Inverse problems of vibrational spectroscopy

Compendium

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Introduction

Many problems of physical chemistry belong to the class of inverse problems, in which from known experimental data of the object we need to determine some of its properties based on a certain model connecting these properties with measured characteristics. Inverse problems typically lead to mathematical models that are not well-posed in the sense of Hadamard, i.e. to the ill-posed problems. This means that they may not have a solution in the strict sense, solutions may not be unique and/or may not depend continuously on the input data. Mathematical problems possessing such properties are called *ill-posed problems*, mostly due to the nonstability of solutions with respect to data perturbations. The theory of ill-posed problems (advanced by A. N. Tikhonov and his scientific school in 1960s) investigates and develops the effective stable numerical (regularization) methods for the solution of the ill-posed problems. In the background of this theory lies an understanding of the underdetermined character of the ill-posed problems and a concept of the regularizing operator (algorithm).

Molecular force fields provide very important information about molecular structure and molecular dynamics and may be determined within harmonic approximation from experimental data of vibrational (infrared and Raman) spectroscopy by solving the so-called inverse vibrational problem. Rapid progress in quantum mechanical calculations of theoretical harmonic force fields provides new ways for more accurate interpretation of experimental data as well as new possibilities for development of empirical force field calculations. The latter are particularly important for the large-size molecules for which accurate *ab initio* calculations are impossible, so that empirical methods based on a solving an inverse vibrational problem still remain the best available source of force field parameters.

Fast progress in the investigation of rather large nanomolecules requires development of special approaches for solving inverse vibrational problems moving far beyond traditional methods based on the least-squares procedures. Analysis of large molecular systems (when a force constant matrix F is constructed from previously evaluated force constants of model compounds) runs across difficulties of possible incompatibility of the results determined by different authors and by means of different numerical methods within different approximations (force field models). These difficulties are related to nonuniqueness and instability of the solution of inverse vibrational problem as well as to incompatibility of available experimental data with the harmonic model.

In the course we discuss how a priori model assumptions and ab initio quantum mechanical calculations may be used for constructing regularizing algorithms for the calculation of molecular force fields. We have proposed a principally new formulation of a problem of searching for the molecular force field parameters using all experimental data available and quantum mechanical calculation results and taking into account the a priori known constraints for force constants. The essence of approach is that we suggest (using given experimental data and its accuracy) to find by means of stable numerical methods the approximations to the so-called *normal pseudosolution*, i.e. matrix F which is the nearest by chosen Euclidean norm to the given force constant matrix F^0, satisfies the set of a priori constraints D and is compatible with experimental data Λ_δ with regard for the possible incompatibility of the problem.

Within this approach, the results will tend to be as close to quantum mechanical data as the experiment allows. From mathematical point of view, the algorithm should provide approximations to the solution that tend to the exact solution when experimental data becomes more extensive and accurate. Imposing certain restrictions on the matrix of force constants (in our case it is a requirement of the closeness of solution to the matrix F^0) allows to obtain unique solution from the variety of possible choices.

The course consists of 7 lectures presenting foundations of the modern approaches to solving inverse problems arising in vibrational spectra data processing and includes:

- Classical theory of small vibrations.
- Molecular force fields and experimental sources of information. Mathematical model of molecular vibrations. Formulation of inverse vibrational problem.
- Generalized coordinates in normal coordinate analysis.
- Regularizing algorithm for solving the inverse vibrational problem.

- Constraints on the values of force constants based on quantum mechanical calculations.Generalized inverse structural problem. Computer implementation.
- Examples of molecular force field calculations within different models.

Course literature

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Course plan.

- Lecture 1: Physical models of molecular vibrations. Classical theory of small vibrations.
- Lecture 2: Mathematical model for molecular vibration analysis. Direct and inverse problems.

- Lecture 3: Vibrational problem in internal coordinates. Models of a molecular force field. Construction of the auxiliary matrices
- Lecture 4: The mathematical formulation of the inverse vibrational problem.
- Lecture 5: Regularizing algorithms for solving the inverse vibrational problems.
- Lecture 6: Constraints on the values of force constants based on quantum mechanics. Generalized inverse structural problem. Computer implementation..
- Lecture 7: Joint treatment of ab initio and experimental data in molecular force field calculations.

Course problems.

It is assumed that a student would solve one project. Computations performed by standard accessible software (MATLAB) illustrating the solutions are encouraged for the projects. The project includes solving problems connected with vibrational spectroscopy. The students should present a written report on the solved problems.

1. PHYSICAL MODEL OF MOLECULAR VIBRATIONS. CLASSICAL THEORY OF SMALL VIBRATIONS.

The vibrational spectrum of a substance appears as a result of interaction of infrared electromagnetic radiation with the substance. This interaction changes the vibrational component of the total molecular energy. The vibrational spectrum of a molecule is a characteristic and complicated function of its geometric structure, nuclei masses and electron density distribution, i.e., of intramolecular forces. The physical consideration of vibrational spectra and their models may use two approaches {classical and quantum mechanical. In other words, molecules belong to quantum systems whose behavior in certain cases may be described by classical theory. To solve vibrational problems, one can often use simple approximations of classical mechanics. The classical theory considers the vibrational spectrum of a molecule to result from small vibrations of a system of linked material points. At the same time, some problems of the molecular spectroscopy, for example, the intensity of vibrational bands, the appearance of combined frequencies and overtones cannot be properly formulated and solved by means of classical physics. In these cases, it is necessary to apply the approximations of quantum mechanics.

It is well known that classical mechanics, generally speaking, is inapplicable to the treatment of atoms and molecules because this theory cannot explain the fact of their stability.

Indeed, a resting or uniformly and linearly moving system of charged particles (nuclei and electrons) cannot have a stable equilibrium. On the other hand, a dynamic system of charged particles (of the solar system type) also cannot exist because, according to classical electrodynamics, accelerating charges have to radiate energy, which immediately leads to falling of the electrons into the nuclei. Thus, we may consider atoms and molecules as systems of charged material points only in quantum mechanics.

Nevertheless, some essential peculiarities of vibrational motion of a molecule may be derived from the simplified classical analysis. In many cases this analysis yields results which coincide with those obtained in quantum mechanics, although more descriptive. In addition, the classical analysis allows us to essentially simplify the quantum mechanical consideration.

So, consider a molecule as a classical system of N material points ("atoms" or "nuclei") with the masses $M_1, \dots, M_N$ placed in a certain force field such that the potential energy of the system is a function $U(\vec{R}'_{01}, \dots, \vec{R}'_{0N})$. Here $\vec{R}'_{0i}$ $(i = 1, \dots, N)$ are the radius vectors of material points in a certain fixed inertial frame of reference (laboratory system). The force field includes electrostatic interaction between nuclei and a certain effective field created by all the electrons of the molecule. In this statement of the problem we do not consider individual electrons. The sense of the field U will be completely clarified in the quantum mechanical statement. Here we shall only note the following.

1. The potential energy $U(\vec{R}'_{01}, \dots, \vec{R}'_{0N})$ has to be independent of rotations and motion of the coordinate system (it is the corollary of the fact that the field is created by the particles of the system themselves).

2. The equilibrium configuration $\{\vec{R}_1^0, \dots, \vec{R}_N^0\}$ must exist where the potential energy U is minimal (this reflects the fact of existence of the stable molecule).

Further, let us agree to denote the vector by a column of three numbers (its Cartesian components), for example

$$\vec{R}'_i = \begin{pmatrix} R'_{i1} \\ R'_{i2} \\ R'_{i3} \end{pmatrix}$$

We introduce the scalar product of two vectors

$$(\vec{x}, \vec{y}) = \vec{x} * \vec{y} = \sum_{\alpha=1}^{3} x_\alpha y_\alpha ,$$

Where the sign * denotes transposition (i.e. x* is a row vector), and also, the vector product

$$\vec{r} = [\vec{x}, \vec{y}],$$

defined by relations

$r_1 = x_2 y_3 - x_3 y_2, \quad r_e = x_3 y_1 - x_1 y_3, \quad r_3 = x_1 y_2 - x_2 y_1.$

We shall also use vectors of arbitrary dimensions, treating them as columns.

For consideration of motion of the nuclei we should compose the Lagrange function

$$L = \frac{1}{2} \sum_{i=1}^{N} M_i (\dot{R}_i^{'}, \dot{R}_i^{'}) - U(\vec{R}_1^{'}, \dots, \vec{R}_N^{'} \qquad (1)$$

and solve the Lagrange equations

$$\frac{d}{dt} \frac{\partial L}{\partial \dot{\vec{R}}_i^{'}} = \frac{\partial L}{\partial \dot{\vec{R}}_i^{'}} \qquad (i = 1, \dots, N) \qquad (2)$$

with certain initial conditions.

In general, equations (2) describe three distinct kinds of nuclear motion: the parallel transfer (or translation motion), the rotation of the nuclear system as a whole and the relative motions of nuclei. We are primarily interested in considering the vibrations (i.e., the relative motions) of nuclei within the molecule. Since we are primarily interested in considering the vibrations (i.e. the relative motions) of nuclei, it is convenient to separate, at least approximately, the different types of motion in the molecule. For this purpose, we introduce the coordinate system connected with the molecule.

Let the equilibrium configuration of the molecule $\{\vec{R}_1^0, \dots, \vec{R}_N^0\}$ be nonlinear (such molecules will be called normal). Introduce the new coordinate system (noninertial, because it rotates with the molecule), where the coordinates of the radius vectors are denoted as $\vec{R}_1, \dots, \vec{R}_N$. Since further we shall consider the small vibrations of nuclei near the equilibrium positions, it is convenient to introduce the nuclear displacements $\Delta\vec{R}_i$ so that $\vec{R}_i = \vec{R}_i^0 + \Delta\vec{R}_i \qquad (i = 1, \dots, N).$

We shall require that $\Delta\vec{R}_i$ does not change, when the molecule is moving or rotating as a whole. This leads to the Eckart conditions

$$\sum_i M_i \Delta\vec{R}_i = 0, \qquad \sum_i M_i \left[\vec{R}_i^0, \Delta\vec{R}_i\right] = 0. \qquad (3)$$

The first of these conditions implies the vanishing of the linear momentum of the system for vibrational motion. The second equation resembles the disappearance of the angular momentum, but is not exactly the same. The difference follows from the impossibility of separating the rotational and vibrational motions completely.

Due to the six conditions (3) , the relative (vibrational) motion of nuclei has $n = 3N - 6$ degrees of freedom. Since Eqns. (3) are linear, we may introduce n generalized coordinates $\{q_1, \dots, q_n\}$* so that

$$\Delta\vec{R}_i = \sum_{k=1}^{n} \vec{A}_{ik} q_k, \qquad (i = 1, 2, \dots, N). \tag{4}$$

Here the matrix $\vec{A}$ with vector elements has to satisfy the restrictions which follow from (3) :

$$\sum_{i=1}^{N} M_i \vec{A}_{ik} = 0, \qquad \sum_{i=1}^{N} M_i [\vec{R}_i^0, \vec{A}_{ik}] = 0, \quad k = 1, 2, \dots\cdots, n. \tag{5}$$

For the following consideration, it is convenient to choose the axes of coordinates for the molecular system so that their origin is at the center of masses of the equilibrium configuration. This means the condition $\sum_{i=1}^{N} \vec{R}_i^0 = 0$, and the inertia tensor of this configuration is diagonal.

Further we shall assume these conditions to be true. It is convenient to characterize the molecule's translation by translation of the center of masses, which has coordinates $\vec{R} = \frac{1}{M}\sum_{i=1}^{N} M_i \vec{R}_i^{'}$, where $M = \sum_{i=1}^{N} M_i$ and the rotation is determined by the Eulerian angles $\{\theta_1, \theta_2, \theta_3\}$.

These angles determine the rotational matrix *C* such that $G_{\alpha\beta} = (\vec{e}_\alpha, \vec{i}_\beta) \quad (\alpha, \beta = 1,2,3)$. Here $\vec{e}_\alpha$ are the basis vectors of the laboratory coordinate system, and $\vec{i}_\beta$ are the basis vectors of the molecule coordinate system. Thus, instead of 3*N* Cartesian coordinates $\{\vec{R}_1^{'}, \dots, \vec{R}_N^{'}\}$ we introduce the new coordinates $\{\vec{R}, \theta, q\} = \{\vec{R}, \{\theta_1, \theta_2, \theta_3\}^*, \{q_1, q_2, \dots, q_n\}^*\}$. The relations between the Cartesian coordinates and the new coordinates are as follows

$$\vec{R}_i^{'} = \vec{R} + C(\theta)\vec{R}_i = \vec{R} + C(\theta)(\vec{R}_i^0 + \sum_{k=1}^{n} \vec{A}_{ik} q_k). \tag{6}$$

To simplify the following discussion, we shall assume that the molecule does not participate in either translation or rotation. This means that instead of (6) we have $\vec{R}_i^{'} = \vec{R}_i$ and instead of (1) we have

$$L = \frac{1}{2}\sum_{i=1}^{N} M_i (\dot{\vec{R}}_i)^2 - U(\vec{R}_1^{'}, \dots, \vec{R}_N^{'}). \tag{7}$$

Making the change of variables $\vec{R}_i = \vec{R}_i^0 + \sum_{k=1}^{n} \vec{A}_{ik} q_k$, we obtain

$$L = \frac{1}{2}\sum_{k,l=1}^{n} T_{kl} \dot{q}_k \dot{q}_l - V(q_1, \dots, q_n) \tag{8}$$

Here, *V(q)* denotes the potential energy $U(\vec{R}_1(q), \dots, \vec{R}_N(q))$, and

$$T_{kl} = \sum_{i=1}^{N} M_i (\vec{A}_{ik}, \vec{A}_{il}) \qquad (9)$$

denotes the matrix of the kinetic energy of vibrations .

For quantum mechanical applications it is convenient to introduce the Hamilton function. For this purpose we have to replace $\dot{q}_k$ in (8) by the generalized momenta $p_k = \frac{\partial L}{\partial \dot{q}_k} \quad (k = 1,...,n)$. As a result we obtain

$$H = \frac{1}{2} \sum_{k,l=1}^{n} G_{kl}\, p_k\, p_l + V(q_1,...,q_n)\,, \qquad (10)$$

where $G = T^{1}$ is the so-called kinematic coefficients matrix, $p_k = \sum_{l=1}^{n} T_{kl} \dot{q}_l, \quad \dot{q}_k = \sum_{l=1}^{n} G_{kl}\, p_l$.

The Hamilton equations $\dot{p} = -\frac{\partial H}{\partial q}, \quad \dot{q} = \frac{\partial H}{\partial p}$

give $\dot{p}_k = -\frac{\partial V}{\partial q_k}$,

whence $\ddot{q}_k = \sum_{l=1}^{n} G_{kl}\, \dot{p}_l = -n \sum_{l=1} G_{kl} \frac{\partial V}{\partial q_l}$.

Introduce $V(q)$ as the series

$$V(q) = V_0 + \sum_{i=1}^{n} \left.\frac{\partial V}{\partial q_i}\right|_{q=0} q_i + \sum_{k,l=1}^{n} \left.\frac{\partial^2 V}{\partial q_k \partial q_l}\right|_{q=0} q_k q_l + O(q^3)\,.$$

Such representation assumes the smallness of the system vibrations near the equilibrium position. Since for $q_1 = \ldots = q_n = 0$ the potential energy $V(q)$ has a minimum, this series may be written in the form

$$V(q) = \frac{1}{2} \sum_{k,l=1}^{n} F_{kl}\, q_k q_l + O(q^3)\,. \qquad (11)$$

Here, the fixed energy shift is omitted as unessential for the further treatment. The matrix F with the elements $F_{kl} = \left.\frac{\partial^2 V}{\partial q_k \partial q_l}\right|_{q=0} \quad (k,l = 1,2,...,n)$

is called the matrix of the force constants. In this case

$$\frac{\partial V}{\partial q_l} = \sum_{m=1}^{n} F_{lm} q_m,$$

whence

$$\ddot{q}_k + \sum_{l=1}^{n}\sum_{m=1}^{n} G_{kl}F_{lm}q_m = 0$$

or

$$\ddot{q}_k + \sum_{m=1}^{n} (GF)_{km}q_m = 0, \qquad k = 1, 2, \cdots, n. \tag{12}$$

We shall seek for the periodic solutions to this equation. For this purpose, we present $q_k(t)$ in the form

$$q_k(t) = l_k \cos(\omega t + \varphi). \tag{13}$$

The substitution of (13) into (12) leads to the eigenvalue problem

$$(GF - \omega^2 E)l = 0 \tag{14}$$

where by l is denoted the amplitude vector $l = \{l_1, l_2, ..., l_n\}^*$. Thus, the eigenvalues of GF are the squares of frequencies of the molecular normal vibrations.

The eigenvectors of (14) determine the modes of vibrations, i.e., the relative values of coordinates in the initial moment and (because of (13)) in any other moment. Since the matrix GF has the dimension $n \times n$, it has n eigenvalues, though not all of them are essentially different, and some of them may be multiple in accordance with the degeneracy of the vibrational energy level. Multiplying equation (14) by $G^{-1/2}$ from the left, we obtain

$$G^{1/2}Fl - \omega^2 G^{-1/2}l = 0 \quad \text{or} \quad (G^{1/2}FG^{1/2})(G^{-1/2}l) = \omega^2 (G^{-1/2}l).$$

This eigenvalues problem for the symmetrical matrix $G^{1/2}FG^{1/2}$ has the same eigenvalues as (14) and exactly n eigenvectors $r^{(1)}$, … , $r^{(n)}$, which may be chosen orthogonal. Therefore, as matrix G is nonsingular, the problem (14) also has n eigenvectors, where

$$l^{(k)} = G^{1/2}r^{(k)} \qquad (k = 1, 2, \cdots, n).$$

The problem (14) may be interpreted as the problem of simultaneous reduction of two quadratic forms to the canonical form. Introduce the matrix L with the columns $l^{(1)}$, … , $l^{(k)}$. From the above, it follows that $L = G^{1/2}R$, where R is the orthogonal matrix. Making the change of variables

$$q_k = \textstyle\sum_{l=1}^{n} L_{kl}Q_l,$$

we obtain instead of (8)

$$L = \frac{1}{2}\sum_{k,l=1}(L^*TL)_{kl}\dot{Q}_k\dot{Q}_l - \frac{1}{2}\sum_{k,l=1}(L^*FL)_{kl}Q_kQ_l.$$

Taking into account that

$$L^*TL = R^*G^{1/2}T^{1/2}T^{1/2}G^{1/2}R = R^*R = E,$$

i.e., $(L^*TL)_{kl} = \delta_{kl}$, δ_{kl} is the Kronecker symbol:

$$\begin{cases} = 1 & \text{for} \quad k = l \\ = 0 & \text{for} \quad k \neq l \end{cases},$$

and from the equation

$$G^{1/2}FG^{1/2}R = R\Lambda \qquad (\Lambda = \operatorname{diag}\{\omega_1^2, \cdots, \omega_n^2\})$$

it follows that

$$L^*FL = R^*G^{1/2}FG^{1/2}R = R^*R\Lambda = \Lambda.$$

Finally, we obtain

$$L = \frac{1}{2}\sum_{k=1}^{n} \dot{Q}_k^2 - \frac{1}{2}\sum_{k=1}^{n} \omega_k^2 Q_k^2.$$

Introducing the generalized momenta

$$P_k = \partial L / \partial \dot{Q}_k = \dot{Q}_k,$$

we obtain the following form for the Hamilton function:

$$H = \frac{1}{2}\sum_{k=1}^{n} (P_k^2 + \omega_k^2 Q_k^2). \tag{16}$$

The Hamilton (or Lagrange) equations of motion lead to the system

$$\ddot{Q}_k + \omega_k^2 Q_k = 0,$$

the solutions of which are the known functions of the harmonic oscillator in classical mechanics

$$Q_k = Q_k^0 \cos(\omega_k t + \varphi_k).$$

The coordinates $Q_1, \dots, Q_n$ are usually called the *normal coordinates*. The calculation of the molecular vibrations is called the *normal coordinate analysis*. Thus, the molecular vibrations are represented as the superposition of n independent vibrations, each characterized by its own frequency ω_k and mode $l(k)$ or by the normal coordinate Q_k. Note that in the normal coordinates, the kinematic coefficient matrix G and the force constants matrix F are both diagonal.

