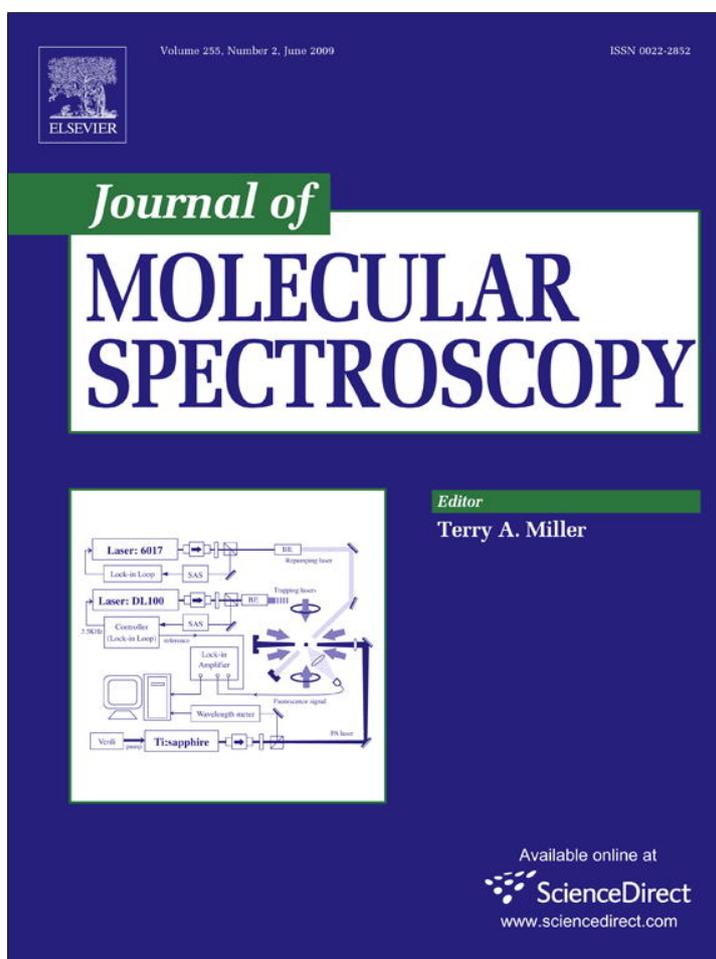


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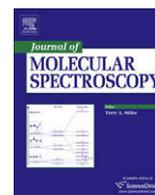
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On the determination of the intramolecular potential energy surface of polyatomic molecules: Hydrogen sulfide and formaldehyde as an illustration

O.N. Ulenikov^{a,*}, E.S. Bekhtereva^a, C. Leroy^b, O.V. Gromova^b, A.L. Fomchenko^a

^aDepartment of Physics, Laboratory of Molecular Spectroscopy, Tomsk State University, Lenin av., 36 RU-634050 Tomsk, Russia

^bInstitut Carnot de Bourgogne-UMR 5209 CNRS, Université de Bourgogne B.P. 47870, F-21078 Dijon Cedex, France

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ABSTRACT

We present here an approach for determining the Hamiltonian of polyatomic molecules that allows one to successfully solve the problem of potential energy surface (PES) determination via construction and diagonalization of a Hamiltonian matrix of large dimension. In the suggested approach, the Hamiltonian is very simple and can be used both for any “normal” polyatomic molecule and for any isotopic species of a molecule. Molecules with two to four equivalent X–Y bonds are considered, and for illustration of the efficiency of the suggested approach, numerical calculations are made for the three-atomic (hydrogen sulfide) and four-atomic (formaldehyde) molecules.

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1. Introduction

One of the most important problems in the field of molecular physics, which deals with the study of the vibrational–rotational properties of polyatomic molecules, is the problem of the determination of the intramolecular potential energy surface (PES) of a molecule in a given electronic state. This problem is very important because knowledge of the PES is vital in order to solve the vibration–rotation Schrödinger equation for a molecule:

$$H\psi_{\alpha} = E_{\alpha}\psi_{\alpha}, \quad (1)$$

which then allows one to use the obtained eigenvalues, E_{α} , and eigenfunctions, ψ_{α} , for many problems in physics and chemistry.

