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A multipole interaction theory of electric polarization of atomic and molecular assemblies

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The polarization of an assembly of polarizable units in the presence of an arbitrary external electric field and the fields of the permanent and induced electric multipole moments of the units is treated by the method of Cartesian polytensors, which formally include the contributions of multipoles of all orders. The linear polarizabilities of the system of all orders and the electrostatic energy of the system are derived in terms of a set of relay polytensors, which express the multipole moments of all orders induced in each unit by the external electric field gradients of all orders at each other unit. The relay polytensors are calculated by a matrix method from the inherent multipole polarizabilities and positions of the units. The net charges on the units are allowed to be unconstrained, constrained to a fixed net charge of the system, or fixed to permanent values. General-order multipole polarizabilities are derived for two types of bodies which are treated as units in assemblies for numerical calculations: (i) homogeneous dielectric and conducting spheres, which are shown to bear a close analogy to atoms and ions; and (ii) polyatomic molecules in which the atoms are characterized by isotropic point dipole polarizabilities. Numerical examples illustrate the importance of higher order induced multipole effects in ion-atom pair energies, anisotropies of molecular pairs, and optical rotations of simple chiral assemblies.

I. INTRODUCTION

This paper presents a classical theory of electric multipole polarization of an assembly of polarizable units in the presence of an arbitrary external field. The units may be atoms, molecules, or groups of atoms in molecules. The assembly may be a polyatomic molecule, a pair of colliding atoms or molecules, or any larger aggregate of units meeting certain conditions. The units are assumed to interact with each other only by way of the electric potentials and potential gradients of their charge distributions. Charge transfer among units is permitted.

Much progress has been made in recent years in the theory of several phenomena by means of an essentially similar classical model, though in most cases the electric potentials of the units have been truncated at the dipole term. The model has been referred to variously as a dipole interaction model,¹ a monopole-dipole interaction model,² and a dipole-induced-dipole model.³ The model has proven useful, though not precise, in accounting for observed molecular dipole and quadrupole polarizabilities,¹ hyperpolarizabilities,⁴ optical rotations,¹ electronic absorption and circular dichroic spectra,⁵ Raman scattering intensities,⁶ electrostatic energies,^{7,8} and collision-induced light scattering.^{3,9}

The present study formally extends the theory to include interactions of multipole moments of all orders. The method lends itself readily to numerical calculations at any desired level of truncation of the multipole series. There are two ways in which it is anticipated that this might improve the usefulness of the model. First, the theory permits a more realistic treatment of assemblies in which the distances between units are not large compared to the dimensions of the units, as for colliding pairs or for neighboring groups within a polyatomic molecule. Second, it permits greater flexibility in defining the boundaries of the interacting units. For example, a complex molecule may be treated as an assembly of atoms, as in the atom dipole interaction model, or

as an assembly of larger functional groups. In the latter case the computational problem may be simpler because of the smaller number of units, while an accuracy comparable to the former case may be achieved through use of a higher level of truncation of the multipole series. These possibilities are explored in this paper by some illustrative calculations of ion-atom induction energies, pair polarizabilities of simple systems, and optical rotations of chiral assemblies.

There is an extensive research literature on molecular multipole interactions, and I will cite here only a few examples which have brought out the significance of higher multipole interactions in important phenomena. Buckingham's¹⁰ treatment of intermolecular forces identified the terms in the permanent and induced multipole moments which are important in a variety of systems. Stigter and Schellman¹¹ calculated the rotational strength of a quadrupole-allowed electronic transition in the presence of a chiral electric multipole field. Buckingham and Stiles¹² introduced quadrupole polarizability terms into the theory of the dynamic-coupling mechanism for optical activity. Buckingham and Tabisz¹³ treated polarizability interactions in molecular pairs by a first-order perturbation treatment which includes dipole, quadrupole, and octupole polarizabilities. Logan¹⁴ treated the molecular dipole and quadrupole contributions to the dielectric behavior of a fluid in a nonuniform field. Examples of chemical applications of molecular multipole potentials were given in a recent collection of papers edited by Politzer and Truhlar.¹⁵

The object here is to develop a general means of calculating the polarization behavior of a system from the positions, permanent moments, and higher-order polarizabilities of its parts. For the most part the geometry of the system is regarded as fixed, and problems of ensemble averaging are neglected. We also bypass the quantum mechanical basis for the polarizabilities of the units, regarding these as phenomenological coefficients which may be available from a var-

iety of experimental and theoretical sources. The numerical applications of the theory described here are chosen to illustrate the quantitative significance of higher order induced multipole effects in various phenomena where little is known of such effects from previous work.

The present treatment takes a compact form by the use of Cartesian polytensors to simplify expressions involving series of tensor products. The properties of polytensors and a preliminary account of their use in treating multipole interactions have been given elsewhere.¹⁶ A recent generalized treatment of electric multipole moments and multipole polarizabilities has been given,¹⁷ and will play an important part in the present paper.

Sections II–VII cover the main mathematical derivations. Sections VIII–XIII deal with numerical examples. The Appendices contain a number of supplementary derivations.

II. THE MULTIPOLE INTERACTION PROBLEM

Our system is composed of an assembly of N units in some fixed geometry. Each unit consists of a charge distribution which is contained within a spherical region (the “circumsphere”) which does not overlap with the circumsphere of any other unit. (This restriction is necessary for the validity of the multipole expansions of the potentials of the units.¹⁸) The center of the circumsphere of unit i is located at \mathbf{r}_i . The n th rank (or n th order) electric multipole moment of unit i about \mathbf{r}_i is

$$\boldsymbol{\mu}_i^{(n)} = (n!)^{-1} \int_V \rho(\mathbf{r}) (\mathbf{r} - \mathbf{r}_i)^n dV, \quad (1)$$

where $\rho(\mathbf{r})$ is the charge density at point \mathbf{r} , the expression $(\mathbf{r} - \mathbf{r}_i)^n$ denotes the direct, or polyadic, product of the n factors $\mathbf{r} - \mathbf{r}_i$, and the integration is over the volume V of the circumsphere. The multipole moment polytensor of unit i is the column vector¹⁶

$$\mathbf{M}_i = \begin{pmatrix} \boldsymbol{\mu}_i^{(0)} \\ \boldsymbol{\mu}_i^{(1)} \\ \boldsymbol{\mu}_i^{(2)} \\ \vdots \end{pmatrix}, \quad (2)$$

where each tensor $\boldsymbol{\mu}_i^{(n)}$ is arranged as a columnar array of its components in canonical order.¹⁶ Formally, \mathbf{M}_i and related polytensors are regarded here as infinite arrays, though they are truncated at some desired tensor rank for numerical applications. A sequence of tensors in the column vector form of Eq. (2) is a first degree polytensor.¹⁶

The electrostatic potential ϕ_{ij} of unit j at a point \mathbf{r}_i outside its circumsphere is given by the multipole expansion¹⁹

$$\phi_{ij} = \sum_{n=0}^{\infty} \mathbf{t}_{ij}^{(n)} \cdot \mathbf{n} \cdot \boldsymbol{\mu}_j^{(n)}, \quad (3)$$

where $\cdot \mathbf{n} \cdot$ denotes an n -fold tensor contraction and

$$\mathbf{t}_{ij}^{(n)} = (-1)^n \nabla_i^n |\mathbf{r}_i - \mathbf{r}_j|^{-1}, \quad (4)$$

where $\nabla_i \equiv \partial/\partial \mathbf{r}_i$. We define a first degree polytensor \mathbf{t}_{ij} as the sequence $\mathbf{t}_{ij}^{(0)}, \mathbf{t}_{ij}^{(1)}, \mathbf{t}_{ij}^{(2)}, \dots$. From Eqs. (3) and (4), the total potential ϕ_i at \mathbf{r}_i may be expressed as

$$\phi_i = \phi_i^0 + \sum_{j=1}^N \mathbf{t}_{ij} \cdot \mathbf{M}_j, \quad (5)$$

where ϕ_i^0 is the potential due to external charges, the prime indicates that the summation excludes the term $j = i$, and the dot product denotes a polytensor contraction,¹⁶ which is equivalent in this case to an inner product of column vectors.

The n th order field gradient at \mathbf{r}_i is

$$\mathbf{F}_i^{(n)} = -\nabla_i^n \phi_i. \quad (6)$$

The electric field polytensor \mathbf{F}_i is the column vector composed of the sequence $\mathbf{F}_i^{(0)}, \mathbf{F}_i^{(1)}, \mathbf{F}_i^{(2)}, \dots$. The dependence of all multipole moments on all field gradients, through the linear terms in the gradients, may be expressed in the form

$$\mathbf{M}_i = \mathbf{M}_{00i} + \mathbf{P}_i \cdot \mathbf{F}_i, \quad (7)$$

where \mathbf{P}_i is the polarizability polytensor of unit i and \mathbf{M}_{00i} is the multipole moment polytensor of unit i in the absence of all other units and in the absence of an external field (the “intrinsic” multipole moments). \mathbf{P}_i is a polytensor of second degree,¹⁶ defined as the matrix

$$\mathbf{P}_i = \begin{bmatrix} \mathbf{p}_i^{(0,0)} & \mathbf{p}_i^{(0,1)} & \mathbf{p}_i^{(0,2)} & \dots \\ \mathbf{p}_i^{(1,0)} & \mathbf{p}_i^{(1,1)} & \dots & \\ \mathbf{p}_i^{(2,0)} & \dots & & \\ \vdots & & & \end{bmatrix}, \quad (8)$$

where¹⁷

$$p_{i,\alpha_1 \dots \alpha_n, \beta_1 \dots \beta_m}^{(n,m)} = (\partial \mu_{i,\alpha_1 \dots \alpha_n}^{(n)} / \partial F_{i,\beta_1 \dots \beta_m}^{(m)})_0, \quad (9)$$

where Greek indices denote Cartesian components and the subscript 0 indicates that the derivative is evaluated at zero value of all field gradients. The polarizability tensor $\mathbf{p}_i^{(n,m)}$ is of rank $n + m$ and is regarded as a rectangular matrix whose rows are indexed by the canonical array of sets $\alpha_1 \dots \alpha_n$ and whose columns are indexed by the canonical array of sets $\beta_1 \dots \beta_m$. [The set $\beta_1 \dots \beta_m$ is written in opposite order on the two sides of Eq. (9) because the expansion of Eq. (7) gives a series of tensor contractions which take the conventional form $\mathbf{p}_i^{(n,m)} \cdot \mathbf{m} \cdot \mathbf{F}_i^{(m)} = p_{i,\alpha_1 \dots \alpha_n, \beta_1 \dots \beta_m}^{(n,m)} F_{i,\beta_1 \dots \beta_m}^{(m)}$, where summation over repeated Greek indices is implied.] In a static field $\mathbf{p}_i^{(n,m)}$ is symmetric with respect to interchange of rank indices n, m ¹⁷; i.e., $\mathbf{p}_i^{(n,m)} = \mathbf{p}_i^{(m,n)T}$ where T denotes the transpose. Consequently, \mathbf{P}_i is also symmetric. Some further important properties of \mathbf{P}_i are discussed in Appendix A.

Let \mathbf{D}_i be the polytensor gradient operator composed of the sequence of operators $1, \nabla_i, \nabla_i^2, \dots$. Let \mathbf{T}_{ij} be a second degree polytensor defined by the direct product

$$\mathbf{T}_{ij} = \mathbf{D}_i \mathbf{t}_{ij}. \quad (10)$$

The tensor elements of \mathbf{T}_{ij} are thus

$$T_{ij}^{(m,n)} = (-1)^n \nabla_i^m |\mathbf{r}_i - \mathbf{r}_j|^{-1}, \quad m, n = 0, 1, 2, \dots \quad (11)$$

Using Eqs. (5), (6), and (10), we have

$$\mathbf{F}_i = \mathbf{E}_i - \sum_{j=1}^N \mathbf{T}_{ij} \cdot \mathbf{M}_j, \quad (12)$$

where $\mathbf{E}_i = -\mathbf{D}_i \phi_i^0$, the external electric field polytensor.

The multipole interaction problem may now be cast into a simple matrix form with the help of the following matrices:

$$\mathcal{M} = \begin{bmatrix} \mathbf{M}_1 \\ \vdots \\ \mathbf{M}_N \end{bmatrix}, \quad (13)$$

$$\mathcal{E} = \begin{bmatrix} \mathbf{E}_1 \\ \vdots \\ \mathbf{E}_N \end{bmatrix}, \quad (14)$$

$$\mathcal{P} = \begin{bmatrix} \mathbf{P}_1 & 0 & \cdots \\ 0 & \mathbf{P}_2 & \cdots \\ \vdots & & \mathbf{P}_N \end{bmatrix}, \quad (15)$$

$$\mathcal{T} = \begin{bmatrix} 0 & \mathbf{T}_{12} & \cdots & \mathbf{T}_{1N} \\ \mathbf{T}_{21} & & & \\ \vdots & & & \\ \mathbf{T}_{N1} & \mathbf{T}_{N2} & \cdots & 0 \end{bmatrix}. \quad (16)$$

Inserting Eq. (12) into Eq. (7), we obtain

$$\mathcal{M} = \mathcal{M}_{00} + \mathcal{P}(\mathcal{E} - \mathcal{T}\mathcal{M}), \quad (17)$$

where \mathcal{M}_{00} is the matrix of intrinsic moments \mathbf{M}_{00i} . Equation (17) is solved for \mathcal{M} in the form

$$\mathcal{M} = \mathcal{M}_{00} + \mathcal{B}(\mathcal{E} - \mathcal{T}\mathcal{M}_{00}), \quad (18)$$

where

$$\mathcal{B} = (\mathcal{I} + \mathcal{P}\mathcal{T})^{-1}\mathcal{P}, \quad (19)$$

where \mathcal{I} is the identity matrix. The permanent multipole moments \mathcal{M}_0 (the moments in the absence of an external field) are found from Eq. (18) by setting $\mathcal{E} = 0$:

$$\mathcal{M}_0 = (\mathcal{I} - \mathcal{B}\mathcal{T})\mathcal{M}_{00}. \quad (20)$$

By combining Eqs. (18) and (20) we obtain the alternative form

$$\mathcal{M} = \mathcal{M}_0 + \mathcal{B}\mathcal{E}. \quad (21)$$

In polytensor form, Eq. (21) is

$$\mathbf{M}_i = \mathbf{M}_{0i} + \sum_{j=1}^N \mathbf{B}_{ij} \cdot \mathbf{E}_j, \quad (22)$$

where \mathbf{B}_{ij} is a second degree polytensor element of \mathcal{B} . We refer to \mathbf{B}_{ij} as a "relay polytensor," because it expresses the multipole moments which are relayed to unit i by the external field gradients at unit j .

