MULTIPOLE FORMALISM FOR INTERMOLECULAR AND INTRAMOLECULAR INTERACTIONS

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The multipole formalism in the theory of intermolecular interactions is reviewed and the reasons for its success in applications in condensed media are analyzed. The question of the effective size of the multipoles is discussed. The effective length of the dipole moment of the water molecule is calculated on the basis of the Duncan-Pople model. The multi pole formalism is used for the first time to describe intramolecular interactions in the approximation of small electronic overlapping. The dipole and quadrupole moments of 36 diatomic molecules and bonds were calculated, and the computed values agree fairly well with experiment. The mechanism of formation of the chemical bond in diatomic molecules is discussed on the basis of the dipole-quadrupole interaction of the atoms.

INTRODUCTION

The optics of atmospheric gases and vapors is determined not only by the structure and optical properties of their constituent molecules but also by intermolecular interactions (IMI). In the case of the atmosphere there are two characteristic peculiarities. First, the atmosphere contains primarily light fractions of gases and vapors, i.e., the atomic and molecular weights of the particles are usually small. For this reason diatomic and triatomic molecules with comparatively simple structure predominate among the molecules present in the atmosphere. Second, for completely understandable reasons, the earth's atmosphere is not a dense gas, such as that obtainable under laboratory conditions under pressures of hundreds of thousands of atmosphere. Therefore pair collisions of particles are most likely to occur in the earth's atmosphere, and this simplifies substantially the problem of applying the statistical theory.

The two features indicated above should be. determining in the study of the processes involved in atmospheric optics. It is obvious that the power of the exact theory in describing the structure of molecules and IMI can be realized only if an appropriate approximation enabling numerical results to be obtained from the theory is made. In the case of atoms and simple molecules which interactby means of pair forces the multipole approximation is just such an approximation. Historically the multipole approximation appeared within the framework of electrodynamics, but it is also widely employed in modern quantum theory.

H. Lorentz was evidently first to represent molecules as point dipoles. As far back as 1880, in his classical work,[1] H. Lorentz took into account the IMI in a cubic lattice of dipoles and he derived an expression for the local electric field in such a lattice. The approach proposed by Lorentz was so popular that in works on solid-state physics, which laid the foundation of this science at the beginning of this century, the multipole formalism is standard in any discussion of IMI in a crystal lattice (see, for example, Ref. 2). One should not think, however, that the multipole formalism was employed in solid-state physics only at the dawn of its creation: the concept of dipoles and quadrupoles are necessary in both the modern literature in discussions of energy transfer processes in crystals and the theory of excitons with small radius.[3]

Multipole representations play a special role in the description of the intermolecular forces, in particular, intermolecular interaction potentials. The classical works of Debye,[4] Keesom,[5] and Lennard-Jones[6] explained not only the nature of Van-der—Waals forces in liquids and crystals, but they also made it possible to develop the theory of the dielectric constant of polar liquids in the language of multipoles. Prior to the works of F. London,[7] however, the origin of the attractive forces between nonpolar molecules was unclear. Wang made the first step toward an explanation.[8] Soon after the creation of quantum mechanics he showed that an attractive force should exist between two hydrogen atoms and this force should vary as R^{-7} at large distances R. London, however, developed the quantum-mechanical theory of dispersion forces acting between any atoms and molecules; he showed that the leading term in the potential of the dispersion forces varies as R^{-6}, and he derived a simple expression for the constant of this potential C_6 in the approximation of equal energy denominators. The classification of attractive intermolecular forces is now conducted completely in the language of multipoles.[9,10]

While the nature of attractive forces is explained by the interaction of electric multipoles, the repulsive forces acting between molecules are determined by electronic overlapping arising at short distances R. These forces are traditionally described by the methods of quantum chemistry, in which a multipole expansion is usually not employed. Quantum chemistry also studied intramolecular interactions, in particular, the nature of the chemical bond between atoms and molecules.

The division of IMI into long- and short-range became standard long ago.[9,10] There arises, however, the nontrivial question: where are the conditions for long-range forces realized? In condensed media – liquids and crystals – the intermolecular distances R are close to the diameters of the molecules σ. In gases molecules practically do not interact in the process of drifting and in collisions they approach to distances $R \geq \sigma$ owing to the deformation of the electron shells). Why then does the multipole formalism describe correctly in such a case the physical effects in all media? Moreover, the multipole language makes it possible to construct a quantitative theory, while the quantitative successes of quantum chemistry are limited to the simplest diatomic molecules.

The purpose of this paper is to analyze the limits of applicability of the multipole expansion and to determine why it is successful in describing the IMI at short distances. In addition, for the' first time an attempt is made to employ the multipole formalism for describing intramolecular interactions also. This can be done in the approximation of small overlapping of the electronic wave functions of the atoms. Although the molecules themselves cannot exist without electronic overlapping, an important question is what stimulates the appearance of the electronic overlapping itself under conditions of strong interelectronic and intermolecular repulsion. The calculation of the dipole and quadrupole moments of diatomic molecules, performed below based on the multipole formalism, demonstrates, first of all, the definite universality and applicability of this formalism not only at large distances R but also at short (intramolecular) distances. Second, this calculation answers the question posed above regarding the reasons for the appearance of a chemical bond in molecules. Finally, the discrepancy between theory and experiment shows the limits of applicability of the multipole description, i.e., it shows the contribution of spontaneous multipole fluctuations of the electron density of atoms to the formation of the electric moments of molecules and the contribution of exchange forces associated with the overlapping of the electron clouds of the atoms.