Quantum mechanics, in principle, allows us to predict all molecular spectra without any experimental information except charges, masses and spins of the particles. It is natural because quantum mechanics was created to describe the simplest spectra. At present, when we describe more complicated systems, consisting of point particles, it works as well.

In consideration of a molecule as a quantum system, we restrict ourselves by the nonrelativistic Schrodinger equation, and we shall not consider spins of particles (except for certain conditions imposed by spins on the parity of wave functions). Such a treatment holds for molecules consisting of not too heavy atoms.

Physical characteristic of molecular system – dynamic variables which characterize the molecule are subdivided into two groups complemented each other – space coordinates and time from one side and energy and momentums from other side. Quantum mechanics formalism is based on the operator theory. Associated with each measurable parameter in a physical system is a quantum mechanical operator. Such operators arise because in quantum mechanics you are describing nature with waves (the wave function) rather than with discrete particles whose motion and dynamics can be described with the deterministic equations of Newtonian physics. Part of the development of quantum mechanics is the establishment of the operators associated with the parameters needed to describe the system. The main properties of operators: they should be linear and self-adjoined (conjugated). Operators should result in real quantities of observed values, it means that operators should be Hermitian.

Table 1. Operators of some physical values

Physical value	Operator
Coordinate $x \to \hat{x}$	x
Any function of position, such as x, or potential V(x) Coordinate function $f(x) \to \hat{f}(x)$	$f(x)$
X component of momentum $\vec{p}_x \to \hat{p}_x$	$i\hbar \frac{\partial}{\partial x}$,
Vector of momentum $\vec{\mathrm{p}} \to \hat{\mathrm{p}}$	$-i\hbar(\mathrm{i}\frac{\partial}{\partial x} + \mathrm{j}\frac{\partial}{\partial y} + \mathrm{k}\frac{\partial}{\partial z}) \equiv -i\hbar\nabla$
Function of momentum vector $f(\vec{p}) \to \hat{f}(p)$	$f(\hat{p})$
Operator of kinetic energy $\hat{T}$	$-\frac{\hbar^2}{2m}\nabla^2$ ($m -$ particle mass)

With every physical observable there is associated a mathematical operator which is used in conjunction with the wavefunction. Suppose the wavefunction associated with a definite quantized value (eigenvalue) of the observable is denoted by y_n (an eigenfunction) and the operator is denoted by Q. The action of the operator is given by

$$Q\Psi_n = q_n\Psi_n \qquad (17)$$

The mathematical operator Q extracts the observable value q_n by operating upon the wavefunction which represents that particular state of the system. This process has implications about the nature of measurement in a quantum mechanical system. Any wavefunction Ψ_n for the system can be represented as a linear combination of the eigenfunctions y_n (basis set postulate), so the operator Q can be used to extract a linear combination of eigenvalues multiplied by coefficients related to the probability of their being observed (expectation value postulate).

Quantum mechanics, in principle, allows us to predict all molecular spectra without any experimental information except charges, masses and spins of the particles. The basic equation of quantum mechanics or the stationary Schrodinger equation is formulated as the eigenvalue problem

$$\widehat{H}\Psi = E\Psi \qquad (18)$$

Here, the Hamilton operator $\widehat{H}$ is obtained from the expression for classical particle energy (written by means of coordinates and momenta) by substituting the coordinates and momenta with the corresponding operators. For example, for a point electron in the field of a positive charge (the nucleus), i.e., for the simplest model of the hydrogen atom, the stationary Schrodinger equation has the form

$$\widehat{H}\Psi = \frac{\hat{\bar{p}}^2}{2m}\Psi - \frac{e^2}{r}\Psi$$

Here e, m are the charge and mass of the electron respectively, $\hat{\bar{p}}$ is the momentum operator, r is the distance from the origin (where the positive charge is placed). In coordinate representation, the operator of the momentum squared is equal to $\hat{\bar{p}}^2 = -\hbar^2\nabla$, where $\hbar$ is the Planck constant ($\hbar = h/2\pi$), and ∇ is the Laplace operator. In Cartesian coordinates it can be written as

$$\Delta\Psi = \frac{\partial^2\Psi}{\partial x^2} + \frac{\partial^2\Psi}{\partial y^2} + \frac{\partial^2\Psi}{\partial z^2},$$

and in spherical coordinates as

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}$$

If we impose certain conditions on the function Ψ, we obtain the eigenvalue problem for the differential operator. This particular problem was solved in the 1920s. As a result, the following energy levels were found

$$E_n = -\frac{m_e^{4}}{2\hbar^2 n^2}\text{, where } n = 1,2,3, \ldots .$$

In the case of a molecule, when kinetic and potential energies are expressed in the operator form, we should solve the Shrodinger equation of the form:

$$\left[\sum_k \frac{1}{2m}\hat{p}_k^2 + \sum_i \frac{1}{2M}\hat{p}_i^2 + U\right]\Psi = E\Psi \quad , \qquad (19)$$

where function Ψ depends on the coordinates of all the electrons $\vec{r}_1,\ldots,\vec{r}_{N_e}$, and the nuclei $\vec{R}_1,\ldots,\vec{R}_N$. The operator $\hat{p}_k^2$ denotes differentiating Ψ by coordinates of the k (k=1, …, N_e), and $\hat{p}_i^2$ denotes differentiating by coordinates of the i-th nucleus. (i=1, …, N). M_i –is the mass of the i-th nucleus. The potential energy U of the system may be represented in the form

$$U=U_{ee} + U_{nn} + U_{ne}, \qquad (20\ )$$

where

$U_{ee} = \frac{1}{2}\sum_{j\neq k}\frac{e^2}{\left|\vec{r}_j - \vec{r}_k\right|}$ corresponds to the electron repulsion;

$U_{ne} = -\sum_{i,k}\frac{Z_i e^2}{\left|\vec{R}_i - \vec{R}_k\right|}$ corresponds to the attraction of electrons and nuclei (Zi is the charge of i-the nucleus in electron charge units, i.e. its atomic number), and

$U_{nn} = \frac{1}{2}\sum_{j\neq k}\frac{Z_k Z_j e^2}{\left|\vec{R}_j - \vec{R}_k\right|}$ corresponds to the nuclei repulsion.

It is fundamentally hard to solve equation (19). Even for the case of two electrons (the helium atom) this equation cannot be solved analytically. The numerical solution comes across many difficulties, too. For example, we may represent a one-dimensional function for a numerical calculation either as its values at the grid points, or to define it by means of some parameters.

Let K parameters be introduced. For the helium atom the functionΨ^a depends on nine arguments (six electron coordinates and three nucleus coordinates); therefore, it will require K^9 parameters. Even for small K, say, K = 10, to find 10^9 parameters is unrealistic even for future computers. The molecules, that we are interested in may have dozens of nuclei and several hundred electrons.

So, simplifications are necessary to make the problem solvable. As a result, we may lose the accuracy of calculation and the value of such calculation may decrease substantially.

On the other hand, some molecule characteristics may be determined from experiment, using very simple models, which do not require extremely difficult calculations. If we succeed in constructing such models, this may also be considered as the spectrum interpretation. Finally, we may make a simplified quantum mechanical calculation replacing those values that are most difficult to calculate by parameters determined from experiment.

In practice, all three approaches are used. They are called nonempirical (or *ab initio*, when experimental data are not used), empirical (when the basis of calculation is the experimental data), and semiempirical (when the experimental data are used only for estimating some of the parameters).

To construct the mathematical model we have to separate the different types of particle motion in the equation (19). Indeed, a molecule may move and rotate in the space as a whole, and change its shape because of the intramolecular motion (vibration of the nuclei, etc.) Therefore, it is sensible to separate, even approximately, all these motion types. Also we need to separate the motion of nuclei and electrons in order to consider, first, more simple models.

Using this approach, the vibrational energy arises as the component of the total molecule energy, represented (with translation energy excluded) in the first approximation as

$$E = E_e + E_v + E_r.$$

Here, E_e is the electron energy, E_v is the vibrational energy, and E_r is the rotational energy. The orders of these quantities are $1 : \sqrt{\ } m_e/M : m_e/M$ ($m_e/M = 10^{-3} - 10^{-5}$), where m_e is the electron rest mass, M is the sum of the nuclear masses of the molecule). Such separation of energy is possible if $E_e >> E_\upsilon >> E_r$.

Three types of spectra correspond to three energy components.

1. Rotational spectra arise in the far infrared (IR) and microwave electromagnetic spectrum regions, when we have transitions between the rotational levels of the given vibrational and given electron states.

2. Vibrational{rotational spectra arise in IR region of the electromagnetic spectrum, when we have transitions from rotational levels of the given vibrational state to the rotational levels of another vibrational state, the electron state being fixed.

3. Electronic spectra or electronic-vibrational-rotational spectra. They correspond to transitions from the various rotational and vibrational levels of one electronic state to the diffrent rotational and vibrational levels of another electronic state. They are observed in the visible and ultraviolet regions.

Besides these three types of spectra, there are also spectra of electron-spin resonance and nuclear-magnetic, nuclear quadruple and gamma-resonance, which are not considered here.

In an exact treatment, besides electron, vibrational and rotational components of the total molecule energy there arise terms connected with electronic-vibrational, electronic-rotational and vibrational-rotational interactions.

We shall consider the simplified quantum mechanical statement of the problem of molecular vibrations. Assume that the rotational motions and translations of the molecule's nuclei have no influence on vibrations, and electronic motion is taken into account as creating a certain equivalent force field. Thus, we are to solve the same problem as was considered above but for the quantum mechanical model. Considering this simplified statement is useful since the results obtained remain valid in more general cases.

For stationary vibrational states, the Schrodinger equation is written as follows:

$$\widehat{H}_\upsilon \Psi_\upsilon = E_\upsilon \Psi_\upsilon$$

where the Hamilton operator is obtained from the expression (10) for classical particle energy (written by means of coordinates and momenta) by substituting the coordinates and momenta with the corresponding operators.

The substitution leads to the equation

$$\frac{1}{2}\sum_{k,l=1}^{n} G_{kl}\hat{p}_k\hat{p}_l\Psi + V(q_1,\cdots,q_n)\Psi = E\Psi.$$

To solve this equation, it is useful to transfer to the normal coordinates. As a result we obtain

$$\frac{1}{2}\sum_{k=1}^{n}(\hat{P}_k^2 + \omega_k^2 {Q_k}^2)\Psi = E\Psi.$$

or in other form

$$\left[\frac{1}{2}\sum_k\left(\hat{P}_k^2 + \lambda\ Q_k^2\right) - E\right]\Psi = 0 \qquad (21)$$

Here, we have used the representation of $V(q)$ in the form (11):

$$V(q) = \frac{1}{2}\sum_{k,l=1}^{n} F_{kl}q_k q_l + O(q^3).$$

Thus, we have to solve n independent problems of harmonic oscillators.

$$\frac{1}{2}\hat{P}_k^2\Psi_k + \frac{1}{2}\omega_k^2 Q_k^2\Psi_k = E_k\Psi_k \qquad (k = 1,\ldots\ n), \qquad (22)$$

where $\Psi_k = \Psi_k(Q_k)$ and then to obtain

$$E = \sum_{k=1}^{n} E_k, \qquad \Psi = \prod_{k=1}^{n} \Psi_k(Q_k).$$

The solution to each of the problems (22) is well-known. It is expressed as the eigenfunctions

$$\Psi_k(Q_k) = \mathrm{const}\cdot e^{-x^2/2} H_{v_k}(x),$$

where $H_{\upsilon k}$ are the Hermite polynomials, $x = \sqrt{\omega_k / \hbar Q_k}$, $E_{\upsilon k} = \hbar\omega_k(\upsilon_k + 1/2)$ (υ_k =0, 1, …) are the eigenvalues of the energy. The levels of vibrational energy of the molecule are characterized by n quantum numbers υ_k =0, 1, ….. $\omega_k = \sqrt{\lambda_k}$, and λ_k are eigenvalues of matrix *GF*.

The levels of vibrational energy of the molecule in harmonic approximations are characterized by *n* quantum numbers υ_k (*n*=3*N*-6, *N* – number of atoms in a molecule):

$$E_\upsilon(\upsilon_1, \upsilon_2, \upsilon_3, \ldots, \upsilon_n) = \sum_{k=1}^{n} h\omega_{ek}\left(\upsilon_k + \frac{d_k}{2}\right)$$

The wave function of a molecule is expressed as a product of eigenfunctions of harmonic oscillators $\psi_{\upsilon k}$:

$$\Psi_\upsilon = \prod \psi_{\upsilon_k}(Q) = N_{\upsilon_k}\left[\prod_{k=1}^{n} H_{\upsilon k}(Q_k^0)\right]\left[\exp\left(-\frac{1}{2\hbar}\sum_{k=1}^{n}(\lambda_k^{1/2}Q_k^2)\right)\right],$$

where N_υ is normalizing factor; $H_{\upsilon k}$ are the Hermite polynomials, $Q_k^0 = Q_k(\lambda_k^{1/2}Q_k^2)$.

Transitions between different vibrational levels are determined as

$$hv = E_i^{'} - E_k^{''} = hc\sum_{k=1}^{n}\omega_{ik}(\upsilon_i^{'} - \upsilon_k^{''})$$

Where $E_i^{'}$ is an energy of upper state and $E_k^{''}$ is an energy of lower state. According to selection rules for a harmonic oscillator, the absorption is allowed for transitions with $\Delta\upsilon_k = 1$. Therefore, the absorbed frequencies are equal to

$$\frac{E^{\upsilon_k} - E^{\upsilon'_k}}{\hbar} = \omega_k \Delta\upsilon_k = \omega_k,$$

i.e. they are the same as in the classical case. The transitions between the levels with other $\Delta\upsilon \neq 0$ will give overtones or combined frequencies. Within the limits of the simplified quantum mechanical approach we may calculate the mean square amplitudes of vibrations for the different types of interatomic distances which are very important in investigating molecular structure.

Choose any pair of nuclei (*i; j*) in a molecule and consider the squared distance $\overline{D}_{ij}^2 = \left\langle \left(\vec{R}_i - \vec{R}_j \right)^2 \right\rangle$ averaged over all the vibrational states. Since

$$\vec{R}_i = \vec{R}_i^0 + \sum_{k-1}^{n} \vec{A}_{ik} q_k$$

and in the equilibrium configuration $\overline{D}_{ij}^2 = \left\langle \left(\vec{R}_i^0 - \vec{R}_j^0 \right)^2 \right\rangle$, then for the mean square of the vibration amplitude we have

$$\left\langle d_{ij}^2 \right\rangle = \left\langle (D_{ij} = \overline{D}_{ij})^2 \right\rangle = \left\langle \left(\sqrt{(\vec{R}_i^0 - \vec{R}_j^0} \right) + \sum_k (\vec{A}_{ik} - \vec{A}_{jk}) q_k)^2 \right\rangle =$$

$$\frac{1}{\left| \vec{R}_i^0 - \vec{R}_j^0 \right|^2} \sum_{k,l=1}^{n} (\vec{R}_i^0 - \vec{R}_j^0, \vec{A}_{ik} - A_{jk})(\vec{R}_i^0 - \vec{R}_j^0, \vec{A}_{il} - A_{jl}) \langle q_k q_l \rangle + O(q^4).$$

Finally, after a series of transformations

$$\langle d_{ij}^2 \rangle = \sum_{k,l}^{n} H_{ij}^k H_{ij}^l (L \Delta L^*)_{kl}, \tag{23}$$

where Δ = diag{Δ1, Δ2, … Δ*n*} and the matrix *H* is determined by the formulas

$$H_{ij}^k = \frac{(\mathbf{R}_i^0 - \mathbf{R}_j^0, \mathbf{A}_{ik} - \mathbf{A}_{jk})}{|\mathbf{R}_i^0 - \mathbf{R}_j^0|} \tag{24}$$

and depends only on the geometry of equilibrium configuration of the molecule.

If consider the full statement of vibrational problem we should begin from the analysis of vibrational-rotational interaction because the main difference between the complete statement of the molecular vibration problem and that considered above is consideration of vibrational-rotational interaction.

2. MATHEMATICAL MODEL FOR MOLECULAR VIBRATION ANALYSIS. DIRECT AND INVERSE PROBLEMS

We consider a mathematical model which connects experimentally determined values with the theoretical parameters. In the strict sense, these parameters may contain only charges and masses of nuclei and electrons of a molecule. Solving equation (18) we should obtain the equilibrium configuration of molecule {$\mathbf{R}^0$}. For this configuration, we have to construct the matrix of kinematic coefficients *G* and then expand the adiabatic potential by the powers of vibrational coordinates

$$V(q) = \frac{1}{2}\sum_{k,l=1}^{n} F_{kl} q_k q_l + O(q^3).$$

At this stage the following calculations are possible:

(a) of the frequencies of normal vibrations - as the eigenvalues of the

$$GFL=L\mathit{\Lambda}, \tag{25}$$

(b) of the mean square amplitudes of vibrations of all internuclear distances

$$\langle d_{ij}^2 \rangle = \sum_{k,l}^{n} H_{ij}^k H_{ij}^l (L\Delta L^*)_{kl}, \tag{26}$$

(c) of Coriolis constants (when we have the degenerate vibrational levels)

$$\zeta_{\lambda\mu} = \sum_{i,k,l} M_i [\mathbf{A}_{ik}, \mathbf{A}_{il}] L_{k\lambda} L_{l\mu}; \tag{27}$$

(d) of the centrifugal distortion constants

$$\tau_{\alpha\beta\gamma\delta} = -\frac{1}{2 I_{0\alpha} I_{0\beta} I_{0\gamma} I_{0\delta}} \sum_{k,l=1}^{n} F_{kl}^{-1} J_{\alpha\beta}^{(k)} J_{\gamma\delta}^{(l)}. \tag{28}$$

In all these calculations it is assumed that the nuclear masses, the equilibrium molecular configuration, and the force constant matrix *F* are known. If we need to analyze phenomena dependent on the next terms of *V* (*q*) expansion, we calculate the corresponding corrections by means of perturbation theory methods.

