ON HIGHER-ORDER MOLECULAR ENERGIES

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A consistent and general tensor formalism is developed, allowing to compute easily the higher-order energies arising from various molecular interactions. In the case of interaction between a multipolar molecule and an external, in general inhomogeneous electric or magnetic field, the higher-order energies are calculated from quantum-mechanical perturbation theory to the fourth order approximation inclusively. Also, general expressions for the first, second, third and fourth-order energies of interactions between multipolar unlike molecules of a multi-component system are obtained in a classical picture. The formalism proposed can be of use in computing various effects involving multipole interactions, as shown here on the example of the tensorial part of the excess free energy of multi-component systems.

1. Introduction

The long-range intermolecular potential energy consists in general of three parts: (i) the Keesom electrostatic part representing interaction between permanent dipoles, quadrupoles, *etc.*, (ii) the Debye-Falkenhagen inductional part arising from interactions of the permanent dipole or quadrupole of one molecule with the dipole induced in another molecule, and (iii) the London dispersional energy resulting from mutual polarization of the electron clouds of neighbouring nonoverlapping atoms or molecules, *e. g.* from induced dipole--induced dipole interaction.

Various aspect of the respective intermolecular energies have been discussed in detail and developed in suitable approaches by several authors (see Refs. [1—15] and the papers cited there). In general, the electrostatic potential of an electric charge distribution can be written explicitly as a multipole expansion in terms of spherical harmonic functions [5]. Carlson and Rushbrooke [3] showed that the multipole expansion of intermolecular electrostatic energy can be obtained by applying irreducible tensor algebra (see also [5]). Subsequently, Fontana [7] combined the theory of angular momentum with irreducible tensor

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formalism and calculated by this method the second-order dispersional inter-atomic energy. The earliest tensor formalism for the multipole series of electrostatic potential was given by Frenkel [12] and later by Jansen [13], whose general and concise tensor notation we use in the present paper (the tensor formalism used in our previous papers [14] is less compact and not so convenient for the definition of 2^n-pole moments $\boldsymbol{N}^{(n)}$ and n-th rank interaction tensors $\boldsymbol{T}^{(n)}$ as given by Jansen).

Quite generally, an electric field (external, atomic or molecular) induces in atoms or molecules not only a dipole moment, but also a quadrupole and higher-order moments. Thus, the changes in the electric charge distribution of an atom or molecule due to an electric (generally inhomogeneous) field can be characterized by a series of multipole polarizabilities [12, 15, 16]. In this connection, the need may be felt of a tensor formalism allowing to derive, in a concise and simultaneously general manner, the higher-order energies, as well as the higher-order electric multipole moments induced in molecular systems by strong inhomogeneous electric fields. For the case of an external electric field, the higher-order energies of an isolated molecule are computed in this paper to within the fourth- order approximation of quantum-mechanical perturbation theory. First, second and third-order multipole polarizability tensors are introduced and their diagonal matrix elements are given in explicit form. Also, a general relation betwen the $(s+1)$th-order energy and the s-th-order multipole moment induced in a molecule by an external electric field is derived.

We also propose a classically conceived tensor formalism useful for computing the total intermolecular energy, for the general case of multi-component systems of unlike multipolar molecules. Namely, in addition to the energy arising from electrostatic interaction of the permanent 2^n-pole moments with other permanent 2^n-pole moments, we take into account the higher-order interactions between the permanent 2^n-pole moments of molecules and the 2^n-pole moments of respective orders induced by them in other molecules of the system. However, we do not consider here the dispersional energy discussed recently by a number of authors in second-order [6—9] and third-order approximation [10, 11].

The tensor formalism developed in the present paper can be applied for computing various measurable effects in which molecular interactions of multipole type are sufficiently apparent. Investigation of such effects is liable to provide information on permanent as well as induced multipole molecular moments. As an a example we give a general equation for the tensor of electric permittivity of a gas in a strong electric field as well as evaluations of various tensorial contributions to the excess free energy of multi-component systems.

2. Interaction of a molecular system with an external electric field

We consider a molecular system consisting of point particles with electric charges e_1, e_2, ..., e_ν. The position of the charge e_ν with respect to the origin 0 of the reference system x, y, z (chosen within the molecular system) is represented by the vector $\boldsymbol{r}_\nu$. If the molecular system is in an external electric field with the potential φ_ν at $\boldsymbol{r}$, the potential energy of electrostatic interaction is given by the well-known expression

$$V = \sum_\nu e_\nu \varphi(\boldsymbol{r}_\nu). \tag{1}$$

Assuming that the field varies but slowly in the region of the molecular system we can expand (1) as a Taylor series around 0 and obtain finally

$$V = -\sum_{n=0}^{\infty} \frac{1}{n!}\, \boldsymbol{N}^{(n)}[n]\boldsymbol{E}^{(n)}, \tag{2}$$

wherein [13]

$$\boldsymbol{N}^{(n)} = \sum_{\nu} e_{\nu} \boldsymbol{r}_{\nu}^{n} \tag{3}$$

is the n-th rank electric moment operator and

$$\boldsymbol{E}^{(n)} = -\{\boldsymbol{\nabla}^{n}\varphi(\boldsymbol{r})\}_{0} \tag{4}$$

is the intensity of the external electric field of degree n at the origin 0; Δ is the differential operator; in (2), the symbol $[n]$ in Jansen's notation denotes n-fold contraction of the product of two n-th-rank tensors $\boldsymbol{N}^{(n)}$ and $\boldsymbol{E}^{(n)}$.

In contradistinction to Jansen's definition of (3), we introduce here the following definition of the permanent 2 -pole electric moment of a molecular system [17].

$$\boldsymbol{M}^{(n)} = \sum_{\nu} e_{\nu} r_{\nu}^{n} \boldsymbol{Y}^{(n)}(\boldsymbol{r}_{\nu}), \tag{5}$$

wherein the operator $\boldsymbol{Y}^{(n)}$ of degre n (its properties resemble those of spherical harmonic function) is given by

$$\boldsymbol{Y}^{(n)}(\boldsymbol{r}) = \frac{(-1)^{n}}{n!}\, r^{n+1}\, \boldsymbol{\nabla}^{n}\left(\frac{1}{r}\right)$$

$$= \frac{1}{n!\, r^{n}}\, \{(2n-1)!!\, \boldsymbol{r}_{1}\boldsymbol{r}_{2}\ldots\boldsymbol{r}_{n} - (2n-3)!!\, r^{2}\sum \boldsymbol{U}_{12}\boldsymbol{r}_{3}\ldots\boldsymbol{r}_{n} +$$

$$+ (2n-5)!!\, r^{4}\sum \boldsymbol{U}_{12}\boldsymbol{U}_{34}\boldsymbol{r}_{5}\ldots\boldsymbol{r}_{n} - (2n-7)!!\, r^{6}\sum \boldsymbol{U}_{12}\boldsymbol{U}_{34}\boldsymbol{U}_{56}\boldsymbol{r}_{7}\ldots\boldsymbol{r}_{n} + \ldots +$$

$$+ (-1)^{k}(2n-2k-1)!!\, r^{2k}\sum \boldsymbol{U}_{12}\ldots\boldsymbol{U}_{2k-1,\,2k}\boldsymbol{r}_{2k+1}\ldots\boldsymbol{r}_{n} + \ldots\}, \tag{6}$$

where $\boldsymbol{U}_{12}$ is the second-rank unit tensor, and $\Sigma \boldsymbol{U}_{12}\boldsymbol{r}_{3}\ldots\boldsymbol{r}_{n}$ etc. are sums of the terms obtained from the one written out above by interchanging the suffixes 1, 2, ... n, the number of such terms amounting to $n!/\{2^{k}(n\text{-}2k)!k!\}$. In particular, we obtain from (6) for the operators of successive degrees