MULTI POLE EXPANSION

The interaction between atoms and molecules of any type, including chemical reactions, are basically of an electrical nature. For this reason the IMI can be described correctly if the Coulomb interaction of all constituent electric charges e_i of electrically neutral systems (atoms and molecules) can be analyzed.

The multipole formalism arises naturally in writing down the potential of an electrically neutral system at distances R outside the boundaries of this system. Let the charges e_i be located at distances r_i from some chosen center of the charge system. Then, according to Coulomb's law, the electric potential generated by the system at a distance R from its center is given by

$$V(\vec{R}) = \sum_i \frac{e_i}{|\vec{R} - \vec{r}_i|}. \tag{1}$$

it is more convenient to expand the function $\left|\vec{R} - \vec{r}_i\right|^{-1}$ in a series (Neumann's expansion), but in so doing two regions must be distinguished: a) $r_i < R$ and b) $r_i > R$.

It is important to stress that in both cases the expansion can be made regardless of the magnitude of the parameter r/R or R/r. The so-called one center expansion is obtained with the help of the spherical functions:

$$V(R,\ \theta,\ \varphi) = \sum_{n=0}^{\infty} \frac{(n - |m|)!}{(n + |m|)!} P_n^m (\cos\theta)\, e^{-im\varphi} \times$$
$$\times \left[\frac{1}{R^{n+1}} \sum_{\substack{i \\ (r_i<R)}} e_i r_i^n P_n^m (\cos\theta_i)\, e^{im\varphi_i} + \right.$$
$$\left. + R^n \sum_{\substack{i \\ (r_i>R)}} \frac{e_i}{r_i^{n+1}} P_n^m (\cos\theta_i)\, e^{im\varphi_i} \right]. \tag{2}$$

The first term on the right side of Eq. (2), which gives the expansion of the potential (1) in the region outside the boundaries of the charge system, leads to the multipole formalism. The second term could be termed an expansion in "inverse multipoles". Unfortunately the latter expansion is not widely used (though it is described in detail in Chapter 12 of Ref. 11); it can, however, in principle, be used to describe intramolecular interactions.

The relation (2) can be written in a more compact form with the help of the operator $\vec{\nabla}$:

$$V(\vec{R}) = \sum_{n=0}^{\infty} \frac{(-1)^n}{n!} \left[\sum_i e_i (\vec{r}_i \cdot \vec{\nabla})^n \left[\frac{1}{R} \right] + \right.$$
$$\left. + \sum_i e_i (\vec{R} \cdot \vec{\nabla}_i)^n \left[\frac{1}{r_i} \right] \right]. \tag{3}$$

We expand the function $V(\vec{R} + \vec{r}_j)$ around the point $\vec{R}$ in a series in powers of $\vec{r}_j$:

$$V(\vec{R} + \vec{r}_j) = V(\vec{R}) + \vec{\nabla}V\cdot\vec{r}_j + \frac{1}{2}\vec{\nabla}(\vec{\nabla}V):\vec{r}_j\vec{r}_j + \dots \tag{4}$$

Multiplying this expression by e_j and summing over all charges j of the second molecule we obtain an expression for the interaction energy of two molecules, i.e., the intermolecular pair interaction potential:

$$V_{int}(\vec{R}) = \sum_j e_j V(\vec{R} + \vec{r}_j). \tag{5}$$

The multipole expansion of the potential V_{int} is obtained by substituting Eq. (4) into Eq. (5) and using the first term on the right side of Eq. (3) for $V(\vec{R})$:

$$V_{int}(\vec{R}) = \sum_{n_1=0}^{\infty}\sum_{n_2=0}^{\infty}\frac{(-1)^{n_1+n_2}}{n_1!\,n_2!}\vec{N}^{(n_1)}[n_1]\vec{T}_{12}^{(n_1+n_2)}[n_2]\vec{N}^{(n_2)}. \tag{6}$$

The following notation has been introduced in Eq. (6): [12]

$$\vec{N}^{(n)} = \sum_i e_i\vec{r}_i^{\,n} = \int \rho(\vec{r})\,\vec{r}^{\,n}\,d\vec{r} \tag{7}$$

is the tensor of the multipole moment of order n ($\rho(\vec{r})$ is the charge density in the molecule);

$$\vec{T}_{12}^{(n)} = -\vec{\nabla}^n\left[\frac{1}{R}\right] \tag{8}$$

is the n-pole interaction tensor; and, $[n]$ denotes contraction with respect to the n indices of two neighboring tensors.