Since equation (18) cannot be solved directly, we have to simplify this problem. In detail these simplifications are considered in the survey of nonempirical (*ab initio*) and semiempirical quantum mechanical methods. The latter use the fitting parameters to determine which experimental data are utilized. Using an empirical approach means that we do not solve (18) at all; in this case we assume that the equilibrium configuration of a molecule is known (for example, from the experimental data). All the elements of the force constant matrix are considered as parameters derived from the experimental data. To define them, the equations (25)-(28) connecting this data with the elements F_{ij} are used. Some of these parameters may be set *a priori* from physical considerations or from symmetry conditions. This reduces the number of values to be determined. A similar approach consists of approximating the potential *V* (*q*) by the given functions which contain empirically determined parameters.

When deducing relations (25)-(28), we have not considered the terms in expansion of V (q) of the order higher than second. Thus, the obtained model cannot take into account the anharmonicity effects. Besides, we did not consider nonadiabatic effects (in accordance with deduction used for approximation). Nevertheless, in most cases this model allows us to obtain the force constant matrix F consistent with all experimental data available.

To a large extent, the value of the empirical approach is determined by the degree of universality of the obtained force constants (i.e., if they can be transferred to the similar molecules). Such transfer is often possible. This allows us to synthesize the matrix for more complicated molecules and to predict their properties related to vibrations.

During the last 2-3 decades numerous attempts were undertaken to compute the force fields directly from Schrodinger's equation. The use of very restrictive assumptions was (and still is) necessary to make such computations technically possible. These restrictions influence very strongly on the accuracy of results because an increasing number of atoms in a molecule (and correspondingly, of the number of vibrational degrees of freedom for nuclear motion) complicates significantly the solution of the problem and decreases the accuracy of calculations. In relatively few cases it is feasible to carry out *ab initio* calculations which can predict frequencies within the limits of experimental error (say, e.g., within the 1% errors of the usual harmonic approximation). Nevertheless, it is possible to predict the further rapid progress of *ab initio* calculations, and below we consider some new ways of utilizing even the not-so-accurate results of *ab initio* calculations that are routinely available today.

The development of *ab initio* force field calculations in the past decade has been extremely rapid. Within the Hartree-Fock (HF) self-consistent-field framework (representing a moderate level of nonrelativistic theory), such calculations are routinely possible for rather large molecules (say, 10-30 atoms) at moderate basis set levels. But this method does not take into account an electron correlation, so the problem of obtaining improved theoretical results (with errors comparable to those of experiment) remains a major challenge for theoretical chemists. The accuracy of HF calculations is rather far from experimental limits, and these calculations often give rather appreciable errors in geometry (~0.05 □ in bond lengths, ~5° in bond angles) and in molecular force constants (~10% error) determined by the shifts of calculated frequencies in a comparison with experimental frequencies.

Recent rapid progress in the extending force constant calculations to higher levels of theory has been associated with the introduction of analytic derivative methods (initially for gradients, subsequently for second order and higher derivatives) to replace the older numerical methods. Rapid progress in quantum mechanical calculations of harmonic force fields for moderate size molecules with inclusion of electron correlation at MP2 (perturbation theory) and DFT (Density Functional Theory) levels provides fundamental new possibilities for more accurate interpretation of experimental data as well as improves methods for empirical force field calculations.

All these *ab initio* calculations are of great importance for the development of theoretical models of molecular structure and dynamics, and they have additional practical importance in a view of the joint treatment of theoretical and experimental data. Recent years have demonstrated rapid development of quantum-chemistry calculation techniques and the powerful QM software packages (GAUSSIAN, QChem, Gamess, etc.) have opened new ways to mass-scale quantum chemical calculations of polyatomic molecules, their potential surfaces, and quadratic force fields. *Ab initio* quantum-mechanical calculations ensure obtaining information that has a clear physical meaning. When performed at a high theoretical level (taking into account electron correlation, etc.), such calculations are capable of satisfactorily reproducing patterns of experimental structural and vibrational spectroscopy data. However, in a case of large molecular systems the best *ab initio* results significantly differ from experimental values, and this makes one use special empirical corrections (so-called scale factors. This reduces *ab initio* calculations to the level of semiempirical approximations and causes the loss of important physical information. An approach that guarantees obtaining solutions which reflect the most important properties of *ab initio* potential surfaces is therefore preferable.

Since we cannot solve (18) directly, we have to simplify this problem. The question arises how to find the main parameters characterizing the molecule without complicated calculations of the wave functions and energy levels, using instead the data obtained from experiment. Let us first define the requirements concerning these parameters using the above considerations.

When deducing the equations of motion for a molecule we have seen that the main role is played by the force field $V(q_1, \ldots, q_n)$ obtained from the eigenvalue equation (23). Due to the fact that solving this equation is usually hard, we may set a problem for determining $V(q_1, \ldots, q_n)$ from the experiment. It should be noted that the determination of all the force field is not a solvable problem, since the spectral properties are related only to some characteristics of $V(q)$. On the other hand, since the function $V(q)$ is required only for prediction of spectral (and geometric) properties of the molecule, it suffices to determine only essential characteristics of $V(q)$ for this problem.

The essential property of the potential function $V(q)$ is that the position of its global minimum determines the equilibrium configuration of the molecule's nuclei. Further, as follows from equation (23), the frequencies of the small vibrations of the nuclei (in harmonic approximation) may be determined using the matrix of the second derivatives in the equilibrium configuration - the force constant matrix F with elements:

$$f_{ij} = \left. \frac{\partial^2 V}{\partial q_i \partial q_j} \right|_{q=q^0}, \quad i, j = 1, ..., n,$$

where q^0 stands for the equilibrium configuration. This matrix allows us to calculate the vibrational-rotational and centrifugal corrections to spectra and the mean square amplitudes of nuclear vibrations.

Note that the representation of the molecule as a set of harmonic oscillators allows us to determine thermodynamical properties of the substance as well. For this purpose we do the same as when deducing the formula for the mean square amplitudes. The thermodynamic functions depend on the frequencies of molecular vibrations and, therefore, may be calculated if the matrix of force constants is known.

Thus, to determine the geometry and the vibrational properties of the molecule it suffices to know only the principal characteristics of $V(q)$: its minimum and the second derivatives at the point of minimum. Long before computers were invented, which allowed us to calculate more complicated molecules than hydrogen molecule, attempts had been undertaken to model the potential $V(q)$ in order to describe the properties of molecular spectra. The simplest method of such simulation is setting the function V from *a priori* concepts (based on experience and intuition) and then fitting the empirical parameters to obtain correspondence with the experimental results.

Assume that the molecule consists of balls connected by springs (mechanical model). In this case, the parameters will be the rigidity coefficients of the springs. In the more complicated model, we may add springs between springs and so on (in order to account for the noncentral forces). The best models are those based on assumptions taken from experience, for example:

1. The valence bonds have (for each given pair of atoms, accounting for the distribution of valence units and enclosure) approximately constant length. The potential for them is more rigid than for the other structure parameters.
2. The interactions of nonbonded atoms are essentially weaker (usually they are simulated by empirical potentials which describe the interaction of the free atoms).
3. For each bonded atom in a certain valence state there exist admitted ideal values of valence bond angles. The deviations of real angles from these values lead to an increase in the energy.

Simple models of the force field are meaningful if the potentials functions used in them are uniform and the number of empirical parameters is not too large. Besides, we would prefer that the parameters preserve their values for a certain class of molecules. In this case, evaluating the parameters for sufficiently simple molecules, we may predict the structure and the force fields for more complicated molecules.

Further, we shall assume that the equilibrium geometrical configuration of the molecule is known. The force field, may be represented as a Taylor series at the minimum point of $V\,(q^0)$:

$$V(q_1,...,q_n)=V(q_1^0,...,q_n^0)+\frac{1}{2}\sum_{iju}F_{ij}(q_i-q_i^0)(q_j-q_j^0)+...$$

and, if the coordinates q are chosen so that they vanish at the equilibrium point,

$$V(q_1,...,q_n)=\frac{1}{2}\sum_{iju}F_{ij}q_iq_j\,.$$

In this expression, we have omitted the term of zero order with respect to q_1, … , q_n. It is an insignificant constant shift of energy levels. The terms of the first order are absent because the expansion is taken at the minimum point. The terms of higher orders are responsible for the vibration anharmonicity. As we have seen from the above analysis, the corrections to the energy due to anharmonicity have the order of $\sqrt{m/M}$ relative to the energies of the vibrational spectrum. Here, m and M are the masses of an electron and a nucleus respectively. Numerically this value alters from 2% for the hydrogen atom down to fractions of one percent for other atoms, which is substantially greater than the error of measuring vibrational frequencies. For example, anharmonicity of C-H bond stretching vibrations leads to the frequency shift of ~ 100 cm^{-1} (the frequency itself is of the order of 3000 cm^{-1}); at the same time the measurement errors are by far less than 1 cm^{-1}. Rigorous accounting for the vibrational anharmonicity is a complicated problem and requires special analysis. We shall not do such accounting, considering the measured vibrational frequencies harmonic and therefore limiting ourselves to finding a certain effective harmonic force field.

To analyze the vibrational spectra, it is necessary to construct the force constant matrix F using experimental data. Indeed, in this case, we may determine the vibrational frequencies and their modes, i.e. (in the classical analogy) the vectors of the nuclear displacements from the equilibrium states for each normal vibration.

Note once more that the matrix F may be useful to predict the vibrational properties of a molecule only if its elements more or less preserve their values in similar structural fragments of different molecules. In this case, we may use the known elements of the force constant matrix (obtained, for example, from analysis of simple molecules), to construct the corresponding matrix for a complicated molecule and determine its vibrational properties. Since characteristic frequencies do exist, it appears that at least for some molecules, some elements of the force constant matrix really possess the required transfer properties.

The experimental data may be insufficient for complete determination of the force constant matrix. Indeed, we have $n = 3N- 6$ nuclear coordinates (N is the number of atoms); therefore, the matrix F contains at most $n(n + 1)/2$ unknown elements (because the matrix is symmetrical). Note that for symmetrical molecules the number of force constants is less and is determined by the type of symmetry. For large molecules, the number of force constants is quite large. Therefore, to construct matrix F, we must take into account some *a priori* concepts based on experience. The most important of these concepts are the choice of internal generalized coordinates, and the properties of the force constants in this coordinate system (including transfer properties). These problems will be considered later.

The most direct method which uses all the available experimental data to determine F is solving the nonlinear operator equation

$$AF=\Lambda \tag{29}$$

where Λ is a set of all the experimentally measured values; A is the operator which puts into correspondence to each symmetric matrix F the set of calculated values, corresponding to these data (according to formulae (25)-(28) and so on). The operator A is completely determined by nuclei masses and the equilibrium geometric configuration of the molecule. Note that the set of experimental data may contain information on many isotopic species of the molecule, since in the approximation considered, F does not depend on atomic masses.

From (25)-(28) it follows that the relation between F and calculated parameters Λ is quite complicated and, at any rate, requires us to solve the eigenvalue problem (14). As a result, even the solution of direct problem (25), i.e. the calculation of vibrational spectrum characteristics with the known matrix F, is practically impossible without using computers.

These difficulties are even greater for the inverse problem. Moreover, practically always, the problem of determining F from (29) is either underdetermined or incompatible, or both. Equation (29) may be incompatible for two reasons:

a) the inconsistency of the harmonic approximation model, since the real molecular vibrations are always more or less anharmonic;

b) using approximate experimentally measured values Λ and the parameters of molecular equilibrium configuration.

As a result, instead of (29) we need to set the problem of finding

$$\min_F \|AF - \Lambda\| \tag{30}$$

Where $\| . \|$ is a norm in the space of vectors Λ, for example

$$\|\Lambda\| = \left(\sum_k \Lambda_k^2 p_k \right)^{1/2}$$

and $p_k > 0$ are some weights. This means that instead of a solution of (29) we have to seek its pseudosolution.

Underdeterminancy of the problem and (related to it) instability of the solution with respect to small perturbations of input data lead to the necessity of using the approaches developed in the theory of ill-posed problems. To avoid the instability, it is possible to introduce the physically stipulated *a priori* constraints. These may either narrow down the set of matrices F, where the value $\|AF - \Lambda\|$ is being minimized, or help to formulate the principle for choice from the set of admissible solutions of (30).

We shall use the following formulation of the inverse problem: let, instead of the exact values A and Λ, we are given their approximations $\tilde{A}$ and $\tilde{\Lambda}$ (the measure of approximation will be defined later), and the accuracy estimates for these approximations be characterized by the parameter η. It is required to construct the approximations F_η to the exact solution $\bar{F}$:

$$\min_{F \subset Q} \|F - F^0\|_F, \qquad Q = \{F : F \subset D, \quad \|AF - \Lambda\| = \min_{f \subset D} \|Af - \Lambda\|\} \qquad (31)$$

such that $F_\eta \to \bar{F}$ when $\eta \to 0$.

Here $\|\,.\,\|_F$ is a norm in the space of symmetric matrices F; D is the set of *a priori* constraints; F^0 is an *a priori* given matrix.

Note that if (29) is uniquely solvable then matrix $\bar{F}$ is its solution.

We shall perform the analysis of the problem of determining F using the experimental data in several stages, since introducing each kind of experimental data, generally speaking, changes the properties of operator A.

When considering certain problems of vibrational spectroscopy we shall show the cases of underdeterminancy and incompatibility of these problems; therefore, the statement in the form (31) (determined by D and the matrix F^0 in the problem setting), the problem of choosing the generalized coordinates is a unique challenge. This question is closely related to the force fields models which are widely used in the calculations of molecular vibrations in order to reduce the underdeterminancy of the problem.

It should be noted, however, that extreme narrowing of the set D, where we seek the solution to problem (31), leads to growing incompatibility of the problem, i.e. (29) is satisfied less and less. More details on mathematical model and statements of problems arising in data processing of vibrational spectra will be considered in the following discussions.

3. VIBRATIONAL PROBLEM IN INTERNAL COORDINATES. MODELS OF A MOLECULAR FORCE FIELD. CHOICE OF GENERALIZED COORDINATES.

We have already shown that solution of the Schrodinger equation and finding the adiabatic potential (or force field) of a molecule encounter substantial difficulties. These difficulties increase even further when we move on from small (2-5 atoms) to large polyatomic molecules. Even nowadays, basic information on force fields with satisfactory accuracy may be obtained only from experimental data. However, in this case, the complete force field within the simplest model usually used (purely harmonic vibrations, adiabatic approximation) cannot in general be obtained, even if additional data (Coriolis constants, centrifugal distortion constants, mean vibrational amplitudes, etc.) is available. Therefore, the force field is usually approximated by a certain (not very numerous) set of parameters which should be determined from experimental data. The analysis and choice of the models, which give results consistent with the experiment may clarify the atomic interaction in molecules.

Let us consider briefly the main force field models used in molecular vibrations analysis. The simplest approximation is the central-force field model, where the forces act along the lines connecting each pair of atoms, depend only on internuclear distances, and satisfy the Hooke law. Even without any assumptions on the character of dependency of $V(q)$ on coordinates, it is easy to show that for the simplest molecule, for example, the molecule of water H_2O, two parameters characterizing interactions H-O and H-H in the equilibrium state are insufficient to reproduce all three vibrational frequencies of the molecule. Besides, for certain molecules there exist deformations that do not lead to changes in any interatomic distances (to within the terms of the second order). Such an example is the linear molecule CO_2.For this molecule , the OCO angle bending leads to very slight change in the O-O interatomic change. Such vibrations must be considered as having potential function of the form (ΔR^4), and their frequencies should have higher order of smallness with respect to bond stretching vibrations. Practice shows, however, that the frequencies of stretching and bending vibrations do not differ significantly. Nevertheless, the central force field model may be successfully applied to ionic compounds.

A more realistic model is the valence force field model. Here we assume that the forces which act on the nuclei prevent the interatomic distances between bonded atoms from changing, and, also, keep bond angles constant and prevent torsion around the bonds.

If we introduce the internal coordinates as deviations of the mentioned distances and angles from their equilibrium values, the force constant matrix would take the diagonal form. Such a model describes all forms of molecular vibrations, but its accuracy is unsatisfactory. It is easy to see from the example of H_2O for which both described models are equivalent (since the bond angle H-O-H is uniquely determined by three interatomic distances). We cannot find such a diagonal force field which satisfactorily reproduces the vibrational spectrum of the water molecule.

But if we admit the assumptions (used in the valency force model) on which distortions of the equilibrium molecular configuration have most influence on its energy, then the force constant matrix in the introduced internal coordinates has to be close to a diagonal matrix. The following elaboration of this model considers small off-diagonal elements in the force constant matrix. We shall refer to such approximation of the potential function as a modified (or generalized) valence force field.

Which off-diagonal elements are to be considered as non-zero is determined both by physical considerations and intuition. For example, a large distance between two structural fragments of a molecule gives a good reason for neglecting corresponding off-diagonal elements in the force constant matrix. The existence of characteristic vibrational frequencies for certain atomic groups (for example, fragments CH_2, CH_3, etc.), if the equilibrium geometry of this group is preserved, indicates that the off-diagonal elements of force constant matrix F, which describe the interaction of vibrations of these fragments with the vibrations of the rest of the molecule, are small.

We may also assume that the force constants of separate molecular fragments should be preserved in similar molecules. This follows from the basic assumptions of the classical theory of chemical structure, involving concepts of bonded and non-bonded interactions, bond orders, monotone changes of physicochemical properties in a series of related molecules (Tatevskii, 1973). If force constants do not change significantly when the corresponding structural fragment is transferred from one molecule to another, we speak of transferability of the force constants. Note that transferability does not always take place, and should be used very cautiously in practical calculations.

If we do not impose *a priori* conditions on the elements of the matrix F, the obtained model of general harmonic force field in essence ceases to be a model because the only remaining assumption is the applicability of adiabatic approximation and of the vibrational harmonicity related to it. In this case, each set of linearly independent internal coordinates (note that they must be linear with respect to atomic displacements) would lead to equivalent results.

The force field models considered above are most popular in practical calculations of force fields and analysis of normal vibrations of polyatomic molecules. But there are many other models involving modified simple force fields. The best known are the force fields of Urey-Bradley and Urey-Bradley-Shimanouti which consider both simple valence force field (i.e., they introduce diagonal force constants of bonds stretch and bond angle deformations) and central-type forces. The off-diagonal constants of such generalized force field are defined by the interactions of unbounded atoms.

Note that the force constant matrix (in the independent coordinates), as well as the adiabatic potential, may be (in principle) determined uniquely. Therefore, if we had a sufficient set of experimental data or if we might perform sufficiently accurate theoretical calculations, the introduction of the above model assumptions would become unnecessary.

However, in most cases, the experimental information is insufficient to determine the force constants matrix uniquely. This leads to introduction of the various model assumptions. The order of magnitude of the matrix F coefficients, their transferability and other properties are subject to experimental verification and may be used as a basis for the described models. The further accumulation of both experimental information and the results of theoretical research may alter the view on the validity of a particular model.

