

Topics in Current Chemistry

Fortschritte der
chemischen Forschung

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58

New Theoretical Aspects

A. Julg

Description of Molecules Using
Point Charges and Electric Moments

R. S. Butler · P. A. D. deMaine

Automatic Chemical Reaction
Analysis

R. Geick

IR Fourier Transform Spectroscopy



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This series presents critical reviews of the present position and future trends in modern chemical research. It is addressed to all research and industrial chemists who wish to keep abreast of advances in their subject.

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Röntgen- strukturanalyse organischer Verbindungen

Eine Einführung

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Beugung von Röntgenstrahlen in Kristallen.
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wendung von Fourier-Reihen bei der Kristall-
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Die Röntgenstrukturanalyse liefert auch von komplizierten organischen Molekülen anschauliche Bilder. Ihre methodischen Grundlagen gelten vielfach als „schwierig“, doch gelingt es den Verfassern zu zeigen, daß nicht nur die Methode, sondern auch die mathematisch-physikalische Auswertung der Meßresultate in unseren Tagen zu einem Routineverfahren geworden sind. Das Werk vermittelt Grundlagen, beschreibt die experimentelle Technik, zeigt Beispiele und gibt eine Anleitung für mathematisch Ungeübte.

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W. Bähr, H. Theobald
Organische Stereochemie
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In den letzten Jahren sind in der organischen Stereochemie viele Begriffe neu geprägt und einige ältere neu definiert oder modifiziert worden. Sie zu sammeln und möglichst kurz wiederzugeben, ist das Ziel dieses Buches. Die Sammlung umfaßt 89 Hauptbegriffe mit ca. 300 Definitionen in alphabetischer Reihenfolge. Der Schwerpunkt liegt auf Definitionen der statischen Stereochemie.

Das Buch ist für alle diejenigen bestimmt, die sich rasch über stereochemische Begriffe und Definitionen informieren wollen. Es wendet sich also nicht nur an Studierende und Studierende der Chemie, sondern auch an Biochemiker, Molekularbiologen, Biologen und Mediziner.

D. Hellwinkel

Die systematische Nomenklatur der Organischen Chemie

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VIII, 170 Seiten. 1974
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Es wird gezeigt, wie man chemischen Verbindungen eindeutige und international verständliche Namen zuordnet, beziehungsweise wie sich aus Verbindungsnamen die Konstitutionsformeln ergeben. Da sich jetzt auch die deutschen Chemie-Zeitschriften auf die von der IUPAC entwickelte systematische Nomenklatur festgelegt haben, wird niemand mehr ohne entsprechende Grundkenntnisse auskommen können, sei er Chemiker, Biologe, Mediziner oder Physiker.

J. Schurz

Physikalische Chemie der Hochpolymeren

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Das Buch behandelt Prinzipien, Gesetze und Methoden der physikalischen Chemie

der Hochpolymeren. Neben der Thermodynamik und Konformation von Polymeren in Lösung werden auch ihr Fließverhalten und Untersuchungsmethoden für Molekülgröße und Molekülgestalt besprochen. Auch konzentrierte Lösungen vom Netzwerktyp werden erörtert. Bei festen Polymeren werden kristalliner, Glas- und gummielastischer Zustand diskutiert sowie entsprechende Phasenübergänge, wobei auf rheologische Gesichtspunkte ausführlich eingegangen wird. Das Buch wendet sich vor allem an Studenten der Chemie und Physik, ist aber auch für Biochemiker und Physiologen interessant. Die Probleme werden weitgehend unter dem Blickwinkel der technischen Anwendung gesehen.

H. Preuss, F. L. Boschke

Die chemische Bindung

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In diesem Buch wird eine weitgehend strenge Wissenschaftlichkeit mit einer möglichst einfachen Darstellungsweise (die im wesentlichen qualitativ ist) verknüpft. Wesentliche mathematische Kenntnisse werden nicht gefordert. Das Buch wendet sich an alle Chemiker sowie besonders an Chemie-Studenten.

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On the Description of Molecules Using Point Charges and Electric Moments

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I. Introduction

The idea of electrical charge in molecules is a very old one. Since it has always been connected with the general theory of molecules and of chemical reactions, its history reflects the same changes in perspective.