Presently there are two main methods to obtain the PES of a molecule. The first way is the use of direct *ab initio* calculations (see, e.g., Refs. [1–8]). Direct methods allow for the production of a high quality topography of the multidimensional potential surface of a molecule (see, e.g., [9] and references therein). At the same time, there are many problems in molecular physics and attendant applied sciences that require not only qualitative but highly accurate quantitative knowledge of PES-parameters. However, as numerical estimations show, even errors of $\sim 0.1\%$ in the values of the main PES-parameters can lead to errors of the order of 20–30 cm^{-1} , e.g., in the harmonic frequencies. If we

take into account that the accuracies in the determination of vibrational–rotational line positions (and, as a consequence, vibrational–rotational energies) in modern experiments are $10^5 - 10^6$ times greater, it is clear that even the best results of direct PES-calculations should be improved on the basis of the modern experimental data.

The second group of methods (methods of quantitative PES determination) may be called “variational” methods because they use highly accurate experimental vibrational–rotational data as initial data in the fitting procedures of the PES-parameters (see, e.g., [10–25]). In this case, even the best among the modern modifications of variational methods are not free of large imperfections that strongly restrict their application to molecules with more than three or four atoms. The most important problem is the huge dimensions of the Hamiltonian matrices used during the diagonalization process (moreover, these dimensions dramatically increase when the number of atoms increases). Extensive efforts have been made to solve this problem partially (see, e.g. Refs. [11–13,26]). The second problem is connected with the proper choice of vibrational coordinates used in the molecular Hamiltonian. This last point is very important for at least two reasons:

(a) Firstly, it is known that different sets of internal coordinates are used to achieve the best representation of the kinetic part of the Hamiltonian for molecules with different numbers of atoms and/or different symmetries. In those cases, the investigation attempts to redefine new vibrational coordinates (see, e.g., Refs. [23–25], [27–29]). In fact, currently there is only one universal scheme for presentation of the kinetic part of the molecular Ham-

* Corresponding author. Fax: +7 049 20 24 39 2581.

E-mail addresses: Ulenikov@phys.tsu.ru (O.N. Ulenikov), ulenikov@mail.ru (O.N. Ulenikov).

iltonian for arbitrary polyatomic molecules, using the so-called normal coordinates, see, e.g., [30,31]. However, as will be discussed below, the normal coordinates are not suitable for the problem of determination of the molecular PES. Thus, it would be suitable to suggest a set of vibrational coordinates that, on the one hand, would be universal and would allow for the possibility to represent the kinetic part of the molecular Hamiltonian in a unique and simple form applicable for any polyatomic molecule and, on the other hand, would be free of the inconveniences of the normal coordinates.

(b) The second, and even a more important reason for a proper choice of internal vibrational coordinates of a molecule, is as follows. As mentioned above, the most important difficulty for the application of traditional schemes for polyatomic molecules is the huge dimensions of the Hamiltonian matrices, which have to be constructed and diagonalized many times. As discussed below, the eigenvalues of matrices of such dimensions can be obtained with satisfactory accuracy by using a special perturbation scheme; however, the success of the perturbation scheme directly depends on the ratio between the diagonal and nondiagonal elements of the matrix. This point strongly depends on the complexity of the initial Hamiltonian: the less complex the Hamiltonian is, the more efficient the diagonalization procedure is. For all of these reasons, it would be suitable to suggest a set of internal vibrational coordinates that would allow one not only to present the molecular Hamiltonian in a unique form, but would be as simple as possible for a further construction and diagonalization of the Hamiltonian matrix.

2. Vibrational Hamiltonian of a polyatomic molecule: application to XY_2 molecules with two equivalent bonds

In the present contribution we suggest an approach that is very simple to use and expands (in comparison with the standard schemes) the number of molecules to which it can be successfully applied. The main advantage of the suggested approach is, first of all, in the introduction of vibrational coordinates that allow us to represent the kinetic operator as well as the potential function of a molecule in a simple form, and, on that basis, allow us to use an efficient perturbation scheme for the diagonalization of Hamiltonian matrices of large dimension.

We start with a general remark that the success of the construction and subsequent diagonalization of a Hamiltonian matrix of huge dimension directly depends on the basic functions that are used in the construction of the Hamiltonian matrix. Indeed, if we assume that the basic functions are the eigenfunctions of the complete Hamiltonian, then the Hamiltonian matrix will be exactly diagonal independent of its dimension. This implies that the closer the basic functions are adapted to the Hamiltonian's eigenfunctions, the more efficient the process of construction and the subsequent diagonalization of the Hamiltonian matrix is. In this case, the better the basic functions are adapted to the eigenfunctions, the smaller the absolute values of the ratios of the nondiagonal matrix elements to the diagonal ones are. As a consequence, the preceding statement implies that perturbation theory can be successfully applied to the problem of matrix diagonalization in spite of its large dimension. To summarize, one should expect that the main question in the procedure of construction and further diagonalization of a huge dimension Hamiltonian matrix is, "how to produce a set of basic functions that would be as closely as possible adapted to the Hamiltonian's eigenfunctions?"