$$Y^{(0)}(r) = 1,$$

$$\boldsymbol{Y}^{(1)}(\boldsymbol{r}) = r^{-1}\boldsymbol{r}_{1},$$

$$\boldsymbol{Y}^{(2)}(\boldsymbol{r}) = \frac{1}{2}\, r^{-2}(3\boldsymbol{r}_{1}\boldsymbol{r}_{2} - r^{2}\boldsymbol{U}_{12}),$$

$$\boldsymbol{Y}^{(3)}(\boldsymbol{r}) = \frac{1}{2}\, r^{-3}\{5\boldsymbol{r}_{1}\boldsymbol{r}_{2}\boldsymbol{r}_{3} - r^{2}(\boldsymbol{U}_{12}\boldsymbol{r}_{3} + \boldsymbol{U}_{23}\boldsymbol{r}_{1} + \boldsymbol{U}_{31}\boldsymbol{r}_{2})\},$$

$$\boldsymbol{Y}^{(4)}(\boldsymbol{r}) = \frac{1}{8}\, r^{-4}\{35\boldsymbol{r}_{1}\boldsymbol{r}_{2}\boldsymbol{r}_{3}\boldsymbol{r}_{4} - 5r^{2}(\boldsymbol{U}_{12}\boldsymbol{r}_{3}\boldsymbol{r}_{4} + \boldsymbol{U}_{23}\boldsymbol{r}_{4}\boldsymbol{r}_{1} + \boldsymbol{U}_{34}\boldsymbol{r}_{1}\boldsymbol{r}_{2} +$$

$$+ \boldsymbol{U}_{14}\boldsymbol{r}_{2}\boldsymbol{r}_{3} + \boldsymbol{U}_{13}\boldsymbol{r}_{2}\boldsymbol{r}_{4} + \boldsymbol{U}_{24}\boldsymbol{r}_{1}\boldsymbol{r}_{3}) + r^{4}(\boldsymbol{U}_{12}\boldsymbol{U}_{34} + \boldsymbol{U}_{13}\boldsymbol{U}_{24} + \boldsymbol{U}_{14}\boldsymbol{U}_{23})\}, \ldots \tag{7}$$

With the help of definition (5), the multipole expansion (2) can be written as follows:

$$V = -\sum_{n=0}^{\infty} \frac{2^n n!}{(2n)!} M^{(n)}[n] E^{(n)}.$$ (8)

This expression represents the general form of the potential energy of interaction between the permanent 2^n-pole electric moment of a molecule and an external electric field of degree n.

In particular, equation (8) becomes in a sufficient approximation

$$V = -M^{(0)}E^{(0)} - M^{(1)} \cdot E^{(1)} - \frac{1}{3} M^{(2)} : E^{(2)} - \frac{1}{15} M^{(3)} \vdots E^{(3)} - \frac{1}{105} M^{(4)} :: E^{(4)},$$ (9)

where the first term is the energy of the unipole moment $M^{(0)}$ (or total charge of the molecular system) in a zero-degree field $E^{(0)}$ (or potential-φ) and the subsequent terms correspond, respectively, to interactions between the dipole moment $M^{(1)}$ and first-degree field $E^{(1)}$ (or uniform field $E = -\nabla\varphi$), quadrupole moment $M^{(2)}$ and second-degree field $E^{(2)}$ (or field gradient ∇E), octopole moment $M^{(3)}$ and third-degree field $E^{(3)}$ (gradient of field gradient $\nabla\nabla E$), hexadecapole moment $M^{(4)}$ and fourth-degree field $E^{(4)} = \nabla\nabla\nabla E$, etc.

3. Higher-order energies in perturbation theory

We now recur to quantum-mechanical perturbation theory for the calculation of higher-order energies of interactions between a molecule and external electric field. In this case the total Hamiltonian of a molecule is $H = H_0 + V$ with H_0 denoting the Hamiltonian of the nonperturbated isolated molecule; V is the perturbation Hamiltonian of the molecule subjected to the external electric field and in general is given by (8).

The perturbated wave function ψ can be expanded in successive orders of approximation as

$$\psi_g = \sum_{s=0}^{\infty} \sum_k c_{kg}^{(s)} \psi_k^{(0)}.$$ (10)

The energy of a molecular system in its perturbated ground state g can then be expressed as follows:

$$W_g = \sum_{s=0}^{\infty} W_g^{(s)} = W_g^0 + W_g^{(1)} + W_g^{(2)} + W_g^{(3)} + W_g^{(4)} + \dots .$$ (11)

Here $c_{kg}^{(0)} = \delta_{kg}$, whereas the remaining coefficients $c_{kg}^{(s)}$ for $s \geqslant 1$ and $k \neq g$ are of the form

$$c_{kg}^{(1)}(W_g^0 - W_k^0) = V_{kg} = \int \bar{\psi}_k^{(0)} V \psi_g^{(0)} d\tau,$$

$$c_{kg}^{(2)}(W_g^0 - W_k^0) = \sum_{l \neq g} V_{kl} c_{lg}^{(1)} - c_{kg}^{(1)} V_{gg},$$

$$c_{kg}^{(3)}(W_g^0 - W_k^0) = \sum_{l \neq g} (V_{kl} c_{lg}^{(2)} - c_{kg}^{(1)} V_{gl} c_{lg}^{(1)}) - c_{kg}^{(2)} V_{gg}, \dots,$$ (12)

with $W_g^0 - W_k^0 = \hbar\omega_{gk}$ denoting the difference between the energy eigenvalues of the ground state g and the excited state k of the molecular system in the absence of an external field and $\psi_g^{(0)}$ and $\psi_k^{(0)}$ are the respective eigenfunctions of the Hamiltonian H_0; V_{kg} is the matrix element of V.

By the general equation (8), the first-order energy of the perturbated molecule is

$$W_g^{(1)} = V_{gg} = -\sum_{n=1}^{\infty} \frac{2^n n!}{(2n)!} M_{gg}^{(n)}[n] E^{(n)}, \tag{13}$$

whereas the second and higher-order energies are given by

$$W_g^{(s+1)} = \sum_{k \neq g} V_{gk} c_{kg}^{(s)}, s = 1, 2, \ldots . \tag{14}$$

From Eqs. (12) and (14) we obtain for the second-order energy

$$W_g^{(2)} = -\hbar^{-1} \sum_{k \neq g} \omega_{kg}^{-1} V_{gk} V_{kg}, \tag{15}$$

which by using the explicit form of V given by (8) may be written as follows:

$$W_g^{(2)} = -\frac{1}{2} \sum_{n=1}^{\infty} \sum_{n_1=1}^{\infty} \frac{2^{n+n_1} n! n_1!}{(2n)! (2n_1)!} E^{(n)}[n]^{(n)} A_{gg}^{(n_1)}[n_1] E^{(n_1)}, \tag{16}$$

where we have introduced the tensor

$$^{(n)}A_{gg}^{(n_1)} = \hbar^{-1} \sum_{k \neq g} \omega_{kg}^{-1} (M_{gk}^{(n)} M_{kg}^{(n_1)} + M_{gk}^{(n_1)} M_{kg}^{(n)}). \tag{17}$$

With the following definition of the first-order multipole moment (or induced moment):

$$\overset{(1)}{M_{gg}^{(n)}} = \sum_{n_1=1}^{\infty} \frac{2^{n_1} n_1!}{(2n_1)!} \, ^{(n)}A_{gg}^{(n_1)}[n_1] E^{(n_1)}, \tag{18}$$

the second-order energy of (16) can be written symbolically in the simpler form

$$W_g^{(2)} = -\frac{1}{2} \sum_{n=1}^{\infty} \frac{2^n n!}{(2n)!} E^{(n)}[n] \overset{(1)}{M_{gg}^{(n)}}. \tag{19}$$

From the definition (18) we see that the tensor of rank $n + n_1$ with matrix elements (17) characterizes the linear or first-order polarization of the 2^n-pole electric moment due to an electric field of degree n_1. Thus, the tensor $^{(n)}A^{(n_1)}$ can be termed the first-order multipole polarizability tensor of an isolated molecule, or in brief, its multipole polarizability tensor.