As a result of his discovery of electrolysis, Davy built a theory around the idea that chemical combination resulted from electrostatic attraction between electrically charged particles, the electrical charge appearing when the particles came together ¹⁾. Berzelius developed this idea in 1819 and proposed a general theory of reactions, according to which the charges were already present in atoms ²⁾ and every atom had both electricities, positive and negative, more or less concentrated around the poles. This led him to classify the elements according to their prevailing electrical state, positive or negative: oxygen, chlorine, etc. were negative; hydrogen, the metals, etc. were positive.

This theory was strongly contested by Dumas and his school, who showed in 1834 that a chlorine atom, which should have been negative according to Berzelius, could replace a (positive) hydrogen atom in molecules as acetic acid or the hydrogen carbides ³⁾. A great controversy followed, the chemists being divided into two camps: those interested in the so-called mineral molecules, partisans of the electrical theory of Berzelius, and those who studied the so-called organic molecules, for which Dumas theory of substitution seemed necessary.

This unsatisfactory situation lasted till the end of the nineteenth century, when the electron was discovered ⁴⁾ and the structure of atoms clarified. Now chemistry entered a new era. The old intuitive idea of affinity between atoms was replaced by the idea of affinity of atoms for electrons. Each atom was characterized by its attractive or repulsive power for electrons ⁵⁾. It followed that in a molecule, if two atoms had a different attractive power, the binding between these two atoms was polar, even if the molecule was not completely ionized ⁶⁾. At the same time the idea was slowly forced upon chemists by experience that all reactions must be preceded by ionic dissociation of molecules, the polar bonds dissociating of course more easily than the non-polar bonds ⁷⁾.

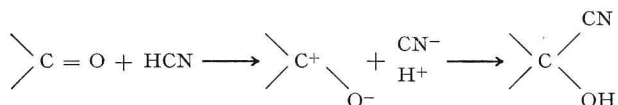
Finally, about 1920, Lewis explicitly attributed the formation of bonds to electron pairs, and thus completed the general description of molecules ⁸⁾; he introduced the distinction between homopolar or covalent and ionic bonds.

This way of viewing molecular structure and chemical reactions bridged the two opposing theories of Berzelius and Dumas. Its success was extraordinary, as is well known ⁹⁾. For instance, hydrolysis of methyl iodide was explained by dissociation of water in ions H^+ and OH^- , followed by replacement of iodine (negative) by the OH^- ions:

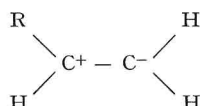


But this theory proved useful mainly in the field of addition reactions: for example, for the carbonyl group, the sites of addition of asymmetric reactants could be predicted from the signs of the ions into which they dissociated and from the polarities, negative for oxygen and positive for carbon, which resulted from

their different power of attraction for electrons. The double bond of CO took the ionic form C^+O^- :

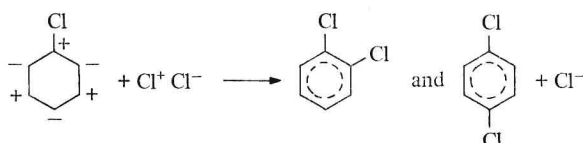


Experiments showed on the other hand that a hydricid molecule could be fixed by an asymmetrically substituted $C=C$ double bond with a well defined orientation (Markovnikov's rule) ¹⁰⁾. Hydrogen was directed to the more substituted carbon atom. This fact was explained by the polarization



of the double bond. By analogy with the carbonyl group, it was possible to conclude that the most substituted carbon atom was the one least rich in electrons.

In the same way the orientation rules for the second substitution on the benzene ring ¹¹⁾ found a simple explanation if alternant polarity on the ring was assumed ¹²⁾ to result from the electron-attracting or -repelling power of the first substituent. For example,