In applications only the first few terms of the expansion in Eq. (6) is usually employed:

$$V_{int}(\vec{R}) = \vec{d}_1\cdot\vec{T}_{12}^{(2)}(\vec{R})\cdot\vec{d}_2 + \frac{1}{2}\vec{d}_1\cdot\vec{\nabla}\vec{T}_{12}^{(2)}(\vec{R}):\vec{q}_2 - \frac{1}{2}\vec{d}_2\cdot\vec{\nabla}\vec{T}_{21}^{(2)}(\vec{R}):\vec{q}_1 - \frac{1}{4}\vec{q}_1:\vec{\nabla}\vec{\nabla}\vec{T}_{12}^{(2)}(\vec{R}):\vec{q}_2 + \dots \tag{9}$$

where

$$\vec{d} = \sum_i e_i\vec{r}_i = \int \rho(\vec{r})\,\vec{r}\,d\vec{r} \tag{10}$$

is the dipole moment of the system;

$$\vec{q} = \sum_i e_i\vec{r}_i\vec{r}_i = \int \rho(\vec{r})\,\vec{r}\vec{r}\,d\vec{r} \tag{11}$$

is the quadrupole moment tensor; and,

$$\vec{T}_{12}^{(2)}(\vec{R}) = \vec{T}_{21}^{(2)}(\vec{R}) = -\vec{\nabla}\vec{\nabla}\left[\frac{1}{R}\right] = \frac{1}{R^3}\left[\vec{I} - \frac{3\vec{R}\vec{R}}{R^2}\right] \tag{12}$$

is the dipole-dipole (DD) interaction tensor. The latter tensor is usually expressed as follows in terms of components:

$$T_{\alpha\beta}^{(2)}(R) = -\nabla_\alpha\nabla_\beta\left[\frac{1}{R}\right] = \frac{1}{R^5}(R^2\delta_{\alpha\beta} - 3R_\alpha R_\beta)$$

$$(\alpha, \beta = x, y, z). \tag{13}$$

The expression $\vec{\nabla}\vec{T}_{12}^{(2)}(\vec{R}) = -\vec{\nabla}\vec{\nabla}\vec{\nabla}\left[\frac{1}{R}\right]$ is a tensor of rank three

$$T_{\alpha\beta\gamma}^{(3)}(R) = \frac{3}{R^7}\left[5R_\alpha R_\beta R_\gamma - R^2\left[R_\alpha\delta_{\beta\gamma} + R_\beta\delta_{\alpha\gamma} + R_\gamma\delta_{\alpha\beta}\right]\right], \tag{14}$$

Describing the dipole-quadrupole (DQ) interaction/

The multipole expansion (6) of the (IMI) interaction is valid when $r_i + r_j < R$, i.e., when the two charge systems do not overlap. Cases of partial and complete overlapping of the charges are described in Ref. 11.

It is obvious that the number of terms to which the series (9) can be limited depends on how small the parameter $(r_i + r_j)/R$ is. The convergence of the series (9) itself has for all practical purposes not been studied. If, however, the potential (9) is employed in the quantum perturbation theory, then when the wave functions of the interacting molecules do not overlap their interaction energy can be represented in the form of the series

$$E(R) = -\sum_n \frac{C_n}{R^n}, \tag{15}$$

the first terms of which were first studied by London.[7] With regard to the series (15), it is known[13,10] that it is asymptotic or semiconverging, i.e., it diverges (according to D'Alembert's criterion) for any finite R. For sufficiently large R, however, the experimental values- of $E(R)$ can be described with good accuracy by the first few terms of the series(15), i.e., interactions of dipoles, quadrupoles, and octapoles. In this case there appears the surprising situation, but not uncommon in physics, when the first few terms of diverging series correctly describe physical quantities.

EFFECTIVE DIMENSIONS OF MOLECULAR MULTI POLES

As mentioned above, intermolecular interactions are described in the classical and quantum theory primarily in the language of multipoles. Of necessity, the multipole formalism is employed in the physics of condensed media, since IMI are significant precisely in such media. Multipoles can be validly used until the electronic overlapping in atoms and molecules becomes significant. Since the repulsion forces are connected precisely with this overlapping the relative role of overlapping can be estimated from the contribution of the repulsive forces to the total IMI energy. It is well known[14] that in molecular crystals the contribution of repulsive forces to the binding energy of the crystals is two times smaller than the contribution of attractive forces while in ionic crystals it is ten times smaller. Therefore in thermodynamic equilibrium in crystals (and especially in liquids) the effects due to electronic overlapping are relatively weak and the multipole expansion of the IMI potential V_{int} can be employed.

Why then in such a case do dipoles, i.e., the first term of the multipole expansion (9), make the main contribution to physical effects? This question can be answered if the effective dimensions of the molecular multipoles are known. Ideal and real dipoles are distinguished.[11]. If the effective length of a dipole $l \ll R$ (where R is the distance from the center of the dipole to the point at which its field is calculated), then the dipole is ideal, i.e., it is a “point” dipole. It is obvious that $a \ll R$ (where a is the linear size of the quadrupole) and the contribution of the quadrupole to the multipole expansion (9) becomes much less than the contribution of the dipole. Thus the answer to the question posed is obvious; one need only calculate the effective length of the dipole l.

First of all, we note that there are only three types of dipole moments of particles. First, the fluctuations of the electron density in atoms and molecules (owing to zero-point oscillations in quantum systems) create stochastic short-lived (instantaneous) dipole moments d_{in}s. They arise in dipole transitions of atoms and molecules into excited states; because of them attractive dispersion forces operate between particles. Second, an electric field E induces in neutral systems an induced dipole moment d_{ind}. Finally, molecules without a center of inversion have permanent dipole moments d_0. In all cases the effective length of the dipole l is introduced based on the relation $d = ql$, where $\pm q$ are the effective charges located at the tips of the dipole.