In third-order perturbation theory we obtain by (12) and (14) for $s = 2$

$$W_g^{(3)} = \hbar^{-2} \{ \sum_{k \neq g} \sum_{l \neq g} \omega_{kg}^{-1} \omega_{lg}^{-1} V_{gk} V_{kl} V_{lg} - \sum_{k \neq g} \omega_{kg}^{-2} V_{gk} V_{kg} V_{gg} \}. \tag{20}$$

or by using the explicite form of (8)

$$W_g^{(3)} = -\frac{1}{6} \sum_{n=1}^{\infty} \sum_{n_1=1}^{\infty} \sum_{n_2=1}^{\infty} \frac{2^{n+n_1+n_2} n! \, n_1! \, n_2!}{(2n)! \, (2n_1)! \, (2n_2)!} \times$$

$$\times E^{(n)} [n] \, {}^{(n)}B_{gg}^{(n_1+n_2)} [n_1+n_2] \, E^{(n_1)} E^{(n_2)}, \tag{21}$$

if the following tensor of rank $n+n_1+n_2$ is introduced:

$${}^{(n)}B_{gg}^{(n_1+n_2)} = \hbar^{-2} \sum_P P(n, n_1, n_2) \{ \sum_{k \neq g} \sum_{l \neq g} \omega_{kg}^{-1} \omega_{lg}^{-1} M_{gk}^{(n)} M_{kl}^{(n_1)} M_{lg}^{(n_2)} -$$

$$- \sum_{k \neq g} \omega_{kg}^{-2} M_{gk}^{(n)} M_{kg}^{(n_1)} M_{gg}^{(n_2)} \}, \tag{22}$$

where $\sum_P P(n, n_1, n_2, \ldots)$ is a symmetrizing operation denoting summation over all permutations of $n, n_1, n_2, \ldots$

In the same way we obtain from Eqs (8), (12) and (14) the following expression for the fourth-order energy:

$$W_g^{(4)} = -\frac{1}{24} \sum_{n=1}^{\infty} \sum_{n_1=1}^{\infty} \sum_{n_2=1}^{\infty} \sum_{n_3=1}^{\infty} \frac{2^{n+n_1+n_2+n_3} n! \, n_1! \, n_2! \, n_3!}{(2n)! \, (2n_1)! \, (2n_2)! \, (2n_3)!} \times$$

$$\times E^{(n)} [n] \, {}^{(n)}C_{gg}^{(n_1+n_2+n_3)} [n_1+n_2+n_3] \, E^{(n_1)} E^{(n_2)} E^{(n_3)}, \tag{23}$$

where the tensor of rank $n+n_1+n_2+n_3$ is of the form

$${}^{(n)}C_{gg}^{(n_1+n_2+n_3)} = \hbar^{-3} \sum_P P(n, n_1, n_2, n_3) \{ \sum_{k \neq g} \sum_{l \neq g} \sum_{m \neq g} \omega_{kg}^{-1} \omega_{lg}^{-1} \omega_{mg}^{-1} M_{gk}^{(n)} M_{kl}^{(n_1)} M_{lm}^{(n_2)} M_{mg}^{(n_3)} -$$

$$- \sum_{k \neq g} \sum_{l \neq g} \omega_{kg}^{-1} \omega_{lg}^{-1} [\omega_{kg}^{-1} M_{gk}^{(n)} M_{kg}^{(n_1)} M_{gl}^{(n_2)} M_{lg}^{(n_3)} + \omega_{lg}^{-1} M_{gk}^{(n)} M_{kl}^{(n_1)} M_{lg}^{(n_2)} M_{gg}^{(n_3)} +$$

$$+ \omega_{kg}^{-1} M_{gg}^{(n)} M_{gk}^{(n_1)} M_{kl}^{(n_2)} M_{lg}^{(n_3)}] + \sum_{k \neq g} \omega_{kg}^{-3} M_{gk}^{(n)} M_{kg}^{(n_1)} M_{gg}^{(n_2)} M_{gg}^{(n_3)} \}. \tag{24}$$

The third-order and fourth-order energies of (21) and (23) can also be written in the following compact form:

$$W_g^{(3)} = -\frac{1}{3} \sum_{n=1}^{\infty} \frac{2^n n!}{(2n)!} \, E^{(n)} [n] \, \overset{(2)}{M}{}_{gg}^{(n)}, \tag{25}$$

$$W_g^{(4)} = -\frac{1}{4} \sum_{n=1}^{\infty} \frac{2^n n!}{(2n)!} \, E^{(n)} [n] \, \overset{(3)}{M}{}_{gg}^{(n)}, \tag{26}$$

where we have introduced the second-order 2^n-pole electric moment

$$\overset{(2)}{M}{}_{gg}^{(n)} = \frac{1}{2} \sum_{n_1=1}^{\infty} \sum_{n_2=1}^{\infty} \frac{2^{n_1+n_2} n_1! \, n_2!}{(2n_1)! \, (2n_2)!} \, {}^{(n)}B_{gg}^{(n_1+n_2)} [n_1+n_2] \, E^{(n_1)} E^{(n_2)} \tag{27}$$

and the third-order 2^n-pole electric moment

$$\overset{(3)}{M}{}^{(n)}_{gg} = \frac{1}{6} \sum_{n_1=1}^{\infty} \sum_{n_2=1}^{\infty} \sum_{n_3=1}^{\infty} \frac{2^{n_1+n_2+n_3} n_1! \, n_2! \, n_3!}{(2n_1)! \, (2n_2)! \, (2n_3)!} \times$$

$$\times \, {}^{(n)}C^{(n_1+n_2+n_3)}_{gg} \, [n_1+n_2+n_3] \, E^{(n_1)} E^{(n_2)} E^{(n_3)}. \tag{28}$$

According to the explicit form of Eqs. (27) and (28) we can consider ${}^{(n)}B^{(n_1+n_2)}$ as the second-order multipole polarizability tensor and ${}^{(n)}C^{(n_1+n_2+n_3)}$ as the third-order multipole polarizability tensor of a molecule subjected to an intense electric field.

From Eqs. (18), (27) and (28) we obtain in a good approximation

$$\overset{(1)}{M}{}^{(n)}_{gg} = {}^{(n)}A^{(1)}_{gg} \cdot E^{(1)} + \frac{1}{3} \, {}^{(n)}A^{(2)}_{gg} : E^{(2)} + \frac{1}{15} \, {}^{(n)}A^{(3)}_{gg} \vdots E^{(3)} + \frac{1}{105} \, {}^{(n)}A^{(4)}_{gg} :: E^{(4)} + ..., \tag{29}$$

$$\overset{(2)}{M}{}^{(n)}_{gg} = \frac{1}{2} \left\{ {}^{(n)}B^{(1+1)}_{gg} : E^{(1)} E^{(1)} + \frac{2}{3} \, {}^{(n)}B^{(1+2)}_{gg} \vdots E^{(1)} E^{(2)} + \frac{1}{9} \, {}^{(n)}B^{(2+2)}_{gg} :: E^{(2)} E^{(2)} + ... \right\}, \tag{30}$$

$$\overset{(3)}{M}{}^{(n)}_{gg} = \frac{1}{6} \left\{ {}^{(n)}C^{(1+1+1)}_{gg} \vdots E^{(1)} E^{(1)} E^{(1)} + \frac{1}{3} \, {}^{(n)}C^{(1+1+2)}_{gg} :: E^{(1)} E^{(1)} E^{(2)} + ... \right\}. \tag{31}$$

The expansion of (29) ${}^{(n)}A^{(1)}$, ${}^{(n)}A^{(2)}$, ${}^{(n)}A^{(3)}$, ... contains multipole polarizability tensors characterizing the polarization caused in a multipolar molecule by electric fields of the first, second, third, ... degree, respectively. Similarly, the first terms in Eqs. (30) and (31) with multipole tensors ${}^{(n)}B^{(1+1)}$ and ${}^{(n)}C^{(1+1+1)}$ describe the second and third-order polarization produced in the molecular multipoles by the second and third power of the uniform field, respectively. In special cases the expansions (29)—(31) yield for $n = 1, 2, 3, ...$ the dipole, quadrupole, octopole, *etc.* moments of first, second and third order, respectively.