Some comments on the above results are in order:

(1) The form of the solution given by Eq. (21) is similar to that found previously²⁰ for the dipole interaction model, which included only the first order multipoles. The intrinsic moments are incorporated here in a manner similar to that of Camail *et al.*²¹ for the dipole case.

(2) The multipole moments \mathbf{M}_i expressed by Eq. (22) are taken with respect to the origin \mathbf{r}_i . Since the moments are origin dependent¹⁷ (except for the lowest-order nonvanishing moment), one cannot simply sum \mathbf{M}_i over all units to obtain the multipole moments of the system. The calculation of the properties of the system will be dealt with below.

(3) For uniformity, the formalism here includes the net charges $\mu_i^{(0)}$ without constraining them to constant values or to a constant total value for the system. In effect, the units are regarded as "grounded," so that their charges may vary independently. However, realistic applications of the theory

are expected to be of the following types. (i) The net charges of the units are fixed, so that all $\mathbf{p}_i^{(0,n)} = \mathbf{p}_i^{(n,0)} = 0$. The problem is then simplified by elimination of the zero-rank tensors from the polytensors in Eqs. (7) and (12). (ii) The net charges of the units are constrained to give a fixed net charge of the system, so that charges can be exchanged among units. This constraint is introduced into the formalism in Appendix B.

(4) If the polytensors are truncated by deletion of tensors of rank greater than L , then the matrices \mathcal{P} , \mathcal{T} , and \mathcal{B} are of order $N(3^{L+1} - 1)/2$, which is unnecessarily large when $L > 1$. The symmetry of the tensors with respect to certain permutations of component indices makes a substantial reduction of the matrix order possible by elimination of redundant components. The above equations then take a somewhat different form, as described in Appendix C.

(5) All tensors implicit in Eq. (17) are expressed in coordinate systems that are unrotated with respect to each other. Since the properties of the units \mathbf{M}_{00i} and \mathbf{P}_i are likely to be expressed in local coordinate systems chosen for convenience, it will usually be necessary to carry out rotational transformations of these polytensors. Appendix D supplies further information on this procedure.

III. SYSTEM ENERGY IN A STATIC FIELD

A straightforward application of the preceding results is in the calculation of the energy \mathcal{W} of the assembly in a static field. \mathcal{W} is the work performed on the system in transferring the isolated units from positions in field-free space to their final positions in the arbitrary external field. \mathcal{W} is the sum of two terms, the work V required to polarize the units to their final states and the work U required to transfer the units so polarized to their final positions. From a previous derivation¹⁷ and from Eq. (7), the polarization work V_i for unit i in polytensor notation is

$$\begin{aligned} V_i &= \frac{1}{2} \mathbf{F}_i \cdot \mathbf{P}_i \cdot \mathbf{F}_i \\ &= \frac{1}{2} \mathbf{F}_i \cdot (\mathbf{M}_i - \mathbf{M}_{00i}). \end{aligned} \quad (23)$$

The sum of V_i over all units is, therefore,

$$V = \frac{1}{2} \mathcal{F}^T (\mathcal{M} - \mathcal{M}_{00}), \quad (24)$$

where \mathcal{F} is the column matrix of $\mathbf{F}_1, \dots, \mathbf{F}_N$. To calculate U , we imagine a process in which the units are introduced one by one into their final positions, so that the field at each position is the external field plus the fields of all units previously introduced. The work on unit i against the external field is $-\mathbf{E}_i \cdot \mathbf{M}_i$. The work on unit i against the field \mathbf{f}_{ij} (a polytensor) of unit j at \mathbf{r}_i is $-\mathbf{f}_{ij} \cdot \mathbf{M}_i$. As in previous derivations,^{7,8} U is calculated by introducing the units in the order 1, 2, ..., N and in the order $N, N-1, \dots, 1$ and equating the results for the two cases. The result is

$$\begin{aligned} U &= - \sum_{i=1}^N (\mathbf{E}_i + \frac{1}{2} \mathbf{f}_i) \cdot \mathbf{M}_i \\ &= - (\mathcal{E} + \frac{1}{2} \mathbf{f})^T \mathcal{M}, \end{aligned} \quad (25)$$

where

$$\mathbf{f}_i = \sum_{j=1}^N \mathbf{f}_{ij}, \quad (26)$$

and \mathcal{L} is the column matrix of $\mathbf{f}_1, \dots, \mathbf{f}_N$. We now make use of Eq. (18) and the relation

$$\mathcal{F} = \mathcal{E} + \mathcal{L} = \mathcal{E} - \mathcal{T}\mathcal{M}, \quad (27)$$

to obtain, from Eqs. (24) and (25),

$$W = -\frac{1}{2} \mathcal{E}^T \mathcal{M}_{00} - \frac{1}{2} (\mathcal{E} - \mathcal{T}\mathcal{M}_{00})^T \times [\mathcal{M}_{00} + \mathcal{B}(\mathcal{E} - \mathcal{T}\mathcal{M}_{00})]. \quad (28)$$

Equation (28) gives the energy in terms of the geometry of the system, the properties of the isolated units, and the external field. The expression includes the terms for interactions among all multipole moments of all orders, both intrinsic and induced.

In the absence of an external field Eq. (28) becomes

$$W = \frac{1}{2} \mathcal{M}_{00}^T \mathcal{T}(\mathcal{F} - \mathcal{B}\mathcal{T})\mathcal{M}_{00}. \quad (29)$$

If the units have no intrinsic multipole moments, Eq. (28) becomes

$$W = -\frac{1}{2} \mathcal{E}^T \mathcal{B} \mathcal{E}. \quad (30)$$

Equation (30) gives the energy change of the system in the process of polarization. Since the process is spontaneous, W must be negative for any \mathcal{E} . Therefore, \mathcal{B} is a positive definite matrix. The same conclusion applies to the general case of Eq. (28), since the polarization energy there has the form of Eq. (30) with \mathcal{E} replaced by $\mathcal{E} - \mathcal{T}\mathcal{M}_{00}$.

IV. SYSTEM POLARIZABILITIES IN A STATIC FIELD

Let $\hat{\mu}_i^{(n)}$ be the n th order multipole moment of unit i about the system origin. It has been shown elsewhere¹⁷ that the transformation of multipole moments under translation of the origin from $\mathbf{r} = \mathbf{r}_i$ to $\mathbf{r} = 0$ is given by

$$\hat{\mu}_i^{(n)} = \sum_{h=0}^n (h!/n!) \sum_{P(n,h)} \mathbf{r}_i^{n-h} \mu_i^{(h)}, \quad (31)$$

where the sum over $P(n,h)$ is the sum over all partitions of n component indices into sets of h and $n-h$ indices. The multipole moments of the system about its origin are obtained by summing $\hat{\mu}_i^{(n)}$ over all i . From Eqs. (22) and (31) the system moments are

$$\begin{aligned} \mu^{(n)} &= \mu_0^{(n)} + \sum_{i=1}^N \sum_{j=1}^N \sum_{h=0}^n \sum_{k=0}^{\infty} (h!/n!) \\ &\times \sum_{P(n,h)} \mathbf{r}_i^{n-h} \mathbf{B}_{ij}^{(h,k)} \cdot \mathbf{k} \cdot \mathbf{E}_j^{(k)}, \end{aligned} \quad (32)$$

where the permanent moment $\mu_0^{(n)}$ is the sum of the permanent moments of the units about the system origin.

The system polarizabilities $\mathbf{p}^{(n,m)}$ are defined by the equivalent of Eq. (9), replacing $\mathbf{F}_i^{(m)}$ with $\mathbf{E}^{(m)}$, the external field gradient evaluated at $\mathbf{r} = 0$. We wish to calculate $\mathbf{p}^{(n,m)}$ by expressing the $\mathbf{E}_j^{(k)}$ of Eq. (32) as a Taylor series in $\mathbf{E}^{(m)}$:

$$\mathbf{E}_j^{(k)} = \sum_{m=k}^{\infty} [(m-k)!]^{-1} \mathbf{r}_j^{m-k} \cdot (m-k) \cdot \mathbf{E}^{(m)}. \quad (33)$$

Equation (33) is based on the fact that $\mathbf{E}^{(m)} = \nabla^{m-k} \mathbf{E}^{(k)}$, which introduces the permutation symmetry of the gradient operator. Thus it is desirable to express $\mathbf{p}^{(n,m)}$ by the symmetry-constrained derivative¹⁷

$$p_{\alpha_1 \dots \alpha_n \beta_1 \dots \beta_m}^{(n,m)} = g(\beta_1 \dots \beta_m)^{-1} (\partial_s \mu_{\alpha_1 \dots \alpha_n}^{(n)} / \partial E_{\beta_1 \dots \beta_m}^{(m)})_0, \quad (34)$$

where

$$g(\beta_1 \dots \beta_m) = m! / n_1! n_2! n_3!, \quad (35)$$

where n_i is the number of i 's in the set $\beta_1 \dots \beta_m$. From Eq. (33) we find

$$\begin{aligned} \partial_s E_{j, \gamma_1 \dots \gamma_k}^{(k)} / \partial E_{\beta_1 \dots \beta_m}^{(m)} &= [(m-k)!]^{-1} \\ &\times \sum_{N\{\beta\}} \mathbf{r}_{j, \beta_1} \dots \mathbf{r}_{j, \beta_{m-k}} \delta_{\gamma_1 \beta_{m-k+1}} \dots \delta_{\gamma_k \beta_m}, \end{aligned} \quad (36)$$

where $\delta_{\gamma\beta}$ is the Kronecker delta and the sum over $N\{\beta\}$ is the sum over all permutations of the indices $\beta_1 \dots \beta_m$ when their numerical values are given. Eq. (36) holds for $m \geq k$; the derivative vanishes for $m < k$. The derivatives of $\mu^{(n)}$ are transformed by the relation

$$(\partial_s \mu^{(n)} / \partial \mathbf{E}^{(m)})_0 = \sum_{j=1}^N \sum_{k=0}^{\infty} (\partial \mu^{(n)} / \partial \mathbf{E}_j^{(k)})_0 \cdot \mathbf{k} \cdot (\partial_s \mathbf{E}_j^{(k)} / \partial \mathbf{E}^{(m)}). \quad (37)$$

Equations (32)–(37) then give

$$\begin{aligned} \mathbf{p}^{(n,m)} &= \sum_{i=1}^N \sum_{j=1}^N \sum_{h=0}^n \sum_{k=0}^m (h!k!/n!m!) \\ &\times \sum_{P(n,h)} \sum_{P(m,k)} \mathbf{r}_i^{n-h} \mathbf{B}_{ij}^{(h,k)} \mathbf{r}_j^{m-k}, \end{aligned} \quad (38)$$

where the sum over $N\{\beta\}$ in Eq. (36) has been replaced by the sum over $P(m,k)$, using a relation applicable to sums of direct products of totally symmetric tensors of ranks k and $m-k$ [Ref. 17, Eq. (41)]. It is understood that the partitions indicated by $P(n,h)$ involve the component indices of \mathbf{r}_i^{n-h} and those corresponding to rank index h of $\mathbf{B}_{ij}^{(h,k)}$, while the partitions indicated by $P(m,k)$ involve the component indices of \mathbf{r}_j^{m-k} and those corresponding to rank index k of $\mathbf{B}_{ij}^{(h,k)}$.

It is shown in Appendix E that \mathcal{B} is a symmetric matrix in the static field case. Consequently,

$$\mathbf{B}_{ij}^{(h,k)T} = \mathbf{B}_{ji}^{(k,h)}. \quad (39)$$

It follows from Eq. (38) that

$$\mathbf{p}^{(n,m)T} = \mathbf{p}^{(m,n)}. \quad (40)$$

This relation has been proven on energetic grounds,¹⁷ and thus serves a check on the validity of Eq. (38). A further confirmation of Eq. (38) may be found by calculating $\mathbf{p}^{(n,m)}$ from the appropriate second derivative of W with respect to field gradients,¹⁷ starting with Eq. (28).

The following are examples of Eq. (38):

$$p^{(0,0)} = \sum_{ij} \mathbf{B}_{ij}^{(0,0)}. \quad (41)$$

$$p_{\alpha}^{(0,1)} = p_{\alpha}^{(1,0)} = \sum_{ij} [\mathbf{B}_{ij}^{(0,0)} r_{j,\alpha} + \mathbf{B}_{ij,\alpha}^{(0,1)}], \quad (42)$$

$$\begin{aligned} p_{\alpha\beta}^{(1,1)} &= \sum_{ij} [\mathbf{r}_{i,\alpha} \mathbf{B}_{ij}^{(0,0)} r_{j,\beta} + \mathbf{r}_{i,\alpha} \mathbf{B}_{ij,\beta}^{(0,1)} \\ &+ \mathbf{B}_{ij,\alpha}^{(1,0)} r_{j,\beta} + \mathbf{B}_{ij,\alpha\beta}^{(1,1)}], \end{aligned} \quad (43)$$

$$\begin{aligned} p_{\alpha\beta\gamma}^{(1,2)} &= p_{\beta\gamma\alpha}^{(2,1)} = \sum_{ij} [\frac{1}{2} \mathbf{r}_{i,\alpha} \mathbf{B}_{ij}^{(0,0)} r_{j,\beta} r_{j,\gamma} + \frac{1}{2} \mathbf{r}_{i,\alpha} \mathbf{B}_{ij,\beta}^{(0,1)} r_{j,\gamma} \\ &+ \frac{1}{2} \mathbf{r}_{i,\alpha} \mathbf{B}_{ij,\gamma}^{(0,1)} r_{j,\beta} + \frac{1}{2} \mathbf{B}_{ij,\alpha}^{(1,0)} r_{j,\beta} r_{j,\gamma} + \frac{1}{2} \mathbf{B}_{ij,\alpha\beta}^{(1,1)} r_{j,\gamma} \\ &+ \frac{1}{2} \mathbf{B}_{ij,\alpha\gamma}^{(1,1)} r_{j,\beta} + \mathbf{r}_{i,\alpha} \mathbf{B}_{ij,\beta\gamma}^{(0,2)} + \mathbf{B}_{ij,\alpha\beta\gamma}^{(1,2)}]. \end{aligned} \quad (44)$$

These expressions are simplified when net charges are constrained in certain ways. For example, if the net charges of all units are fixed, then all $\mathbf{B}_{ij}^{(n,m)}$ with $n = 0$ or $m = 0$ vanish. If all input polytensors \mathbf{P}_i and \mathbf{T}_{ij} are truncated by deletion of tensors of rank indices greater than L , then Eq. (38) is simplified in that all terms with $h > L$ or $k > L$ are deleted. The extensively studied dipole interaction model corresponds to truncation at $L = 1$, and the monopole terms are usually omitted, leaving only the $\mathbf{B}_{ij}^{(1,1)}$ terms in Eq. (38). The following are examples of Eq. (38) for this case.

$$p_{\alpha\beta}^{(1,1)} = \sum_{ij} B_{ij,\alpha\beta}^{(1,1)}, \quad (45)$$

$$p_{\alpha\beta\gamma}^{(1,2)} = p_{\beta\gamma\alpha}^{(2,1)} = \frac{1}{2} \sum_{ij} [B_{ij,\alpha\beta}^{(1,1)} r_{j,\gamma} + B_{ij,\alpha\gamma}^{(1,1)} r_{j,\beta}], \quad (46)$$

$$p_{\alpha\beta\gamma\delta}^{(1,3)} = p_{\beta\gamma\delta\alpha}^{(3,1)} = \frac{1}{6} \sum_{ij} [B_{ij,\alpha\beta}^{(1,1)} r_{j,\gamma} r_{j,\delta} + B_{ij,\alpha\gamma}^{(1,1)} r_{j,\beta} r_{j,\delta} + B_{ij,\alpha\delta}^{(1,1)} r_{j,\beta} r_{j,\gamma}], \quad (47)$$

$$p_{\alpha\beta\gamma\delta}^{(2,2)} = \frac{1}{4} \sum_{ij} [r_{i,\alpha} B_{ij,\beta\gamma}^{(1,1)} r_{j,\delta} + r_{i,\beta} B_{ij,\alpha\gamma}^{(1,1)} r_{j,\delta} + r_{i,\alpha} B_{ij,\beta\delta}^{(1,1)} r_{j,\gamma} + r_{i,\beta} B_{ij,\alpha\delta}^{(1,1)} r_{j,\gamma}]. \quad (48)$$

Equation (45) has been employed extensively in previous studies.^{1,20} Equation (46) leads to the uniform field quadrupole polarizability expression derived elsewhere¹ when $\mathbf{p}^{(2,1)}$ is converted to traceless form.¹⁷ The traceless forms of the higher rank tensors may likewise be obtained by the general procedure given earlier,¹⁷ though for numerical calculations it would seem simpler to carry out this conversion after computing the unabridged polarizabilities as given above.