As was shown earlier, to solve the problem of molecular vibrations, we need to introduce $n = 3N- 6$ (or $n = 3N- 5$ for linear molecules) independent coordinates. We shall not limit ourselves to exactly n coordinates but consider the sets of $n_f \geq n$ coordinates (which, nevertheless, are always assumed to contain exactly n independent coordinates). The problem of excluding the redundant coordinates will also be analyzed. Generally speaking, the choice of coordinates has no principal significance because each set of coordinates should yield the same energy levels and vibrational frequencies. However, this choice begins to play an important role when underdetermined inverse problems are considered.

Indeed, let us formulate the problem of determining the force constant matrix F with the elements $F_{ij} = \partial^2 V \big/ \partial q_i \partial q_j$,

or, which is the same, the quadratic term of adiabatic potential

$$V^{(2)} = \frac{1}{2}\sum_{kl} F_{kl} q_k q_l \,. \qquad (32)$$

As a rule, for polyatomic molecules, we cannot determine in a unique way all $n(n+1)/2$ elements due to the lack of experimental data. The symmetry of molecules reduces the number of parameters to be found, but, simultaneously, it diminishes the number of independent expermentally determined values. Therefore, in this situation, it is natural to solve the inverse problem for the narrow subset of matrices F which satisfy certain physical constraints. For this reason, it is desirable that the elements of the force constant matrix should have a more or less simple physical meaning, and the chosen generalized coordinates be connected with really existing interactions in the molecule. For this reason, it is desirable that the greatest part of potential (32) would be concentrated in a narrow set of expansion terms (in order that the remaining terms might be either omitted or determined as corrections to the principal terms, etc.).

This ideology leads to construction of the so-called internal coordinate system closely related to the molecular structure. If the coordinate system reflects the peculiarities of intramolecular forces, then the main role in producing the vibrations will be played by relatively few elements of F.

For example, in chemistry, it is well known that there is a significant difference between interaction energies of bonded and remote atoms, and that bond angles tend to preserve their ideal values (within the accuracy of the used model and experimental errors) for common functional groups in a large number of compounds.

The internal coordinate system (or internal displacement coordinates) should therefore include the following elements:
1) changing the bond lengths (i.e. the distances between the nuclei for bonded atoms),
2) changing the bond angles (the so-called bending coordinates),
3) changing the angles between a bond and the plane of the pair of other bonds (or the atomic triple connected by this pair of bonds): the so-called out-of plane bending,
4) changing the dihedral angles between the atomic triple planes (bond pairs planes), or torsion.

Sometimes certain combinations of the above-mentioned coordinates 1-4 are also used as internal coordinates. Different types of internal coordinates are illustrated for some molecules.

As a rule the internal displacement coordinate system is widely used in normal coordinate analysis. Besides, it is possible to consider the alternative coordinate systems:
a) the system which includes the changes of all internuclear distances:
their number is $C^2_N = N(N-1)/2$, while the number of independent coordinates is still $3N - 6$. The exclusion of dependent coordinates may be done by accounting for geometric constraints,
b) the Cartesian coordinate system, which consists of $3N$ displacements of all the nuclei along the axes x, y, z in a certain Cartesian coordinate system. In this system, 6 coordinates are to be excluded because the molecule does not rotate or translate as a whole.

Note that both the internal coordinates and the coordinates of changing internuclear distances are nonlinear with respect to the Cartesian displacements of nuclei, whereas for simplicity of analysis it is convenient to use the linear coordinates, as was done above. Therefore, instead of the introduced internal coordinates it is convenient to use the linear terms of their expansion with respect to the Cartesian displacements of nuclei. For small vibrations, such an approach is equivalent to using the nonlinear coordinates. In case of anharmonic vibrations, there is no such equivalence. However, questions related to anharmonicity are not considered here. Everywhere below we assume that the internal coordinates are linear with respect to nuclear displacements.

4. CONSTRUCTION OF THE AUXILIARY MATRICES. THE MATRIX OF KINEMATIC COEFFICIENTS.

When considering the theory of molecular vibrations it was shown that, together with the force constant matrix *F*, the main role in vibrational motion is played by the matrix of kinematic coefficients $G = T^{-1}$, where *T* is defined by formula (9) :

$$T_{kl} = \sum M_i (\vec{A}_{ik}, \vec{A}_{il}) . \tag{33}$$

The matrix *G* has a direct physical sense: it is the matrix of kinetic energy of a molecule in the momentum representation. Calculation of *G* is even simpler than that of matrix *T*. Earlier we have introduced the matrix $\vec{A}$ connecting the Cartesian components of nuclear displacements from the equilibrium state with the generalized coordinates *q*

$$\Delta \mathbf{R}_i = \sum_{k=1}^{n} \mathbf{A}_{ik} q_k, \qquad (i = 1, 2, \cdots, N), \tag{34}$$

Evidently, the inverse transformation also exists and is linear:

$$q_k = \sum (\vec{B}_{ki}, \Delta \vec{R}_i) \quad (k = 1, 2, \dots, n) . \tag{35}$$

Due to the independence of generalized coordinates $q_1, \dots, q_n$, the following equality

$$\sum_{i=1}^{N} (\vec{B}_{ki}, \vec{A}_{il}) = \delta_{kl} \qquad (k = 1, \dots, n). \tag{36}$$

holds and is obtained by substitution of (34) into (35).

We must impose constraints on the matrix $\vec{B}$ because when the molecule is translated (i.e. when $\Delta \vec{R}_1 = \Delta \vec{R}_2 = \dots = \Delta \vec{R}_N$) and is rotated as a whole around any axis (i.e. when $\Delta \vec{R}_i = [\omega, \vec{R}_0^0]$ for an arbitrary vector ω) the coordinates *q* do not have to be changed. It is easy to show that these constraints may be written as follows:

$$\sum_{i=1}^{N} \mathbf{B}_{ki} = 0, \quad \sum_{i=1}^{N} [\mathbf{R}_i^0, \mathbf{B}_{ki}] = 0 \quad (k = 1, \dots, n), \tag{37}$$

i.e. they are somewhat simpler than conditions on $\vec{A}$ (5) since they do not depend on atomic masses. Conditions (36) and (5) must completely define the matrix $\vec{A}$ through the known matrix $\vec{B}$ satisfying conditions (37).

Since $\vec{B}$ is independent of the atomic masses (relations (35) and (37) which determine $\vec{B}$ are purely geometrical) it may be applied more widely than $\vec{A}$. For different reasons, the using the matrix *G* is also more convenient than using *T*.

Kinetic energy of nuclei movement can be written as scalar

$$-\sum_i \frac{\hbar^2}{2m}\left(\frac{\partial}{\partial\Delta\vec{R}_i},\frac{\partial}{\partial\Delta\vec{R}_i}\right). \qquad (38)$$

If we use the internal coordinates { $q_1, \dots, q_n$ } then

$$\frac{1}{2}\sum_{k,l}\widehat{p}_k\left(\sum_i\frac{1}{M_i}\left(\frac{\partial q_k}{\partial\vec{R}_i},\frac{\partial q_i}{\partial\vec{R}_i}\right)\right)\widehat{p}_l\ . \qquad (39)$$

So, if we know the equilibrium configuration of a molecule the elements of matrix G can be calculated on a base of geometry relations. The formulas for calculations of $\vec{B}$ and G matrix elements are presented in textbooks on molecular vibrations. We consider an example of constructing matrix G and some other matrices.

In Cartesian coordinates matrix G has the diagonal form with reciprocal atomic masses

$$G_r = diag\{\varepsilon_1,\varepsilon_2,\dots,\varepsilon_n\};\quad \varepsilon_i = \frac{1}{m_i}\ ; \qquad (40)$$

m_i – mass of *i*-th atom, *i=1,2, ..., N*; *N* is a number of atoms in a molecule.

Matrix G is symmetrical and positively definite matrix.

Consider the relation between matrices A and B which allows us to determine the matrix *G* directly. We shall seek for this dependence as

$$\left|\vec{A}\right| = \varepsilon\vec{B} * X\ \text{, or}\ \vec{A}_{ik} = \frac{1}{M_i}\sum_{i=1}^{n}\vec{B}_{li}X_{lk}\ ,$$

where *X* is an arbitrary matrix to be determined. In this case, conditions (5) immediately follow from (37). To determine *X*, substitute *A* into (36):

$$\delta_{kl} = N\sum_{i=1}(\vec{B}_{ki}\vec{A}_{il}) = \sum_{i=1}^{N}\frac{1}{M_l}\sum_{j=1}^{n}(\vec{B}_{ki}B_{ji})X_{jk} = \sum_{j=1}^{N}X_{jk}(\sum_{i=1}^{N}\frac{1}{M_i}(\vec{B}_{ki}\vec{B}_{jk}))\ ,$$

i.e. $\vec{B}\varepsilon B * X = E,\quad X * (\vec{B}\varepsilon B)X = E,$ where *E* is a unit matrix of *nxn* dimension.

Substitution of $\vec{A}$ into (33) gives

$T = \vec{A} * \varepsilon^{-1}\vec{A} = X * \vec{B}\varepsilon\vec{B} * X = X^* = X$,

whence $\vec{B}\varepsilon B^* = X^{-1} = T^{-1} = G$. So, for calculating the matrix *G*, we have the next expression $G = \vec{B}\varepsilon\vec{B}*$, or

$$G_{kl} = \sum_{i=1}^{N} \frac{1}{M_i} (\vec{B}_{ki}, \vec{B}_{li}), \qquad (40)$$

And for calculating the matrix $\vec{A}$ through matrix $\vec{B}$ the next formula can be written

$$\vec{A} = \varepsilon\vec{B}*T \text{ , or } \vec{A}_{ik} = \frac{1}{M_i} \sum_{i=1}^{n} \vec{B}_{li} T_{lk} \text{ .}$$

Since elements of matrix $\vec{B}$ are independent of the atomic masses (relations (37) and (39)) which determine $\vec{B}$ are purely geometrical) it may be applied more widely than $\vec{A}$. For different reasons, the use the matrix *G* is also more convenient than *T*.

All the previous analysis was performed under the assumption that the relative displacements of nuclei $\Delta\vec{R}_1, \dots, \Delta\vec{R}_N$ are described by $n = 3N$-6 (or by $3N$-5 for a linear molecule) independent internal coordinates $\{q_1, \dots, q_n\}$. In certain cases the use of only independent coordinates is inconvenient (in particular, for the transfer of force constants to the other molecules, when we are dealing with linear combinations of force constants and, also, when we use the symmetry coordinates). So in many cases the redundant coordinates are preferable.

In a case of using the redundant coordinates, there arise two main questions concerning

a) the physical sense of matrices of kinetic and potential energy in redundant systems of coordinates; and

b) the possibility of solving the problems on molecular vibrations immediately in a redundant coordinate system (without excluding the redundant coordinates).

We define the force constant matrix in redundant coordinates for the given molecule as matrix *F* for which the quadratic form 1/2(*q*, *Fq*) is equal to the corresponding quadratic form in independent coordinates, if among the coordinates $q_1, \dots, q_{n_f}$ in the quadratic form for molecular potential energy

$$V = \frac{1}{2} \sum_{k,l=1}^{n_f} F_{kl} q_k q_l \qquad (41)$$

there are only *n* independent coordinates and redundant coordinates are excluded.

The number of redundancies between coordinates is equal ot $m=n_f-n$ and these redundancies can be written in a form

$$\sum_{k=1}^{n_f} w_{ik} q_k = 0, \qquad i = 1, 2, \dots, m \qquad (42)$$

The symmetry of quadratic form $1/2(q, Fq)$ corresponds to the symmetry of the molecule for all (not only those allowed by conditions (42) virtual increments of coordinates.

Note that the matrix F in the redundant coordinates is not defined uniquely.

Symmetry properties play a significant role in the theory and calculations of molecular vibrations. The analysis of symmetry allows us to classify the vibrations, to determine the degenerate energy levels (or multiple frequencies), to clarify the activity of various vibrations in infrared and Raman spectra, to substantially simplify the so-called normal coordinate analysis (calculations of vibrational frequencies and modes), and to solve certain inverse problems of vibrational spectroscopy.

Each molecule can be characterized by the set of space rearrangements transforming it into itself. Such rearrangements are called symmetry transformations or symmetry operations. Later, we shall consider the symmetry of equations and functions. Therefore, it is convenient to define the symmetry transformations as the corresponding coordinate transformations. For example, for the water molecule the symmetry transformations are

a) rotation about the axis O_z through the angle 180° (C_2),

b) reflection in the plane O_{xy} (σ_υ),

c) reflection in the plane O_{yz} (the axis O_x is orthogonal to the plane of ($\sigma_\upsilon^{'}$).

We should also mention the identical transformation, which does not change the coordinates. This is evidently a symmetry transformation for any molecule.

The set of all molecular symmetry operations, including the identical transformation, constitute the so-called symmetry point group to which the given molecule belongs. The actions of such sets of symmetry transformations or corresponding coordinate transformations are described by mathematical group theory.

5. THE MATHEMATICAL FORMULATION OF THE INVERSE VIBRATIONAL PROBLEM.

We consider the equilibrium configuration of the molecule which satisfies the relation

$$\frac{\partial U}{\partial q} = 0,$$

and if we define coordinates $\{ q_1, q_2, ..., q_n \}$ so that $q_1 = q_2 = ... = q_n = 0$ in the equilibrium configuration, the following expansion is valid:

$$V(q_1,...,q_n) = V_0 + \frac{1}{2}\sum_{i,j=1}^{n} f_{ij} q_i q_j + \mathrm{O}\left(\|q\|^3\right) \qquad (43)$$

where U_0 is a certain constant, and the force constants

$$f_{ij} = \frac{\partial^2 V}{\partial q_i \partial q_j}, \quad i, j = 1, ..., n$$

constitute a positive definite matrix F determining all the molecular characteristics connected with small vibrations.

Mathematically, the concept of the force field may be obtained through the adiabatic theory of perturbations with the use of a small parameter related to the ratio of electron mass to the mass of nuclei, and it can be shown that in a certain approximation the nuclei may be treated as particles moving in the force field determined by the potential energy function (2).

There are two main purposes for using a molecular force field: (*a*) to check validity of various model assumptions commonly used by spectroscopists for approximation of the potential function; (*b*) to predict the vibrational properties of certain molecules (including those not yet observed) using fundamental properties of the force field such as its isotopic invariance and the approximate transferability of specific force constants in a series of related compounds.

The spectral frequencies ω_i are the main type of experimental data on molecular vibrations. They are connected with the matrix of force constants F by the eigenvalue equation

$$GFL = L\Lambda \tag{44}$$

where $\Lambda = \mathrm{diag}\{\omega_1^2, \ldots, \omega_n^2\}$ is a diagonal matrix consisting of the squares of the molecular normal vibrational frequencies, and G is the kinetic energy matrix in the momentum representation which depends only on nuclear masses and the equilibrium configuration (assumed to be known within specified limits of error). The matrix L characterizes the form of each normal vibration, i.e., the relative amplitudes of vibrations in terms of classical mechanics.

While (44) is the main source of data determining the force constants, it is evident that (except for diatomic molecules) the $n(n+1)/2$ parameters of F cannot be found from n frequencies ω_1, ..., ω_n. This has led, on the one hand, to attempts to use certain model assumptions concerning the structure of the matrix F, and, on the other hand, to introduction of additional experimental data. Within the approximations considered, the force field of the molecule is independent of the nuclear masses, and hence for the spectra of m molecular isotopic species we have, instead of (44), the system

$$(G_i F)L_i = L_i \Lambda_i, \qquad . \tag{45}$$

where the subscript i = 1,2, ..., m indicates the isotopomers. Usually, the introduction of isotopomers leads to a limited number of independent equations in system (24), thus leaving the inverse problem underdetermined. Important additional information on the molecular force is provided by Coriolis constants ζ which characterize the vibrational-rotational interaction in the molecule. They are connected with matrix F in terms of the eigenvectors L of the problem (34):

$$\zeta = \frac{1}{M^2} L^* \mathrm{AMA}^* L \qquad (46)$$

where ζ is a matrix with vector elements consisting of the Coriolis constants, M is a diagonal matrix consisting of the nuclear masses, M is the sum of nuclear masses of the molecule, and A is a matrix with transpose A* connecting the Cartesian displacements of atoms with coordinates q, which can be found from the equilibrium configuration of the molecule. In a similar manner we can write the dependencies of other measured values on the matrix F, such as the mean-square amplitudes of the vibrations (obtained from gas-phase electron diffraction) which may be calculated from the eigenvalues and eigenvectors of (23). The above-mentioned experimental quantities (frequencies of isotopomers, Coriolis constants, mean-square amplitudes), while not so easily obtainable, are particularly important because their values do not depend on additional unknown parameters of any kind (unlike, e.g., the calculation of intensities in vibrational spectra).

The mean square amplitudes of vibrations of all internuclear distances are also determined by molecular force field.

$$\left\langle d_{ij}^2 \right\rangle = \sum_{k,l=1}^{n} H_{ij}^k H_{ij}^l (L\Delta L^*)_{kl} \qquad (47)$$

where L is the eigenvector matrix for (44), Δ = diag $\{\Delta_k\}$, $\Delta_k = \frac{\hbar}{2\omega_k} \coth \frac{\hbar\omega_k}{2KT}$

and matrix H is completely determined by the equilibrium configuration; In all these calculations it is assumed that the nuclear masses, the equilibrium molecular configuration, and the force constant matrix F are known.

We shall consider (44) - (47), or some part of them, depending on the available experimental data, as a single operator equation

$$AF = \Lambda \qquad (48)$$

where the nonlinear operator A maps the real symmetrical matrix F to the set of eigenvalues of (44) (or (45)), the Coriolis constants, ζ, (46), the mean square amplitudes, etc.. This set of data may be represented as a vector in the finite-dimensional space R^l, where l is a number of known experimental data. Also, we consider the matrix F as a vector in the finite-dimensional space Z, consisting either of the elements of the matrix F or of the quantities by means of which this matrix can be parametrized.

$F \in Z \in R^{n(n+1)/2}$ (Z is a set of possible solutions) is the unknown force constant matrix (real and symmetrical), $\Lambda \in R^m$ represents the set of available experimental data (vibrational frequencies, etc.) determined within δ error level: $\|\Lambda - \Lambda_\delta\| \le \delta$. A is a nonlinear operator which maps matrix F on the Λ.

Note that (48) in general does not satisfy any of the conditions of the well-posedness of the problem considered above.

1) Solvability.

It is possible to shoe that, for example, system (45) (determined for different molecular isotopomers) is compatible only when the condition

$$\det G_i \big/ \det \Lambda_i = \text{const}, \qquad i = 1,2,..m. \tag{49}$$

is satisfied (m is the number of isotopomers). This may be violated both by virtue of errors in measurement of the Λ_i, and due to inaccurate specification of the molecular geometry G_i, or, when exact experimental data are not available, because of the anharmonicity of the vibrations ignored by the operator of (48). Therefore, a matrix F reproducing the frequencies of all isotopomers within the limits of experimental errors does not exist.

2) The uniqueness of the solution of the problem.