A fundamental remark must be made at this point. If it is so that charges direct an electrically charged reactant towards certain points of a molecule when an ionic process takes place, the approach itself of a reactant changes the initial charge distribution in the molecule because of the electrical field it creates. This is the polarization phenomenon. It follows, for instance, in the case of the carbonyl group mentioned above, that if the negative charge situated in the neighborhood of the oxygen nucleus attracts the H^+ ion, and the positive charge of carbon attracts the CN^- ion, without the effect of the field created by this ion, the negative charge of oxygen will decrease to complete ionization ($\text{C}^+ - \text{O}^-$) when at least one of the two ions H^+/CN^- is sufficiently close. If the charges present in the isolated molecule are sufficiently large, their value will determine the point of attack; this is produced for instance for the methylation of azulene by ICH_3 . The CH_3^+ ion will come on carbon 1 (or 3) ¹³⁾ which is strongly negatively charged. ¹⁴⁾ Under the action of the field created by CH_3^+ , a -1 charge will appear at that point. On the other hand, in a molecule such as naphthalene, where the net charges are very weak ¹⁵⁾, the point of attack of a positive ion (SO_3H^+ for instance) will be conditioned by the ease with which a $+1$ charge appears on the α position ¹⁶⁾.

Another example is provided by pyrrole ¹⁷⁾. When an ionic process takes place, the charges are clearly not the only factor. In addition, it is well known

today that several reactions exist which do not take place according to an ionic mechanism: the Kharash effect ¹⁸⁾, *i.e.* the fixation of a molecule of hydracid on a double C=C bond in the opposite sense of that predicted by the Markovnikov rule, the substitution reactions by chlorine in saturated hydrocarbons, etc. Nevertheless, the notion of electrical charges present in the isolated molecules retains a great interest for the chemist in interpreting a large number of reactions.

It is also interesting to note that, parallel to the researches of chemists, physicists also have been interested in the problem of charges in molecules, but in a global form, and had in fact succeeded in obtaining important results.

Considering a molecule as equivalent from the electrostatic point of view to a dipole, which could be polarized under the effect created by its neighbors, Mosotti and Clausius, and independently from each other Lorentz and Lorenz ¹⁹⁾, obtained the general connection between the dielectric constant of a substance in the gas state and its dipole moment:

$$\frac{4\pi N}{9kT} \mu^2 = \left(\frac{\epsilon - 1}{\epsilon + 2} - \frac{n^2 - 1}{n^2 + 2} \right) \frac{M}{d}$$

Later, Onsager generalized this equation by extending it to the case of liquids ²⁰⁾. As a result of the work of Debye who in 1912 formulated the principle of experimental determination of electric dipole moments ²¹⁾, several results were obtained. Nevertheless, the chemists had no way of extracting the values of the electrical charges whose association was suggested by the existence of a dipole moment.

Parallel to these studies, the study of real gases had led to the introduction of interaction forces between molecules, responsible for the differences between real fluids and perfect gases. These forces could be attributed to an electrostatic origin: dipole force, polarization and orientation effects ²²⁾.

Thus, the non-uniform repartition of positive and negative charges in a molecule was a well-established fact. The crucial problem remained of determining their exact distribution. Two important results were nevertheless obtained: one quantitative result, the value of the dipole moment, the other only a qualitative but equally important result, the signs and the relative order of charges situated in the neighborhoods of different nuclei. To go beyond that, it was necessary to have recourse to a theory capable of successfully attacking the problem of molecular structure itself. This was the role of quantum mechanics.

II. Description of Molecules According to Quantum Mechanics

A. Quantum Theory

Without entering into details, it is necessary to recall the general characteristic methods of Quantum Mechanics in order clearly to understand the problem to be solved ²³⁾.

The idea of trajectory in the classical sense of particles forming the system is not introduced. All the information available on the motion of particles is reduced to knowledge of a function of the coordinates of the particles and of time—called

wave function associated to the system: $\Psi(q, t)$. The square of the absolute value of this function, $|\Psi|^2$, represents the probability of finding the particles in the points of coordinates q , at the time t . In an isolated system with a well defined energy, this probability does not depend on time, but only on the coordinates q . The system is then declared to be in a stationary state.

Our experiments refer necessarily to a large number of systems, atoms or molecules. As far as they can be considered as independent systems, *i.e.* as having the same characteristics, the result of a measurement made at the macroscopic scale will give the average of the results which would be obtained by carrying out a very large number of microscopic measurements after a single system. It follows that in a molecule the square of the modulus of the wave function associated with the electrons will be interpreted as giving the density of a continuous repartition of negative charge. This is what we call the "electron cloud". The dynamic model is replaced by a static model.