To answer this question we divide the Hamiltonian into two parts:

$$H = H_0 + h; \quad (2)$$

where H_0 is a zero-order operator and h is a perturbation. In this case, the use of different coordinate sets leads to different separa-

tions of the Hamiltonian, H , into two parts. This implies that a special choice of the coordinate representation can provide a good set of basic functions for the problem of construction and diagonalization of the Hamiltonian matrix: the smaller the ratio of the perturbation operator, h , to the zero-order Hamiltonian, H_0 , the closer the eigenfunctions of the Hamiltonian H_0 will be adapted to the eigenfunctions of the whole Hamiltonian, H .

We consider the vibrational Hamiltonian of an arbitrary polyatomic molecule.¹ Generalization of the results to the rotational-vibrational problem can be made without difficulty after solving the vibrational problem. Also, we will limit our consideration to an isolated, non-degenerate electronic state in the frame of the Born–Oppenheimer approximation because, in this approximation, an intramolecular potential function is isotopically invariant. As a consequence, it allows us to consider jointly all isotopic species of a molecule. This is important for the problem of the determination of the molecular PES because it allows for the possibility to use all of the experimental information about different isotopic species of a molecule, which means increasing the number of initial experimental data involved in the procedure of the PES determination. We also will limit our present consideration to molecules that are free of large amplitude vibrations. Extension of the frame of those approximations will be additionally discussed.

Because the vibrational Hamiltonian, H , of a molecule consists of two parts: the "kinetic" operator, T , and the potential function, V ,

$$H = T + V, \quad (3)$$

it is necessary to mention something concerning the most suitable representations of both terms. In order to take into account our wish to jointly consider different isotopic species of a molecule, the so-called curvilinear vibrational coordinates, Δr (changes of bond lengths) and $\Delta \alpha$ (changes of angles between bonds), which are isotopically invariant, are most suitable for the representation of the potential function, V , in the Hamiltonian Eq. (3). For simplicity of understanding we consider initially a three-atomic molecule, XY_2 of the C_{2v} symmetry (see Fig. 1). In this case, the potential function of the XY_2 (C_{2v}) molecule can be written as:

$$\begin{aligned} V = & \frac{1}{2}f_{rr}(\Delta r_1^2 + \Delta r_3^2) + \frac{1}{2}f_{\alpha\alpha}\Delta\alpha^2 + f_{rr'}\Delta r_1\Delta r_3 + f_{r\alpha}(\Delta r_1 + \Delta r_3)\Delta\alpha \\ & + \frac{1}{6}f_{rrr}(\Delta r_1^3 + \Delta r_3^3) + \frac{1}{6}f_{\alpha\alpha\alpha}\Delta\alpha^3 + \frac{1}{2}f_{rrr'}(\Delta r_1^2\Delta r_3 + \Delta r_3^2\Delta r_1) \\ & + \frac{1}{2}f_{rr\alpha}(\Delta r_1^2 + \Delta r_3^2)\Delta\alpha + f_{r\alpha\alpha}(\Delta r_1 + \Delta r_3)\Delta\alpha^2 \\ & + f_{rr'\alpha}\Delta r_1\Delta r_3\Delta\alpha + \dots \end{aligned} \quad (4)$$

Here, f_{\dots} are the parameters of the intramolecular potential function. It is important that the curvilinear coordinates, Δr and $\Delta \alpha$, be easily connected with different other types of vibrational coordinates used for the description of vibrations in polyatomic molecules.

As for the kinetic part, T , of the Hamiltonian in Eq. (3), it was mentioned above that, at least one type of vibrational coordinates exists that allows one to represent the kinetic operator in an exact form. In that representation the kinetic operator is very simple and valid for any polyatomic molecule under the framework of our consideration. Normal coordinates, Q_i ,² fulfill this condition (see, e.g., Ref. [31]). In this case, the operator, T , has the following form:

$$T \equiv T_1 + T_2 = \sum_{\lambda} \frac{P_{\lambda}^2}{2} + \frac{1}{2} \sum_{\alpha\beta} \mu_{\alpha\beta} G_{\alpha} G_{\beta}. \quad (5)$$

¹ Some aspects of the approach discussed below and its applications to the three- to five-atomic molecules have been presented in Refs. [32,33].