If we know only the vibrational frequencies of one isotopomer of the molecule, (48) reduces to the inverse eigenvalue problem; hence, when G is not singular it follows that as solution of (48) we may take any matrix of the form

$$F = G^{-1/2} C^{*} \Lambda C G^{-1/2} \tag{50}$$

where C is an arbitrary orthogonal matrix (for example it may be chosen as rotation matrix in the next form.

$$C^k = \begin{array}{cccccccccccc}
 & & & i & & & & j & & & & \\
1 & & & & & & & & & & & \\
 & 1 & & & & & & & & & & \\
 & & \ddots & & & & & & & & & \\
 & & & \cos\varphi_{ij}^{(k)} & & & & \sin\varphi_{ij}^{(k)} & & & & i \\
 & & & & \ddots & & & & & & & \\
 & & & & & 1 & & & & & & \\
 & & & & & & \ddots & & & & & \\
 & & & -\sin\varphi_{ij}^{(k)} & & & & \cos\varphi_{ij}^{(k)} & & & & j \\
 & & & & & & & & 1 & & & \\
 & & & & & & & & & \ddots & & \\
 & & & & & & & & & & 1 &
\end{array}$$

To choose a definite solution it is necessary to use additional information or to take into account some model assumptions.

3) <u>The stability of the solution with respect to the perturbations of Λ and *A*</u>.

An example of such instability may be easily constructed for a system of the form (45).

Note that (48) in general does not satisfy any of the conditions of the well-posedness of the problem considered above.

This problem belongs to the class of nonlinear ill-posed problems (it does not satisfy any of three well-posedness conditions by Hadamard) and in the general case (except the diatomic molecules) may have non-unique solution or no solutions at all (incompatible problem), solutions may be unstable with respect to the errors in operator *A* and set of experimental data Λ. The theory of regularization methods for nonlinear problems was developed in the last two decades and applied to the inverse problems of vibrational spectroscopy.

The difficulties which arise during the force field calculations (which are related to the nonuniqueness of solutions and the instability of the solution with respect to the perturbations of experimental data) have been discussed earlier and various special model assumptions have been proposed based on the intuition of the investigator. The absence of stability and uniqueness of the solution has often led to significant differences in the force field parameters of the same molecule. This has caused difficulties in the comparison and transferability of the force fields in series of related compounds and has made the physical interpretation of the experimental data much more obscure.

The molecular force field plays an important role in determining the properties of a molecule, in particular its vibrational spectrum. Many approximations have been proposed for the calculation of a complete quadratic force field and many computational programs have been created and used in practice. Usually, the ill-posed character of inverse vibrational problems has led to some degree of subjectivity, related basically to constraints imposed on the solution to ensure physically meaningful results. In this way various models of the molecular force fields have been proposed and a great number of force field matrices have been calculated for various series of compounds. These matrices are chosen to satisfy either experimental data or a priori known, but not explicitly formulated, criteria of the physically meaningful solution.

As a result, a situation exists (in particular, for complicated polyatomic molecules) when various so-called spontaneous methods for solving inverse problems lead to inconsistent force fields due to different criteria for the physical feasibility of solutions used by various investigators, and to the instability (with respect to small perturbations in the input information) of numerical methods used to solve the inverse problem.

It is very important in the elucidation of any arbitrariness in the calculated force constants to use stable solutions of the inverse vibrational problem which have some specific properties. What is meant by "specific properties" of the force constants or, in other words, what additional limitations on the values of force constants can be imposed while solving the inverse problem?

In practice, chemists and spectroscopists often use certain model assumptions, arising from the classical theory of chemical structure, involving the monotonic changing of the physico-chemical properties in a series of related molecules and the preservation of the properties of separate molecular fragments in the various compounds, taking into account nearest surrounding. It is the transferability of the force constants which related to these properties.

The most important idea of regularization theory is that every time we find that experimental data is insufficient for the unique and stable determination of some (or all) molecular parameters, we should employ some kind of external knowledge or experience. In some cases it is desirable to formulate these considerations as explicit additional restrictions on the set of possible solutions. When it is impossible, a more flexible approach is to choose the solution that is in a certain sense nearest to some a priori defined parameter set. This set may not necessarily conform to the experiment, but should be based on data complementary to the experiment.

This external evidence may be derived from the general ideas (for example, molecular force field models, or data on similar molecular structures), or, preferably, be based on ab initio calculations. An inverse vibrational problem is formulated as a problem of finding the so-called normal solution (or normal pseudo-(quasi-)solution in the case of incompatibility of input data) of a nonlinear operator equation (48).

Now we consider possible ways of the formalizing these model considerations to use them in the force-constant calculation. For example, model assumptions may be taken into account a priori by choice of a given matrix F^0 (see below). In the framework of the so-called valence force field some off-diagonal elements of the matrix F may be taken to be equal to zero, reflecting the assumption of insignificance of some intramolecular interactions. For related molecules we can introduce some in-pair equalities of force constants for similar fragments, some elements of F may be known from preliminary calculations, etc.. Therefore, we can formulate the inverse vibrational problem in the following way.

We need to find, among the set of force constant matrices satisfying (48), the matrix which will be the nearest to some a priori given matrix F^0 (i.e., to find the so-called normal solution). In the case of an inconsistent problem (within harmonic approximation, this may happen in the joint treatment of the spectra of isotopomers, or including additional experimental data) it is possible to find the matrix F for which the distance from AF to Λ is minimal, i.e., to find the so-called pseudosolution of the problem. When the pseudosolution is also nonunique, we must proceed as in the case of nonuniqueness of the solution - i.e., we choose from all possible pseudosolutions the one which is nearest to the given force field F^0 (the normal pseudosolution).

We now arrive at the following formulation of the inverse problem taking into account the principle formulated above for choosing the solution. Suppose, we are given (48) and the operator A which maps the symmetric, and positive definite matrix F to the set of molecular vibrational frequencies squared (possibly including data for isotopomers of the molecule), and of the mean vibrational amplitudes, Coriolis constants etc., which may be taken from experiments. The dimension of the vector Λ is determined by the number of experimental data. Since the symmetric matrix F is determined by $n(n+1)/2$ elements we can consider the unknown force constants as a vector of dimension $n(n+1)/2$. Then the operator A acts from the Euclidean space $R^{n(n+1)/2}$ into the Euclidean space R^l. In these spaces we can introduce the following norms:

$$\|F\| = \left(\sum_{ij}^{n} f_{ij}^{2}) \right)^{1/2} , \qquad \|\Lambda\| = \left(\sum_{k=1}^{l} \lambda_k^2 \rho_k \right)^{1/2} ,$$

where $\rho_k > 0$ are the positive weights, f_{ij} are the elements of matrix F, λ_k $(k= 1,...l)$ are the components of Λ.

The operator A is continuous for all problems considered. However, (48) may have nonunique solutions, or no solution at all, due to the anharmonicity of vibrational frequencies.

Suppose, we are given the matrix F^0 (vector of dimension $n(n+1)/2$). It is necessary to find the normal pseudosolution of (48):

that is, we find an element $F = \bar{F}_n$ for which $\min \|F - F^0\|$ is reached provided that $\|AF - \Lambda\| = \mu$, where $\mu = \inf\limits_{F \in D} \|AF - \Lambda\|$ and D is the closed set of a priori constraints on the values of the force constants. If no constraints are imposed, then $D = R^{n(n+1)/2}$.

The element F^0 should be specified from a priori considerations of the possible solutions, including both the approximate quantum mechanical calculations and other ideas (for example, the transferability of the force constants among similar fragments in a series of related compounds).

The desired solution is a matrix $F^{\alpha} \in Z$ that reproduces experimental data within given error level and is the nearest in the Euclidean metrics to some given matrix F^0. All necessary model assumptions (explicit and implicit) concerning the form of force field may be taken into account by the choice of some given *a priori* matrix of force constants F^0 and a pre-assigned set D of *a priori* constraints on values of the force constants. This set defines a form of matrix F in the framework of the desired force field model (i.e., with specified zero elements, equality of some force constants, etc.). If no *a priori* data constrains the form of solution, then D coincides with the set Z.

Let us denote the solution (vector) to be found as $\bar{F}_n$, if this vector is nonunique then a set of such vectors will be denoted as $\{ \bar{F}_n \}$. It is easy to see that if (48) is solvable then $\mu = 0$, and it remains to find the solution of (48) which is the nearest to the given vector F^0. But we do not know the exact form of either the vector Λ or operator A (the matrix G or matrices G_i). We only have the vector Λ_δ, determined from experimental data such that $\|\Lambda_\delta - \Lambda\| \le \delta$ (where $\delta > 0$ is the experimental error) and the operator A_h approximates the operator A, $h \ge 0$ is a parameter characterizing the proximity of A_h to A. The uncertainty in operator A is related to errors of determination of the matrix G (or G_i) calculated using experimental data on the geometrical parameters of the equilibrium configuration quoted with errors. Therefore, the problem of the solution of (48) arises when we do not know exact forms of A and Λ, but only their approximations A_h, Λ_δ, and their errors (h, δ) and it is necessary to find the vector $F_{h,\delta}$ approximating the exact solution $\bar{F}_n$. The difficulties in solving this problem are related to its ill-posed character.

The modern theory of solving ill-posed problems was founded by A.N.Tikhonov and developed by many. When one designs stable methods for solving ill-posed problems there should be the understanding that ill-posed problems are generally underdetermined. To solve such problems one has to use additional information and formulate the criteria for choosing approximate solutions. If such criteria are formulated and mathematically formalized, it is possible to construct stable methods of solving ill-posed problems - so-called *regularizing algorithms*. We shall attempt to explain what the construction of a regularizing algorithm means, beginning with the example of solving a system of linear algebraic equations.

6. WHAT IS THE REGULARIZING ALGORITHM?

We have found that the inverse vibrational problem is ill-posed, and have formulated a criterion for choosing the solution from among the set of possibilities - the normal pseudosolution (in the general case). Now the problem arises of constructing a stable numerical method (regularizing algorithm) for the given problem.

For clearer analysis of the difficulties which arise while solving nonlinear problems such as (48) , we start with the simpler problem of solving a system of two linear algebraic equations. Using this problem we shall find out what the words "to find the normal solution (pseudosolution)" mean.

Let us consider the system

$$\begin{cases} x + y = 1 \\ x + y = 1. \end{cases}$$

The normal solution for this system is the nearest one to the center of coordinates. It is easy to find that the normal solution is (1/2 , 1/2).

This system may be written in standard form

$$Az = u \tag{51}$$

where *u* is a given vector, *z* is the vector sought and A is the matrix

$$A = \{a_{ij}\},\ i = 1,...,m,\ j = 1,...,n.$$

That is, for system (51)

$$A = \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}, z = \begin{pmatrix} \mathrm{x} \\ \mathrm{y} \end{pmatrix}, u = \begin{pmatrix} 1 \\ 1 \end{pmatrix}, n = m = 2.$$

The problem of searching for the normal solution is formulated as the problem of minimizing ||*z*|| on the set of solutions

$$\{ z:\ Az = u \}.$$

In 1801-1806 Gauss and Legendre independently proposed the least-squares method for solving systems of linear equations. Instead of solving (51) it is possible to find the minimum of the function $\Phi(z) = \| A z - u \|^2$. Such a problem is always solvable. If $\min \Phi(z) = \mu = 0$ then the vector z on which the minimum is reached is obviously the solution of (51), and, conversely, any solution of (51) is the minimum of $\Phi(z)$ with $\mu = 0$. To find the minimum of $\Phi(z)$ it is necessary to calculate the derivatives of $\Phi(z)$ with respect to the components of z, and to equate them to zero. This yields the system of so-called *normal equations*:

$$A^* Az = A^* u \qquad (52)$$

where A^* is the adjoint of the matrix A. This system has a solution for any u.

For system (51)

$$A^* = A = \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix},\ A^* A = \begin{pmatrix} 2 & 2 \\ 2 & 2 \end{pmatrix},\ A^* u = \begin{pmatrix} 2 \\ 2 \end{pmatrix}$$

and we obtain the system

$$\begin{cases} 2x + 2y = 2 \\ 2x + 2y = 2, \end{cases}$$

which is equivalent to system (51).

The normal solution of the system (51) may be found using the method of pseudoinversion of Moore-Penrose, where the pseudoinverse matrix A is determined as

$$A^+ = \lim_{\alpha \to 0+} (A^* A + \alpha E)^{-1} A^*.$$

Let us calculate the value of this limit for system (51). First we find that

$$\det (A^* A + \alpha E) = \alpha (4 + \alpha).$$

Next,

$$\begin{pmatrix} 2+\alpha & 2 \\ 2 & 2+\alpha \end{pmatrix}^{-1} \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} = \begin{pmatrix} 1/(4+\alpha) & 1/(4+\alpha) \\ 1/(4+\alpha) & 1/(4+\alpha) \end{pmatrix}$$

and hence

$$A^{+} = \lim_{\alpha\to 0+0}\begin{pmatrix} 1/(4+\alpha) & 1/(4+\alpha) \\ 1/(4+\alpha) & 1/(4+\alpha) \end{pmatrix} = \begin{pmatrix} 1/4 & 1/4 \\ 1/4 & 1/4 \end{pmatrix}.$$

The normal solution of the system (51) is

$$\bar{z} = A^{+}u = A^{+}\begin{pmatrix} 1 \\ 1 \end{pmatrix} = \begin{pmatrix} 1/2 \\ 1/2 \end{pmatrix}.$$

So, in solving the system of linear equations with the exactly given matrix A it is possible to use the pseudoinversion method to obtain the normal solution.

Note that $\Phi(z)$ has only global minimum. The case is possible when $\mu > 0$ and system (51) has no solutions. Then it is necessary to formulate the problem of searching for the solution in terms of the least-squares method. The problem of finding the pseudosolution uses the vector $\bar{z}$, on which the minimum of $\Phi(z)$ is reached:

$$\bar{z} = \operatorname{argmin}\| Az - u\|^{2} \to A^{*}A\bar{z} = A^{*}u\,.$$

If this equation has a nonunique solution then the problem is formulated as the problem of finding the normal pseudosolution, i.e. the pseudosolution nearest to the origin of the coordinate system. The problem of finding the normal pseudosolution may be written as to find $\min\| z \|$, while $\| Az - u \| = \mu = \min\| Az - u \|$, or (equivalently) $A^{*}Az = A^{*}u$. This problem may be solved (if we know the matrix A exactly) by the pseudoinversion method yielding $z = A^{+}u$. Note that, if $\det(A^{*}A) \neq 0$ then $A^{+}=(A^{*}A)^{-1}A^{*}$. If system (51) has a unique solution then this solution is the normal pseudosolution, and the pseudoinverse matrix coincides with the inverse $A^{+}=A^{-1}$.

Let us consider the system (51) with the same matrix A and the right hand side

$$u = \begin{pmatrix} 1/2 \\ 3/2 \end{pmatrix}.$$

This system has no solutions but it is easy to see that the normal equations (52) for the system are the same as we considered above. So the normal pseudosolution of this system is

$$z = \begin{pmatrix} 1/2 \\ 1/2 \end{pmatrix}.$$

and may be found as above.

Were these the only difficulties, our problems would be solved and for construction of the normal pseudosolution of system (51) it would be sufficient to use the pseudoinversion method. If the system has a solution then the normal solution would be reached, if the solution were unique then this is the solution that would be found. However, the pseudoinversion has very unpleasant properties which were discovered soon after the method was proposed.

It was found that the pseudoinversion method is unstable with regard to errors in matrix A. What would happen if the coefficients of x and y (i.e., the matrix A) were not known exactly, but only with some errors? This means that instead of the exact matrix A the matrix A_h with elements $\{a_{ij}+h_{ij}\}$ is known, h_{ij} being the errors in the entries of the matrix A_h. Consider system (51). Suppose, for example,

$$A_h = \begin{pmatrix} 1 & 1 \\ 1 & 1+\varepsilon \end{pmatrix}, \quad h_{22} = \varepsilon \neq 0.$$

Then A_h is a non-singular matrix and the corresponding system of equations is

$$\begin{cases} x + y = 1 \\ x + (1+\varepsilon)y = 1. \end{cases} \tag{53}$$

For $\varepsilon \neq 0$ the unique solution of (53) is

$$z_h = \begin{pmatrix} 1 \\ 0 \end{pmatrix}.$$

For this square nonsingular matrix $A_h^+ = A_h^{-1}$, so the pseudoinversion method gives the same solution, and this solution does not tend to the normal solution of the exact system

$$\begin{pmatrix} 1/2 \\ 1/2 \end{pmatrix}$$

when h tends to zero. It is clear that the negligible deviation in one of the system coefficients of (51) has led to a completely different normal solution. Thus, the problem of finding the normal solution (or pseudosolution) of the perturbed system is unstable with regard to errors in the matrix A, and such errors naturally occur if the matrix A is obtained from experiments or is calculated on a computer.

This is an example of an ill-posed problem. The problem of constructing a stable algorithm for finding the normal solution of the perturbed system (53) arises, such an algorithm must guarantee the convergence of the solutions obtained to the exact normal solution of the unperturbed system (51) when errors tend to zero. Algorithms of this type can be constructed by means of the Tikhonov regularization method. Let us write the problem in the following form:

$$A_h z = u_\delta, \tag{54}$$

$$\|A - A_h\| \le h, \ \|u - u_\delta\| \le \delta,$$

where A and u are the exact matrix and vector of the right-hand part, and $h \ge 0$, $\delta > 0$ are the errors. To simplify notation, designate $\eta = (h, \delta)$. We wish to construct a stable method for solving system (54) using approximate data A_h, u_δ and η, that is, we wish to find an approximate solution z_η, such that $z_\eta \to \bar{z}_n$ when $\eta \to 0$, where $\bar{z}_n$ is the exact normal solution (pseudosolution) of system (51). Such stable method is called a regularizing algorithm. In general one can determine the regularizing algorithm in the following way: $R(A_h, u_\delta, h, \delta)$ is the regularizing algorithm (or regularizing operator) for solving (51) if R is defined for any vector u_δ, matrix A_h, nonnegative numbers δ, h, and

$$z_\eta = R(A_h, u_\delta, h, \delta) \underset{\eta \to o}{\to} \bar{z}_n. \tag{55}$$

where $(A_h, u_\delta, h, \delta)$ represents the minimal necessary information for the construction of the regularizing algorithm. For finite dimensional problems it is possible to neglect the error δ, but construction of regularizing algorithms without knowledge of h is impossible. If some additional information about the solution is known it is useful to include it in the formulation of the problem, and this will generate another regularizing algorithm, or even the problem could become well-posed (in this case it could be solved without knowledge of errors δ, h). For example, if from *a priori* considerations the rank of the matrix A or A^+ (that is, the number of non-zero eigenvalues of the matrix A^+ or, equivalently, the singular values of the matrix A) is known, this knowledge may be used for the construction of the regularizing algorithm. In practice the rank of A is usually unknown.