It is important to remember that in all three cases an electrically neutral system has a dipole moment only if charges of opposite sign are separated, i.e., the centers of gravity of the positive and negative charges do not coincide. The distance between these centers of gravity is the effective length of dipole:

$$l = |\vec{r}_{+q} - \vec{r}_{-q}|, \tag{16}$$

where the radius vectors $\vec{r}_{\pm q}$ are measured from an arbitrarily chosen center.

The displacement of the center of the electronic density Δr caused by quantum fluctuations must be small compared with the size r_0 of the orbitals of valence electrons which determine the effective quantum-mechanical dimensions of atoms and molecules. Otherwise a quantum system would be unstable and it would ionize continuously.

The dimensions l_{ind} of the induced dipoles are negligibly small. For example, placing a hydrogen atom in a strong field $E = 3 \cdot 10^4$ V/cm, we find $l_{ind} = \dfrac{d_{ind}}{e} = \dfrac{\alpha E}{e} = 1.4 \cdot 10^{-13}$ cm, where $\alpha = 0.67 \cdot 10^{-24}$ cm^3 is the polarizability of the atom. Even if the field displaces not the entire electron charge e but rather only part of the electron density, the size of the dipole l_{ind} is several orders of magnitude smaller than the Bohr radius of the atom a_B. In the field of a light wave the induced dipoles are indeed ”point-like”. This fact should be underscored, since it is often stated that the dimensions of induced dipoles are comparable to the dimensions of atoms and molecules.

This error also occurs in the literature on the dimensions l of the dipoles of molecules which have a permanent dipole moment d_0. In this case l_0 is simply identified with the diameter of the molecule σ. For example, in the case of a heteronuclear diatomic molecule AB it is assumed that the length of the dipole l_0 is equal to the length of the bond R_{AB}. In so doing it is forgotten that even in the case of a strong ionic bond in a molecule A^+B^- the highest electron density is concentrated not at the center of the ion B^- but rather in the space between the nuclei, which is what makes the chemical bond itself possible. For this reason the centers of gravity of the positive and negative charges once again turn out to be displaced relative to the nuclei and the distance l_0 becomes less than R_{AB}.

We shall demonstrate what was said above for the example of the water molecule, for which we have the Duncan and Pople quantum-mechanical model of the electron density distribution (Ref. 11, pp. 788–789). The coordinates of the center of gravity of charges of a given sing are determined by the formula

$$\vec{r}_{\pm q} = \frac{\sum\limits_i (\pm q_i)\, \vec{r}_i}{\sum\limits_i (\pm q_i)}. \tag{17}$$

In the case of the H_2O molecule the dipole moment is oriented along the bisector of the valence angle, and the bisector is chosen as the z axis. The core of the oxygen atom, according to this model, has a charge of +6e and lies at the origin of coordinates ($z_0 = 0$). Then the coordinates of the protons are $z_H = z_{H'} = 0.586$ (in Å). The coordinates of the two pairs of binding electrons are $z_{-2e} = 0.355$ and the coordinates of the two pairs of uncharged electrons are $z_{-2e}' = -0.158$. Then, according to Eq. (17), the coordinates of the centers of gravity of the charges are

$$z_{+q} = \frac{2e \cdot 0.586 + 6e \cdot 0}{2e + 6e} = 0.1465 \text{ Å};$$

$$z_{-q} = \frac{2(-ze) \cdot 0.355 + 2(-2e) \cdot (-0.158)}{2(-2e) + 2(-2e)} = 0.0985 \text{ Å}.$$

From here we find the length of the equivalent dipole moment of the H_2O molecule from the formula (16):

$$l_0(H_2O) = z_{+q} - z_{-q} = 0.048 \text{ Å}. \tag{18}$$

The diameter of the H_2O molecule $\sigma = 2.76$ Å,[15] whence $l_0/\sigma = 0.017$, i.e., the dipole is 57.6 times shorter than the diameter of the molecule.

Thus in all cases the effective sizes of the dipoles are many times smaller than the sizes of the particles themselves. This means that an electrically neutral system (molecule) behaves electrically in the space outside it as a point multipole, whose dimensions l are many times smaller than the distances R to the neighboring molecules. For this reason, under conditions when the electronic densities of the molecules do not overlap, the multipole formalism can be used without any restrictions for any $R > \sigma$. Since the parameter l/R is always very small, the first few terms of the multipole expansion already give good results for the IMI energy $E(R)$ in Eq. (15). The effects of the electronic overlapping diminish with distance exponentially, as a result of which the conditions under which the multipole formalism is applicable already obtain in condensed media.

MULTI POLES AND INTRAMOLECULAR INTERACTIONS

Intramolecular interactions are responsible for the electric characteristics of molecules: polarizability, dipole moments, and quadrupole moments. The calculation of the electric moments of diatomic molecules is a fundamental problem, since for polyatomic molecules results can be obtained from the moments of diatomic bonds based on the vector additivity scheme. Unfortunately, in modern quantum chemistry it is practically impossible to calculate the moments of diatomic molecules and bonds with a reasonable number of trial basis wave functions, even with the help of fast computers.[16]

The successes of the multipole formalism in the theory of IMI suggest that it can be used to describe intramolecular interactions. This can be done, as pointed out above, only if the electronic overlapping of the wave functions of the interacting atoms, which is responsible for the existence of the chemical bond itself, is neglected. Generally speaking, electronic overlapping is sometimes completely neglected (Hückel's method) in quantum chemistry also in order to obtain a physical result.