Neumann²² has derived explicit expressions for the traceless forms of $\mathbf{p}^{(1,1)}$, $\mathbf{p}^{(2,1)}$, and $\mathbf{p}^{(3,1)}$ for tetrahedral XY_4 and octahedral XY_6 molecules in terms of the isotropic atom dipole polarizabilities. His results should be obtainable as special cases of Eqs. (45)–(47).

V. SYSTEM POLARIZABILITIES IN A TIME-DEPENDENT FIELD

The development in Sec. II is formally exact for the system in a static field. The object of this section is to extend the same treatment to an arbitrary time-dependent external field, but in doing so we make the following approximations in order to minimize additional complexity. (i) The multipole field tensors are the static field expressions as in Eq. (11). This omits retardation effects and effects associated with the vector potential of time-dependent induced multipole moments. For a dipole moment induced by the electric field of a light wave, these effects are small at distances which are small compared to the wavelength of the light.²³ Since higher-order multipole effects become significant primarily at small interunit distances, we assume without proof that the dynamic contributions to the multipole fields can be neglected in the systems of interest here. (ii) Effects of the magnetic field associated with a time-dependent electric field are not explicitly included. Effects of certain time derivatives of the magnetic field and its gradients are included indirectly as a result of the Maxwell equations relating these quantities to the electric field ($c\nabla \times \mathbf{E} = -\dot{\mathbf{B}}$ and $c\nabla \times \mathbf{H} = \dot{\mathbf{D}} + 4\pi\mathbf{j}$).

However, magnetic moments induced by the magnetic field itself, through the first-order magnetic susceptibilities of the units, are omitted.

Our main object here is to derive the system polarizabilities for the time-dependent field case from Eq. (21). The derivation differs from that in the static field case in the following ways.

First, the tensors $\mathbf{E}_i^{(m)}$ are no longer totally symmetric because they are not derived from a scalar potential. Instead, the polytensor \mathbf{E}_i consists of the tensors

$$\mathbf{E}_i^{(0)} = \sum_{n=0}^{\infty} (n!)^{-1} \mathbf{r}_i^n \cdot \mathbf{n} \cdot \mathbf{E}^{(n)}, \quad (49)$$

$$\mathbf{E}_i^{(1)} = -\nabla_i \phi_i^0 - \dot{\mathbf{A}}_i/c, \quad (50)$$

$$\mathbf{E}_i^{(m)} = \nabla_i^{m-1} \mathbf{E}_i^{(1)}, \quad m = 1, 2, \dots, \quad (51)$$

where \mathbf{A}_i is the vector potential of the external field at \mathbf{r}_i and c is the velocity of light. In Eq. (49) $\mathbf{E}_i^{(0)}$ is a scalar having the dimensions of a potential, but is in general different from $-\phi_i^0$. From Eqs. (50) and (51) it follows that $\mathbf{E}_{i,\beta_1 \dots \beta_m}^{(m)}$ is symmetric with respect to permutations among $\beta_1 \dots \beta_{m-1}$ only. We refer to such a tensor as “semisymmetric” with respect to permutation of component indices. [The undefined quantity $\mathbf{E}^{(0)}$ in Eq. (49) is the arbitrary additive constant in the potential at $\mathbf{r} = 0$.]

Second, the polarizabilities are again defined by Eq. (9), but the derivative is taken under the condition of adherence to the equations of motion for the system, and not under the condition of internal equilibrium as in the static-field case.¹⁷ For a field with sinusoidal time dependence, $\mathbf{p}_i^{(n,m)}$ then becomes a complex function of the frequency. The major formal distinction from the static field case is that $\mathbf{p}_i^{(n,m)}$ is, in general, not necessarily symmetric with respect to permutation of the rank indices n and m , since the proof of that symmetry rests on the condition of internal equilibrium.¹⁷ Furthermore, it follows from Eqs. (9) and (51) that $p_{i,\alpha_1 \dots \alpha_n \beta_1 \dots \beta_m}^{(n,m)}$ is totally symmetric in the index sets $\alpha_1 \dots \alpha_n$ and $\beta_1 \dots \beta_{m-1}$, but is semisymmetric in the set $\beta_1 \dots \beta_m$.

As in the static field case, the system multipole moments are given by Eq. (32). Due to the semisymmetry of the field gradients, the symmetry-constrained form of the polarizability analogous to Eq. (34) is

$$p_{\alpha_1 \dots \alpha_n \beta_1 \dots \beta_m}^{(n,m)} = g(\beta_1 \dots \beta_{m-1})^{-1} (\partial_s \mu_{\alpha_1 \dots \alpha_n}^{(n)} / \partial E_{\beta_1 \dots \beta_m}^{(m)})_0. \quad (52)$$

The Taylor series of Eq. (33) remains valid for $k = 0, 1, 2, \dots$, as a result of the definitions in Eqs. (49)–(51). However, in place of Eq. (36) we have

$$\begin{aligned} \partial_s E_{j,\gamma_1 \dots \gamma_k}^{(k)} / \partial E_{\beta_1 \dots \beta_m}^{(m)} \\ = [(m-k)!]^{-1} \sum_{N\{\beta\}} r_{j,\beta_1} \dots r_{j,\beta_{m-k}} \delta_{\gamma_1 \beta_{m-k+1}} \dots \delta_{\gamma_k \beta_m}, \end{aligned} \quad (53)$$

where the sum over $N\{\beta\}$ is the sum over all permutations of the set $\beta_1 \dots \beta_{m-1}$ when their numerical values are specified. The final result is

$$p_{\alpha_1 \dots \alpha_n \beta_1 \dots \beta_m}^{(n,m)} = \sum_{i=1}^N \sum_{j=1}^N \sum_{h=0}^n (h!/n!) \cdot \sum_{P(n,h)} r_{i,\alpha_1} \dots r_{i,\alpha_n-h}$$

$$\times \left\{ (m!)^{-1} B_{ij, \alpha_n - h + 1 \dots \alpha_n}^{(h,0)} + \sum_{k=1}^m [(k-1)!/(m-1)!] \right. \\ \left. \times \sum_{P(m-1, k-1)} B_{ij, \alpha_n - h + 1 \dots \alpha_n \beta_m \dots \beta_{m-k+1}}^{(h,k)} r_{j, \beta_m - k} \dots r_{j, \beta_1} \right\}, \quad (54)$$

which is derived from Eqs. (32), (33), (37), (52), and (53), transforming the sum over $N\{\beta'\}$ as in the case of Eq. (38) for $k \geq 1$, but treating the $k = 0$ term separately. In Eq. (54) it is understood that the partitions $P(n, h)$ are made on the indices $\alpha_1 \dots \alpha_n$, and the partitions $P(m-1, k-1)$ are made on the indices $\beta_1 \dots \beta_{m-1}$.

Equation (54) gives the same expressions as the static field formula, Eq. (38), for $\mathbf{p}^{(n,0)}$ and $\mathbf{p}^{(n,1)}$, since there is no question of permutation of component indices corresponding to the second rank index in these cases. Thus Eqs. (41)–(44) can be obtained from Eq. (54) for all cases shown except $\mathbf{p}^{(1,2)}$. The latter tensor is an important one for optical activity, and is discussed in the next section.

VI. MOLECULAR ROTATORY PARAMETER

We consider here the optical activity of an isotropic distribution of identical systems of the type under consideration. A treatment of the macroscopic dipole polarization of the medium leads to the conclusion that the optical rotation and circular dichroism are proportional to the real and imaginary parts, respectively, of a molecular rotatory parameter β .²⁴ The following expression has been derived for β by calculating the isotropic average induced dipole moment, assuming that the dimensions of the system are small compared with the wavelength of the light²⁵:

$$\beta = \frac{1}{6} p_{\alpha\beta\gamma}^{(1,2)} \epsilon_{\alpha\beta\gamma}, \quad (55)$$

where $\epsilon_{\alpha\beta\gamma}$ is the permutation tensor. From Eq. (54) we obtain the following form for $\mathbf{p}^{(1,2)}$ when zero-rank tensors are omitted:

$$p_{\alpha\beta\gamma}^{(1,2)} = \sum_{i,j} [B_{ij, \alpha\beta}^{(1,1)} r_{j,\gamma} + B_{ij, \alpha\beta\gamma}^{(1,2)}]. \quad (56)$$

This expression is not in general symmetric in the indices $\beta\gamma$, though such symmetry is present for achiral systems. Equations (55) and (56) give β in terms of the relay tensors $\mathbf{B}_{ij}^{(1,1)}$ and $\mathbf{B}_{ij}^{(1,2)}$. The optical rotation and circular dichroism arising from the $\mathbf{B}_{ij}^{(1,1)}$ terms have been calculated for many molecules using dipole interaction models.^{1,5} These terms correspond to the terms in Kirkwood's²⁶ quantum mechanical theory of optical activity arising from pairs of electric dipole transition moments on different units.²⁵ The $\mathbf{B}_{ij}^{(1,2)}$ terms include higher order terms found by Buckingham and Stiles.¹² They are found when the multipole polytensors are truncated at rank $L > 2$. These include the terms $\mathbf{B}_{ii}^{(1,2)}$, which correspond to the terms which Kirkwood called the "internal rotatory parameters" of the units. A term $\mathbf{B}_{ij}^{(1,2)}$ for $i \neq j$ represents the dipole moment induced in unit i by the field gradient $\mathbf{E}_j^{(2)}$ at unit j . Such terms appear to be related to Kirkwood's terms arising from pairs of electric and magnetic dipole transition moments on different units, though the precise relationship remains to be found.

The multipole interaction model introduces a new way of looking at the mechanisms responsible for optical activity.

The relay tensors of all ranks, as given by Eq. (19), contain contributions from interactions among electric multipole moments of all ranks through the truncation level L . Thus neither the $\mathbf{B}_{ij}^{(1,1)}$ nor the $\mathbf{B}_{ij}^{(1,2)}$ term can be attributed entirely to a particular type of multipole interaction, as both terms depend on L .

The mechanisms which contribute to β by way of Eqs. (55) and (56) do not include effects of the static fields of permanent multipole moments in the system, as these do not affect the relay tensors. Thus the one-electron mechanism of Condon *et al.*²⁷ is omitted. It would be possible to include this mechanism as an inherent property of the appropriate units through the input polarizabilities $\mathbf{p}_i^{(1,2)}$, but this would not be equivalent to a direct calculation of the effects of the static fields. The one-electron mechanism is nonlinear, as it depends on polarization which is proportional to the fields of both the static multipoles and the light wave. The appropriate classical formalism for such an effect at the induced dipole level is contained in the theory of Sundberg.²⁸

VII. POLARIZABILITIES OF HOMOGENEOUS SPHERES

A spherical sample of a homogeneous substance, either a conductor or a dielectric, is a body whose multipole polarizabilities can be easily calculated. Assemblies of such spheres will be used to illustrate the results of the preceding sections. The purpose of this section is to derive the necessary polarizabilities and to draw an interesting parallel between the multipole polarizabilities of homogeneous spheres and atoms. The method used is similar in principle to those in classic textbook treatments²⁹ of the static polarization of homogeneous spheres, though I have been unable to find a previous treatment that yields polarizabilities of all orders in a general static field. Cartesian tensors are used here in place of the spherical tensors usually employed in order to be consistent with the preceding sections.

A body is placed in a vacuum in which there is a potential ϕ^0 due to external charges, given by the Taylor series

$$\phi^0(\mathbf{r}) = - \sum_{n=0}^{\infty} (n!)^{-1} \mathbf{E}^{(n)} \cdot \mathbf{n} \cdot \mathbf{r}^n, \quad (57)$$

where $\mathbf{E}^{(n)} = -\nabla^{(n)} \phi^0(0)$. A relation which facilitates the development in terms of Cartesian tensors is the following expression of the potential ϕ^s of the body as a similar power series in \mathbf{r} :

$$\phi^s(\mathbf{r}) = \sum_{n=0}^{\infty} r^{-2n-1} \mathbf{M}^{(n)} \cdot \mathbf{n} \cdot \mathbf{r}^n. \quad (58)$$

The coefficients $\mathbf{M}^{(n)}$ are the traceless multipole moments of the body about the origin. Equation (58) is derived from Eq. (3) in Appendix F. In the present case the body is a sphere of radius a centered at the origin, for which Eq. (58) is valid when $r > a$.