On the basis of Eqs. (19), (25) and (26) we can write the following general relation:

$$W^{(s+1)}_g = - \frac{1}{s+1} \sum_{n=1}^{\infty} \frac{2^n n!}{(2n)!} \, E^{(n)}[n] \overset{(s)}{M}{}^{(n)}_{gg}, \tag{32}$$

between the $(s+1)$th-order energy and s-th-order 2^n-pole electric moment defined in general by

$$\overset{(s)}{M}{}^{(n)}_{gg} = \frac{1}{s!} \sum_{n_1=1}^{\infty} ... \sum_{n_s=1}^{\infty} \frac{2^{n_1+...+n_s} n_1! ... n_s!}{(2n_1)! ... (2n_s)!} \, {}^{(n)}A^{(n_1+...+n_s)}_{gg} [n_1+...+n_s] \, E^{(n_1)} ... E^{(n_s)} \tag{33}$$

with ${}^{(n)}A^{(n_1+...+n_s)}$ denoting the multipole polarizability tensor of order s.

The numerical values of diagonal matrix elements of the second and third-order multipole polarizability tensors of (22) and (24) can be calculated directly by the methods discussed in the paper of Dalgarno [16] for the case of first-order multipole polarizability.

4. The energy of intermolecular interactions

We consider two nonoverlapping molecular systems p and q which have in general 2^n-pole and 2^m-pole electric moments, respectively. The vector connecting the centres of these interacting molecular systems is $\boldsymbol{r}_{pq}$, and $\boldsymbol{r}_{p\nu}$ and $\boldsymbol{r}_{q\mu}$ are radius vectors of their electric charges $e_{p\nu}$ and $e_{q\mu}$. The potential $\varphi(\boldsymbol{r}_{pq})$ at the centre of the q-th molecular system due to all the electric charges of the p-th molecular system is defined as

$$\varphi(\boldsymbol{r}_{pq}) = \sum_{\nu} \frac{e_{p\nu}}{|\boldsymbol{r}_{pq} - \boldsymbol{r}_{p\nu}|}, \tag{34}$$

which for $r_{p\nu} < r_{pq}$ may be expanded in a series in powers of $r_{p\nu}/r_{pq}$,

$$\varphi(\boldsymbol{r}_{pq}) = \sum_{n=0}^{\infty} (-1)^n \frac{2^n n!}{(2n)!} \boldsymbol{M}_p^{(n)}[n] \, \boldsymbol{\nabla}^n \left(\frac{1}{r_{pq}} \right), \tag{35}$$

where $\boldsymbol{M}_p^{(n)}$ is the 2^n-pole electric moment of a molecular system p defined by Eq. (5) if e_ν is replaced by $e_{p\nu}$ and $\boldsymbol{r}_\nu$ by $\boldsymbol{r}_{p\nu}$.

We now introduce the definition of an electric field $\boldsymbol{F}_q^{(m)} = -\boldsymbol{\nabla}^m \varphi(\boldsymbol{r}_{pq})$ of degree m at the centre of the molecular system q, obtaining by the expansion (35)

$$\boldsymbol{F}_q^{(m)} = \sum_{n=0}^{\infty} (-1)^n \frac{2^n n!}{(2n)!} \boldsymbol{M}_p^{(n)}[n]^{(n)}\boldsymbol{T}_{pq}^{(m)}, \tag{36}$$

wherein the tensor of rank $n+m$

$$^{(n)}\boldsymbol{T}_{pq}^{(m)} = -\boldsymbol{\nabla}^{n+m} \left(\frac{1}{r_{pq}} \right) = (-r_{pq})^{-(n+m+1)} \, \boldsymbol{Y}^{(n+m)} (\boldsymbol{r}_{pq}) \tag{37}$$

describes (2^n-pole) — (2^m-pole) type interactions between molecules p and q. Here, $\boldsymbol{\nabla}^{n+m}$ is directed from molecule p to q so that $^{(n)}\boldsymbol{T}_{pq}^{(m)} = (-1)^{n+m} \,^{(m)}\boldsymbol{T}_{qp}^{(n)}$, and $\boldsymbol{Y}^{(n+m)}(\boldsymbol{r}_{pq}) = (-1)^{n+m} \, \boldsymbol{Y}^{(n+m)} (\boldsymbol{r}_{qp})$ is defined by (6) or (7) if n is replaced by $n+m$ and $\boldsymbol{r}$ by $\boldsymbol{r}_{pq}$.

Similarly, the energy of electrostatic interaction between the two molecular systems

$$u_{pq} = \sum_{\nu} \sum_{\mu} \frac{e_{p\nu} e_{q\mu}}{|\boldsymbol{r}_{pq} - \boldsymbol{r}_{p\nu} + \boldsymbol{r}_{q\mu}|} = \sum_{\mu} e_{q\mu} \varphi(\boldsymbol{r}_{pq} + \boldsymbol{r}_{q\mu}) \tag{38}$$

may be expanded into the following form [13, 17];

$$u_{pq} = -\sum_{n=0}^{\infty} \sum_{m=0}^{\infty} (-1)^n \frac{2^{n+m} n! \, m!}{(2n)! \, (2m)!} \boldsymbol{M}_p^{(n)}[n]^{(n)}\boldsymbol{T}_{pq}^{(m)} [m] \boldsymbol{M}_q^{(m)}, \tag{39}$$

which simplifies, by Eq. (36), to the form

$$u_{pq} = -\sum_{m=0}^{\infty} \frac{2^m m!}{(2m)!} \, \boldsymbol{F}_q^{(m)} [m] \boldsymbol{M}_q^{(m)} = -\sum_{n=0}^{\infty} \frac{2^n n!}{(2n)!} \boldsymbol{M}_p^{(n)} [n] \, \boldsymbol{F}_p^{(n)}. \tag{40}$$

We now generalize these equations to the case of a multi-component system containing $N_1, N_2, \ldots N_i, \ldots$ molecular systems of the first, second, $\ldots$ i-th species, and obtain for the total first-order (or electrostatic) energy of molecular interactions

$$\overset{(1)}{U} = -\frac{1}{2} \sum_{ij} \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} (-1)^n \frac{2^{n+m} \, \boldsymbol{n}! \, m!}{(2\boldsymbol{n})! \, (2m)!} \, M_{pi}^{(n)}[\boldsymbol{n}]^{(n)} T_{pq}^{(m)}[m] M_{qj}^{(m)}, \quad (41)$$

or in consistent form,

$$\overset{(1)}{U} = -\frac{1}{2} \sum_{j} \sum_{q=1}^{N_j} \sum_{m=0}^{\infty} \frac{2^m m!}{(2m)!} \, \boldsymbol{F}_{qj}^{(m)}[m] \boldsymbol{M}_{qj}^{(m)}. \quad (42)$$

Here, $\boldsymbol{F}_{qj}^{(m)}$ is the total electric field of degree m at the centre of the molecular system q of species j due to the electric multipoles of all the other molecular systems and can be obtained directly from (36) by summation over all molecular systems except the given q-th; namely, we have

$$\boldsymbol{F}_{qj}^{(m)} = \sum_{i} \sum_{p=1}^{N_i} \sum_{n=0}^{\infty} (-1)^n \frac{2^n \boldsymbol{n}!}{(2\boldsymbol{n})!} \, M_{pi}^{(n)}[\boldsymbol{n}]^{(n)} T_{pq}^{(m)} \quad (43)$$

with the multipole tensor $M_{pj}^{(n)}$ now referring to the p-th molecular system of species i.