Overlapping is itself, however, usually accepted as fact and question of why the electron density is concentrated in the space between the nuclei, i.e., why the atoms are attracted toward one another, is never asked.

The multipole formalism gives an answer to this question. This will be discussed below. Addressing the problem of calculating the dipole and quadrupole moments of diatomic molecules and bonds, we must study the process of two atoms drawing together from large distances R up to equilibrium internuclear distances in the molecule R_e. As long as there is no overlapping the attraction of the atoms is determined by the correlation of their electric densities which arises owing to the interaction of the instantaneous fluctuating atomic dipoles and quadrupoles. When the electron densities start to overlap the multipole interaction does not vanish completely, but remains owing to the nonoverlapping atomic cores.

The indicates multipole interaction of the atoms induces in them dipole and quadrupole moments, whose quantum-mechanical average remains nonzero in second-order perturbation theory. Since we do not know how to take into account the effects of overlapping and exchange without knowing the wave functions of the atoms, we can study the dipole interaction of atoms at large distances R and extrapolate the obtained result to R_e. In this manner we avoid the need to take into account the effects of overlapping, but the entire calculation will, naturally, be approximate. The discrepancy between the computed values of the moments and the experimental values characterizes the relative role of the ignored effects of overlapping.

The fact that dipole and quadrupole moments appear in a pair of interacting atoms has in itself been known for a long time,[9] but a quantitative theory has not been constructed. To construct such a theory we shall start from the interaction Hamiltonian

$$\hat{H}_{\text{int}} = \hat{H}_{\text{DD}} + \hat{H}_{\text{DQ}} = \\ = \hat{\vec{d}}_1 \cdot \vec{T}^{(2)}_{12} \cdot \hat{\vec{d}}_2 + \frac{1}{2}\hat{\vec{q}}_1 : \vec{T}^{(3)}_{12} \cdot \hat{\vec{d}}_2 + \frac{1}{2}\hat{\vec{q}}_2 : \vec{T}^{(3)}_{21} \cdot \hat{\vec{d}}_1, \qquad (19)$$

associated with the first three of the expansion (9). The DD interaction tensor $\vec{T}^{(2)}_{12}$ and the DQ interaction tensor $\vec{T}^{(3)}_{12} = -\vec{T}^{(3)}_{21}$ are given by Eqs. (13) and (14).

In the approximation under study, when there are no effects due to electron exchange between atoms, the wave function $\psi^{(0)}$ of the molecules in zeroth-order with respect to the interaction (19) need not be antisymmetrized with respect to each pair of electrons, i.e., the wave function can be written as a simple product of the wave functions of the atoms.[9] In this case, in the second-order perturbation theory with respect to $\hat{H}_{\text{DD}}$ the diagonal matrix element $\left\langle \psi_0 \middle| \vec{Q} \middle| \psi_0 \right\rangle$ gives the quadrupole moment $\vec{Q}(R)$ of the pair of atoms, and in second order with respect to the product of Hamiltonians $\hat{H}_{\text{DD}}$ $\hat{H}_{\text{DQ}}$ the matrix element $\left\langle \psi_0 \middle| \vec{d} \middle| \psi_0 \right\rangle$ gives the dipole moment $\vec{d}(R)$. The wave function ψ_0 of the ground state of the system in second-order perturbation theory has a quite complicated form, but the diagrammatic rules for the interaction of atom-molecule systems[17] make it possible to write down the indicated matrix elements immediately:

$$\vec{Q}(R) = \vec{Q}_{12}(R) + \vec{Q}_{21}(R) = \\ = \sum_{\chi_1 \neq o_1} \sum_{\substack{\lambda_1 + \mu_2 \neq \\ \neq o_1 + o_2}} \frac{(\vec{Q}_1)_{o_1\chi_1} (\vec{d}_1)_{\chi_1\lambda_1} \cdot \vec{T}^{(2)}_{12} \cdot (\vec{d}_2)_{o_2\mu_2}}{(E_{o_1} + E_{o_2} - E_{\lambda_1} - E_{\mu_2})} \times$$

$$\times \frac{(\vec{d}_1)_{\lambda_1 0_1} \cdot \vec{T}^{(2)}_{12} \cdot (\vec{d}_2)_{\mu_2 0_2}}{(E_{0_1} - E_{\chi_1})} +$$

$$+ \sum_{\substack{\chi_1+\mu_2\neq \\ \neq 0_1+0_2}} \sum_{\substack{\lambda_1+\mu_2\neq \\ \neq 0_1+0_2}} \frac{(\vec{d}_1)_{0_1\chi_1} \cdot \vec{T}^{(2)}_{12} \cdot (\vec{d}_2)_{0_2\mu_2} (\vec{Q}_1)_{\chi_1\lambda_1}}{(E_{0_1} + E_{0_2} - E_{\chi_1} - E_{\mu_2})} \times$$