We consider first the case of a conducting sphere. The boundary conditions that the total potential $\phi^0 + \phi^s$ be (i) equal to a constant C within the sphere and (ii) continuous at the surface of the sphere lead to the following relation, obtained by applying Eqs. (57) and (58) at the surface.

$$\sum_{n=0}^{\infty} [a^{-n-1} \mathbf{M}^{(n)} - (a^n/n!) \mathbf{E}^{(n)}] \cdot \mathbf{n} \cdot \hat{\mathbf{r}}^n = C, \quad (59)$$

where $\hat{\mathbf{r}}$ is the unit vector \mathbf{r}/r . The summand in Eq. (59) is of

the form $\mathbf{A}^{(n)} \cdot \mathbf{n} \cdot \mathbf{r}^n$, where $\mathbf{A}^{(n)}$ is a totally symmetric tensor which is traceless in all pairs of indices. Such a form is a surface spherical harmonic of degree n , since it is r^{-n} times an n th degree homogeneous polynomial which satisfies Laplace's equation.³⁰ Since surface spherical harmonics of different degrees are independent, Eq. (59) implies $\mathbf{A}^{(n)} \cdot \mathbf{n} \cdot \mathbf{r}^n = 0$ and $\mathbf{A}^{(n)} \cdot \mathbf{n} \cdot \mathbf{r}^n = 0$ for $n > 0$. The last expression is a homogeneous polynomial of degree n in x, y, z , having $(n+1)(n+2)/2$ linearly independent terms, whose coefficients must vanish. These coefficients are the components of the compressed tensor¹⁶ $\bar{\mathbf{A}}^{(n)}$. From the form of $\bar{\mathbf{A}}^{(n)}$ in Eq. (59), we find, for $n > 0$,

$$\bar{\mathbf{M}}^{(n)} = (a^{2n+1}/n!) \bar{\mathbf{E}}^{(n)}. \quad (60)$$

Equation (60) holds for $n=0$ as well if $C=0$, as for a grounded conductor. The coefficient of $\bar{\mathbf{E}}^{(n)}$ defines a scalar polarizability which will be denoted π_n :

$$\pi_n = a^{2n+1}/n! \quad (61)$$

The case $\pi_1 = a^3$ is a familiar result for the dipole polarizability of a conducting sphere.³¹ The fact that Eq. (60) does not include terms in $\bar{\mathbf{E}}^{(m)}$ with $m \neq n$ means that polarizabilities of mixed rank vanish.

We consider next the case of a dielectric sphere with dielectric constant ϵ . The potential within the sphere is now the sum of the potential ϕ^0 and the potential ϕ^i due to the charge distribution in the dielectric. We may write

$$\phi^i(\mathbf{r}) = - \sum_{n=0}^{\infty} (n!)^{-1} \mathbf{e}^{(n)} \cdot \mathbf{n} \cdot \mathbf{r}^n, \quad (62)$$

where $\mathbf{e}^{(n)} = -\nabla^n \phi^i(0)$. Equation (62) holds for $r < a$, while Eq. (58) still holds for the potential of the sphere when $r > a$. The boundary conditions are (i) the continuity of the total potential at the surface of the sphere,

$$\lim_{r \rightarrow a-} (\phi^i + \phi^0) = \lim_{r \rightarrow a+} (\phi^s + \phi^0), \quad (63)$$

and (ii) the continuity of the component of the dielectric displacement normal to the surface of the sphere,

$$\lim_{r \rightarrow a-} \epsilon \partial(\phi^i + \phi^0)/\partial r = \lim_{r \rightarrow a+} \partial(\phi^s + \phi^0)/\partial r. \quad (64)$$

Application of Eqs. (63) and (64) to Eqs. (57), (58), and (62) results in two relations which equate power series in \mathbf{r} . By equating coefficients of linearly independent terms and eliminating terms in $\mathbf{e}^{(n)}$ between the two relations, one obtains

$$\bar{\mathbf{M}}^{(n)} = \pi_n \bar{\mathbf{E}}^{(n)}, \quad (65)$$

where the scalar polarizability is now

$$\pi_n = (\epsilon - 1) a^{2n+1} / (\epsilon + 1 + n^{-1}) n!, \quad (66)$$

for $n = 1, 2, \dots$ (π_0 is not obtained.) The case $\pi_1 = (\epsilon - 1)a^3/(\epsilon + 2)$ is the familiar result for the dipole polarizability of a dielectric sphere.³¹ Equation (66) reduces to Eq. (61) in the limit $\epsilon = \infty$, corresponding to a conductor. Again, the polarizabilities of mixed rank vanish.

The relation between the scalar polarizability π_n and the tensor $\mathbf{p}^{(n,n)}$ required by the foregoing theory is discussed in Appendix G.

It is of interest to compare the multipole polarizabilities of homogeneous spheres with values calculated for various

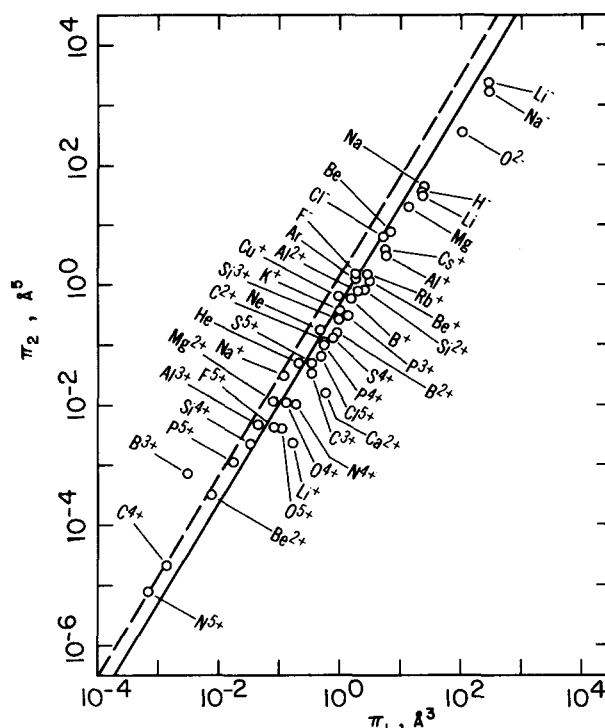


FIG. 1. Quadrupole polarizability π_2 vs dipole polarizability π_1 for atoms and ions (Refs. 33 and 34). (—) Present theory for homogeneous conducting spheres. (---) Present theory for homogeneous dielectric spheres with $\epsilon = 2$.

atoms (neutral and charged) using quantum mechanical perturbation theory. It is already well known from experimental data that atom dipole polarizabilities are of the order of magnitude of the radius cubed,³² as for spheres. Langhoff and Hurst³³ have given theoretical polarizabilities for numerous species through the octupole level, and Ha³⁴ has compiled additional results for dipole and quadrupole polarizabilities. It is shown in Appendix H that the polarizabilities reported are equivalent to $n!\pi_n$. The atom data are plotted in Figs. 1 and 2, where the sphere radius has been eliminated as a variable by regarding the higher order polarizabilities π_2 (quadrupole) and π_3 (octupole) as functions of the dipole polarizability π_1 . The straight lines show these functions as calculated from Eq. (61) for conducting spheres and Eq. (66) for spheres with $\epsilon = 2$. The atom data show some scatter about these lines, but there is clearly a strong parallel between the behavior predicted for homogeneous spheres and for atoms. Some of the scatter is undoubtedly due to theoretical uncertainty, since discrepancies among theoretical results for the same species of the order of 100% are common. (Where discrepancies were reported, the value used in Figs. 1 and 2 is the average of the highest and lowest values.) The fact that the dielectric and conducting sphere lines are so nearly similar means that the graphs are insensitive to the nature of the substance, and this fact is probably one reason why the atom data and homogeneous sphere data are similar.

The similarity of atoms and homogeneous spheres through the octupole level suggests that atom polarizabilities of still higher orders may be estimated from equations for spheres. The dipole polarizability of an atom is often

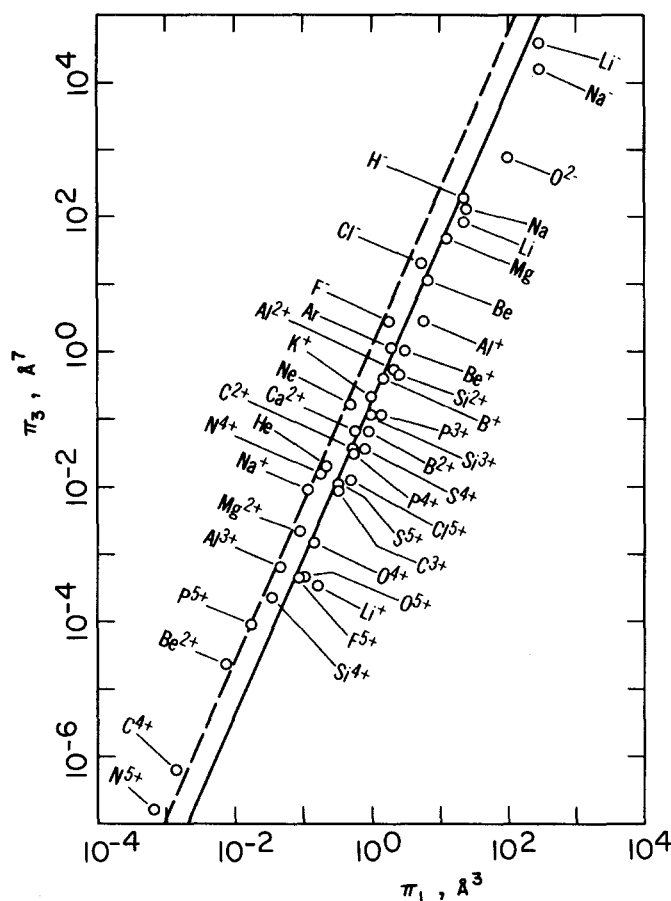


FIG. 2. Octupole polarizability π_3 vs dipole polarizability π_1 for atoms and ions (Ref. 33). (—) Present theory for homogeneous conducting spheres. (---) Present theory for homogeneous dielectric spheres with $\epsilon = 2$.

known, and can be used to determine the effective sphere radius, which is the main parameter required. The conducting sphere model does not require a dielectric constant, and appears to represent the bulk of the atom data better than spheres of low dielectric constant. Several problems in multipole interactions in assemblies of conducting spheres are treated in the following sections. The main object is to illustrate higher order effects on relatively simple models, but it might be assumed that the results are relevant to the behavior of assemblies of atoms as well.

VIII. COMPUTATIONAL METHODS

The calculations described in the following sections were carried out on a National Advanced Systems AS/6 computer using double precision arithmetic. The major step is the computation of the \mathcal{P} matrix of Eq. (19). Programs were written to do this using the compressed forms in Eqs. (C3) and (C4) and the semicompressed form in Eq. (C8). Zero-rank tensors were omitted from the polytensors in these equations, since the net charges and potentials do not play a role in most of the problems treated. The formula of Cipriani and Silvi³⁵ for $\nabla^n r^{-1}$ was used to construct \mathcal{T} [Eq. (16)]. The higher polarizabilities needed for \mathcal{P} [Eq. (15)] were obtained by the methods of Sec. VII and Appendix G when the units were conducting spheres. In several of the examples the units are taken to be assemblies of conducting

spheres or atoms, requiring for \mathcal{P} the higher rank polarizabilities of the assemblies about their local origins. These were obtained by carrying out the multipole interaction calculation for each such assembly, using Eq. (38) or Eq. (54) to give the unit polarizabilities. The major matrix manipulations were carried out using Linpack³⁶ subroutines for inversions and IMSL³⁷ subroutines for multiplications.

IX. POTENTIAL OF A PAIR OF POLARIZED SPHERES

As an elementary application of the multipole interaction theory, the electrostatic potential in the region surrounding a pair of conducting spheres which are polarized by a uniform external field will be considered here. The behavior of the potential is helpful in visualizing the significance of the various induced multipole moments.

The system consists of two conducting spheres of radius 1.0 \AA with their centers separated by a distance of 2.2 \AA , a distance chosen so that higher order multipole interactions would be present to a moderate degree. The system is placed in a uniform external electric field directed parallel to the line between sphere centers. (See Fig. 3.) The uniform field induces a dipole moment, but no other multipole moment, in each of the spheres, according to the results of Sec. VII. However, each polarized sphere produces a nonuniform field which induces higher multipole moments in its neighbor. We will consider the resulting multipole expansion of the potential of the system given by Eq. (3).

The potential may be conveniently calculated by either a one-center expansion or a two-center expansion, the number of centers being the number of units into which the system is subdivided. The two-center expansion is the sum of the multipole potentials of each sphere about its center, and is convergent in the region outside both spheres. The one-center expansion is the multipole expansion of the whole system about its origin, chosen as the midpoint between sphere centers, and is convergent in the region outside the circumsphere of the system.

Either expansion requires the calculation of the relay polytensors, which is done by means of Eq. (C4), using sphere polarizability polytensors truncated at $L = 5$. The multipole moments are then obtained from the polarizabilities of Eq. (38) in the one-center expansion and from Eq. (22) in the two-center expansion.

Figure 3 shows contour maps of the potential in a plane containing the sphere centers, with the two-center expansion in the top row and the one-center expansion in the bottom row. The potential of the external field is not included. ϕ_n denotes the potential of the n th order multipole moment or moments of the units. The first three nonvanishing terms and their sum are shown for each expansion. For the one-center expansion only odd-order terms are nonvanishing. (This is because the "unit" is subject only to the uniform external field, and $\mathbf{p}^{(n,1)} = 0$ for even n when the system has a center of inversion symmetry.) The following are some notable features of Fig. 3.

(1) Two familiar properties of the individual multipole terms are evident: (i) the range in which ϕ_n is significant decreases with increasing n due to its dependence on $r^{-(n+1)}$,³⁸ and (ii) the potentials show the nodal lines charac-

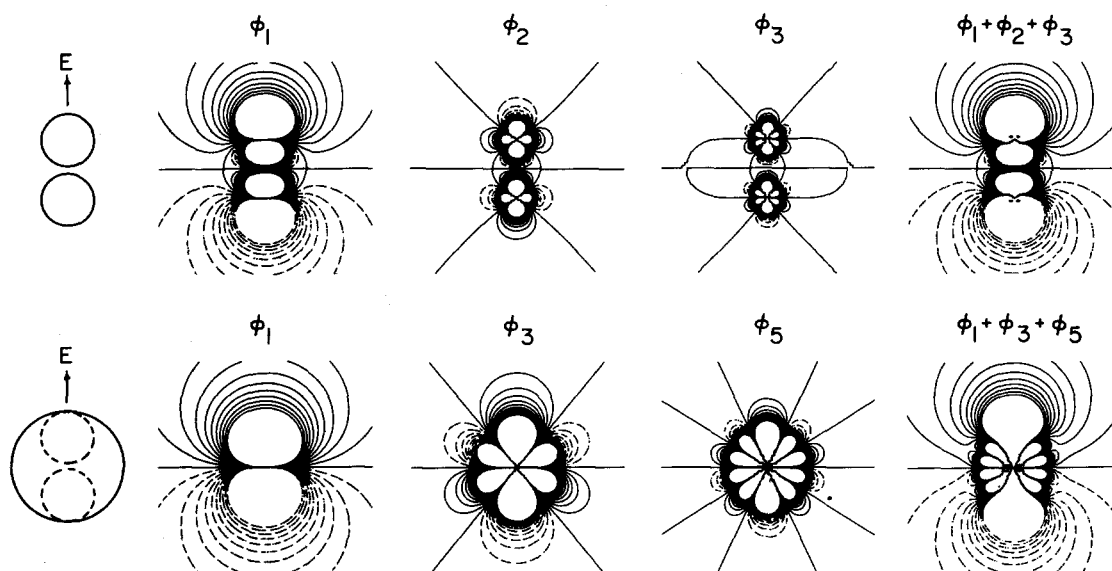


FIG. 3. Electrostatic potentials of induced multipole moments of a pair of conducting spheres in a uniform external field E parallel to the line through the sphere centers. Top row: two-center potentials of sphere multipole moments about their own centers. Bottom row: one-center potentials of system multipole moments about the midpoint between sphere centers. Contours are at intervals of $0.05 \text{ \AA} \cdot E$ from $-0.5 \text{ \AA} \cdot E$ to $+0.5 \text{ \AA} \cdot E$. Negative potentials are indicated by dashed contours. The spheres are drawn to scale at the left. The large circle in the lower left diagram shows the circumsphere of the system.

teristic of spherical harmonic functions.^{38,39}

(2) The total potential is fairly well approximated by the ϕ_1 term in the two-center expansion but not in the one-center expansion. This reflects the generally more rapid convergence of the multipole series as the number of expansion centers increases.