The higher-order or inductional intermolecular energies can be formally written on a classical level in a form analogical to equation (32) if the external electric field is replaced by (43) and provided the problem is restricted to multipole polarizabilities in the first power only. In this way we have for the $(s+1)$-order energy of intermolecular interactions $(s = 1, 2, \ldots)$

$$\overset{(s+1)}{U} = -\frac{1}{s+1} \sum_{j} \sum_{q=1}^{N_j} \sum_{m_1=1}^{\infty} \frac{2^{m_1} m_1!}{(2m_1)!} \, \boldsymbol{F}_{qj}^{(m_1)}[m_1] \overset{(s)}{\boldsymbol{M}}_{qj}^{(m_1)}, \quad (44)$$

where $\overset{(s)}{\boldsymbol{M}}_{qj}^{(m_1)}$ is the s-th-order multipole moment of the molecular system q of species j.

Since the first-order multipole moment $\overset{(1)}{\boldsymbol{M}}_{qj}^{(m_1)}$ can be expressed as follows:

$$\overset{(1)}{\boldsymbol{M}}_{qj}^{(m_1)} = \sum_{m_2=1}^{\infty} \frac{2^{m_2} m_2!}{(2m_2)!} \, {}^{(m_1)}A_{qj}^{(m_2)}[m_2] \boldsymbol{F}_{qj}^{(m_2)}, \quad (45)$$

we obtain from (44) for the second-order intermolecular energy

$$\overset{(2)}{U} = -\frac{1}{2} \sum_{j} \sum_{q=1}^{N_j} \sum_{m_1=1}^{\infty} \sum_{m_2=1}^{\infty} \frac{2^{m_1+m_2} m_1! \, m_2!}{(2m_1)! \, (2m_2)!} \, \boldsymbol{F}_{qj}^{(m_1)}[m_1] \, {}^{(m_1)}A_{qj}^{(m_2)}[m_2] \, \boldsymbol{F}_{qj}^{(m_2)}, \quad (46)$$

where ${}^{(m_1)}\boldsymbol{A}_{qj}^{(m_2)}$ is the first-order multipole polarizability tensor of an isolated molecule q of species j.

On substituting in (46) the molecular electric field of (43) we obtain in explicite form

$$\overset{(2)}{U} = -\frac{1}{2} \sum_{ijk} \sum_{p=1}^{Ni} \sum_{q=1}^{Nj} \sum_{r=1}^{Nk} \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \sum_{m_1=1}^{\infty} \sum_{m_2=1}^{\infty} (-1)^{n_1+m_2} \frac{2^{n_1+n_2+m_1+m_2} n_1! \, n_2! \, m_1! \, m_2!}{(2n_1)! \, (2n_2)! \, (2m_1) \, !(2m_2)!} \times$$

$$\times \, M_{pi}^{(n_1)} [n_1] \, {}^{(n_1)}T_{pq}^{(m_1)} [m_1] \, {}^{(m_1)}A_{qj}^{(m_2)} [m_2] \, {}^{(m_2)}T_{qr}^{(n_2)} [n_2] \, M_{rk}^{(n_2)}. \tag{47}$$

Third-order energy of intermolecular interactions is given by Eq. (44) as follows:

$$\overset{(3)}{U} = -\frac{1}{6} \sum_{ijk} \sum_{q=1}^{Nj} \sum_{m_1=1}^{\infty} \sum_{m_2=1}^{\infty} \sum_{m_3=1}^{\infty} \frac{2^{m_1+m_2+m_3} m_1! \, m_2! \, m_3!}{(2m_1)! \, (2m_2)! \, (2m_3)!} \times$$

$$\times \, F_{qj}^{(m_1)} [m_1] \, {}^{(m_1)}B_{qj}^{(m_2+m_3)} [m_2+m_3] \, F_{qj}^{(m_2)} F_{qj}^{(m_3)}, \tag{48}$$

or, by (43), in the following explicite form:

$$\overset{(3)}{U} = -\frac{1}{6} \sum_{ijkl} \sum_{p=1}^{Ni} \sum_{q=1}^{Nj} \sum_{r=1}^{Nk} \sum_{s=1}^{Nl} \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \sum_{n_3=0}^{\infty} \sum_{m_1=1}^{\infty} \sum_{m_2=1}^{\infty} \sum_{m_3=1}^{\infty} \times$$

$$\times (-1)^{n_1+m_2+m_3} \frac{2^{n_1+\ldots+m_3} n_1! \, \ldots \, m_3!}{(2n_1)! \, \ldots \, (2m_3)!} \, M_{pi}^{(n_1)} [n_1] \times$$

$$\times \, {}^{(n_1)}T_{pq}^{(m_1)} [m_1] \, {}^{(m_1)}B_{qj}^{(m_2+m_3)} [m_2+m_3] \, {}^{(m_2)}T_{qr}^{(n_2)} [n_2] \, M_{rk}^{(n_2)} \, {}^{(m_3)}T_{qs}^{(n_3)} [n_3] \, M_{sl}^{(n_3)}. \tag{49}$$

Similarly, with respect to the general equation (44), we have for the fourth-order energy of intermolecular interactions

$$\overset{(4)}{U} = -\frac{1}{24} \sum_{j} \sum_{q=1}^{Nj} \sum_{m_1=1}^{\infty} \sum_{m_2=1}^{\infty} \sum_{m_3=1}^{\infty} \sum_{m_4=1}^{\infty} \frac{2^{m_1+m_2+m_3+m_4} m_1! \, m_2! \, m_3! \, m_4!}{(2m_1)! \, (2m_2)! \, (2m_3)! \, (2m_4)!} \times$$

$$\times \, F_{qj}^{(m_1)} [m_1] \, C_{qj}^{(m_2+m_3+m_4)} [m_2+m_3+m_4] \, F_{qj}^{(m_2)} F_{qj}^{(m_3)} F_{qj}^{(m_4)}, \tag{50}$$

where the total molecular electric field $F_{qj}^{(m)}$ of degree m is given by Eq. (43).

It is clear that by appropriate simplifying assumptions we can obtain directly from the general expansions of (41) and (47) the special results derived previously by Debye, Keesom and others [2, 4, 5, 15] as well as the result including explicitely the anisotropy in th e dipole polarizability of a molecule [14].

5. Applications of the tensor formalism

The tensor formalism developed in Section 3 can be applied to calculate the tensor of electric permittivity ε of a gas in the presence of an intense electric field. Let ϱ be the number density of molecules of a gas. We have the general equation [18, 19]

$$(\boldsymbol{\varepsilon}-\boldsymbol{U}) \cdot \boldsymbol{E} = 4\pi\varrho \sum_{n=1}^{\infty} (-1)^{n-1} \frac{2^n n!}{(2n)!} \, \boldsymbol{\nabla}^{n-1} [n-1] \, M_T^{(n)}, \tag{51}$$

where

$$M_T^{(n)} = \sum_g \{M_{gg}^{(n)} + \overset{(1)}{M_{gg}^{(n)}} + \overset{(2)}{M_{gg}^{(n)}} + \overset{(3)}{M_{gg}^{(n)}} + ...\}\varrho_{gg} \qquad (52)$$

is the total multipole moment obtained by averageing its diagonal matrix element with the density matrix $\varrho_{gg} = \exp\{-W_g/kT\}/\underset{g}{\Sigma}\exp\{-W_g/kT\}$ over all occupied states g of a molecule in the presence of the external electric field.