We shall proceed in the following way. First we give the description of the whole set of approximate solutions of (54) and then formulate the criteria for selecting the definite approximate solution from this set. Consider first the case when $h = 0$ (this means that the matrix A is given exactly) and $\mu = 0$ (which means that the system is consistent). Then the set of approximate solutions of (54) can be determined as a set of vectors for which the inequality $\|A_h z - u_\delta\| \le \delta$ is satisfied. Let us designate this set as Z_η. (Obviously $\bar{z}_n \in Z_\eta$, where $\bar{z}_n$ is the exact normal solution of (54)). If we choose from this set a vector z_δ, deviating minimally from zero, it can be proved that $z_\delta \to \bar{z}_n$ when $\delta \to 0$. In the general case for $h \ge 0$ and $\mu \ge 0$, the determination of the set of approximate solutions is somewhat more complicated: $z \in Z_\eta$ if z is compatible with the inequality

$$\| A_h z - u_\delta \| \le \delta + h\| z \| + \tilde{\mu}_\eta, \qquad (56)$$

where $\tilde{\mu}_\eta$ is an upper estimate for μ, such that $\tilde{\mu}_\eta \ge \mu$, $\tilde{\mu}_\eta \to \mu$ when $\eta \to 0$. $\tilde{\mu}_\eta$ may be calculated, for example, in the following way :

$$\tilde{\mu}_\eta = \min\left(\delta + h\| z \| + \| A_h z - u_\delta \|\right).$$

Now a new problem emerges: find $z_\eta \in Z_\eta$ such that

$$z_\eta = \operatorname{argmin} \| z \|, \quad z \in Z_\eta \qquad (57)$$

that is, choose a vector which is nearest to zero and satisfies the inequality (56). Such a vector exists and is unique. The choice of the vector z_η in this way is called the generalized discrepancy method. It may be proved that $z_\eta \to \bar{z}_n$ when $\eta \to 0$.

Consider another way of stable constructing the normal pseudosolution of (54). The following function is the so-called Tikhonov's functional:

$$M^\alpha[z] = \| A_h z - u_\delta \|^2 + \alpha \| z \|^2 \qquad (58)$$

($\alpha > 0$ is the regularization parameter). The first part of $M^\alpha[z]$ is the *discrepancy* which shows how well the vector satisfies the equation $A_h\, z = u_\delta$. The second part estimates the deviation of solution from zero (the so-called “stabilizer” of Tikhonov's functional). Let us consider the extreme problem of finding min $M^{\alpha}[z]$. The solution of this problem exists for any α>0 and is unique. We shall denote it as z_{η}^{α}.

To find the extremum z_{η}^{α} known methods for the minimization of the quadratic functionals in finite-dimensional spaces may be used, for example, the method of conjugate gradients. Or we can calculate the gradient of $M^{\alpha}[z]$:

$$\left(M^{\alpha}[z]\right)' = 2\left(A_h^* A_h z + \alpha z - A_h^* u_\delta\right) \tag{59}$$

and get an equation for the extreme z_{η}^{α} as a stationary point of the functional $M^{\alpha}[z]$:

$$\left(M^{\alpha}[z]\right)' = 0,$$

or, equivalently,

$$\left(A_h^* A_h + \alpha E\right) z = A_h^* u_\delta . \tag{60}$$

The solution of this equation is

$$z_{\eta}^{\alpha} = \left(A_h^* A_h + \alpha E\right)^{-1} A_h^* u_\delta .$$

This is similar to the pseudoinversion method but α is not decreased to zero in an arbitrary manner, its value must be connected with h and δ. Taking into account the specific character of the matrix $\left(A^* A + \alpha E\right)$ (it is symmetric and positive definite) effective numerical methods may be used to invert it. It is necessary to make value of the parameter α dependent on the errors in a way that such that $z_{\eta}^{\alpha} \to \bar{z}_n$ when $\eta \to 0$. This may be done in various ways, we shall consider only one of them. For the extremals of functional (58) we shall define the function

$$\rho_{\eta}(\alpha) = \left\| A_h z_{\eta}^{\alpha} - u_\delta \right\| - \tilde{\mu}_{\eta} - (\delta + h\|z\|). \tag{61}$$

This function is called the generalized. Let

$$\|u_\delta\| > \tilde{\mu}_{\eta} + \delta. \tag{62}$$

In the opposite case, z_{η}, which is the approximate normal pseudosolution of (51), must naturally be put equal to zero.

It turns out that $\rho_\eta(\alpha)$ is continuous when $\alpha > 0$, increases monotonically, and its values fill the interval $\left(-\delta, \| u_\delta \| - \delta - \tilde{\mu}_\eta\right)$. Therefore the equation

$$\rho_\eta(\alpha) = 0 \tag{63}$$

has a unique root. Let us call this root $\alpha(\eta)$. Well-known methods for solving such transcendental equations with monotone continuous functions of one variable may be used to find this root, (for example, the method of bisection, the method of the golden section or other methods).

It can be proved that $z_\eta^{\alpha(\eta)} \to \bar{z}_n$ when $\eta \to 0$, so that the constructed algorithm is a regularizing in the sense of Tikhonov. Such a strategy for choosing the parameter of regularization is called the *generalized discrepancy principle*. If we recall the generalized discrepancy method (57), it turns out that the solution of the problem (57), i.e., z_η, is equal to $z_\eta^{\alpha(\eta)}$, which is the extreme of Tikhonov's functional with the value of parameter α chosen by means of the generalized discrepancy principle. That is, the generalized discrepancy method and the generalized discrepancy principle are equivalent.

7. NONLINEAR ILL-POSED PROBLEMS

In this section we consider nonlinear ill-posed problems in the finite-dimensional (for simplicity) case. We begin with the following example the main problem for us is an operator equation

$$Az = u, \; z \in D \subseteq Z, \; u \in U, \tag{64}$$

where D is a set of constraints, Z and U are metric spaces. Let $D = Z = U = R$, where R is the space of real numbers with the norm $\| z \| = | z |$. Fix positive numbers α_0, z_0, u_0 and define the continuous nonlinear operator A: $Z \to U$:

$$Az = \begin{cases} \left[a_0\left(z_0^2 - z^2 + z(z_0 - z)\right)\right]^{1/2} + u_0, & \text{if} \quad 0 \le z \le z_0; \\ \left[a_0\left(z_0^2 - z^2\right)\right]^{1/2} + u_0, & \text{if} \quad z > z_0; \\ a_0^{1/2} z_0 + z^2 + u_0, & \text{if} \quad z < z_0. \end{cases} \tag{65}$$

Consider (64) with the data (A, u). It has the unique solution $\bar{z} = z_0$. We introduce Tikhonov's functional

$$M^{a}[z] = \| Az - u\|^2 + a\| z\|^2, \; z \in D \subseteq Z, \; a > 0, \tag{66}$$

and consider the variational problem: for fixed $\alpha>0$, find an element $z^{\alpha} \in D$ such that

$$M^{\alpha}\left[z^{\alpha}\right] = \inf\left\{M^{\alpha}[z]: \, z \in D\right\}. \tag{67}$$

Then problem (67) with data (A, u_0) from (65)has the solution

$$z^{\alpha} = \{z_0 \text{ for } 0 < \alpha < \alpha_0, \, [0, z_0] \text{ for } \alpha = \alpha_0, \; 0 \text{ for } \alpha > \alpha_0\}.$$

Hence, the discrepancy

$$\beta(\alpha) = \left\|Az^{\alpha} - u_0\right\| = \begin{cases} 0 & \text{for } 0 < \alpha < \alpha_0; \\ u_0 & \text{for } \alpha > \alpha_0. \end{cases}$$

and the equation

$$\beta(\alpha) = \delta \tag{68}$$

for choosing the regularization parameter α by the discrepancy principle has no solution in the ordinary sense for any δ, satisfying $0 < \delta < u_0$.

This example shows that the discrepancy principle generally gives no possibility of choosing the value of the regularization parameter for nonlinear problems. Similar difficulties arise in other strategies involving an a posteriori choice of the regularization parameter. These difficulties are connected with the nonuniqueness of the solution of (67) for the nonlinear case. This nonuniqueness leads to another difficulty. Let us assume that the regularization parameter $\alpha(\delta) > 0$ is chosen and problem (67) has more than one minimizer for $\alpha = \alpha(\delta)$. The question is whether it is possible to take an arbitrary element $z^{\alpha(\delta)}$ as an approximate solution or if a special choice of such an element is needed. Our example shows that if we choose $\alpha(\delta)$ as a solution of (68) in general sense, i.e., as a "jump" point of a monotone function $\beta(\alpha)$ over δ, then the "unsuccessful" choice of $z^{\alpha(\delta)}: \; z^{\alpha(\delta)} = 0,$ from the set of the extremals corresponding to this $\alpha(\delta)$ can result in the approximate solutions $z^{\alpha(\delta)}$ not converging to the exact solution $\bar{z} = z_0$. Thus, the algorithm for Tikhonov's regularization method of solving nonlinear problem (64) should in general contain along with the rule for choosing the parameter $\alpha(\delta)$ also a rule for selecting $z^{\alpha(\delta)}$ from the set of solutions of (67) for $\alpha = \alpha(\delta)$.

Let us give the general formulation of Tikhonov's scheme of constructing a regularizing algorithm for solving the main problem: for the operator (64) on *D* find $z^* \in D$ for which

$$\rho\left(Az^*,u\right) = \inf\left\{\rho\left(Az,u\right):\ z \in D\right\} \equiv \mu \qquad (69)$$

(ρ is the distance in the metric space *U*). We call such a z^* a *quasisolution* for problem (64). In the case *D* = *Z* problem (69) gives a pseudosolution of (64). If the measure of incompatibility is equal to zero, then the solutions of (69) are the solutions of (64) on the set *D*. The quasisolution problem (69) may be ill-posed. Namely, problem (69) may not be solvable, and if a solution of (69) exists, it may be nonunique or unstable (with respect to perturbations of the data (*A, u*)) in the metric of *Z*.

We assume that to some element $u = \bar{u}$ there corresponds a nonempty set $Z^* \subseteq D$ of quasisolutions and that Z^* may consist of more than one element. Furthermore, we suppose that a functional $\Omega(z)$ is defined on *D* and bounded below:

$$\Omega(z) \ge \Omega^* \equiv \inf\left\{\Omega(z):\ z \in D\right\} \ge 0.$$

The Ω-optimal quasisolution problem for (64) is as follows: find $\bar{z} \in Z^*$ such that

$$\Omega(\bar{z}) = \inf\left\{\Omega(z)\ : z \in Z^*\right\} \equiv \bar{\Omega}. \qquad (70)$$

We denote the set of Ω-optimal quasisolutions of (64) by $\bar{Z}$. If *D* = *Z*, then $\bar{Z}$ is the set of the Ω-optimal pseudosolutions of (64). For simplicity we use only the term "pseudosolution" below.

We suppose that, instead of the unknown exact data $\left(A, \bar{u}\right)$, we are given approximate data $\left(A_h, u_\delta\right)$ which satisfy the following conditions:

$$u_\delta \in U,\ \rho\left(\bar{u}, u_\delta\right) \le \delta,\ A_h \in \mathbf{A}, \rho\left(Az, A_h z\right) \le \psi\left(h, \Omega(z)\right) \quad \forall z \in D.$$

Here the function ψ represents the known measure of approximation of the precise operator *A* by the approximate operator A_h, and $A_h \in \mathbf{A}$, a class of admissible operators. We are given also numerical characterizations h, $\delta \geq 0$ of the "closeness" of (A_h, u_δ) to (A, u). The main problem is to construct from the approximate data (A_h, u_δ ,h δ) in (64) an element $z_\eta = z_\eta\left(A_h, u_\delta, h, \delta\right) \in D$ which converges to a member of the set $\bar{Z}$ of Ω-optimal solutions as $\eta = \left(h, \delta\right) \to 0$.

Let us formulate our basic assumptions:

1) The class A consists of the operators A continuous from D to U.

2) The functional $\Omega(z)$ is lower semicontinuous (for example, continuous) on D:

$$\forall z_0 \in D,\ \forall\left\{z_n\right\} \in D:\ z_n \to z_0 \Rightarrow \lim_{n\to\infty} \inf \Omega(z_n) \geq \Omega(z_0).$$

3) If K is an arbitrary number such that $K \geq \Omega^*$, then the set

$$\Omega_K = \left\{\ z \in D\!:\ \Omega(z) \leq K\ \right\}$$

is compact in Z.

4) The measure of approximation $\psi(h,\Omega)$ is assumed to be defined for $h \geq 0,\ \Omega \geq \Omega^*$, to depend continuously on all its arguments, to be monotonically increasing with respect to Ω for any $h > 0$, and to satisfy the equality $\psi(0,\Omega) = 0,\ \ \forall\, \Omega \geq \Omega^*$.

Conditions 1) - 3) guarantee that $\bar{Z}$ is nonempty. Tikhonov's scheme for constructing of a regularizing algorithm is based on using the smoothing functional

$$M^\alpha[z] = f\left[\rho\left(A_h z, u_\delta\right)\right] + \alpha\Omega(z),\quad z \in D,\ \ \alpha > 0 \tag{71}$$

in the conditional extreme problem (67). Here $f(x)$ is an auxiliary function. A common choice is $f(x) = x^m, m \geq 2$.

We denote the set of extremals of (67) which correspond to a given $\alpha > 0$ by Z^α. Again, conditions 1) - 3) imply that Z^α is nonempty. The scheme of constructing an approximation to the set $\bar{Z}$ includes: (*i*) the choice of the regularization parameter $\alpha_\eta = \alpha_\eta\left(A_h, u_\delta, h, \delta\right)$, (*ii*) the specification of the set Z^{α_η} corresponding to α_η, and a special selection of an element z^{α_η} in this set. We take the element z^{α_η} chosen in this way as a solution of the main problem.

Procedures (*i*), (*ii*) must be accomplished so as to guarantee the convergence $z^{\alpha\eta} \to \bar{Z}$ as $\eta \to 0$. Thus, Tikhonov regularizing algorithms differ from each other by the method of choosing α_η and by the method of selecting $z^{\alpha\eta}$. Sometimes the latter procedure is not necessary, and one can take an arbitrary element $z^{\alpha\eta}$ from $Z^{\alpha\eta}$ as an approximate solution. In this case we say that the corresponding Tikhonov algorithm is *simple*.

It is in this way that the generalized analogs of a posteriori parameter choice strategies are used. For their formulations we define some auxiliary functions and functionals for $\alpha > 0$, and $z^\alpha \in Z^\alpha$:

$$
\begin{aligned}
&\gamma(\alpha) = \Omega(z^\alpha),\ \beta(\alpha) = \mathrm{f}\left[\rho\left(A_h z^\alpha\ ,\ u_\delta\right)\right] \equiv I\left(z^\alpha\right),\\
&\varphi(\alpha) = M^\alpha\left[z^\alpha\right], \pi(\alpha) = \mathrm{f}\left[\psi\left(h,\gamma(\alpha)\right) + \delta + \mu_\eta\right] \equiv \Pi\left(z^\alpha\right),\\
&\rho(\alpha) = \beta(\alpha) - \pi(\alpha) \equiv \mathrm{P}\left(z^\alpha\right), \qquad (72)\\
&\varepsilon(\alpha) = \varphi(\alpha) - f\left\{\mu_\eta + \left[\psi\left(h,\gamma(\alpha)\right) + \delta\right]^p\right\} \equiv E\left(z^\alpha\right),\\
&p = \mathrm{const}, 0 < p < 1.
\end{aligned}
$$

Here $\mu_\eta = \inf\left\{\rho\left(A_h z,\ u_\delta\right) + \psi\left(h,\Omega(z)\right) + \delta : z \in D\right\}$ is a generalized measure of incompatibility for nonlinear problems having the properties: $\mu_\eta > \mu,\ \mu_\eta \to \mu$ as $\eta \to 0$. All the functions (72) (except φ) are generally many-valued. They have the following properties.

Lemma . If the functions $\gamma, \beta, \pi, \rho, \varepsilon$ are single-valued and continuous everywhere for $\alpha > 0$ except perhaps for a countable set of their common points of discontinuity of the first kind, which are points of multiple-valuedness, then there exists at least two elements z_+^α and z_-^α in the set Z^α such that

$$
\gamma\left(\alpha \pm 0\right) = \Omega\left(z_\pm^\alpha\right),\ \ \rho\left(\alpha \pm 0\right) = \Pi\left(z_\pm^\alpha\right),\ \ \varepsilon\left(\alpha \pm 0\right) = \mathrm{E}\left(z_\pm^\alpha\right)
$$

The functions β,ρ,ε are monotonically nondecreasing and γ,π are nonincreasing. The function φ is single-valued, continuous, and nondecreasing.

The generalized discrepancy principle (GDP) for nonlinear problems consists of the following steps.

(*i*) The choice of the regularization parameter as a generalized solution $\alpha > 0$ of the equation

$$\rho(\alpha) = 0 \tag{73}$$

Here and afterwards we say that α is the generalized solution of (73) for a monotone function ρ if α is the ordinary solution or if is the "jump"-point of this function over 0.

(*ii*) An approximate solution z^{α_η} from the set Z^{α_η} is selected by means of the following rule: let q >1 and C>1 be fixed constants, $\alpha_{1} = {}^{\alpha_\eta}\!/_{q}$ and $\alpha_2 = \alpha_\eta \cdot q$ are auxiliary regularization parameters, and let z^{α_1} and z^{α_2} be extremals of (67) for $\alpha = \alpha_{1,2}$. If the inequality

$$I\left(z^{\alpha_2}\right) \ge C\Pi\left(z^{\alpha_1}\right) - (C-1)\, f\left(\mu_\eta\right) \tag{74}$$

holds for z^{α_1} and z^{α_2}, then any elements $z^{\alpha_1} \in Z^{\alpha_\eta}$, subject to the condition $\mathrm{P}\left(z^{\alpha_\eta}\right) \le 0$ can be taken as the approximate solution. For instance we can take $z^{\alpha_\eta} = z_{-}^{\alpha_\eta}$.

But if

$$\mathrm{I}\left(z^{\alpha_2}\right) < C\Pi\left(z^{\alpha_1}\right) - (C-1)\, f\left(\mu_\eta\right) \tag{75}$$

then we choose z^{α_η} so as to have $\mathrm{P}\left(z^{\alpha_\eta}\right) \ge 0$, for example, $z^{\alpha_\eta} = z_{+}^{\alpha_\eta}$.

Note that we do not need any selection rule if α_η is an ordinary solution of (73). In this case the equality $\mathrm{P}\left(z^{\alpha_\eta}\right) = \rho\left(\alpha_\eta\right) = 0$ holds, and an arbitrary element $z^{\alpha_\eta} \in Z^{\alpha_\eta}$ can be taken as an approximate solution.

Theorem

Suppose that for any quasisolution $z^{*} \in D$ of (64) the inequality

$$\Omega\left(z^{*}\right) > \Omega^{*} = \inf\left\{\Omega(z) : \;\; z \in D\right\}$$

holds. Then (*a*) (73) has a positive generalized solution, (*b*) for any sequence $\eta_n = \left(h_n, \delta_n\right)$ such that $\eta_n \to 0$ as $n \to \infty$, the corresponding sequence $\left\{z_n\right\}$ of approximate solutions, which is found by GDP has the following properties: $z_n \to \bar{Z}$, $\Omega\left(z^{n}\right) \to \overline{\Omega}$ as $n \to \infty$.

In many practical cases it is very convenient to take $\Omega(z) = \|z\|^r$ (r is a constant, r >1). If it is known in addition that (64) has a solution on D, then the value μ_η can be omitted. It can be shown that the GDP in linear and nonlinear cases has a number of optimal.