(3) The total potentials are nearly identical for the two expansions in the region outside the circumsphere of the system (shown by the large circle in the lower left diagram). Marked differences are seen in the region inside the circumsphere, due to the different convergence properties of the expansions in that region.

This example illustrates the relative merits of a few-center vs a many-center multipole expansion. The latter has the advantages of more rapid convergence and a larger region of convergence. The former offers a means of simplifying calculations for large assemblies, particularly when these are composed of recurring subassemblies whose multipole polarizabilities are readily determined. The ways in which these features affect the calculation of various properties are explored in the following sections.

X. DIPOLE POLARIZABILITIES OF MOLECULAR PAIRS

Frommhold⁹ has reviewed the extensive literature on studies of effects of molecular collisions on various properties which depend on the dipole polarizability, including the dielectric constant, the Kerr constant, and light scattering of gases. The collisional effects arise through the effects of intermolecular interactions on both the mean polarizability and the anisotropy of polarizability of the colliding pair. Frommhold concludes that a dipole interaction model is capable of accounting for the observed collisional effects on anisotropies of pairs such as He_2 , Ne_2 , Kr_2 , Xe_2 , and $(\text{CH}_4)_2$, though the model is not suitable for the collisional effects on the mean polarizability. (Hunt⁴⁰ has recently treated the complicating effects of overlap and exchange by means of a

nonlocal polarizability model.) It is relevant to such studies to ask whether higher order multipole interactions within a colliding pair influence the observed collisional effects on the dipole polarizability. We consider here three model systems whose pair polarizabilities can be calculated from the multipole interaction theory. No attempt will be made to calculate the statistical mechanical averages needed for a direct comparison with experimental data, but an indication of the importance of higher order multipole effects will be obtained from the dependence of pair polarizabilities at various intermolecular distances on the level of truncation of the multipole series.

Figure 4 shows the behavior of the simplest system, a pair of conducting spheres of radius 1.0 \AA whose centers are separated by a distance D . The quantities shown are the dipole polarizability components α_{\parallel} , parallel to the line through the sphere centers, and α_{\perp} , perpendicular to that line. (We adopt here a conventional notation for components of the $\mathbf{p}^{(1,1)}$ tensor for an axially symmetric system.) The calculations were carried out at truncation level L from 1–5, indicated by the numbers on the curves. The $L = 1$ calculation is equivalent to the use of the Silberstein⁴¹ equations for the dipole interaction theory of atom pair polarizabilities. It is seen that the higher order contributions are significant only near the contact distance $D = 2 \text{ \AA}$, and here they affect primarily α_{\parallel} . (At $D < 2 \text{ \AA}$ the multipole series is divergent, and the calculations are not physically significant.)

These observations are consistent with the conclusion that the dipole interaction model is reasonably valid for predicting anisotropies of rare gas atom pairs, considering that the higher order multipole effects in rare gas atoms are comparable to those in conducting spheres. Levine and McQuarrie⁴⁴ calculated the dipole polarizability of a pair of conducting spheres by a direct solution of Laplace's equation, and obtained series expressions whose asymptotic limits are easier to determine than that of the multipole series used here.

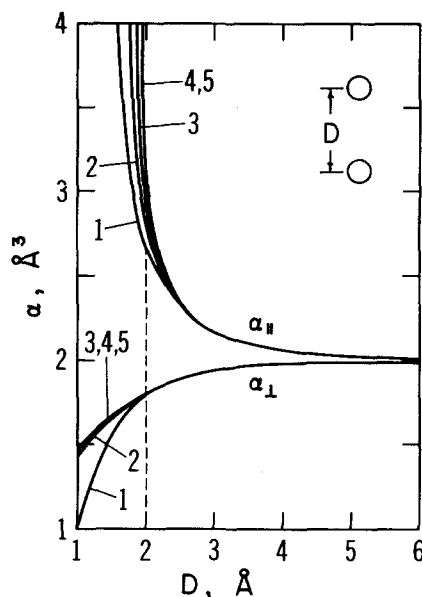


FIG. 4. Dipole polarizability of a pair of conducting spheres of radius 1.0 Å. Numbers on curves show the truncation level L . The vertical dashed line shows the contact distance.

Their numerical results are indistinguishable from the $L = 5$ curves in Fig. 4 through most of the range of D , showing that these curves are indeed near the asymptotic limit. A discrepancy is found in the steeply rising $\alpha_{||}$ curve at the contact distance, where the $(\alpha_{||}, \alpha_{\perp})$ values are $(4.808 \text{ Å}^3, 1.803 \text{ Å}^3)$ in Levine and McQuarrie's results and $(3.149 \text{ Å}^3, 1.803 \text{ Å}^3)$ in the $L = 5$ calculation; such a discrepancy is expected near this point, where the multipole series does not converge completely at $L = 5$.

Figure 4 shows that the effect of the higher order terms is to increase the anisotropy $\alpha_{||} - \alpha_{\perp}$ of a pair of spheres near the contact distance. The application of the dipole interaction model to polarizabilities of covalently bound diatomic molecules²⁰ has shown that the model tends to predict anisotropies which are too large when isotropic atoms are assumed. Evidently this deficiency of the model cannot be corrected solely by invoking higher order multipole polarizabilities. Birge⁴² and Thole⁴³ have proposed modifications of the model which overcome this deficiency.

To take a somewhat more complex system we consider next a pair of diatomic molecules, each of which is a pair of conducting spheres of radius 1.0 Å separated by a distance of 2.2 Å (identical to the system in Fig. 3). Figure 5 shows the principal polarizability components of this system when the axes of the molecules are collinear. The circles show the results of a four-center calculation at truncation level $L = 5$, the most accurate calculation carried out for this system. The solid curves show two-center calculations at the truncation levels indicated. For these cases the units were chosen as the two diatomic molecules, and their polarizability polytensors about the molecular centers were generated from those of spheres by a multipole interaction calculation truncated at $L = 5$. The curves show that the higher order effects are quite significant in the two-center calculation at separations below about 7 Å. At $L = 5$ the curves approximate the four-center results fairly well, indicating that the two-center expansion does converge satisfactorily. Again, the multipole

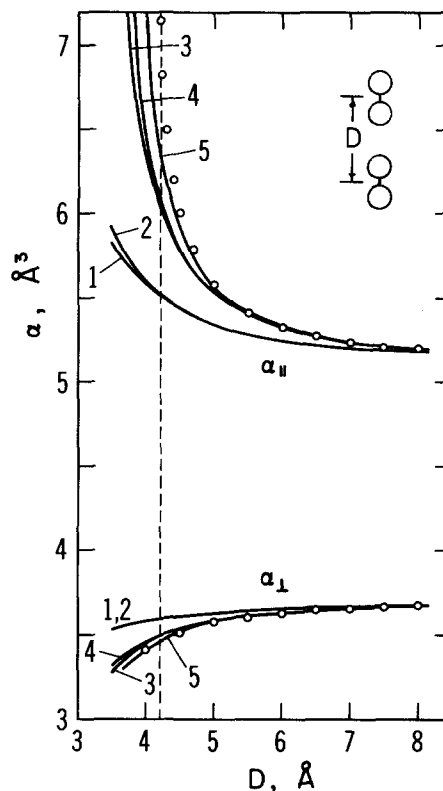


FIG. 5. Dipole polarizability of a pair of diatomic molecules composed of pairs of conducting spheres. (O) Four-center calculations at truncation level $L = 5$. (—) Two-center calculations at truncation levels indicated on curves. The vertical dashed line shows the contact distance.

series diverges below the contact distance of 4.2 Å, and the calculations in that region are not physically significant. Collisional effects on polarizabilities of anisotropic molecules are difficult to treat because of the configurational averaging problem, but from this example it would be expected that a two-center multipole interaction treatment would require terms at least through the octupole ($L = 3$) to obtain reasonable accuracy for diatomic molecules. Lallemand's study⁴⁵ of collisional anisotropy in H_2 suggested that a dipole interaction treatment is suitable for this system, though this was based on the theory for isotropic molecules.

The third system we consider is $(\text{CH}_4)_2$. The purpose is, again, to learn something of the accuracy of the two-center multipole interaction theory at various levels of truncation. To do this we take as the "accurate" model of the system the ten-center atom dipole interaction model, in which each atom is represented by an isotropic point particle having only a dipole polarizability. For the two-center calculations we then use CH_4 polarizability polytensors calculated by a five-center atom dipole interaction model, using Eq. (38) with truncation level $L = 1$. The atom polarizabilities used are the semiempirical values obtained previously:²⁰ 0.135 Å^3 for H and 0.878 Å^3 for C. The molecular structure is regular tetrahedral with C-H bond length 1.095 Å. The circumsphere radius of CH_4 is equal to the C-H bond length for the point-atom model, so the two-center multipole series diverges at separations less than the contact distance, 2.19 Å. Figure 6 shows the results for the configuration in which the second molecule is related to the first by a displacement along a twofold axis. Truncation of the two-center calcula-

tion at $L = 1$ is seen to be accurate only at distances greater than about 5 Å. At shorter distances the two-center calculations at $L = 3$ appear to have converged fairly well to the accurate values, though the $L = 4$ results show some tendency toward oscillation of convergence. It is worth noting that the two-center calculations at $L = 1$ give an anisotropy which is larger than the more accurate results for this system, contrary to the behavior in the two preceding examples. A similar calculation for a configuration of $(\text{CH}_4)_2$ in which the relative displacement is along a threefold axis (not shown) showed the opposite behavior, in which the anisotropy is too small for the $L = 1$ two-center calculation. Thus one might expect some mutual cancellation of these errors in a full averaging over pair configurations.

Buckingham and Hunt⁴⁶ carried out related calculations for a pair of SF_6 molecules, comparing results for 14-center and two-center dipole interaction calculations at separations of molecular centers down to four S-F bond lengths. They found little difference in anisotropies by the two treatments. The results for the CH_4 pair in Fig. 6 are similar in that the ten-center and two-center results differ primarily at distances less than four C-H bond lengths (4.38 Å).

XI. ION-ATOM INDUCTION ENERGIES

We consider here a simple example of the electrostatic energy problem treated in Sec. III, namely, the energy of a pair of conducting spheres, one of which bears a fixed net charge. This system serves as a model for simple ion-atom pairs, and the electrostatic energy given by Eq. (29) is what is usually called the induction energy of the system.⁴⁷ The total potential energy is usually treated as the sum of the induction energy, the dispersion energy, and the short-range repulsion energy. Only the first of these terms is given by clas-

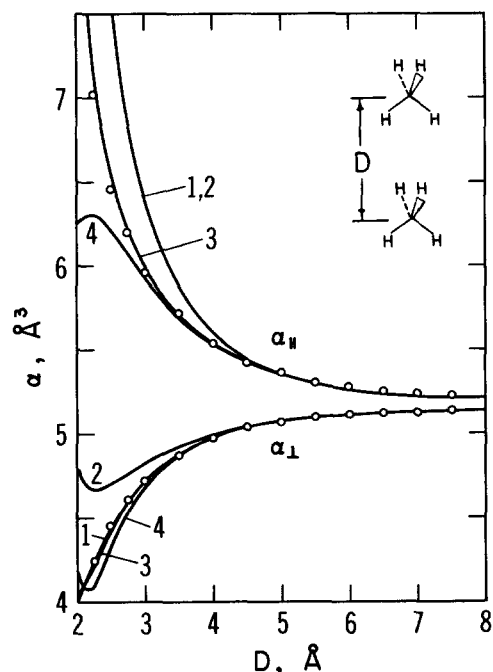


FIG. 6. Dipole polarizability of $(\text{CH}_4)_2$. (O) Ten-center calculations for atom dipole interaction model. (—) Two-center calculations at truncation levels indicated on curves.

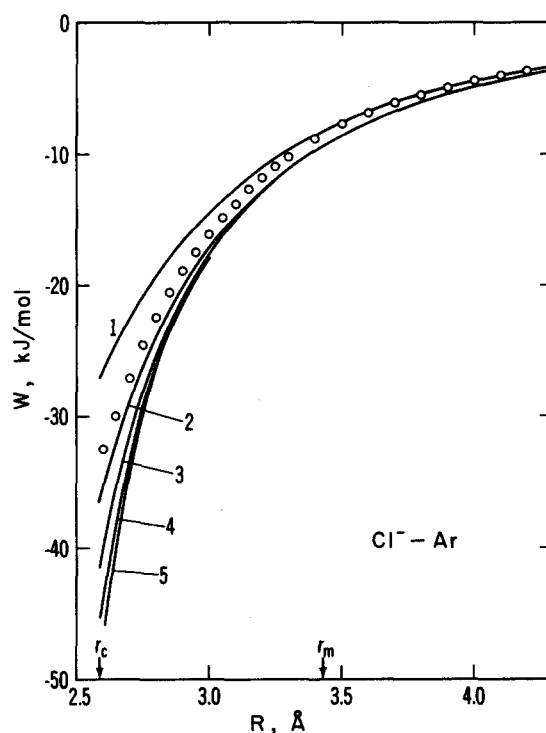


FIG. 7. Induction energy of the Cl^- -Ar pair vs internuclear distance. (O) Kim and Gordon's (Ref. 47) calculations. (—) Present theory for conducting sphere model at truncation levels indicated on curves. Arrows indicate the contact distance r_c and the distance of minimum potential energy r_m .

sical physics, and we confine attention here to that term.