From equation (51) with the expressions (52), (11), (32) and (33) we can compute the nonlinear change caused in the electric permittivity tensor by a strong uniform field, field gradient [15, 20], or fields of higher degree, such as the gradient of a field gradient [21]. We refrain, however, from proceeding to a discussion of these nonlinear effects in the present paper, but wish to draw attention to the fact that the first-order multipole moment of (18) if averaged over all possible orientations of the molecule yields

$$M^{(n)} = a^{(n+n)}E^{(n)}, \qquad (53$$

where

$$a^{(2n)} = a^{(n+n)} = \frac{2^n{}_{\omega}!}{(2n+1)!}\sum_g \varrho_{gg}^{(0)}{}^{(n)}A_{gg}^{(n)}[2n]\,U^n$$

$$= \frac{2^{n+1}n!}{(2n+1)!\,\hbar}\sum_g \sum_{k\neq g}\omega_{kg}^{-1}M_{gk}^{(n)}[n]\,M_{kg}^{(n)}\varrho_{gg}^{(0)} \qquad (54)$$

is the mean value of the 2^n-pole electric polarizability of the molecule due to an electric field of degree n, and $\varrho_{gg}^{(0)}$ is the density matrix in the absence of an external field $i.\,e.$ when $W_g = W_g^0$.

If, in particular, the molecule possesses the axial symmetry, we have [19]

$$M^{(n)}[n]\,M^{(n)} = \frac{(2n)!}{2^n(n!)^2}\{M^{(n)}\}^2, \qquad (55)$$

and Eq. (54) for multipole polarizability assumes the simpler form

$$a^{(2n)} = \frac{2}{n!\,(2n+1)\,\hbar}\sum_g \sum_{k\neq g}\omega_{kg}^{-1}M_{gk}^{(n)}M_{kg}^{(n)}\varrho_{gg}^{(0)}, \qquad (56)$$

where $M^{(n)}$ is the scalar multipole moment of the axially-symmetric molecule. From (54) or (56) we obtain, successively, the dipole polarizability due to a uniform field ($n = 1$), the quadrupole polarazability due to a field gradient ($n = 2$), the octopole polarizability due to the gradient of a field gradient ($n = 3$) $etc.$ (see Ref. [16]).

The formulas derived in Section 4 for the intermolecular energy U will now be applied to computing the excess free energy of multicomponent systems by the method of Longuet-Higgins [22] and Pople [4, 23]. Namely, we have

$$F_{\text{excess}} = F_{\text{central}} + F_{\text{tensorial}}; \qquad (57)$$

considering the tensorial intermolecular energy U to represent a perturbation to the central-force energy. In (57) F_{central} is the contribution to F_{excess} from central intermolecular forces and does not interest us here. The contribution to F_{excess} from the tensorial intermolecular forces can be expanded up to the second-order approximation as follows [4]:

$$F_{\text{tensorial}} = \langle U \rangle - \frac{1}{2kT} (\langle U^2 \rangle - \langle U \rangle^2) + \ldots, \tag{58}$$

where

$$\langle U \rangle = \frac{(N-h)!}{n!} \int \ldots_{(h)} \int \langle U(\mathbf{r}^N) \rangle_\omega \, n^{(h)}(\mathbf{r}^h) \, d\mathbf{r}^h \tag{59}$$

is the statistical average evaluated with the distribution functions $n^{(h)}(\mathbf{r}^h)$ of h molecules of the unperturbed system, and

$$\langle U(\mathbf{r}^N) \rangle_\omega = \frac{1}{\Omega^N} \int \ldots_{(N)} \int U(\mathbf{r}^N, \boldsymbol{\omega}^N) \, d\boldsymbol{\omega}^N \tag{60}$$

is the unweighted average of U over all orientations $\boldsymbol{\omega}^N$ of the N molecules of the system, $\Omega^N = \int_{(N)} \ldots \int d\boldsymbol{\omega}^N$.

In the first approximation (the first term of 58) the first-order and third-order energies of intermolecular interactions (Eqs. 41 and 49) do not contribute to $F_{\text{tensorial}}$, as $\overset{(1)}{U}$ and $\overset{(3)}{U}$ vanish on isotropic averageing as defined by (60). The only non-zero contributions to $F_{\text{tensorial}}$ in the first approximation come from the second- and fourth-order energies given by Eqs. (46) and (50). Namely, we obtain from Eqs. (46), (54) and (60) for the isotropic average of the second-order tensorial energy

$$\overset{(2)}{\langle U \rangle}_\omega = -\frac{1}{2} \sum_j \sum_{q=1}^{N_j} \sum_{m=1}^{\infty} \frac{2^m \, m!}{(2m)!} \, a_{qj}^{(2m)} \langle \boldsymbol{F}_{qj}^{(m)} [m] \, \boldsymbol{F}_{qi}^{(m)} \rangle_\omega, \tag{61}$$

where by (43) and (37) we have

$$\langle \boldsymbol{F}_{qj}^{(m)} [m] \, \boldsymbol{F}_{qj}^{(m)} \rangle_\omega = \sum_i \sum_{\substack{p=1 \\ p \neq q}}^{N_i} \sum_{n=0}^{\infty} \frac{2^{2n}(n!)^2}{(2n)!(2n+1)!} \, (\boldsymbol{M}_{pi}^{(n)} [n] \, \boldsymbol{M}_{pi}^{(n)}) \, (^{(n)}\boldsymbol{T}_{pq}^{(m)} [n+m] \, ^{(n)}\boldsymbol{T}_{pq}^{(m)})$$

$$= \sum_i \sum_{\substack{p=1 \\ p \neq q}}^{N_i} \sum_{n=0}^{\infty} \frac{2^{n-m} (2n+2m)! \, (n!)^2}{(2n)! \, (2n+1)!} \, (\boldsymbol{M}_{pi}^{(n)} [n] \, \boldsymbol{M}_{pi}^{(n)}) \, r_{pq}^{-2(n+m+1)}.$$

On substituting (61) in the definition (59), we finally obtain

$$\overset{(2)}{\langle U \rangle} = -\frac{1}{4} \sum_{ij}{}' x_i x_j \sum_{n=0}^{\infty} \sum_{m=1}^{\infty} \frac{2^n(n!)^2 \, m! \, (2n+2m)!}{(2n)! \, (2m)! \, (2n+1)!} \{ a_i^{(2m)} (\boldsymbol{M}_j^{(n)} [n] \, \boldsymbol{M}_j^{(n)}) +$$

$$+ (\boldsymbol{M}_i^{(n)} [n] \, \boldsymbol{M}_i^{(n)}) \, a_j^{(2m)} \} \iint r_{pq}^{-2(n+m+1)} n_{ij}^{(2)} (\mathbf{r}_p, \mathbf{r}_q) \, d\mathbf{r}_p \, d\mathbf{r}_q, \tag{62}$$

where $n_{ij}^{(2)}(\boldsymbol{r}_p, \boldsymbol{r}_q)$ is the binary distribution function for pairs of molecules p and q of species i and j respectively, and $x_i = N_i/N$ is the molar fraction of the i-th component of the mixture.