$$\times \frac{(\vec{d}_1)_{\lambda_1 0_1} \cdot \vec{T}^{(2)}_{12} \cdot (\vec{d}_2)_{\mu_2 0_2}}{(E_{0_1} + E_{0_2} - E_{\lambda_1} - E_{\mu_2})} +$$

$$+ \sum_{\chi_1\neq 0_1} \sum_{\substack{\lambda_1+\mu_2\neq \\ \neq 0_1+0_2}} \frac{(\vec{d}_1)_{0_1\lambda_1} \cdot \vec{T}^{(2)}_{12} \cdot (\vec{d}_2)_{0_2\mu_2} (\vec{d}_1)_{\lambda_1\chi_1}}{(E_{0_1} + E_{0_2} - E_{\lambda_1} - E_{\mu_2})} \times$$

$$\times \frac{\vec{T}^{(2)}_{12} \cdot (\vec{d}_2)_{\mu_2 0_2} (\vec{Q}_1)_{\chi_1 0_1}}{(E_{0_1} - E_{\chi_1})} + [1 \Leftrightarrow 2]; \tag{20}$$

$$\vec{d}(R) = \vec{d}_{12}(R) + \vec{d}_{21}(R) =$$

$$= \sum_{\chi_1\neq 0_1} \sum_{\substack{\lambda_1+\mu_2\neq \\ \neq 0_1+0_2}} \frac{(\vec{d}_1)_{0_1\chi_1} (\vec{d}_1)_{\chi_1\lambda_1} \cdot \vec{T}^{(2)}_{12} \cdot (\vec{d}_2)_{0_2\mu_2}}{(E_{0_1} + E_{0_2} - E_{\lambda_1} - E_{\mu_2})} \times$$

$$\times \frac{(\vec{q}_1)_{\lambda_1 0_1} : \vec{T}^{(3)}_{12} \cdot (\vec{d}_2)_{\mu_2 0_2}}{(E_{0_1} - E_{\chi_1})} +$$

$$+ \sum_{\substack{\chi_1+\mu_1\neq \\ \neq 0_1+0_2}} \sum_{\substack{\lambda_1+\mu_2\neq \\ \neq 0_1+0_2}} \frac{(\vec{q}_1)_{0_1\chi_1} : \vec{T}^{(3)}_{12} \cdot (\vec{d}_2)_{0_2\mu_2} (\vec{d}_1)_{\chi_1\lambda_1}}{(E_{0_1} + E_{0_2} - E_{\chi_1} - E_{\mu_2})} \times$$

$$\times \frac{(\vec{d}_1)_{\lambda_1 0_1} \cdot \vec{T}^{(2)}_{12} \cdot (\vec{d}_2)_{\mu_2 0_2}}{(E_{0_1} + E_{0_2} - E_{\lambda_1} - E_{\mu_2})} +$$

$$+ \sum_{\chi_1\neq 0_1} \sum_{\substack{\lambda_1+\mu_2\neq \\ \neq 0_1+0_2}} \frac{(\vec{d}_1)_{0_1\chi_1} (\vec{q}_1)_{\chi_1\lambda_1} : \vec{T}^{(3)}_{12} \cdot (\vec{d}_2)_{0_2\mu_2}}{(E_{0_1} + E_{0_2} - E_{\lambda_1} - E_{\mu_2})} \times$$

$$\times \frac{(\vec{d}_1)_{\lambda_1 0_1} \cdot \vec{T}^{(2)}_{12} \cdot (\vec{d}_2)_{\mu_2 0_2}}{(E_{0_1} - E_{\chi_1})} + [1 \Leftrightarrow 2]. \tag{21}$$

where $\vec{d}_{12}$ is the dipole moment induced in the first atom by the second atom and $\vec{d}_{21}$ is the dipole moment induced in the second atom as a result of the interaction with the first atom. Analogous notation was introduced for the quadrupole moments $\vec{Q}_{12}$ and . $\vec{Q}_{21}$. To save space the expressions for $\vec{Q}_{21}$ and $\vec{d}_{21}$ are denoted by the symbol [1 ⇔ 2], which indicates that all indices 1 and 2 in the expressions presented must be interchanged. The energies of the ground and excited states of the atoms are denoted by E_{0_1} and E_{κ_1} (I = 1, 2), respectively. The matrix elements of all operators in the numerators are calculated using the wave functions of the atoms ψ_{κ_1}.

It is obvious that the electric moments of interacting atoms, expressed in terms of the dispersion sums in Eqs. (20) and (21), strictly speaking cannot be expressed in terms of the observed characteristics of free atoms. This is possible in the approximation of equal energy denominators, introduced in quantum mechanics by Unsöld[18] and widely employed in the theory of IMI.[7,9-13] In this approximation the first ionization potential of the atoms are introduced:

$$E_{\chi_1} - E_{0_1} = U_1, \quad E_{\chi_2} - E_{0_2} = U_2, \tag{22}$$

This makes it possible to obtain, by summing, an expression for the polarizability α of free atoms:

$$(d_\mu d_\nu)_{0_1 0_1} = \frac{1}{2} \alpha_1 U_1 \delta_{\mu\nu} \; (i = 1,2;\ \mu,\ \nu = x,\ y,\ z). \tag{23}$$