Kim and Gordon⁴⁷ have treated interatomic potentials in a manner that considers each of the terms individually, and we use their induction energies for the K^+ -Ar and Cl^- -Ar systems to compare with the multipole interaction theory for pairs of conducting spheres. Their Coulombic energy included charge-dipole, charge-quadrupole, and dipole-dipole terms. The sphere radius a for each atom is chosen so that the dipole polarizability a^3 is equal to the polarizabilities used by Kim and Gordon, namely, 1.640 Å^3 for Ar, 1.201 Å^3 for K^+ , and 2.794 Å^3 for Cl^- .

Figure 7 shows the energy W as a function of the internuclear distance R for the Cl^- -Ar pair, using Eq. (29) at the truncation levels indicated on the curves. Figure 8 shows similar results for the K^+ -Ar pair. The circles show Kim and Gordon's induction energies for these systems. Their results are close to the $L = 1$ curves for conducting spheres at large distances because the charge-dipole energy is dominant in both calculations at such distances. Kim and Gordon attribute the deviation of their curves from the charge-dipole curves to a term which is the change in repulsive energy when the centers of the electron shells are displaced from the nuclear positions to their equilibrium positions at a particular internuclear distance. The sign of this term depends on the sign of the charged species, as seen in Figs. 7 and 8. No such term can occur in the present theory because Eq. (29) is quadratic in the charge. However, significant new terms do occur in the present theory at short range. It is apparent from Figs. 7 and 8 that induced multipole moments through the fifth order significantly lower the short range induction energy. The higher multipole effects are important primarily at

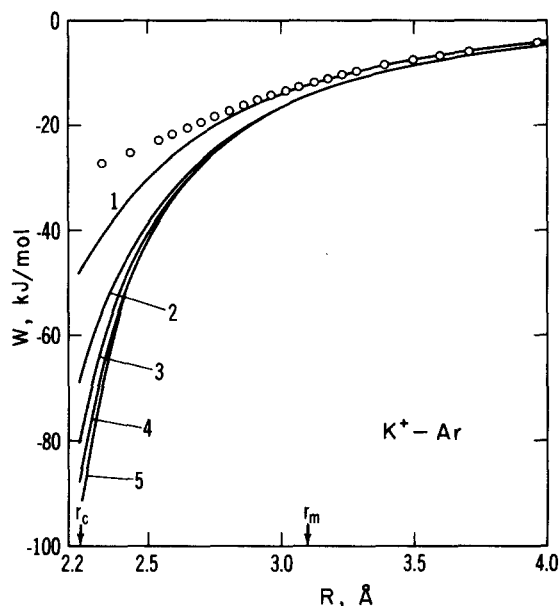


FIG. 8. Induction energy of the K^+-Ar pair vs internuclear distance. (○) Kim and Gordon's (Ref. 47) calculations. (—) Present theory for conducting sphere model at truncation levels indicated on curves. Arrows indicate the contact distance r_c and the distance of minimum potential energy r_m .

distances less than r_m , the position of Kim and Gordon's potential energy minimum, which is the same region in which their repulsive energy contribution to the induction energy is significant. Since the higher multipole polarizabilities of atoms are comparable to those of conducting spheres, one can expect the effects noted here to be present in real systems.

XII. OPTICAL ROTATIONS OF CHIRAL ASSEMBLIES

Some striking demonstrations of the importance of higher order multipole interactions are found in the optical rotations of a variety of simple chiral systems. The intrinsic molar rotation $[m]$ of an isotropic distribution of identical assemblies given is calculated by²⁵

$$[m] = 288\pi^2 N_A \beta / \lambda^2, \quad (67)$$

where N_A is Avogadro's number and λ is the wavelength of the light. Equations (55) and (56) are used to obtain β . The wavelength is chosen as the Na D line, 5893 Å, giving the rotation $[m]_D$.

Figure 9 shows the rotation of a system of four conducting spheres of radius 1.0 Å, placed in a chiral fashion at the corners of an imaginary cube of edge d . The curves represent four-center calculations at the truncation levels shown. It is seen that interactions above the dipole level ($L = 1$) are of major importance throughout the range of d shown. However, the multipole series appears to converge rapidly over most of the range, so that the $L = 2$ level is a fairly good approximation.

Figure 10 shows the rotation of an assembly consisting of a rigid pair of the chiral sphere assemblies of Fig. 9 with $d = 2.2$ Å. The second group is related to the first by a translation D parallel to a cube edge and a 45° rotation about that edge, as shown. This system represents a molecule containing two identical chiral chromophores in a chiral configuration. The curves in Fig. 10 represent eight-center calculations at the truncation levels shown on the curves. The vertical dashed line shows the contact distance.

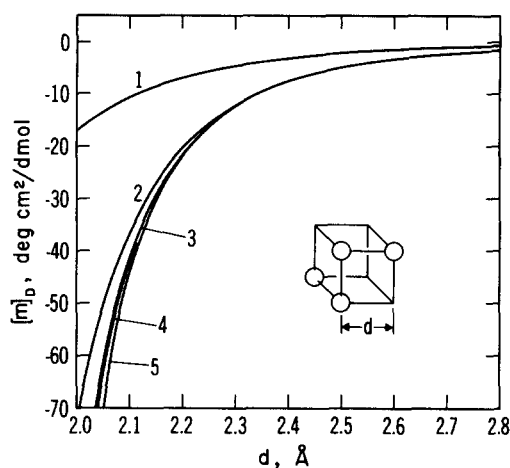


FIG. 9. Optical rotation of a system of four conducting spheres of radius 1.0 Å centered at the corners of a cube as shown. Truncation levels are indicated on curves.

tions of rotation as a function of the translation distance at the truncation levels shown. Again, the interactions above the $L = 1$ level are of major importance, and again the multipole series is rapidly convergent at distances greater than the contact distance of 4.2 Å.

Figure 11 shows two-center calculations for the same system as in Fig. 10. For this purpose the polarizability polytensor of the four-sphere group about the cube center was obtained by a four-center calculation truncated at $L = 5$. The circumsphere of the unit has radius 2.91 Å, and the multipole series diverges below the contact translation distance 5.69 Å. (This is somewhat less than twice the circumsphere radius because the translation is not along the line of centers.) As expected, the multipole series converges much more slowly for the two-center than for the eight-center calculations, though there appears to be satisfactory convergence at $L = 5$ when D is beyond the contact distance. (This conclusion is uncertain because the convergence is oscillatory.) The small magnitude of the $L = 1$ rotations in Fig. 11 is notable. This comes about because the $B_{ij}^{(1,2)}$ terms of Eq.

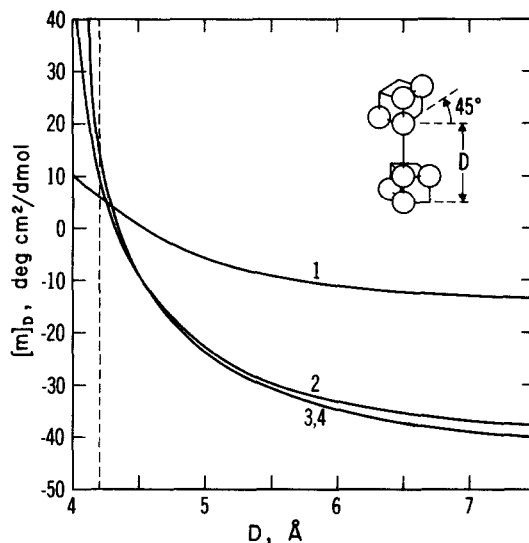


FIG. 10. Optical rotation of a pair of chiral sphere assemblies from eight-center calculations at the truncation levels shown on the curves. The vertical dashed line shows the contact distance.

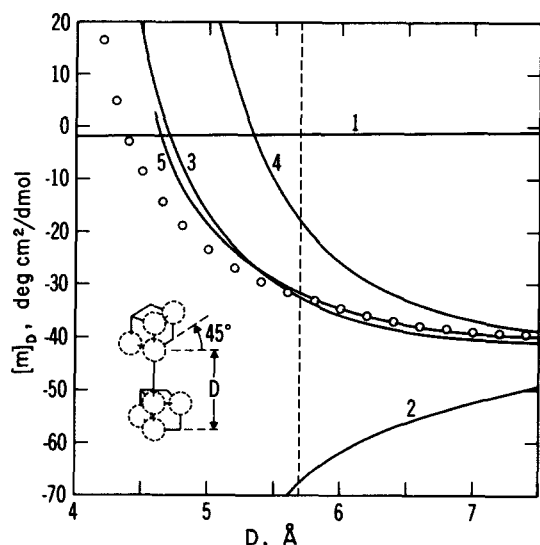


FIG. 11. Optical rotation of the same pair of chiral sphere assemblies as in Fig. 10, using two-center calculations at the truncation levels shown on the curves. (○) Eight-center calculations at $L = 4$ from Fig. 10. The vertical dashed line shows the contact distance of the circumspheres.

(56) are omitted at $L = 1$, thus omitting the intrinsic optical activity of the units. For $L \geq 2$ the rotation at large distances approaches that due solely to the internal rotatory parameters of the units (cf. Sec. VI).

A final example is the system composed of a pair of molecules of the optically active haloform CHFCIBr . The optical rotation of the monomer from the atom dipole interaction theory has been discussed previously.^{1,25} The dimer is a system which is more closely related to real molecules than the sphere assemblies discussed above and serves to compare some practical approximations to the treatment of interactions among inherently chiral chromophores.

Figure 12 shows the calculated rotations of $(\text{CHFCIBr})_2$ in a configuration in which the second molecule is related to the first by a translation through distance D parallel to the C-Br bond. The structure of the monomer is based on regular tetrahedral bond angles and bond lengths²⁵ C-H 1.073 Å, C-F 1.41 Å, C-Cl 1.73 Å, and C-Br 1.93 Å. The circles in Fig. 12 show a 10-center atom dipole interaction calculation, using the semiempirical isotropic atom polarizabilities²⁰ C 0.878 Å³, H 0.135 Å³, F 0.32 Å³, Cl 1.91 Å³, and Br 2.88 Å³. The solid curves show two-center calculations at the truncation levels indicated. (The $L = 1$ two-center rotation vanishes because it omits the inherent chirality of the units and has no other source of chirality.) The polarizability polytensor of CHFCIBr needed for the two-center calculations was obtained by a five-center atom dipole interaction treatment. The origin of the unit was chosen as the center of the sphere which circumscribes the H, F, Cl, and Br nuclei. This is the circumsphere of the point-atom model, having a radius of 1.61 Å. Thus the contact distance is $D = 3.22$ Å, below which the multipole series diverges for the two-center treatment.

Figure 12 shows once again that a two-center calculation requires a number of higher order terms to approximate the accurate ten-center results. The multipole series converges in an oscillatory manner at any given distance above

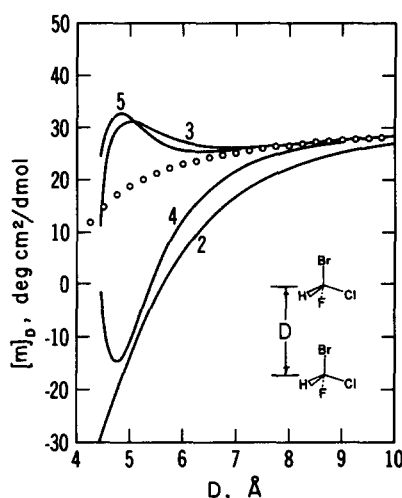


FIG. 12. Optical rotation of $(\text{CHFCIBr})_2$. (○) Ten-center calculations for atom dipole interaction model. (—) Two-center calculations at truncation levels indicated on curves.

5 Å; below that distance convergence is possible, but not clearly evident at the truncation levels shown. The danger in neglecting higher order terms is emphasized by the fact that the incorrect sign of rotation is obtained even at $L = 4$ at short distances.

XIII. CONCLUSIONS

The numerical examples discussed here lead to the following conclusions regarding the treatment of higher-order multipole interactions in the electric polarization of molecular assemblies.

(1) Higher-order multipole interactions are usually significant when interunit distances are comparable to the dimensions of the units. Near the contact distance, terms through at least the fifth-order multipole are significant.

(2) From the standpoint of convergence, a many-center treatment of a given system is preferable to a few-center treatment. This is often true also from the standpoint of computational effort. For example, the ten-center calculations for $(\text{CHFCIBr})_2$ at $L = 1$ required 104 K bytes of storage and 0.5 s of CPU time for each structure, while the two-center calculations at $L = 5$ required 756 K bytes and 11 s per structure. A choice between such extremes may not always be possible, however, since the assignment of units in a given system will depend on the nature of the polarizability data available.

(3) The acquisition of realistic higher-order multipole polarizabilities of atoms and polyatomic units for use in multipole interaction calculations appears to be within reach. The point-atom and conducting sphere models used here illustrate two possible approaches. Such approaches may prove useful in the treatment of large assemblies where the assignment of a polarizability center to each atom is less practical than the subdivision of the assembly into a number of readily characterized polyatomic units.

APPENDIX A: PROPERTIES OF THE POLARIZABILITY POLYTENSOR

Consider a body having polarizability polytensor \mathbf{P} and permanent multipole moment polytensor \mathbf{M}_0 in a static

(polytensor) field \mathbf{E} . The total electrostatic energy of the body is¹⁷

$$W = -\mathbf{M}_0 \cdot \mathbf{E} - \frac{1}{2} \mathbf{P} : \mathbf{E} \mathbf{E}. \quad (\text{A1})$$

The second term on the right is the change in energy due to polarization of the body. Since the polarization is a spontaneous process, this term must be negative. Hence \mathbf{P} is positive definite; i.e., $\mathbf{P} : \mathbf{E} \mathbf{E}$, which is equivalent to the matrix product $\mathbf{E}^T \mathbf{P} \mathbf{E}$, is positive for any matrix \mathbf{E} . This conclusion does not depend on \mathbf{M}_0 , and for the following we assume $\mathbf{M}_0 = 0$.