The wave equation Ψ is a solution of the partial differential equation of Schrödinger ²⁴⁾. The construction of this equation makes use of a mathematical formalism which we shall not treat here.

In principle, owing to its generality, the Schrödinger equation contains the solution of all problems of molecular structure. Unfortunately, it is only integrable in a few special cases, the hydrogen atom for instance.

Thus, in general, one must be content with approximate solutions.

B. Application to Molecules

The specific case of molecules lends itself to a first important simplification. In fact, the very large difference between nuclei and electrons allows reduction of the problem to electrons only. More precisely, the wave function can be determined to describe the electrons for every geometrical configuration of the nuclei. This is the Born-Oppenheimer approximation ²⁵⁾. The knowledge of the purely electronic wave function allows calculation of the total molecular energy including the repulsion energy of the positive nuclei. In general this energy is at a minimum for a particular arrangement of the nuclei. This is the equilibrium geometry around which the molecule will vibrate. Neglecting vibrations, we shall assume in the following that the nuclei are fixed in their equilibrium positions.

The study of the H_2 molecule ²⁶⁾ showed that, in agreement with the prophetic ideas of Lewis ⁸⁾, the two electrons of that molecule do in fact pair together and the resulting electron density is concentrated between the nuclei. Generalizing this result, it is reasonable to try to describe in general a molecule in terms of electron pairs. In the H_2 molecule, with a good approximation, one can describe each of the two electrons by the same spatial function, *i.e.* assign to each electron the same spatial distribution of the charge. The energy obtained under this assumption is actually little different from the exact value ²⁷⁾. By extrapolation, in a general molecule, each electron of every pair will be assigned a space function, the *molecular orbital*, the two electrons of a given pair being described by the same space function (they will differ only by their spins).

This simplifying assumption allows construction of a spatial wave function describing all the electrons of a molecule, having an even number of electrons, in the ground state, in the form of a determinant ²⁸⁾:

$$\psi(1, 2, \dots, n) = \frac{1}{\sqrt{n!}} \begin{vmatrix} \varphi_1(1) \alpha(1) & \varphi_1(1) \beta(1) & \varphi_2(1) \alpha(1) & \dots \\ \varphi_1(2) \alpha(2) & \varphi_1(2) \beta(2) & \varphi_2(2) \alpha(2) & \dots \\ \dots & \dots & \dots & \dots \end{vmatrix} \quad (1)$$

Here, n is the number of electrons, the φ_i 's are the space functions, and α and β are the functions associated with the electron spin. (The choice of the structure of the determinant is imposed by a general theorem of quantum mechanics, which says that the wave function must change its sign when two electrons are interchanged). We leave aside the case of molecules whose levels are not doubly occupied, viz. radicals ²⁹⁾.

The problem is thus reconducted to the determination of the various functions φ_i . A well-known procedure consists in expanding these functions in a basis of conveniently chosen functions ³⁰⁾:

$$\varphi_i = \sum_r c_{ir} \chi_r \quad (2)$$

The coefficients c_{ir} thus introduced are determined by a variational calculation so as to minimize the energy of the system.

The choice of the basis functions χ_r is rather arbitrary. Different types of functions have been proposed and discussed ³¹⁾. We shall not consider this delicate problem. A current choice is to take the functions or *atomic orbitals* associated with electrons in the isolated atoms. For simplicity, we shall take the latter in their real forms.

It is quite obvious that the greater the number of χ_r functions used, the better the representation (2) of molecular orbitals will be. However, in practice, only a relatively small number of functions χ can be introduced. The experience of calculations shows that in general a good approximation is obtained if the atomic orbitals used correspond to the energy levels populated by electrons in the atomic ground states ³²⁾:

1s for H; 1s, 2s, 2p_x, 2p_y, 2p_z, for first-row atoms, etc.

Once the basis functions have been chosen, explicit determination of the φ 's is only a matter of computation. The classical method is Roothaan's self-consistent-field (S.C.F.) ³³⁾, which modern computers make easily applicable.

C. Electron Density in a Molecule

Knowledge of the wave function ψ permits calculation of the various quantities which characterize the molecule. In particular the total electron density appears in the form:

$$\rho^e = 2 \sum_i \varphi_i^2 \quad (3)$$

the factor 2 coming from the fact that each orbital φ_i is associated with two electrons.