8. REGULARIZING ALGORITHMS FOR SOLVING THE INVERSE VIBRATIONAL PROBLEM

The inverse vibrational problem under investigation is nonlinear. Let us consider again (48) in the standard form

$$AF = \Lambda,\ F \in R^{n(n+1)/2},\ \Lambda \in R^l. \tag{76}$$

The existence of the normal (relative to a given a priori estimate F^0) pseudosolution $\overline{F}_n$ of the exact problem (76) may be guaranteed if the operator A includes the operator of the direct vibrational problem for a single molecule. The uniqueness of $\overline{F}_n$ cannot be guaranteed.

How may the error of the approximate operator A_h be estimated? The estimation $\|A - A_h\| \le h$ is impossible because the nonlinear operators have no norm. It is obvious that for the operator of the inverse vibrational problem this error is related to errors of the G matrix. It is possible to obtain an estimate in the form

$$\|AF - A_h F\| \le \psi(h,F),$$

where ψ is a known continuous function, which approaches 0 as the errors of the equilibrium geometry of the molecule decrease to zero. In particular, the estimates may be obtained in the form

$$\psi(h,F) = \psi(h,\|F\|);\ \psi(h,F) = h\|A_h F\|.$$

The error in the right part of (74) is determined as previously.

We arrive to the following formulation of the inverse problem.

Problem I. Suppose we are given (76) where $F \in D \subseteq Z, \Lambda \in U$, Z and U are finite-dimensional spaces, D is a closed set of a priori constraints of the problem, and A is a nonlinear operator continuous in D. It is required to find an approximate solution of (74) when instead of A and Λ, we are given their approximations A_h and Λ_δ such that

$\|\Lambda - \Lambda_\delta\| \le \delta, \|AF - A_h F\| \le \psi(h,F)$ for $F \in D$, here $\psi(h, F)$ is a known continuous function, which approaches zero as $h \to 0$ uniformly for all $F \in D \cap \bar{S}(0,R)$, where $\bar{S}(0,R)$ is a closed ball with center at $F = 0$ and an arbitrary radius R. The error in specifying the operator A involves an error in determining the equilibrium configuration of the molecule, the parameters of which can be found experimentally. Note that Problem I satisfies none of the conditions of correctness of the problem.

We shall consider now the problem of constructing a normal pseudosolution of Problem I with exact right side and operator.

Problem II. It is required to obtain

$$\bar{F}_n = \operatorname{argmin} \left\|F - F^0\right\|, \ F: \ F \in D, \ \|AF - \Lambda\| = \mu,$$

where $\mu = \inf\|AF - \Lambda\|, \ F \in D$.

The element $F^0 \in Z$ should be specified from a priori requirements on the solution, using both approximate quantum mechanical calculations and other ideas (for example, the transferability of the force constants to similar fragments of molecules).

In the case when a unique solution of (74) exists, it is clear that its normal pseudosolution is identical with the solution itself. Taking all the above mentioned into account we can formulate the following problem.

Problem III. Suppose we are given (74), it is required from the approximate data $\{A_h, \Lambda_\delta, h, \delta\}$ to obtain approximations $F_\eta \in D$ to the solution $\bar{F}_n$ of Problem II such that

$$F_\eta \xrightarrow[\eta \to 0]{} \bar{F}_n$$

i.e., the algorithm for finding F should be Tikhonov regularizing.

Now we shall consider the simplest formulation of Problem I.

Problem I'. The vibrational spectrum of a single molecule is known, and in (74) the operator A corresponds to the vector $F \in R^{n(n+1)/2}$ which is made up of the elements of the symmetric matrix F of order n, the ordered set of eigenvalues of the matrix GF. We shall use the ordered set of squares of the molecular vibrational frequencies as the right-hand side $\Lambda \in R^l$.

Problem II'. It is required to find the normal solution

$$\bar{F}_n = \text{argmin}\left\|F - F^0\right\|,\ F \in \left\{F : AF = \Lambda\right\},$$

since Problem I is always solvable, and, furthermore, solutions are nonunique (apart from the case when $n = 1$).

Since the operator A in (74) is completely defined by the specification of the matrix G, we shall estimate the deviation of the approximately specified operator A_h (corresponding to certain G_ξ) from the exact operator A (corresponding to G) by the error in specifying matrix G. We suppose that in a certain matrix norm $\left\|G - G_\xi\right\| \le \xi$.

In the space R^l of the right-hand sides we shall introduce the Euclidean norm with positive weights, while in $R^{n(n+1)/2}$ we use the Euclidean norm. Suppose that instead of the accurate value of the right-hand side Λ we specify Λ_δ, such that $\left\|\Lambda - \Lambda_\delta\right\| \le \delta$.

The following theorems on the stability of Problems I' and II' hold.

Theorem 1. Problem I' is stable in the Hausdorff metric with respect to the perturbations of the operator and the right-hand side.

Here the Hausdorf distance (metrics), $\rho(A,B)$, is determined in the following way: for any closed set A and B in normed space

$$\rho(A,B) = \sup_{x\in A}\inf_{y\in B}\left\|x-y\right\| + \sup_{y\in A}\inf_{x\in B}\left\|x-y\right\|.$$

Theorem 2. If Problem II' has a unique solution, then it is stable to perturbations of the operator and the right-hand side.

Most existing methods of solving inverse problems in vibrational spectroscopy are intended for (44) and (45), i.e., for the cases when only the frequencies of the vibrations of the molecules are used as experimental data. As regards the inverse vibrational problem for one molecule, i.e., solutions of (44), it follows from (50) that the choice of the unique solution from their set corresponds to the choice of a certain orthogonal matrix C. Such selection can be made from a priori considerations (for example, we can use as C the unit matrix or the matrix of eigenvectors of G). This approach suffers from the following drawbacks:

(*a*) it is impossible to take into account the a priori limitations imposed on the elements of the matrix F, (*b*) the results of the calculations are almost never transferable to isotopic varieties of the molecule.

The least-squares method which consists of minimizing $\|A_h F - \Lambda_\delta\|^2$ on a set of a priori constraints is the one most often encountered. However, in the view of the ill-posed nature of the problem, this method cannot be applied directly to solving problems with approximate data. Rather, the method must be regularized by taking into account the possible inconsistency of the problem and also the nonuniqueness of its solutions. If we attempt to find the normal pseudosolutions (with respect to a certain F^0) we arrive at the formulation of the problem described above.

What regularizing algorithms can be proposed for finding a normal pseudosolution? One of them (the generalized discrepancy principle) we described above. Many other approaches one can find in different publications. We have also proposed a modification of the generalized discrepancy principle based on the possibility of estimating the error of the operator in the form

$$\|AF - A_h F\| \le h\|A_h F\|, \; h < 1, \tag{77}$$

which corresponds to specification of the relative error *AF* and is a more convenient estimate for the problem considered than the monotone function ψ.

Suppose F_η^α is an extremum (possibly nonunique) of Tikhonov's functional

$$M^\alpha[F] = \|A_h F - \Lambda_\delta\|^2 + \alpha\|F - F^0\|^2 \tag{78}$$

in the set *D*. The existence of an extreme can be proved. We shall introduce the function

$$\rho_\eta(\alpha) = \|A_h F_\eta^\alpha - \Lambda_\delta\| - \frac{1}{1-h}\left[\hat{\mu}_\eta + k\left(\delta + h\|\Lambda_\delta\|\right)\right]$$

where *k* > 1 is a constant and

$$\hat{\mu}_\eta = \inf_{F \in D}\left\{\|A_h F - \Lambda_\delta\| + \delta + h\|A_h F\|\right\}$$

If the condition

$$\|A_h F^0 - \Lambda_\delta\| > \frac{1}{1-h}\left[\hat{\mu}_\eta + k\left(\delta + h\|\Lambda_\delta\|\right)\right] \tag{79}$$

is satisfied, then the equation $\rho_\eta(\alpha)=0$ has a generalized solution $\alpha_\eta>0$ (i.e., α_η is such that $\rho_\eta(\alpha)>0$ when $\alpha>\alpha_\eta$; $\rho_\eta(\alpha)<0$ when $\alpha<\alpha_\eta$). If α_η is a point of continuity of $\rho_\eta(\alpha)$, we have $\rho_\eta\left(\alpha_\eta\right)=0$. This assertion follows from the monotonicity of $\rho_\eta(\alpha)$ and the limit relations (as $\alpha\to 0$ and $\alpha\to+\infty$).

We shall formulate the algorithm for finding approximations to the normal pseudosolutions of (76). If condition (79) is not satisfied, we take $F_\eta=F^0$ as an approximate solution, in the contrary case we find $\alpha_\eta>0$ (the generalized solution of the equation $\rho_\eta(\alpha)=0$), and assume $F_\eta=F^{\alpha_\eta}$. If the extreme of the functional (78) is non-unique, we choose the one for which

$$\left\|A_h F^{\alpha\eta}-\Lambda_\delta\right\|\le\frac{1}{1-h}\left[\hat{\mu}_\eta+k\left(\delta+h\|\Lambda_\delta\|\right)\right].$$

Theorem 3. The algorithm formulated above is Tikhonov regularizing.

For versions of Problem I in which the estimate of the error of the operator cannot be written in the form (77), but the requirements of Problem I are satisfied we can use the following version of the generalized discrepancy method.

Problem IV. It is required to obtain

$$\inf\left\|F-F^0\right\|,$$
$$F\in\boldsymbol{F}_\eta=\left\{F: F\in D,\ \left\|A_hF-\Lambda_\delta\right\|\le\delta+\psi(h,F)+\hat{\mu}\left(A_h,\Lambda_\delta\right)\right\}$$

where the estimate of the measure of incompatibility of the exact problem from above is

$$\hat{\mu}_\eta=\inf_{F\in D}\left\{\left\|A_hF-\Lambda_\delta\right\|+\psi(h,F)+\delta\right\}.$$

Lemma 1. Suppose the conditions of Problem I are satisfied.
Then $\hat{\mu}_\eta\ge\mu$, and $\hat{\mu}_\eta\to\mu=\inf\limits_{F\in D}\|AF-\Lambda\|$ as $\eta\to 0$.

Lemma 2. Problem IV is solvable for any $\Lambda_\delta\in U$ such that $\left\|\Lambda-\Lambda_\delta\right\|\le\delta$ and for a continuous operator A such that $\left\|A_hF-AF\right\|<\psi(h,F)$.

The proof of this lemma relies on the fact that for all $\eta > 0$, the set $\boldsymbol{F}_\eta$ is nonempty (since $\overline{F}_n \in \boldsymbol{F}_\eta$), closed and bounded.

Theorem 4. The algorithm defined by the extremal Problem IV, is Tikhonov regularizing for Problem I.

9. CONSTRAINTS ON THE VALUES OF FORCE CONSTANTS BASED ON QUANTUM MECHANICAL CALCULATIONS.

In the Tikhonov's regularizing procedure, one can increase the stability and accuracy of the calculated solution F^α by using

a) an extended set of experimental data (including, e.g., Coriolis constants, mean square amplitudes, frequencies of isotopomers or related compounds, etc.),

b) an improved choice of the stabilizer matrix F^0,

c) an improved choice of the constraint set D.

As a particularly effective choice of stabilizer, we have proposed to use an *ab initio* quantum mechanical F^0 matrix in the regularizing procedure. This leads to the concept of regularized quantum mechanical force field (RQM FF), defined as the force constant matrix that is nearest to a corresponding quantum mechanical matrix F^0 and reproduces experimental frequencies within given error level.

The correct choice of constraint set D is also extremely important. Physically stipulated limitations may either decrease the range of acceptable matrices F, or provide criteria for selecting a concrete solution from a set of tolerable ones. An incorrect choice of constraints may lead to increasing incompatibility of the inverse problem, eventually resulting in a pseudosolution having no physical meaning. A set of a priori constraints may arise from several types of limitations on force constant values, e.g. :

1. some force constants may be stipulated on a priori grounds to be a zero,

2. some force constants may be stipulated to satisfy inequalities $a_{ij} \leq f_{ij} \leq b_{ij}$, where a_{ij}, b_{ij} are certain known values,

3. some force constants may be stipulated to be equal in a series of related molecules (or conformers),

4. the final solution may be stipulated to conform to Pulay's scaled force constant matrix, which may also be considered as a kind of constraint.

During the last 30 years numerous attempts were undertaken in the development of quantum mechanical methods for the evaluation of molecular structure and molecular dynamics of polyatomic molecules directly from Schrodinger's equation. The use of very restrictive assumptions was (and still is) necessary to make such calculations computationally realizable. At present, direct calculations of vibrational spectra by quantum mechanical calculations at different levels of theory are very important and widely used for the interpretation of experimental data, especially in case of large molecules.

Among different approaches, the Hartree-Fock (HF) level calculations are routine and available even for very large (consisting of up to hundreds of atoms) systems. But the quality of these calculations is insufficient for the direct comparison of theoretical vibrational frequencies with experimental ones. As a rule, the HF frequencies are overestimated (up to 15%), and these errors have a systematic character for the related compounds. The wide use of quantum mechanical calculations of vibrational spectra and harmonic force fields of polyatomic molecules induced the necessity of making empirical corrections to theoretical data for compatibility with experiment. The most popular approach is the so-called scaling procedure proposed by P. Pulay where the disagreement between experimental and theoretical frequencies was eliminated by introducing a finite (not very large) number of scaling factors. This approach also can be formulated in a form of a priori constraints mentioned above as type 4.

In this approach we can specify the set D as: $D = \{F: F = BF^0B\}$, $B = \mathrm{diag}\{\beta_1,...,\beta_n\}$ (where β_i are the scaling parameters).

Though this scaling procedure (mathematically, it is imposing rather strict limitations on the molecular force field) often does not provide enough freedom to eliminate all discrepancies between calculated and observed data, it has certain advantages that follow from the comparatively small number of adjustable parameters and, consequently, moderate computational resources required to perform force-field refinement. Indeed, it is very attractive to find a limited number of scaling factors for a series of model molecules (assuming their transferability), and use them for correction of the quantum mechanical force constants of more complicated molecular systems. The most popular numerical procedure for calculation (optimization) of scaling factors is the least-squares procedure, but there are a few publications indicating at the non-convergency and instability of this numerical procedure while solving an inverse scaling problem. It is explained by the impossibility of using the traditional numerical methods for solving the nonlinear ill-posed problems.

The following strict mathematical formulation of the inverse scaling problem has been proposed: the problem of finding scaling factors on the base of experimental data is treated as an operator equation similar to (4):

$$AF(\beta) = \Lambda_\delta \tag{80}$$

where β are scaling factors. Let the following norms in the Euclidean space be introduced:

$$\|F\| = \left(\sum_{ij}^{n} f_{ij}^2 \,) \right)^{1/2} \qquad \|\Lambda\| = \left(\sum_{k=1}^{l} \lambda_k^2 \rho_k \right)^{1/2},$$

where $\rho_k > 0$ are certain positive weights, f_{ij} are the elements of matrix F, λ_k ($k = 1, ..., m$) are the components of Λ.

Since problem (5) is also ill-posed, we have to regularize it. We formulate the problem as a requirement to find a solution of (80) , $F_{n,\delta}$, that is nearest (by Euclidean norm) to the quantum mechanical matrix F^0, satisfies experimental data within a given error level δ ($\| A(F(\beta)) - \Lambda_\delta \| \leq \delta$) and has a special form proposed by Pulay. If we consider this problem taking into account its possible incompatibility (within harmonic model), we come to the following formulation:

to find

$$F_{n,\delta} = \arg\min \left\| F - F^0 \right\|$$

where

$$F \in \left\{ F : F \in D = \left\{ F : \quad F = B^{1/2} F^0 B^{1/2} \right\}, \quad \left\| AF - \Lambda_\delta \right\| \leq \mu + \delta \right\}. \tag{81}$$

Here B is a diagonal matrix of scaling factors β_I, and μ is a measure of incompatibility of the problem. It may arise due to the possible anharmonicity of experimental frequencies or the crudeness of the chosen model.

Finding such a solution may be provided by minimization of the Tikhonov functional

$$M^{\alpha}(\beta) = M^{\alpha}[F] = \left\| A_h F - \Lambda_\delta \right\|^2 + \alpha \left\| F - F^0 \right\|^2 \tag{82}$$

where $F = F(\beta)$, and regularization parameter α is chosen in accordance with the generalized discrepancy principle.

As a rule, the assumed limitations on the values of force constants of polyatomic molecules cannot be strictly proved. Nevertheless, numerical quantum mechanical results on molecular force fields can provide useful guidance in choosing realistic force field models for different types of molecules.

The simplicity of the scaling procedure made it extremely popular in recent years. It has been shown that for many molecular fragments scale factors (within a given level of quantum-mechanical method) are approximately constant in a wide range of similar molecules. Force constant scaling factors have been obtained for different sets of coordinates and quantum-mechanical methods, which in most cases allow to approximate experimental frequencies with a reasonable degree of accuracy.

However, the regularized scaling procedure has initially been suggested for the force fields defined in the internal or symmetry (local symmetry) coordinate systems. In the course of spectroscopic and structural research, introduction of the complete system of internal coordinates is the most tedious and time-consuming procedure, especially for the large molecular systems. From quantum chemistry we usually obtain force constant matrix in Cartesian coordinates. Therefore we have proposed the procedure to scale ab initio force field matrix in Cartesian coordinates which allows to avoid introducing internal coordinates.

Within this approach scaling is still given by (81), however, we are not assuming the matrix *B* to be diagonal. Force field matrix in Cartesian coordinates is not automatically independent of the molecular position and orientation as in a case of using internal coordinates. Physically meaningful force constant matrix should therefore satisfy a number of constraints that would eliminate translational and vibrational degrees of freedom in the expression for the potential energy.

Let the force field matrix in Cartesian coordinates is represented as an array of 3x3 submatrices corresponding to each atom:

$$F = \begin{pmatrix} f_{(11)} & f_{(12)} & \cdots & f_{(1N)} \\ f_{(21)} & f_{(22)} & \cdots & f_{(2N)} \\ \cdots & \cdots & \cdots & \cdots \\ f_{(N1)} & f_{(N2)} & \cdots & f_{(NN)} \end{pmatrix} \qquad (83)$$

where *N* is the number of atoms in a molecule. Independence of potential energy of the transltions and rotation of a molecule as a whole leads to the following requirements:

$$\sum_{i=1}^{N} f_{(ij)} = 0, \; \sum_{i=1}^{N} V_i f_{(ij)} = 0, \quad j = 1,2,\ldots,N \qquad (84)$$

where 3x3 submatrices V_i are defined as

$$V_i = \begin{pmatrix} 0 & -Z_i^0 & Y_i^0 \\ Z_i^0 & 0 & -X_i^0 \\ -Y_i^0 & X_i^0 & 0 \end{pmatrix},$$

and X_i^0, Y_i^0, Z_i^0 are Cartesian components of the *i*-th atom equilibrium position.

Imposing constraints (84) reduces the rank of matrix F to 3N-6 (or 3N-5 for linear molecules), thus leaving only vibrational degrees of freedom.