The further calculations are standard. With their help we obtain the following expression for the quadrupole moment $\vec{Q}_{12}$ induced in the first atom:

$$Q_{12\alpha\beta}(R) = \frac{e^3 U_2 (3U_1 + 2U_2)}{10 U_1 (U_1 + U_2)^2} \alpha_2 \times$$

$$\times \sum_k (r_k^4)_{0_1 0_1} (3n_{12\alpha} n_{12\beta} - \delta_{\alpha\beta}) R^{-6}, \tag{24}$$

where $\vec{n}_{12}$ is a unit vector oriented from the center of the first atom to the center of the second atom. Writing an analogous expression for the moment $\vec{Q}_{21}$ and transforming to the experimentally measured zz component of the total tensor $\vec{Q}_{\alpha\beta}$ (the axis of the molecule is chosen as the z axis), we obtain the following expression for the quadrupole moment of a diatomic molecule:

$$Q(R) = Q_{12zz}(R) + Q_{21zz}(R) =$$

$$= \frac{e^3 R^{-6}}{5(U_1 + U_2)^2} \left[\frac{U_2}{U_1} (3U_1 + 2U_2) \alpha_2 \sum_k (r_k^4)_{0_1 0_1} + \right.$$

$$+ \frac{U_1}{U_2}\left(3U_2 + 2U_1\right)\alpha_1 \sum_{1}\left(r_1^4\right)_{0_2 0_2}\Bigg]. \tag{25}$$

Analogous calculations give the following expression for the dipole moment $\vec{d}_{121}$ induced in the first atom:

$$\vec{d}_{12}(R) = \frac{3e^3}{5}\frac{U_2\left(3U_1 + 2U_2\right)}{U_1\left(U_1 + U_2\right)^2}\alpha_2 \sum_{k}\left(r_k^4\right)_{0_1 0_1}\vec{R}^{-7}\,\vec{n}_{21}. \tag{26}$$

Correspondingly, the dipole moment $\vec{d}_{21}$ induced in the second atom is oriented along the vector n_{12}. Since the vector d is oriented, as customarily done,[9-11] from the negative charge to the positive charge the directions of the vectors $\vec{d}_{12}$ and $\vec{d}_{21}$ show that as a result of the DQ interaction of the atoms negative charge accumulates in their interiors in the space between the nuclei.

Thus the DQ interaction, which already arises at distances R where there is still no electronic overlapping, provides the "impetus", consisting of redistribution of the electronic density along the line R_{12}, for the formation of a chemical bond between the atoms. Since the DD and DQ forces are attractive the atoms draw together up to internuclear distances R_e at which further attraction is determined by the electrostatic forces between the nuclei and the electronic density of the overlapping orbitals. The formation of antibonding orbitals can also be explained in an analogous manner, if the formation of the molecule in an excited state is studied.

Without the discovery of the mechanism described above the increase in the electron density in the space between the nuclei must be postulated (as is done in quantum chemistry), and the fact of electron overlapping must itself be regarded as the starting point of the entire theory of the chemical bond. In addition, the reason that interelectronic repulsion does not always lead to accumulation of electron charge only on the outer side of the atoms (which does indeed occur with the formation of antibonding orbitals) is regarded as inexplicable. If it were not for the DQ force, the electron density would always be forced out of the internuclear space and the formation of bonding orbitals would be impossible.

In a diatomic molecule A^+B^- the dipole moment $\vec{d}$ of the molecule must be oriented parallel to the vector $\vec{n}_{21}$. For this reason d will be positive, if we define $d(R) = d_{21}(R) - d_{12}(R)$. If, however, according to this definition d turned out to be negative, then this means that the charge distribution in the molecule has the form A^-B^+. Based on what we have said, we find from Eqs. (25) and (26)

$$d(R) = 3R^{-1}\left[Q_{21}(R) - Q_{12}(R)\right] =$$

$$= \frac{3e^3R^{-7}}{5\left(U_1 + U_2\right)^2}\left[\frac{U_1}{U_2}\left(3U_2 + 2U_1\right)\alpha_1 \sum_{1}\left(r_1^4\right)_{0_2 0_2} -\right.$$

$$\left. - \frac{U_2}{U_1}\left(3U_1 + 2U_2\right)\alpha_2 \sum_{k}\left(r_k^4\right)_{0_1 0_1}\right]. \tag{27}$$

It is obvious that in homonuclear molecule this expression vanishes, i.e., the moments $\vec{d}_{12}$ and $\vec{d}_{21}$ compensate one another. In a molecule of type AB, however, the dipole moment exists only to the extent that the atoms are different (asymmetric).