² In accordance with the general vibration–rotation theory, Refs. [30,31], the normal vibrational coordinates, Q_i , are determined as follows: $r_{N\alpha} = r_{N\alpha}^e + \sum_i m_N^{-1/2} I_{N\alpha i} Q_i$; where $r_{N\alpha}^e$ are the equilibrium coordinates (in cm) of the nuclei of a molecule and the units of the coordinates, Q_i , is $g^{1/2} \times \text{cm}$.

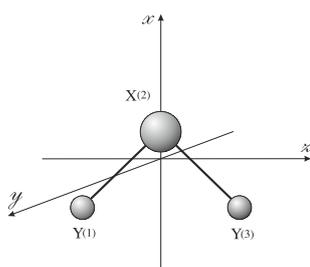


Fig. 1. Structure of the XY_2 (C_{2v}) molecule and definition of the axis used in the present work.

Here $P_\lambda = -\hbar\partial/\partial Q_\lambda$; $\mu_{\alpha\beta}$ and $G_\alpha = \sum_{\lambda\mu} s_{\lambda\mu}^\alpha Q_\lambda P_\mu$ are elements of the matrix of the inverse moments of inertia and the vibrational angular momenta, respectively, which depend on the transformation coefficients, $I_{N\beta\lambda}$, known from the vibration–rotation theory, Ref. [31].

The Hamiltonian of a molecule in the form of Eqs. (3)–(5) can be considered as a suitable basis for the problem of the molecular PES determination. In this case, of course, both parts, T and V , should be transformed to expressions depending on the same set of vibrational coordinates. In this context, three possibilities should be considered:

(a) Curvilinear coordinates, Δr and $\Delta\alpha$, in the potential function, V , as in Eq. (4) can be transformed into the coordinates Q_i , which the kinetic part, T , depends on. Indeed, the vibrational Hamiltonian is expanded in the standard form, Ref. [31]. However, such a Hamiltonian representation is not suitable for the problem of the determination of the molecular PES because of the appearance of extremely large nondiagonal elements in the Hamiltonian matrix. In this case, not only the reduction of large-dimension matrix to submatrices of smaller dimension, but even its direct diagonalization is impossible because of the presence of extremely large anharmonic terms in the Hamiltonian connected with the stretching vibrations. As an example of such extremely large nondiagonal elements in the matrix of the Hamiltonian of the XY_2 (C_{2v}) molecule, the elements of the type $\langle v_1 v_2 v_3 | k_{133} Q_1 Q_3^2 | v_1 \pm 1 v_2 v_3 \rangle$ can be mentioned.

(b) The second possibility is the transformation of the Q_i coordinates (within the kinetic part, T) to the curvilinear coordinates, Δr and $\Delta\alpha$. Such a Hamiltonian presentation was discussed recently in our Refs. [34–36] and, independently, in [37,38]. This method can be applied, in principle, to any “normal” polyatomic molecule. Moreover, the use of the obtained expression to construct the Hamiltonian matrix and then to its diagonalization advantageous in comparison with the procedure discussed in (a). The advantage is the absence of extremely large values of nondiagonal matrix elements caused by the potential function, V , if one uses the Morse coordinates, $y_i = 1 - \exp(-a\Delta r_i)$, instead of the stretching coordinates, Δr_i . At the same time the representation in case (b) leads to a very complicated form of the kinetic operator, T (see above mentioned Refs. [34–38]). As a consequence, the analysis shows that the problems produced by the large values of nondiagonal matrix elements, caused by the potential function, V , in case (a), are transferred to analogous problems that appear from the complicated representation of the kinetic part, T (especially for molecules with more than three atoms).

We stress here, that both cases discussed above, and a third one discussed below, are applicable to arbitrary polyatomic molecules. From this point of view, all three situations satisfy the first goal of two goals of the present study, which is to formulate the Hamiltonian of a molecule in a form that would be applicable to any “normal” polyatomic molecule. At the same time, the second goal to derive a calculation scheme that would provide the possibility to obtain eigenvalues of the large dimension Hamiltonian matrix is not successfully solved by the two first approaches. Therefore, special attention should be devoted to the third point discussed below:

(c) Let us try to find a new type of vibrational coordinates that would allow us to keep the advantages of both the kinetic part, T ,

(as in case (a)) and the potential function, V , (as in case (b)) but would be, more or less, free of their disadvantages. Namely, we would like that this new set of vibrational coordinates keeps a form of the kinetic operator as simple as possible (moreover, if possible, they should allow for the inclusion of the whole operator, T_1 , as in Eq. (5) into the zero-order operator, H_0 , in Eq. (2)) and, at the same time, be free of large values of the nondiagonal matrix elements caused by the potential function, V .