This expression shows that the contribution to the total density of the pair described by the molecular orbital φ_i is $2\varphi_i^2$. Knowledge of the total electron density in every point of space permits the calculation of the center of gravity of the electron cloud. As the position of the center of gravity of the positive charges of the nuclei is easily calculated, the electric dipole moment of the molecule can be immediately derived. On the other hand, the charges as postulated by chemists do not follow directly, for it is not possible to identify a discrete set of charges with the continuous distribution given by calculations.

Another difficulty arises from the quantum representation. Strictly speaking, the electronic cloud extends to infinity, so that a reactant attacking the molecule is never situated outside the electron cloud, *i.e.* outside the molecule. However, owing to the rapid decrease of the electron density as the distance from the nuclei increases, it is justified in practice to assume that the electron cloud is contained in a well-defined finite volume V having dimensions of the same order as the inter-nuclear distances. For instance, 99% of the electron cloud of the H_2 molecule is located inside a revolution ellipsoid with axis 4.5 and radius 1.6 Å. The picture of the molecule as a finite size object, as viewed in classical chemistry, is thus justified even though it is only a very good approximation. The fact that the electron cloud extends to infinity does not produce mathematical difficulties concerning the definition of the electrostatic potential created at any point of space. In fact, the potential created in its center by a charged sphere whose charge density is everywhere finite ($|\rho| \leq |\rho_m|$) and of the same sign, tends to zero with the radius a of the sphere:

$$V = \int_0^a \frac{|\rho|}{r} 4\pi r^2 dr \leq |\rho_m| 2\pi a^2.$$

III. Equivalent Multipoles

As has been mentioned, the electrostatic potential created by the molecule plays an important role in the ionic reactions as well as in molecular interaction phenomena. As the problem has been presented and discussed in detail in an article recently published in this series ³⁴, we shall not discuss it here.

It is quite obvious that the best representation of this potential consists in constructing contour lines maps (Figs. 1, 2). Such pictures are often very effective, but have the limitation that several sections are necessary to represent the potential in space, and they do not lend themselves easily to further calculations. These diagrams, sometimes not easy to interpret, will be discarded by the chemist in favor of a more tangible and familiar description, based on point charges and electric multipoles, especially dipoles. The problem is then to reproduce as well as possible the electrostatic field created by the molecules by means of these point charges and these dipoles.

A. General Expression of the Electrostatic Potential Created by a Molecule

The potential created by a molecule is completely defined by the charge density values in every point of space. This density may be written:

$$\varrho(M) = -\varrho^e(M) + \sum_K N_K \delta(\mathbf{M} - \mathbf{K}) \quad (4)$$

where $\varrho^e(M)$ is the electronic density at point M , defined by the vector \mathbf{M} , N_K is the positive charge of the nucleus whose position vector \mathbf{K} , and δ is the Dirac distribution.

In the following, we shall always assume that the nuclei are fixed. It is well known that the molecule is actually in a perpetual state of vibration, the nuclei oscillating around equilibrium positions corresponding to the minima of energy. We shall suppose that the nuclei are fixed in these positions and we shall define the coordinate system O_{xyz} with reference to them.

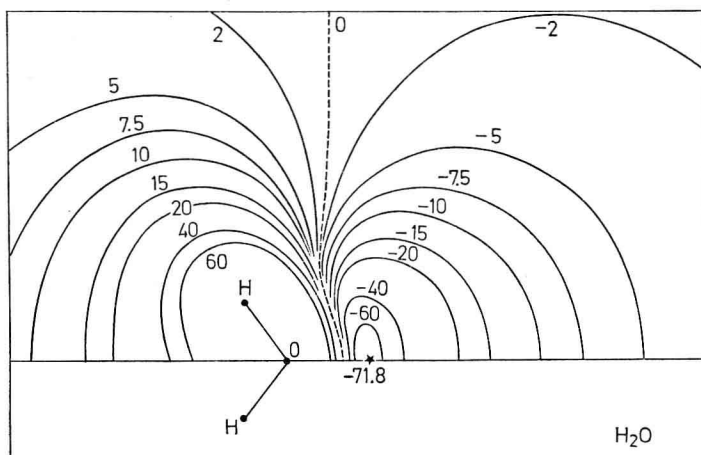


Fig. 1. Electrostatic potential-energy map for H₂O in the molecular plane ³⁴⁾. Values are expressed in kcal-mole