For axially-symmetric molecules we have the relation (55) and Eq. (62) assumes the form

$$\overset{(2)}{\langle U \rangle} = -\frac{1}{4} \sum_{ij} x_i x_j \sum_{n=0}^{\infty} \sum_{m=1}^{\infty} \frac{(2n+2m)!\, m!}{(2n+1)!\,(2m)!} \{a_i^{(2m)}(M_j^{(n)})^2 +$$

$$+ (M_i^{(n)})^2\, a_j^{(2m)}\} \int\int r_{pq}^{-2(n+m+1)}\, n_{ij}^{(2)}(\boldsymbol{r}_p, \boldsymbol{r}_q)\, d\boldsymbol{r}_p\, d\boldsymbol{r}_q, \tag{63}$$

which in the case of molecules possessing only the dipole $M_i^{(1)} = \mu_i$ and quadrupole $M_i^{(2)} = \Theta_i$ moments reduces to the simple formula

$$\overset{(2)}{\langle U \rangle} = -\frac{1}{8} \sum_{ij} x_i x_j \int\int \left\{ ((a_i\mu_j^2 + \mu_i^2 a_j)r_{pq}^{-6} + \frac{3}{2}\,(a_i\Theta_j^2 + \Theta_i^2 a_j)r_{pq}^{-8} + \right.$$

$$\left. 5(q_i\mu_j^2 + \mu_i^2 q_j)r_{pq}^{-8} + 14\,(q_i\Theta_j^2 + \Theta_i^2 q_j)r_{pq}^{-10} \right\} n_{ij}^{(2)}(\boldsymbol{r}_p, \boldsymbol{r}_q)\, d\boldsymbol{r}_p d\boldsymbol{r}_q, \tag{64}$$

where $a_i = a_i^{(2)}$ is the dipole and $q_i = a_i^{(4)}$ — the quadrupole polarizability of the isolated molecule of species i, defined by expression (54) or (56) for $n = 1$ and $n = 2$, respectively.

Averageing of the fourth-order energy $\overset{(4)}{U}$ can be performed in the same way; however for simplicity, we restrict this calculation to the case of dipolar molecules possessing the mean third-order dipole polarizability $c_i = \boldsymbol{U}: {}^{(1)}C_i^{(3)}:\boldsymbol{U}/5$, and finally obtain omitting the term with ternary interactions of the molecules

$$\overset{(4)}{\langle U \rangle} = -\frac{1}{10} \sum_{ij} x_i x_j (c_i\mu_j^4 + \mu_i^4 c_j) \int\int r_{pq}^{-12} n_{ij}^{(2)}(\boldsymbol{r}_p, \boldsymbol{r}_q) d\boldsymbol{r}_p d\boldsymbol{r}_q. \tag{65}$$

In the second-order approximation the average of the square of the first-order energy $\overset{(1)}{U}$ is non-zero and the result is in general given by the formula

$$\overset{(1)}{\langle U^2 \rangle} = \frac{1}{2} \sum_{ij} x_i x_j \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} \frac{2^{n+m}(n!\, m!)^2\,(2n+2m)!}{(2n)!\,(2m)!\,(2n+1)!\,(2m+1)!} \times$$

$$\times (M_i^{(n)}\,[n]\, M_i^{(n)})\,(M_j^{(m)}\,[m]\, M_j^{(m)}) \int\int r_{pq}^{-2(n+m+1)} n_{ij}^{(2)}(\boldsymbol{r}_p, \boldsymbol{r}_q)\, d\boldsymbol{r}_p\, d\boldsymbol{r}_q. \tag{66}$$

A further simplification of the general result of (62) and (66) can be obtained by appropriate assumptions on the type of symmetry of the molecule (e. g. the cases of molecules

with tetrahedral or octahedral symmetry are discussed in Refs. [17, 19, 21]. In some special cases expressions (62) and (66) yield the result derived by Pople [4, 23] and Barker [24].

Other contributions to $F_{\text{tensorial}}$ within the framework of the second approximation come from the terms $\langle \overset{(1)}{U} \overset{(2)}{U} \rangle$, $\langle \overset{(1)}{U} \overset{(3)}{U} \rangle$ etc. if, in averageing these terms, we take into consideration besides binary correlation also ternary or higher correlations as well as the anisotropy of the multipole polarizability tensors. However, we shall restrict these supplementary calculations to the following contribution only:

$$\langle \overset{(1)}{U} \overset{(3)}{U} \rangle = \frac{6}{25} \sum_{ij} x_i x_j \mu_i \mu_j (b_i \mu_j^3 + \mu_i^3 b_j) \int\int r_{pq}^{-12} n_{ij}^{(2)}(\boldsymbol{r}_p, \boldsymbol{r}_q) d\boldsymbol{r}_p d\boldsymbol{r}_q \tag{67}$$

resulting from eqs. (41) and (49) in the simpler case of dipolar molecules possessing the mean second-order dipole polarizability $b_i = \boldsymbol{U}{:}^{(1)}\boldsymbol{B}_i^{(2)} . \boldsymbol{k}/3$, with $\boldsymbol{k}$ denoting the unit vector along the axis of molecular symmetry.

In order to be able to test numerically the foregoing contributions to $F_{\text{tensorial}}$ we have to know the values of the radial averages of r_{pq}^{-n}. To compute the latter, one has to assume some form of the binary distribution function $n_{ij}^{(2)}(\boldsymbol{r}_p, \boldsymbol{r}_q)$. In the special case of moderately dense systems, when the binary distribution function can be expressed as follows:

$$n_{ij}^{(2)}(\boldsymbol{r}_p, \boldsymbol{r}_q) = \varrho^2 \exp\left\{ -\frac{4\varepsilon_{ij}}{kT} \left[\left(\frac{\sigma_{ij}}{r_{pq}}\right)^s - \left(\frac{\sigma_{ij}}{r_{pq}}\right)^t \right] \right\}, \tag{68}$$

we find [17]

$$\int\int r_{pq}^{-n} n_{ij}^{(2)}(\boldsymbol{r}_p, \boldsymbol{r}_q) \, d\boldsymbol{r}_q \, d\boldsymbol{r}_p = \frac{6b_{ij}\varrho}{sy_{ij}^{\frac{4-n}{s}}\sigma_{ij}^n} H_n^{s-t}(y_{ij}), \tag{69}$$

where

$$H_n^{s-t}(y_{ij}) = y_{ij}^{2(2s+3-n)/s} \sum_{m=0}^{\infty} \frac{1}{m!} y_{ij}^{2m(s-t)/s} \Gamma\left(\frac{mt+n-3}{s}\right) \tag{70}$$

with ε_{ij} and σ_{ij} denoting the central forces parameters having the dimensions of an energy and length, respectively, and $y_{ij} = 2(\varepsilon_{ij}/kT)^{\frac{1}{2}}$ and $b_{ij} = \frac{2}{3} \pi N\sigma_{ij}^3$. If in particular $s = 12$ and $t = 6$ i. e. with the 12—6 Lennard-Jones potential, the functions of Eq. (70) reduce to the functions H_n^{12-6} introduced by Pople [4], whereas $s = 18$ and $t = 6$, as well as $s = 28$ and $t = 7$ involve the functions discussed by Saxena and Joshi [25].

In cases when the values of the parameters ε_{ij} and σ_{ij} are known, we can use expression (69) for evaluating numerically the appropriate contribution to $F_{\text{tensorial}}$ given by expansion (58), with (62)—(67). In this way we can obtain information concerning the values of the permanent multipole moments and multipole polarizabilities of unlike molecules of substances.

APPENDIX

Interaction of a molecular system with an external magnetic field

Let a molecular system consist of point particles with masses m_ν and electric charges e_ν without consideration of their spins. The nonrelativistic Hamiltonian of such a molecular system is represented by the well-known equation

$$H = \sum_\nu \left\{ \frac{1}{2m_\nu} \left(\boldsymbol{p}_\nu - \frac{e_\nu}{c} \boldsymbol{A}_\nu \right)^2 + e_\nu \varphi_\nu \right\}, \tag{A. 1}$$

in which $\boldsymbol{p}_\nu$ is the momentum operator of the νth particle and φ_ν and $\boldsymbol{A}_\nu$ are the scalar and vector potentials at the position of the νth particle.