The expressions (25) and (27) contain the parameter $\sum_k (r_k^4)_{00}$, which must be calculated quantum-mechanically. Since we have neglected exchange effects at the outset, it is logical to represent the wave functions $|O_i>(i = 1, 2)$ of the ground state of the atoms in the form of a nonantisymmetrized (Hartree) product of single-electron Slater orbitals (once again by analogy to what is done in the theory of IMI):

$$|0> = \prod_{k=1}^{z}\chi^{(k)}_{n^*,l,m_l}\left(r_k, \theta_k, \varphi_k\right), \tag{28}$$

where z is the number of electrons in the atom. Writing the single-electron orbitals in atomic units:

$$\chi^{(k)}_{n^*,l,m_l}\left(r, \theta, \varphi\right) = Nr^{n^*-1}\exp\left[\frac{-Z^*r}{n^*}\right]Y_{l,m_l}(\theta, \varphi), \tag{29}$$

where n^* and z^* are the effective principal quantum number and the nuclear charge for a given orbital, which are defined according to Slater's rules,[11] and taking into account the fact the wave functions (29) are orthogonal and normalized, the diagonal matrix elements of interest can be put into the form

$$\sum_{k=1}^{z}\left(r_k^4\right)_{00} = \sum_{n,l}\langle r^4\rangle_{n^*,z^*}, \tag{30}$$

where we have transferred from summation over all electrons in the atom to a sum over all orbitals nl of the atom. The averages $\langle r^4\rangle_{n^*,z^*}$ can be easily calculated with the help of the wave functions (29):

$$\langle r^4\rangle_{n^*,z^*} = \frac{1}{4}\left[\frac{n^*}{Z^*}\right]^4 \times$$

$$\times\left(2n^{*2} + 3n^* + 1\right)\cdot\left(2n^{*2} + 7n^* + 6\right). \tag{31}$$

Thus under the approximations made above we were able to express quite simply the electric moments of diatomic molecules in terms of the well-known[19] characteristics of free atoms: the polarizability α and the first ionization potential U. The values of the parameter $\sum_{k=1}^{z}\left(r_k^4\right)_{00}$ and the polarizability of the atoms calculated for the atoms studied are presented in Table I.

TABLE I.

Atom	H	Li	C	N	O	F	Na	Si	S	Cl	Br
$\sum_{k=1}^{Z}(r_k^4)_{00}$, a_B^4	22.50	444.5	60.28	36.33	23.53	16.09	1095.3	345.5	174.21	129.49	27.66
α, Å^3	0.667	24.0	1.75	1.11	0.80	0.48*	24.0	5.50	2.90	3.10 [26]	3.80

TABLE II.

Theoretical and experimental values of the dipole and quadrupole moments of diatomic molecules.

Molecule	$d_0 \cdot 10^{18}$		$Q_0 \cdot 10^{26}$	
	Ther.	Exper. [20]	Ther.	Exper. [21]
Li_2	—	—	14.81	13.80
N_2	—	—	4.29	2.05
O_2	—	—	1.21	1.0
F_2	—	—	0.15	0.17
Cl_2	—	—	1.35	3.23 [22]
HF	2.36	2.34	3.24	3.0
HCl	-1.30	1.11	3.73	3.80
HBr	1.54	0.83	1.28	2.90
LiH	7.35	6.04	7.94	7.34
LiF	7.55	6.60	6.08	5.82
LiCl	5.27	7.07	9.62	—
LiBr	6.47	6.20	5.66	—
CH	2.13	2.80 [23]	4.47	—
CN	3.50	3.94	5.46	—
CO	3.48	2.70 [24]	4.98	—
CF	1.26	1.41	1.38	—
CS	-2.05	±2.0	4.71	—
CSi	-2.36	-1.20	2.85	—
CBr	1.11	1.38	0.99	—
NH	-1.0	-1.31	3.65	—
NO	-0.03	0.16	2.28	2.05
NF	0.20	0.18	0.58	—
OH	-0.96	-1.51	4.36	—
NaF	5.36	8.16	4.04	2.02
NaCl	7.13	8.50	7.92	—
NaBr	6.64	9.17	5.95	—
SiH	5.73	5.93	4.48	—
SiO	5.09	3.10	3.95	—
SiF	2.96	2.27	2.14	—
SiS	1.65	1.73	4.59	—
SN	3.61	1.80	3.31	—
SO	2.51	1.55	2.37	—
ClO	0.60	0.73	1.42	—
ClF	0.38	0.65	0.51	—
ClBr	0.58	0.57	0.63	—

The values of the dipole moment d_0 and quadrupole moment Q_0 of a molecule in the position of equilibrium can be obtained from the corresponding expressions (27) and (25) for the functions $d(R)$ and $Q(R)$ by extrapolating them to the equilibrium distances $R = R_e$ between the nuclei.[19] The theoretical and experimental values$^{20-2}$4 of d_0 and Q_0 are compared in Table II. As we can see, the theory gives a quite good quantitative prediction of the electric moments of the diatomic molecules and bonds. It is significant that the predicted direction of the dipole moment vector d_0 is inconsistent with the generally accepted valuesof the electronegativities of the atoms in only two of 36 cases (HCl and NO). In addition, in quantum-mechanical calculations the problem of the sign (direction) of the dipole moment is one of the most difficult problems.[16]

It is also important to note that extrapolation of the results of the multipole formalism to ultrashort distances $R = R_e$ does not give physically meaningless large values of the d_0 and Q_0; they remain reasonable and close to their experimental values. This serves as additional justification for using the language of multipoles in the theory of IMI in condensed media. In addition, we can see that the electronic overlapping in diatomic molecules does not play a decisive role in the formation of the magnitudes of the electric moments of the molecules.

Thus the multipole formalism describes quantitatively quite correctly both the intermolecular and intramolecular interactions in effects that are not related directly with electronic exchange and overlapping.

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