We now seek to represent \mathbf{P} by a quadratic hypersurface analogous to the polarizability ellipsoid of the dipole polarizability.⁴⁸ \mathbf{P} is a singular matrix because it is composed of tensors which contain a number of sets of identical rows and columns.¹⁶ The compressed form $\bar{\mathbf{P}}$ (Appendix C) is obtained by deleting the redundant rows and columns, and is therefore nonsingular. The compressed multipole moment polytensor is given by

$$\bar{\mathbf{M}} = \bar{\mathbf{P}} \mathbf{g} \bar{\mathbf{E}}, \quad (\text{A2})$$

where \mathbf{g} is the diagonal matrix whose elements are given by Eq. (35) in the canonical order of the elements of compressed polytensors. Let $\bar{\mathbf{E}}$ be constrained to satisfy the "normalization" condition

$$\bar{\mathbf{E}}^T \mathbf{g} \bar{\mathbf{E}} = 1. \quad (\text{A3})$$

Since $\bar{\mathbf{P}}$ is nonsingular, we can write $\mathbf{g} \bar{\mathbf{E}} = \bar{\mathbf{P}}^{-1} \bar{\mathbf{M}}$ from Eq. (A2). Then Eq. (A3) becomes

$$\bar{\mathbf{M}}^T (\bar{\mathbf{P}}^{-1})^2 \bar{\mathbf{M}} = 1, \quad (\text{A4})$$

making use of the fact that $\bar{\mathbf{P}}$ and its inverse are symmetric. Equation (A4) is a quadratic form expressing the locus of all multipole moment components which satisfy the normalized field, Eq. (A3); it represents a hyperellipsoid in the infinite-dimensional space of polytensor components. Equation (A4) reduces to the familiar three-dimensional polarizability ellipsoid when $\bar{\mathbf{M}}$ contains only $\mu^{(1)}$ and $\bar{\mathbf{P}}$ contains only $\mathbf{p}^{(1,1)}$.

Since $\bar{\mathbf{P}}$ is symmetric, there exists an orthogonal matrix \mathbf{K} which transforms $\bar{\mathbf{P}}$ to a diagonal matrix \mathbf{D} by the relation

$$\mathbf{K}^T \bar{\mathbf{P}} \mathbf{K} = \mathbf{D}. \quad (\text{A5})$$

The diagonal elements of \mathbf{D} are the eigenvalues of $\bar{\mathbf{P}}$, and the columns of \mathbf{K} are the corresponding eigenvectors.⁴⁹ Solving Eq. (A5) for $\bar{\mathbf{P}}^{-1}$, we obtain from Eq. (A4),

$$\bar{\mathbf{M}}^T \mathbf{K} (\mathbf{D}^{-1})^2 \mathbf{K}^T \bar{\mathbf{M}} = 1. \quad (\text{A6})$$

Equation (A6) represents the hyperellipsoid in a coordinate system whose axes are given by the eigenvectors (the "principal axes"). When $\bar{\mathbf{E}}$ is parallel to a principal axis, $\bar{\mathbf{M}}$ is parallel to the same axis, and the polarizability, a scalar, is given by the corresponding eigenvalue. Since \mathbf{P} (and hence $\bar{\mathbf{P}}$) is positive definite, the eigenvalues are all positive.

APPENDIX B: FORMULATION WITH FIXED NET CHARGE OF SYSTEM

The calculation of relay polytensors by Eq. (19) when zero-rank tensors are included assumes there is no constraint on the net charges of the units or the system as a whole. A more useful model for isolated systems is that in which the net charge of the system is constant, but in which exchange

of charge among units is permitted. The following treatment of this model is similar in principle to that of Olson and Sundberg² for a classical monopole-dipole interaction model.

Let

$$\mathbf{u} = \begin{bmatrix} 1 \\ 0 \\ 0 \\ \vdots \end{bmatrix}, \quad (\text{B1})$$

a column vector which is truncated at the same level as the multipole polytensors. Let

$$\mathcal{U} = \begin{bmatrix} \mathbf{u} \\ \vdots \\ \mathbf{u} \end{bmatrix}, \quad (\text{B2})$$

where \mathbf{u} is repeated N times. The constancy of the net charge of the system is expressed by

$$\mathcal{U}^T \mathcal{M} = \mathcal{U}^T \mathcal{M}_{00}, \quad (\text{B3})$$

since either side of the equation is the net charge. Equation (B3) constitutes an additional relation among multipole moments. An additional variable is supplied to complete the system of equations by allowing the potential at all points to be varied by an arbitrary additive constant λ . Equation (17) then becomes

$$\mathcal{M} = \mathcal{M}_{00} + \mathcal{P}(\mathcal{E} - \mathcal{T} \mathcal{M} - \lambda \mathcal{U}). \quad (\text{B4})$$

Let

$$\mathcal{C} = \begin{bmatrix} \mathcal{T} + \mathcal{P} \mathcal{T} & \mathcal{P} \mathcal{U} \\ \mathcal{U}^T & 0 \end{bmatrix}, \quad (\text{B5})$$

$$\mathcal{M}' = \begin{bmatrix} \mathcal{M} \\ \lambda \end{bmatrix}, \quad (\text{B6})$$

$$\mathcal{M}'_{00} = \begin{bmatrix} \mathcal{M}_{00} \\ 0 \end{bmatrix}, \quad (\text{B7})$$

$$\mathcal{P}' = \begin{bmatrix} \mathcal{P} & 0 \\ 0 & 1 \end{bmatrix}, \quad (\text{B8})$$

$$\mathcal{E}' = \begin{bmatrix} \mathcal{E} - \mathcal{T} \mathcal{M}_{00} \\ 0 \end{bmatrix}. \quad (\text{B9})$$

Then Eqs. (B3) and (B4) are combined in the equation

$$\mathcal{C}(\mathcal{M}' - \mathcal{M}'_{00}) = \mathcal{P}' \mathcal{E}'. \quad (\text{B10})$$

Solving for \mathcal{M}' ,

$$\mathcal{M}' = \mathcal{M}'_{00} + \mathcal{B}' \mathcal{E}', \quad (\text{B11})$$

where

$$\mathcal{B}' = \mathcal{C}^{-1} \mathcal{P}'. \quad (\text{B12})$$

From the form of the matrices in Eq. (B11) it is seen that the submatrix of \mathcal{B}' which excludes the last row and last column plays the same role in calculating the system properties as \mathcal{B} given by Eq. (19) for the unconstrained case.

APPENDIX C: COMPRESSION OF POLYTENSOR MATRICES

In the static field case, the matrices \mathcal{M} , \mathcal{P} , \mathcal{E} , and \mathcal{T} are all composed of tensors which are totally symmetric in the component indices corresponding to each rank index. Elimination of the redundant components produces the

compressed matrices denoted by an overbar (e.g., $\bar{\mathcal{M}}, \bar{\mathcal{P}}$, etc.). The tensor contractions generated by a product such as $\mathcal{P}\mathcal{E}$ are found by the equivalent product $\bar{\mathcal{P}}\mathcal{G}\bar{\mathcal{E}}$, where \mathcal{G} is the diagonal matrix composed of N identical to \mathbf{g} matrices [Eq. (A2)] on the diagonal.¹⁶ Thus Eq. (17) takes the compressed form

$$\bar{\mathcal{M}} = \bar{\mathcal{M}}_{00} + \bar{\mathcal{P}}\mathcal{G}(\bar{\mathcal{E}} - \bar{\mathcal{T}}\mathcal{G}\bar{\mathcal{M}}). \quad (\text{C1})$$

This may be solved in the form

$$\bar{\mathcal{M}} = \bar{\mathcal{M}}_{00} + \bar{\mathcal{B}}\mathcal{G}(\bar{\mathcal{E}} - \bar{\mathcal{T}}\mathcal{G}\bar{\mathcal{M}}_{00}), \quad (\text{C2})$$

where

$$\bar{\mathcal{B}} = (\mathcal{I} + \bar{\mathcal{P}}\mathcal{G}\bar{\mathcal{T}}\mathcal{G})^{-1}\bar{\mathcal{P}}, \quad (\text{C3})$$

or, equivalently,

$$\bar{\mathcal{B}} = (\bar{\mathcal{P}}^{-1} + \mathcal{G}\bar{\mathcal{T}}\mathcal{G})^{-1}. \quad (\text{C4})$$

Equation (C3) is equivalent to Eq. (19). Equation (C4) provides an alternative algorithm which is possible for compressed matrices because $\bar{\mathcal{P}}$ is nonsingular (see Appendix A). Equation (C4) is similar to the form that has been used in the dipole interaction theory,²⁰ where compression has no effect.

The order of the complete matrices \mathcal{P} , \mathcal{T} , and \mathcal{B} is $N(3^{L+1} - 1)/2$ for truncation at rank L . The compressed matrices are of order $N(L+1)(L+2)(L+3)/6$, which is a substantial reduction in matrix size for $L > 1$.

As noted in Sec. V, the field and polarizability tensors for time-dependent fields are in general semisymmetric, and cannot be reduced to the same extent as symmetric tensors. "Semicompressed" forms of semisymmetric tensors, polytensors, and polytensor matrices are obtained from the complete forms by deletion of redundant components, and are denoted by a superior tilde. In particular, $\tilde{\mathcal{P}}_{\alpha_1 \dots \alpha_n \beta_m \dots \beta_l}^{(n,m)}$ is represented by a rectangular matrix whose rows are indexed by the compressed array of index sets $\alpha_1 \dots \alpha_n$ in canonical order and whose columns are indexed by the semicompressed array of index sets $\beta_m \dots \beta_l$ in canonical order. For the case $n = m = 3$, the compressed canonical array of $\alpha_1 \alpha_2 \alpha_3$ is 111, 211, 311, 221, 321, 331, 222, 322, 332, 333; the semicompressed canonical array of $\beta_2 \beta_3 \beta_1$ is 111, 211, 311, 121, 221, 321, 131, 231, 331, 122, 222, 322, 132, 232, 332, 133, 233, 333. The $\tilde{\mathcal{P}}^{(n,m)}$ matrix has $(n+1)(n+2)/2$ rows and $3m(m+1)/2$ columns. The corresponding polytensor $\tilde{\mathcal{P}}$, when truncated at rank L , has dimensions $(L+1)(L+2)(L+3)/6$ by $L(L+1)(L+2)/2 + 1$.

In order to calculate the product $\mathcal{P}\mathcal{T}$ in Eq. (19) in semicompressed form, we require matrices $\tilde{\mathcal{T}}_{ij, \beta_1 \dots \beta_m \alpha_1 \dots \alpha_n}^{(m,n)}$ in which rows are indexed by the semicompressed array $\beta_1 \dots \beta_m$ and columns by the compressed array $\alpha_1 \dots \alpha_n$. Since $\mathbf{T}_{ij}^{(m,n)}$ is totally symmetric in both index sets by the approximation adopted here for time-dependent fields, the canonical and anticanonical orders of the arrays are identical. $\mathbf{E}^{(n)}$ is not totally symmetric, however, and the rows of \mathcal{E} in equations corresponding to Eqs. (17) and (18) must be in anticanonical order.

To express a tensor contraction such as $\mathbf{p}_i^{(n,k)} \cdot \mathbf{k} \cdot \mathbf{T}_{ij}^{(k,m)}$ in semicompressed form, we define a diagonal matrix $\mathbf{h}^{(k)}$ whose diagonal elements are

$$h(\beta_k \dots \beta_1) \equiv g(\beta_1 \dots \beta_{k-1}), \quad (\text{C5})$$

in semicompressed canonical order of the sets $\beta_k \dots \beta_1$. By the same argument as in the case of compressed tensors,¹⁶ the desired contraction is given by the matrix product $\tilde{\mathcal{P}}_i^{(n,k)} \mathbf{h}^{(k)} \tilde{\mathcal{T}}_{ij}^{(k,m)}$. The semicompressed form of the polytensor contraction $\mathbf{P}_i \cdot \mathbf{T}_{ij}$ is $\tilde{\mathcal{P}}_i \mathbf{h} \tilde{\mathcal{T}}_{ij}$, where \mathbf{h} is the diagonal matrix whose diagonal blocks are $\mathbf{h}^{(1)}, \mathbf{h}^{(2)}, \dots$. The semicompressed form of $\mathcal{P}\mathcal{T}$ is $\tilde{\mathcal{P}}\mathcal{H}\tilde{\mathcal{T}}$, where \mathcal{H} is the diagonal matrix whose diagonal blocks are \mathbf{h} repeated N times.

In semicompressed form Eq. (17) becomes

$$\bar{\mathcal{M}} = \bar{\mathcal{M}}_{00} + \tilde{\mathcal{P}}\mathcal{H}(\bar{\mathcal{E}} - \bar{\mathcal{T}}\mathcal{G}\bar{\mathcal{M}}). \quad (\text{C6})$$

This may be solved in the form

$$\bar{\mathcal{M}} = \bar{\mathcal{M}}_{00} + \tilde{\mathcal{B}}\mathcal{H}(\bar{\mathcal{E}} - \bar{\mathcal{T}}\mathcal{G}\bar{\mathcal{M}}_{00}), \quad (\text{C7})$$

where

$$\tilde{\mathcal{B}} = (\mathcal{I} + \tilde{\mathcal{P}}\mathcal{H}\bar{\mathcal{T}}\mathcal{G})^{-1}\tilde{\mathcal{P}}. \quad (\text{C8})$$

Thus $\tilde{\mathcal{B}}$ is a rectangular matrix of the same dimensions as $\bar{\mathcal{P}}$, and has all the information necessary to construct the semisymmetric system polarizabilities according to Eq. (54).

APPENDIX D: ROTATIONAL TRANSFORMATION OF POLYTENSORS

Let S and S' be Cartesian coordinate systems which are rotated with respect to each other, and let $\lambda_{\alpha\beta}$ be the direction cosine of axis α in system S' with respect to axis β in system S . As shown elsewhere,¹⁶ the matrix which transforms an n th rank tensor in complete form from S to S' is

$$\Lambda_{\alpha_1 \dots \alpha_n \beta_1 \dots \beta_n}^{(n)} = \lambda_{\alpha_1 \beta_1} \dots \lambda_{\alpha_n \beta_n}, \quad (\text{D1})$$

where the row indices $\alpha_1 \dots \alpha_n$ and column indices $\beta_1 \dots \beta_n$ span the complete arrays in canonical order. The transformation matrix for a compressed n th rank tensor is¹⁶

$$\Gamma_{\alpha_1 \dots \alpha_n \beta_1 \dots \beta_n}^{(n)} = \sum_{N\{\beta'\}} \Lambda_{\alpha_1 \dots \alpha_n \beta_1 \dots \beta_n}^{(n)}, \quad (\text{D2})$$

where the row indices $\alpha_1 \dots \alpha_n$ and column indices $\beta_1 \dots \beta_n$ span the compressed arrays in canonical order. By similar methods it may be shown that the transformation matrix for a semicompressed n th rank tensor is

$$\Delta_{\alpha_1 \dots \alpha_n \beta_1 \dots \beta_n}^{(n)} = \sum_{N\{\beta'\}} \Lambda_{\alpha_1 \dots \alpha_n \beta_1 \dots \beta_n}^{(n)}, \quad (\text{D3})$$

where the row indices $\alpha_1 \dots \alpha_n$ and column indices $\beta_1 \dots \beta_n$ span the semicompressed arrays in canonical order (cf. Appendix C), and the sum over $N\{\beta'\}$ is the sum over all permutations of the set $\beta_2 \dots \beta_n$ when their numerical values are specified. (The indices $\beta_2 \dots \beta_n$ are those in which the tensor is symmetric.)