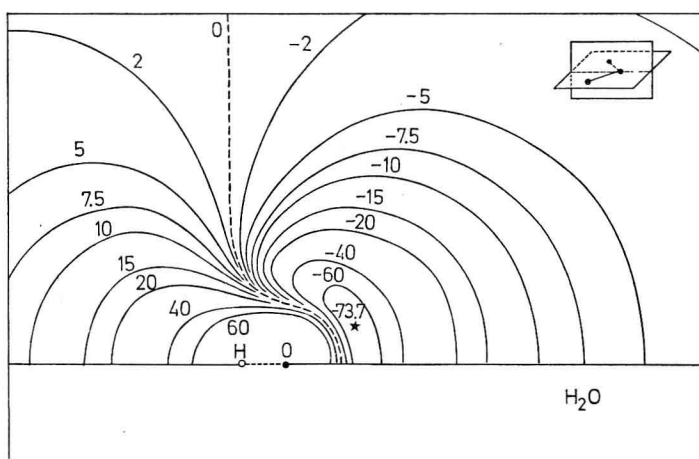


Fig. 2. Potential-energy map for H₂O in the symmetry plane perpendicular to the molecular one ³⁴⁾

A. Julg

The potential created at a point P situated at a distance R from the origin ($OP=R$), in the direction specified by cosines α, β, γ , may be expanded to the powers of R^{-1} according to the classical expression:

$$V_P(R; \alpha, \beta, \gamma) = \frac{1}{R} \int \varrho dv + \frac{1}{R^2} \left[\alpha \int \varrho x dv + \beta \int \varrho y dv + \gamma \int \varrho z dv \right] \quad (5)$$

$$+ \frac{1}{2R^3} \left[\alpha^2 \int \varrho (2x^2 - y^2 - z^2) dv + \dots + 6\alpha\beta \int \varrho xy dv + \dots \right] + \dots$$

(the integrations being taken over the whole space).

The term in $R^{-(n+1)}$ of Eq. (5) corresponds to the potential created by a multipole of order 2^n .

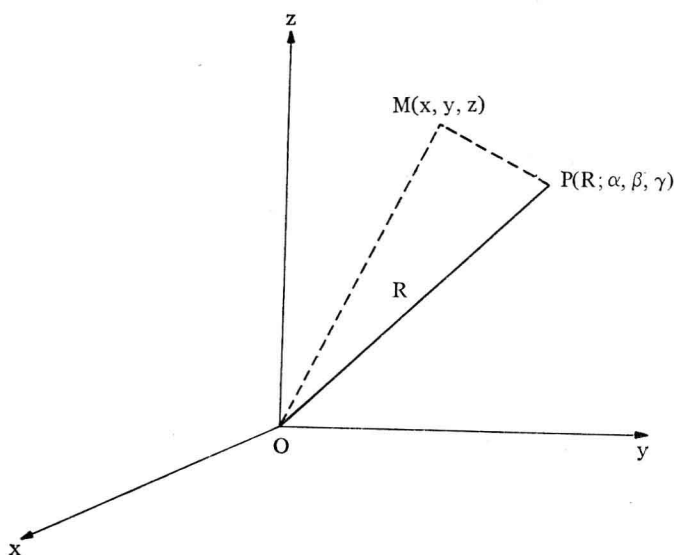


Fig. 3. Notation for the expansion of the potential

B. Study of Multipole Expressions

The expansion Eq. (5), taken in its entirety, is evidently valid regardless of the origin or the orientation of the chosen axis. But it is essential to keep in mind that the various integrals depend on the choice of the reference system. To see this we perform for instance the translation defined by:

$$x \rightarrow x' = x - X, \quad y \rightarrow y' = y - Y, \quad z \rightarrow z' = z - Z.$$

Then, $\int \varrho x dv$ becomes $\int \varrho x' dv = \int \varrho x dv - X \int \varrho dv$, and similar formulas hold for y and z . Thus, if the total charge $\int \varrho dv$ does not vanish, the dipole components $\int \varrho x dv, \dots$, are not invariant upon translation.