In the usual way (A1) can be split into a nonperturbated Hamiltonian H_0 and a perturbated Hamiltonian V, which now represents the interaction of the molecular system with external electric and magnetic fields and may be written in the form of

$$V = V_e + V_m. \tag{A. 2}$$

Here, V_e is the electric part of the perturbation and is given in general by the multipole expansion of Eq. (8), whereas V_m is the magnetic part of the perturbation which can be in general expanded as follows:

$$V_m = V_m^{(1)} + V_m^{(2)} + V_m^{(3)} + V_m^{(4)} + \cdots \tag{A. 3}$$

The magnetic part of the first-order perturbation Hamiltonian has the form (for comparison see Refs. [27], [28])

$$V_m^{(1)} = - \sum_{n=1}^{\infty} \frac{2^n n!}{(2n)!} \boldsymbol{M}_m^{(n)} [n] \boldsymbol{H}^{(n)}, \tag{A. 4}$$

where

$$\boldsymbol{M}_m^{(n)} = \frac{n}{(n+1)c} \sum_\nu e_\nu r_\nu^n \boldsymbol{Y}_\nu^{(n)} \times \dot{\boldsymbol{r}}_\nu \tag{A. 5}$$

is the 2^n-pole magnetic moment of the molecular system, and

$$\boldsymbol{H}^{(n)} = \{\boldsymbol{\nabla}^n \times \boldsymbol{A}_\nu\}_0 \tag{A. 6}$$

is the strength of the external magnetic field of degree n.

By (A. 4) the first-order magnetic energy of the molecular system in the ground state g is

$$W_{mg}^{(1)} = V_{gg}^{(1)} = - \sum_{n=1}^{\infty} \frac{2^n n!}{(2n)!} \boldsymbol{M}_{mgg}^{(n)} [n] \boldsymbol{H}^{(n)} \tag{A. 7}$$

The second-order magnetic perturbation in (A. 1) and (A. 3)

$$V_m^{(2)} = \frac{1}{2c^2} \sum_\nu \frac{e_\nu^2}{m_\nu} (A_\nu \cdot A_\nu), \tag{A. 8}$$

can be expanded as follows

$$V_m^{(2)} = -\frac{1}{2} \sum_{n=1}^\infty \sum_{n_1=1}^\infty \frac{2^{n+n_1} n! \, n_1!}{(2n)!(2n_1)!} H^{(n)}[n]^{(n)}A_d^{(n_1)}[n_1] H^{(n)}, \tag{A. 9}$$

where

$$^{(n)}A_d^{(n_1)} = -\frac{n \, n_1}{(n+1)(n_1+1)c^2} \sum_\nu \frac{e_\nu^2}{m_\nu} r_\nu^{(n+n_1)}(Y_\nu^{(n)} \cdot Y_\nu^{(n_1)} U - Y_\nu^{(n)} Y_\nu^{(n_1)}) \tag{A. 10}$$

is the diamagnetic multipole polarizability operator of an isolated molecule.

In the second-order perturbation theory we have

$$W_g^{(2)} = -\hbar^{-1} \sum_{k \neq g} \omega_{kg}^{-1} V_{gk}^{(1)} V_{kg}^{(1)} + V_{gg}^{(2)}, \tag{A. 11}$$

which because of (A. 4) and (A. 9) can be written as

$$W_{mg}^{(2)} = -\frac{1}{2} \sum_{n=1}^\infty \frac{2^n n!}{(2n)!} H^{(n)}[n] \overset{(1)}{M}{}_{mgg}^{(n)}, \tag{A. 12}$$

where

$$\overset{(1)}{M}{}_{mgg}^{(n)} = \sum_{n=1}^\infty \frac{2^{n_1} n_1!}{(2n_1)!} {}^{(n)}A^{(n_1)}[n_1] H^{(n_1)} \tag{A. 13}$$

is the first-order magnetic multipole moment with

$$^{(n)}A_{mgg}^{(n_1)} = {}^{(n)}A_{dgg}^{(n_1)} + \hbar^{-1} \sum_{k \neq g} \omega_{kg}^{-1}(M_{mgk}^{(n)} M_{mkg}^{(n_1)} + M_{mgk}^{(n_1)} M_{mkg}^{(n)}) \tag{A. 14}$$

the diagonal matrix element of the total magnetic multipole polarizability tensor. The first term in (A. 14) is the diamagnetic part whereas the second — the paramagnetic part of the magnetic multipole polarizability tensor.

Averageing over all possible molecular orientations we obtain from (A. 13)

$$\overset{(1)}{M}{}_m^{(n)} = a_m^{(2n)} H^{(n)}, \tag{A. 15}$$

where

$$a_m^{(2n)} = \frac{2^n n!}{(2n+1)!} \sum_g \varrho_{gg}^{(0)} {}^{(n)}A_{mgg}^{(n)} [2n] U^n \tag{A. 16}$$

is the mean value of the magnetic multipole polarizability consisting the diamagnetic part

$$a_d^{(2n)} = - \frac{2n^2}{n!(n+1)^2(2n+1)c^2} \sum_{\nu} \varrho_{gg}^{(0)} \left\langle g \left| \sum_{\nu} \frac{e_\nu^2}{m_\nu} r_\nu^{2n} \right| g \right\rangle \qquad (A.17)$$

and paramagnetic part

$$a_p^{(2n)} = \frac{2^{n+1}n!}{(2n+1)!\hbar} \sum_{g} \sum_{k \neq g} \omega_{kg}^{-1} M_{kg}^{(n)} [n] M_{kg}^{(n)} \varrho_{gg}^{(0)}. \qquad (A.18)$$

In particular for $n = 1$ Eqs. (A.16)—(A.18) give the well-known result of Van Vleck (1932).

Analogously, one obtains the magnetic energies of third and fourth-order by using the following formulas (see *e. g.* [30]):

$$W_g^{(3)} = \sum_{k \neq g} \{V_{gk}^{(1)} c_{kg}^{(2)} + V_{gk}^{(2)} c_{kg}^{(1)}\} + V_{gg}^{(3)},$$

$$W_g^{(4)} = \sum_{k \neq g} \{V_{gk}^{(1)} c_{kg}^{(3)} + V_{gk}^{(2)} c_{kg}^{(2)} + V_{gk}^{(3)} c_{kg}^{(1)}\} + V_{gg}^{(4)}, \qquad (A.19)$$

where we have now

$$c_{kg}^{(2)}(W_g^0 - W_k^0) = \sum_{l \neq g} V_{kl}^{(1)} c_{lg}^{(1)} - c_{kg}^{(1)} V_{gg}^{(1)} + V_{kg}^{(2)},$$

$$c_{kg}^{(3)}(W_g^0 - W_k^0) = \sum_{l \neq g} (V_{kl}^{(1)} c_{kl}^{(2)} + V_{kl}^{(2)} c_{lg}^{(1)} - c_{kg}^{(1)} V_{gl}^{(1)} c_{lg}^{(1)}) - V_{gg}^{(2)} c_{kg}^{(1)} - c_{kg}^{(2)} V_{gg}^{(1)} + V_{kg}^{(3)}. \qquad (A.20)$$

In the general case, when the total perturbation Hamiltonian of (A.2) is introduced in equation (A.11), (A.19) and (A.20), we find total energies of the second and higher--orders consisting, in addition to the pure parts depending only on the electric or magnetic field, mixed parts dependent simultaneously on the electric and magnetic fields.

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