When scaling procedure (81) is applied to the matrix F in Cartesian coordinates, we may assume that a priori matrix F^0 satisfies the requirements (84). However, this does not necessarily mean that the scaled matrix also satisfies these requirements. To ensure that scaled matrix also contains only vibrational degrees of freedom, the scale matrix B should also satisfy certain conditions:

1) Matrix B similarly to force field matrix in Cartesian coordinates (4) consists of the 3×3 unit submatrices multiplied by certain factors β_{ij} ($i, j, = 1, \ldots, N$):

$$B = \begin{pmatrix} \beta_{11}E & \beta_{12}E & \ldots & \beta_{1N}E \\ \beta_{21}E & \beta_{22}E & \ldots & \beta_{2N}E \\ \ldots & \ldots & \ldots & \ldots \\ \beta_{N1}E & \beta_{N2}E & \ldots & \beta_{NN}E \end{pmatrix}$$

2) The factors β_{ij} are subject to the following constraints:

$$\beta_{ij} = \beta_{ji},$$

$$\sum_{i=1}^{N} \beta_{1i} = \sum_{i=1}^{N} \beta_{2i} = \ldots = \sum_{i=1}^{N} \beta_{Ni} = S = \text{const}. \qquad (85)$$

It is easy to see that conditions (85) allow matrix B to be diagonal only when all β_{ii} are equal. If there exist any extra constraints due to the symmetry or model assumptions, they should be used in addition to (85). In general, matrix B contains $N(N$-1)/2+1 independent parameters, since all diagonal elements may be represented as

$$\beta_{ii} = S - \sum_{j\neq i} \beta_{ij} .$$

On this way we come to the formulation of inverse vibrational problem in a form (81) where a set of a priori constraints D on the molecular force field includes conditions (85). The solution (a set of scaling factors) can be found by minimization of functional (83). Additionally, a set D can include the constraints such as equality of some off-diagonal factors to zero, in-pair equalities of factors, symmetry constraints etc.

There is a lot of publications describing application of numerical methods to solution of the inverse vibrational problem on the base of the least squares procedure. Very often, as criterion of minimization, the authors choose the "best" agreement between experimental and fitted vibrational frequencies. However, there is a doubt if the "best" agreement criterion is meaningful. We should like to note that this criterion is insufficient due to the ill-posed nature of the inverse vibrational problem. Even in the case of a single molecule, it is a well-known fact that there exist an infinite number of solutions, which exactly satisfy any given set of the experimental frequencies. Addition of the expanded experimental information on frequencies of the isotopomers or related molecules may lead to incompatibility of the mathematical problem and result in no solution at all within the conventional harmonic model. This means that, using any minimization procedure for solving the inverse vibrational problem, it is necessary to apply some additional criteria (that can be mathematically formulated) in the minimization procedure to select the unique solution.

10. GENERALIZED INVERSE STRUCTURAL PROBLEM

More complicated procedure was proposed for solving the generalized inverse structural problem (GISP) in the case of joint treatment of the experimental data obtained by different physical methods (vibrational spectroscopy, electron diffraction (ED) data and microwave (MW) spectroscopy).

To implement an integrated procedure of simultaneous refinement of the force field and equilibrium geometry, a dynamic model of a molecule has been created. Based on the general approximation of small vibrations, the model has been extended to include cubic and quartic anharmonic potential terms for proper description of the large-amplitude motion. Within this approach, a molecule is described using a set of equilibrium geometry parameters R, and a molecular force field F represented by the matrices of quadratic, cubic and possibly quartic force constants defined in the framework of a certain nonlinear system of internal coordinates. Both parameter sets R and F can be considered as finite-dimensional vectors.

The model is used to predict experimentally measured values, such as vibrational frequencies ω, electron diffraction intensity $M(s)$, rotational constants $\{A, B, C\}$ obtained from microwave molecular spectra, etc. All of these values are functions of geometric (R) and force field (F) parameters. With experimental data and parameters represented as elements of normalized finite-dimensional spaces, we can formulate the problem of simultaneous refinement of the force field and equilibrium geometry of the molecule as a system of non-linear equations

$$\begin{cases} \omega(F,R) = \omega_{\exp}, \\ M(s,F,R) = M_{\exp}(s), \\ \{A,B,C\}(R,F) = \{A,B,C\}_{\exp} \end{cases} \tag{86}$$

on a set of predefined constraints $F \in D_F$, $R \in D_R$. This system can be extended to include additional experimental evidence when available (for example, data for isotopic species of a molecule sharing the same force field and equilibrium geometry).

Due to experimental errors, lack of experimental data and model limitations, this system of equations (that can be also treated as a finite-dimensional non-linear operator equation) usually fails to define unique solution, often proves to be incompatible and does not provide stability with respect to the errors of input data. To avoid these unfavorable features characteristic to the ill-posed problems, it is necessary to implement a regularizing algorithm for its solution.

We suggest using a regularizing algorithm based on optimization of the Tikhonov's functional

$$\begin{aligned} M^{\alpha}(F,R) = {} & \left\| \omega(F,R) - \omega_{\exp} \right\|^2 + \left\| M(s,F,R) - M_{\exp}(s) \right\|^2 + \left\| \{A,B,C\}(F,R) - \{A,B,C\}_{\exp} \right\|^2 + \\ & + \alpha \left\{ \left\| F - F^0 \right\|^2 + \left\| R - R^0 \right\|^2 \right\} \end{aligned} \tag{87}$$

where in the last ("stabilizer") term F^0 and R^0 represent parameters of *ab initio* force field and equilibrium geometry, respectively. With the appropriate choice of regularization parameter α (that depends on the experimental errors characterized by some numerical parameter δ), it proves possible to obtain approximations converging to a normal pseudosolution of the system (87) when experimental errors tend to zero. These approximations are obtained as extremals $\{F_\alpha, R_\alpha\}$of functional (87).

Now it is appropriate to give a brief summary of the features distinguishing the given approach from the various previously used attempts to solve the similar inverse problem.

1. The approach is aimed at a simultaneous determination of the geometry and force field parameters of a molecule. It combines techniques previously used in IR spectroscopy and ED data analysis. In particular, it allows to use more flexible force field models when fitting ED data, far beyond the usually employed scaling of the ab initio force field.
2. Ab initio data (or any other external data) is automatically "weighed" so as to serve an additional source of information when data supplied by the experiment proves insufficient. There is no need to supply ab initio data with some kind of assumed errors, etc.
3. Molecular geometry is defined in terms of equilibrium distances thus allowing compatibility with spectroscopic models and ab initio calculations. Besides, the self-

consistency of geometrical configuration is automatically maintained at all stages of the analysis.

The complexity of molecular models used in the analysis strongly depends on the availability and quality of the experimental data. Since in most cases vibrational spectra and ED patterns reveal the vibrational motion in a molecule resulting from small deviations of the atoms from their equilibrium positions, most molecular models are based on the assumption of small harmonic vibrations. In some cases of solving GISP within the scaling approximation, it is necessary to include the cubic part of the force field. Similarly, in order to get a set of more reliable cubic force constants it is undoubtedly beneficial to improve empirically the *ab initio* values, e.g. for simplicity by the use of the Pulay harmonic scale factors. Two schemes of cubic constant scaling are generally feasible. Let the *ab initio* quadratic force constant f_{ij}^{0} defined in natural internal coordinates be scaled as follows:

$$f_{ij}(\text{scaled}) = f_{ij}^{0}\beta_i^{1/2}\beta_j^{1/2} \quad ,$$

where β_i and β_j are the harmonic scale factors. Then, reasoning by analogy, the cubic constants scaling mode can be formulated as

$$f_{ijk}(\text{scaled}) = f_{ijk}^{0}\beta_i^{1/2}\beta_j^{1/2}\beta_k^{1/2}$$

or, alternatively,

$$f_{ijk}(\text{scaled}) = f_{ijk}^{0}\beta_i^{1/3}\beta_j^{1/3}\beta_k^{1/3} \quad ,$$

where f_{ijk}^{0} are the unscaled theoretical cubic constants. Both scaling schemes reduce the vibrational problem to the determination of a much smaller number of parameters

The most important step in solving the inverse vibrational problem is formulating a priori constraints on the solution, which are taken from quantum mechanical calculations. Plausible constraints for the force field matrix followed recommendations discussed elsewhere.

11. COMPUTER IMPLEMENTATION

On the basis of the regularizing algorithms described above we have compiled a package of programs for processing spectroscopic data on a computer which has been revised and now has the structure shown below.

The package contains 3 distinct software units. One of them, intended for graphic illustrations of the 3D models of molecules, has no direct output. It shows a rigid molecule rotating in space. At present we plan to extend it to display vibrational modes.

Another program, the *symmetry analyzing routine*, is not absolutely necessary for vibrational calculations but has proved extremely useful when working with molecules including dozens of atoms and possessing relatively high symmetry (for example, C_{60} with icosahedron symmetry). The version of symmetry analysis implemented in our package has following capabilities:

1. Given the equilibrium configuration (Cartesian coordinates of atoms) and masses of the atoms, it defines the symmetry point group of the molecule. In the other mode, when the symmetry group is given a priori, the Cartesian coordinates may be adjusted (if necessary) to correspond to given symmetry properties,

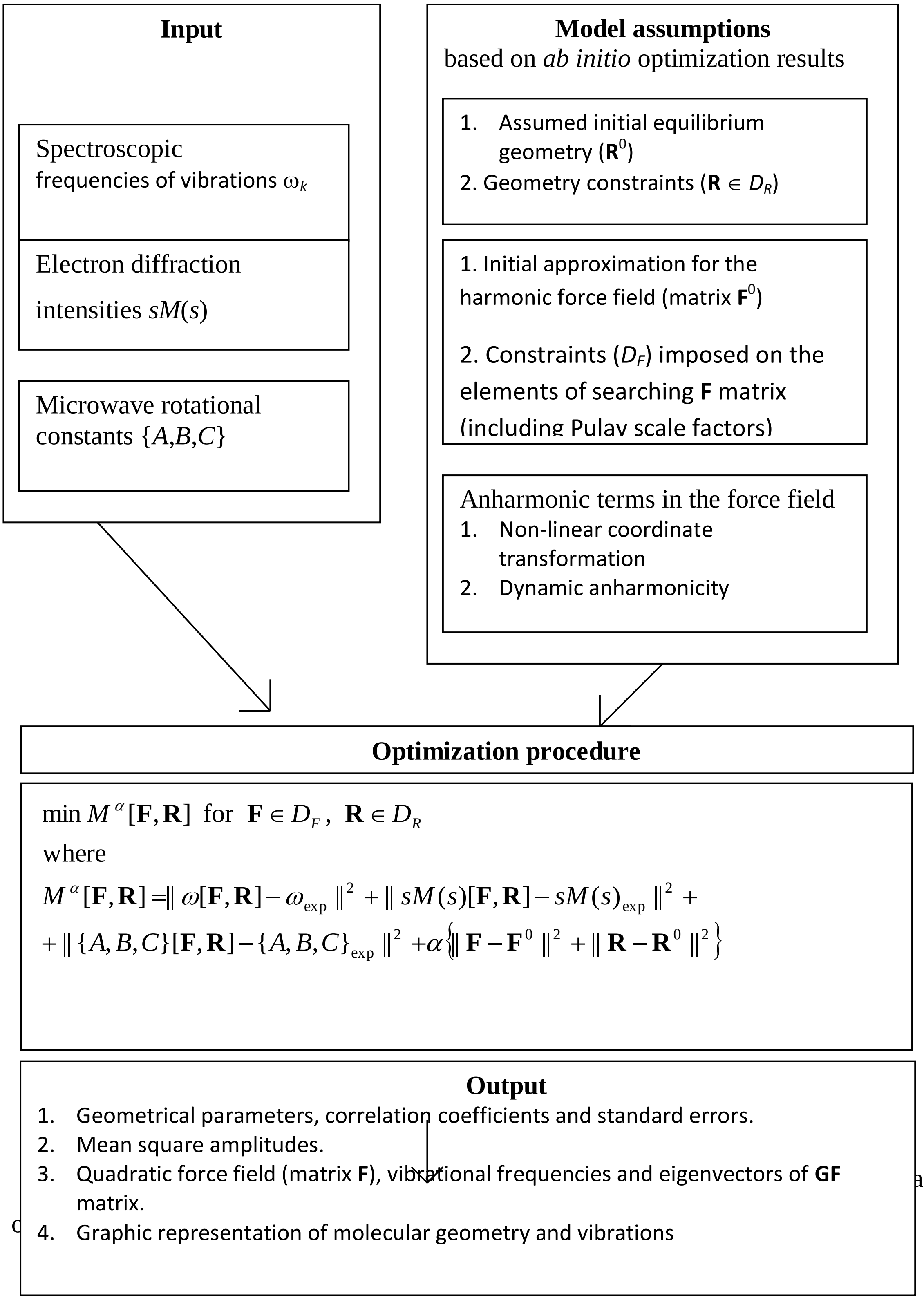
2. The number of normal frequencies of each symmetry is calculated,

3. If the set of internal coordinates is described in the input, then the symmetry coordinates based on this set are constructed. The resulting set of symmetry coordinates is analyzed (e.g., numbers of independent and redundant coordinates of each symmetry are calculated) and outputted to be used in solving direct or inverse vibrational problems.

The main software package known as SPECTRUM has recently undergone important modifications and the current version takes advantages of 64-bit processing and virtual memory management that leads to increases in both the processing rate and in the allowable size of molecules. Progress in these areas has made the processing of molecules of more than 100-200 atoms possible in a reasonable amount of time.

Further improvements were concerned with allowing the input of more kinds of data and the imposition of more and different constraints on the solution of the inverse problem. The general flow of data processing within the program is shown in the following table.

Software package SPECTRUM



Input

Spectroscopic frequencies of vibrations ω_k

Electron diffraction intensities $sM(s)$

Microwave rotational constants $\{A,B,C\}$

Model assumptions
based on *ab initio* optimization results

1. Assumed initial equilibrium geometry ($\mathbf{R}^0$)
2. Geometry constraints ($\mathbf{R} \in D_R$)

1. Initial approximation for the harmonic force field (matrix $\mathbf{F}^0$)
2. Constraints (D_F) imposed on the elements of searching **F** matrix (including Pulay scale factors)

Anharmonic terms in the force field
1. Non-linear coordinate transformation
2. Dynamic anharmonicity

Optimization procedure

$\min M^{\alpha}[\mathbf{F},\mathbf{R}]$ for $\mathbf{F} \in D_F$, $\mathbf{R} \in D_R$

where

$$M^{\alpha}[\mathbf{F},\mathbf{R}] = \| \omega[\mathbf{F},\mathbf{R}] - \omega_{\exp} \|^2 + \| sM(s)[\mathbf{F},\mathbf{R}] - sM(s)_{\exp} \|^2 + \\ + \| \{A,B,C\}[\mathbf{F},\mathbf{R}] - \{A,B,C\}_{\exp} \|^2 + \alpha \left\{ \| \mathbf{F} - \mathbf{F}^0 \|^2 + \| \mathbf{R} - \mathbf{R}^0 \|^2 \right\}$$

Output
1. Geometrical parameters, correlation coefficients and standard errors.
2. Mean square amplitudes.
3. Quadratic force field (matrix **F**), vibrational frequencies and eigenvectors of **GF** matrix.
4. Graphic representation of molecular geometry and vibrations

c

al scheme

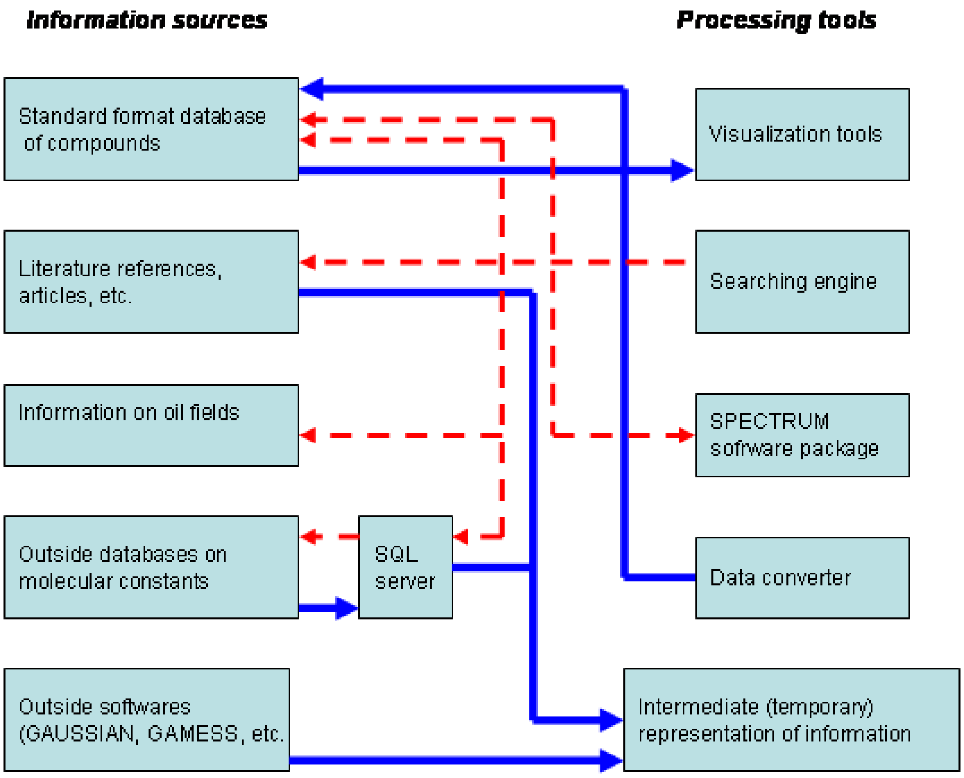


Figure 1. Hybrid type information system ISMOL

Data processing sequence

1. Conversion of input matrices given in Cartesian or internal coordinates to matrices in symmetry coordinates. Verification of matrix symmetry (adjusting,if necessary).

2. Creating, preprocessing and applying specified constraints on matrix *F*.

3 (Inverse problem only). Minimizing Tikhonov functional for the problem with the specified numerical method and appropriate choice of regularization parameter.

4. Solving direct problem for resulting matrix in symmetry coordinates.

5. Constructing force field matrix in internal coordinates.

6. Solving direct problem in internal coordinates.

7. Calculating additional characteristics of interest, such as mean square amplitudes of vibrations and potential energy distribution.

It should be noted that the package allows the processing of more than one molecule at a time (each of them possessing several isotopic species). This is a sensible approach when the model considerations require equivalence between certain force matrix elements. With this kind of constraint specified, these elements are held equivalent throughout the whole process of optimization. This option is of special value for verifying transferability properties of force constants. Additional features of the package include the following: all constraints are applied to matrices in internal coordinates, all the algorithms throughout the package allow internal coordinates to be redundant, redundancy conditions are taken into account automatically, and the regularization parameter is chosen in accordance with the generalized discrepancy principle.

Note also that conversion from Cartesian to internal coordinates may be not unique if coordinates are redundant. In this case, the software package allows two choices:

a) to generate a canonical matrix F (that is, with minimal rank sufficient to represent all vibrational degrees of freedom, $3N$-6 where N is number of atoms),

b) to generate a matrix F with the minimal off-diagonal norm (this is a commonly used model assumption).