Let Λ be a block diagonal matrix whose diagonal blocks are $\mathbf{1}, \Lambda^{(1)}, \Lambda^{(2)}, \dots$, and let matrices Γ and Δ be similarly formed from the blocks $\Gamma^{(n)}$ and $\Delta^{(n)}$, respectively. The transformation of a polarizability polytensor \mathbf{P} in complete form is given by¹⁶

$$\mathbf{P}' = \Lambda \mathbf{P} \Lambda^T, \quad (\text{D4})$$

where the prime denotes the polytensor in system S' . The transformations of the compressed and semicompressed forms are given by¹⁶

$$\bar{\mathbf{P}}' = \Gamma \bar{\mathbf{P}} \Gamma^T, \quad (\text{D5})$$

$$\tilde{\mathbf{P}}' = \Gamma \tilde{\mathbf{P}} \Delta^T. \quad (\text{D6})$$

Equation (D6) follows from the fact that $\tilde{\mathbf{P}}$ is compressed in its rows and semicompressed in its columns.

A property of Δ worth noting is that its inverse is

$$\Delta^{-1} = \mathbf{h}^{-1} \Delta \mathbf{h}. \quad (\text{D7})$$

An important consequence is that a relation such as $\mathbf{M} = \mathbf{P} \mathbf{h} \mathbf{E}$ is transformed to $\bar{\mathbf{M}}' = \tilde{\mathbf{P}} \mathbf{h} \mathbf{E}'$. The proof of these statements is similar to that for the analogous results involving compressed polytensors.¹⁶

APPENDIX E: SYMMETRY OF THE \mathcal{B} MATRIX

We consider here the symmetries that can be derived for the \mathcal{B} matrix given by Eq. (19), examining first the invariance of the matrix under certain interchanges among rows or columns. \mathcal{P} and \mathcal{T} are made up of tensors which are symmetric with respect to certain permutations of component indices, and are hence invariant under interchange of any two rows or any two columns corresponding to component index sets which are such permutations of each other. Let \mathcal{X} be a matrix which interchanges two rows as a prefactor of another matrix or two columns as a postfactor. Let the pairs so interchanged be permutable in \mathcal{P} and \mathcal{T} , in the sense that $\mathcal{X}\mathcal{P} = \mathcal{P}$ and $\mathcal{T}\mathcal{X} = \mathcal{T}$. \mathcal{X} is its own inverse because $\mathcal{X}\mathcal{X} = \mathcal{I}$. Hence,

$$\begin{aligned} \mathcal{X}(\mathcal{I} + \mathcal{P}\mathcal{T})\mathcal{X} &= \mathcal{X}\mathcal{I}\mathcal{X} + \mathcal{X}\mathcal{P}\mathcal{T}\mathcal{X} \\ &= \mathcal{I} + \mathcal{P}\mathcal{T}. \end{aligned} \quad (\text{E1})$$

Therefore,

$$\begin{aligned} [\mathcal{X}(\mathcal{I} + \mathcal{P}\mathcal{T})\mathcal{X}]^{-1} &= \mathcal{X}(\mathcal{I} + \mathcal{P}\mathcal{T})^{-1}\mathcal{X} \\ &= (\mathcal{I} + \mathcal{P}\mathcal{T})^{-1}. \end{aligned} \quad (\text{E2})$$

Consequently,

$$\begin{aligned} \mathcal{X}\mathcal{B} &= \mathcal{X}(\mathcal{I} + \mathcal{P}\mathcal{T})^{-1}\mathcal{P} \\ &= \mathcal{X}(\mathcal{I} + \mathcal{P}\mathcal{T})^{-1}\mathcal{X}\mathcal{X}\mathcal{P} \\ &= (\mathcal{I} + \mathcal{P}\mathcal{T})^{-1}\mathcal{P} = \mathcal{B}. \end{aligned} \quad (\text{E3})$$

If, on the other hand, \mathcal{X} is such that $\mathcal{P}\mathcal{X} = \mathcal{P}$, then

$$\mathcal{B}\mathcal{X} = (\mathcal{I} + \mathcal{P}\mathcal{T})^{-1}\mathcal{P}\mathcal{X} = (\mathcal{I} + \mathcal{P}\mathcal{T})^{-1}\mathcal{P} = \mathcal{B}. \quad (\text{E4})$$

Thus \mathcal{B} is invariant under the same row and column interchanges as \mathcal{P} . For the static field case, this means that $B_{ij, \alpha_1 \dots \alpha_n \beta_m \dots \beta_l}^{(n,m)}$ is invariant under any permutation of the set $\alpha_1 \dots \alpha_n$ or of the set $\beta_1 \dots \beta_m$ (total symmetry). For the time-dependent field case, that tensor is invariant under any permutation of the set $\alpha_1 \dots \alpha_n$ or of the set $\beta_1 \dots \beta_{m-1}$ (semisymmetry).

We consider next the symmetry of \mathcal{B} with respect to transposition of rows and columns. In a static field \mathcal{P} is symmetric because \mathbf{P}_i is symmetric (see Sec. II). \mathcal{T} is symmetric because $\mathbf{T}_{ij}^{(n,m)} = \mathbf{T}_{ji}^{(n,m)T}$, as can be seen from Eq. (11). The compressed matrices $\tilde{\mathcal{P}}$ and $\tilde{\mathcal{T}}$ are likewise symmetric. From Eq. (C4) it is seen that \mathcal{B} is the inverse of a symmetric matrix, and is therefore symmetric. The complete matrix \mathcal{B} is likewise symmetric, since it is generated from $\tilde{\mathcal{B}}$ by repeating rows and columns in a like manner. In a time-dependent field \mathcal{B} is not symmetric in general.

APPENDIX F: EXPANSION OF POTENTIAL IN POWERS OF \mathbf{r}

An expansion of the electrostatic potential of a body in powers of \mathbf{r} will be derived from the multipole expansion¹⁹

$$\phi(\mathbf{r}) = \sum_{n=0}^{\infty} (-1)^n \boldsymbol{\mu}^{(n)} \cdot \mathbf{n} \cdot \nabla^n \mathbf{r}^{-1}. \quad (\text{F1})$$

It has been shown¹⁷ that the traceless multipole moment $\mathbf{M}^{(n)}$ and gradient $\nabla^n \mathbf{r}^{-1}$ can be generated with the help of a “de-tracing operator” \mathcal{T}_n according to

$$\mathbf{M}^{(n)} = \mathcal{T}_n \boldsymbol{\mu}^{(n)}, \quad (\text{F2})$$

$$\nabla^n \mathbf{r}^{-1} = (-1)^n \mathbf{r}^{-2n-1} \mathcal{T}_n \mathbf{r}^n. \quad (\text{F3})$$

\mathcal{T}_n also has the property that $\mathbf{A}^{(n)} \cdot \mathbf{n} \cdot \mathcal{T}_n \mathbf{B}^{(n)} = \mathcal{T}_n \mathbf{A}^{(n)} \cdot \mathbf{n} \cdot \mathbf{B}^{(n)}$, where $\mathbf{A}^{(n)}$ and $\mathbf{B}^{(n)}$ are totally symmetric tensors.¹⁷ Thus Eq. (F1) becomes

$$\phi(\mathbf{r}) = \sum_{n=0}^{\infty} \mathbf{r}^{-2n-1} \mathbf{M}^{(n)} \cdot \mathbf{n} \cdot \mathbf{r}^n. \quad (\text{F4})$$

This expansion plays an important role in the development of Sec. VII.

APPENDIX G: TENSOR FORMS OF SCALAR POLARIZABILITIES

The scalar polarizabilities π_n of Sec. VII may be cast into equivalent tensor forms for use in the equations of the multipole interaction theory, particularly in Eqs. (C3), (C4), and (C7). We define a traceless multipole moment $\mathbf{v}^{(n)}$ by

$$\mathbf{v}^{(n)} = [(2n-1)!!]^{-1} \mathbf{M}^{(n)}, \quad (\text{G1})$$

where $(2n-1)!! = 1 \cdot 3 \cdot 5 \dots (2n-1)$. It can be shown from the properties of the \mathcal{T}_n operator of Appendix F that

$$\mathbf{v}^{(n)} \cdot \mathbf{n} \cdot \nabla^n \mathbf{r}^{-1} = \boldsymbol{\mu}^{(n)} \cdot \mathbf{n} \cdot \nabla^n \mathbf{r}^{-1}, \quad (\text{G2})$$

and

$$\mathbf{v}^{(n)} \cdot \mathbf{n} \cdot \mathbf{E}^{(n)} = \boldsymbol{\mu}^{(n)} \cdot \mathbf{n} \cdot \mathbf{E}^{(n)}. \quad (\text{G3})$$

Thus $\mathbf{v}^{(n)}$ and $\boldsymbol{\mu}^{(n)}$ are equivalent in their contribution to the potential of a body [Eq. (G2)] and in their contribution to the energy of the body in an external field [Eq. (G3)]. Therefore, $\mathbf{v}^{(n)}$ can be substituted for $\boldsymbol{\mu}^{(n)}$ in all equations of the multipole interaction theory. We define a polarizability by

$$\alpha^{(n,m)} = (\partial \mathbf{v}^{(n)} / \partial \mathbf{E}^{(m)})_0. \quad (\text{G4})$$

$\alpha^{(n,m)}$ can be substituted for $\mathbf{p}^{(n,m)}$ throughout the present theory. For homogeneous spheres, the polarizabilities of mixed rank vanish, and we have the compressed form

$$\bar{\mathbf{v}}^{(n)} = \bar{\alpha}^{(n,n)} \mathbf{g}^{(n)} \bar{\mathbf{E}}^{(n)}, \quad (\text{G5})$$

where $\mathbf{g}^{(n)}$ is the diagonal matrix whose diagonal elements are given by Eq. (35). From Eqs. (65), (G1), and (G4), one obtains the desired relation

$$\bar{\alpha}^{(n,n)} = [(2n-1)!!]^{-1} \pi_n \mathbf{g}^{(n)-1}. \quad (\text{G6})$$

Thus both $\bar{\alpha}^{(n,n)}$ and the corresponding polytensor $\bar{\mathbf{P}}$ are diagonal matrices.

For problems involving semisymmetric field gradients, such as the problem of optical activity, we require the semicompressed form $\tilde{\mathbf{P}}$ composed of $\bar{\alpha}^{(n,n)}$, which satisfies the relation

$$\tilde{\mathbf{v}}^{(n)} = \tilde{\alpha}^{(n,n)} \mathbf{h}^{(n)} \tilde{\mathbf{E}}^{(n)}. \quad (\text{G7})$$

[See Eq. (C5) and related text.] While the derivation of scalar polarizabilities in Sec. VII is not rigorous for a time-dependent field (because the field is not derivable from a scalar potential), it will be assumed for the present that the derivation is approximately valid for slowly varying fields. When the equation $M_{\alpha_1 \dots \alpha_n}^{(n)} = \pi_n E_{\alpha_1 \dots \alpha_n}^{(n)}$ is summed over all permutations of the numerical values of $\alpha_1 \dots \alpha_n$, one obtains

$$g(\alpha_1 \dots \alpha_n) \bar{M}_{\alpha_1 \dots \alpha_n}^{(n)} = \pi_n \sum_{V(\alpha_n)} h(\alpha_n \dots \alpha_1) \tilde{E}_{\alpha_1 \dots \alpha_n}^{(n)}, \quad (\text{G8})$$

where the sum over $V(\alpha_n)$ is the sum over all permutations of the numerical values of $\alpha_1 \dots \alpha_n$ which give distinct values of α_n . We define a rectangular matrix $\mathbf{U}^{(n)}$ whose row indices $\alpha_1 \dots \alpha_n$ span the compressed array in canonical order, whose column indices $\beta_1 \dots \beta_n$ span the semicompressed array in canonical order, and whose elements are

$$U_{\alpha_1 \dots \alpha_n \beta_1 \dots \beta_n}^{(n)} = \begin{cases} 1 & \text{if } \beta_1 \dots \beta_n \text{ is a permutation of } \alpha_1 \dots \alpha_n, \\ 0 & \text{otherwise.} \end{cases} \quad (\text{G9})$$

Then Eq. (G8) becomes

$$\mathbf{g}^{(n)} \bar{\mathbf{M}}^{(n)} = \pi_n \mathbf{U}^{(n)} \mathbf{h}^{(n)} \tilde{\mathbf{E}}^{(n)}. \quad (\text{G10})$$

From Eqs. (65), (G1), (G7), and (G8), one finds

$$\tilde{\alpha}^{(n,n)} = [(2n-1)!!]^{-1} \pi_n \mathbf{g}^{(n)-1} \mathbf{U}^{(n)}. \quad (\text{G11})$$

It should be noted that $\tilde{\alpha}^{(n,n)}$ is the semicompressed form of a tensor which is totally symmetric in both index sets. For example, $\tilde{\alpha}_{\alpha\beta\gamma\delta}^{(2,2)} = \tilde{\alpha}_{\alpha\delta\beta\gamma}^{(2,2)}$, according to Eq. (G11).

APPENDIX H: ATOM POLARIZABILITIES FROM PERTURBATION THEORY

The multipole polarizabilities of atoms have been found by several workers^{33,34} using quantum mechanical perturbation theory to calculate the multipole moments induced by the field of a fixed point charge located on the z axis, the atomic nucleus being at the origin. The data reproduced here are based on the following conventions. The n th order multipole moment is defined as³³

$$\mu_{2^n} = - \left\langle \psi \left| \sum_i r_i^n P_n(\cos \theta_i) \right| \psi \right\rangle, \quad (\text{H1})$$

where ψ is the wave function of the atom, (r_i, θ_i) are the spherical polar coordinates of the i th electron, and $P_n(\cos \theta_i)$ is the n th degree Legendre polynomial. The n th order polarizability is defined as³³

$$\alpha_{2^n} = (-1)^n n! \mu_{2^n} / \nabla^n \phi, \quad (\text{H2})$$

where $\nabla^n \phi$ is the n th order gradient of the potential of the fixed charge at the origin, equal in Langhoff and Hurst's³³ development to $(-1)^n (\partial^n \phi / \partial z^n)$. The Cartesian form of Eq. (H1) is obtained using the relation⁵⁰

$$P_n(\cos \theta_i) = [(-1)^n r_i^n + 1/n!] (\partial^n r_i^{-1} / \partial z_i^n), \quad (\text{H3})$$

so that

$$\mu_{2^n} = M_{33 \dots}^{(n)}, \quad (\text{H4})$$

according to the definition of $\mathbf{M}^{(n)}$.¹⁷ From Eqs. (65), (H2), and (H4) it follows that

$$|\alpha_{2^n}| = n! \pi_n. \quad (\text{H5})$$

The π_n values in Figs. 1 and 2 are obtained from the literature values using Eq. (H5).

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