Before we express such a special set of vibrational coordinates, we will note that the set of vibrational coordinates, Δr and $\Delta\alpha$, used in V in Eq. (4) can be connected to the vibrational coordinates, Q_i , used in T in Eq. (5) by the expressions:

$$\Delta r_N = \sum_\lambda C_\lambda^N Q_\lambda + \frac{1}{2} \sum_{\lambda\mu} C_{\lambda\mu}^N Q_\lambda Q_\mu + \frac{1}{6} \sum_{\lambda\mu\nu} C_{\lambda\mu\nu}^N Q_\lambda Q_\mu Q_\nu + \dots \quad (6)$$

and

$$\Delta\alpha = \sum_\lambda C_\lambda Q_\lambda + \frac{1}{2} \sum_{\lambda\mu} C_{\lambda\mu} Q_\lambda Q_\mu + \frac{1}{6} \sum_{\lambda\mu\nu} C_{\lambda\mu\nu} Q_\lambda Q_\mu Q_\nu + \dots \quad (7)$$

Here, r_N ($N = 1, 3$) is the length of the bond $X-Y_N$; α is the interbond angle; λ, μ , and ν may vary between 1 and 3; Q_1 and Q_3 belong to the stretching vibrations and Q_2 belongs to the bending vibration. The C -coefficients in Eqs. (6,7) are known functions of the transformation coefficients, $I_{N\beta\lambda}$, and, for illustration, their analytical expressions for the XY_2 (C_{2v}) molecules are given in Appendix A. The corresponding higher order coefficients, $C_{\lambda\mu}^N$ and $C_{\lambda\mu\nu}^N$, for the XY_2 (C_{2v}) molecule and any coefficients for other types of molecules can be easily obtained if one takes into account Eqs. (6,7) and Eqs. (45–50). From the analysis of the symmetry properties and the values of the C_λ^N -coefficients it is possible to find that the following relations are fulfilled for XY_2 (C_{2v}) molecules: $C_1^1 = C_3^1 > 0$; $C_3^3 = -C_1^3 > 0$; the values of the coefficients C_1^1 and C_3^3 are very close (they practically coincide) to each other; and the absolute values of coefficients C_2^1 and C_2^3 are considerably smaller than the value of C_1^1 . As for the C_λ -coefficients in Eq. (7), they satisfy $|C_1| \ll |C_2|$, and $|C_3| \ll |C_2|^3$ (as an illustration, see Table A1 in Appendix A where numerical values of the C_λ^N -coefficients are presented for the H_2S molecule).

After this remark, let us introduce a new set of vibrational coordinates, R_i , with the help of the following linear transformation:

$$Q_\lambda = \sum_\mu \alpha_{\lambda\mu} R_\mu; \quad (8)$$

where $\alpha_{12} = \alpha_{21} = \alpha_{23} = \alpha_{32} = 0$, $\alpha_{22} = 1$ and

$$\alpha_{11} = \alpha_{13} = \alpha_{33} = -\alpha_{31} = (C_1^1 - C_3^1)^{-1}. \quad (9)$$

From Eqs. (8,9) it is clear that coordinates R_1 and R_3 are connected with the stretching vibrations and R_2 is connected with the bending vibration.⁴

It is important to note that the new coordinates, R_i , introduced in this way keep the main part, T_1 , of the kinetic operator in Eq. (5) in the exact and very simple form:

³ It can be shown that the analogous relations between the C_λ^N and C_λ coefficients are valid for any XY_2 fragment in any polyatomic molecule.

⁴ It should be mentioned that the introduced vibrational coordinates are very close to the curvilinear coordinates, Δr , and the Radau coordinates (see, for example [40,41]). However they are considerably different from both the curvilinear and Radau coordinates as can be clearly seen from Eq. (12) and Appendix B. Indeed, they are not curvilinear coordinates because they differ from Δr_N by addition of $\mathcal{F}(R_1, R_2, R_3)$. On the other hand, the introduced coordinates, R_N , are not the Radau coordinates because (see, for example Eq. (6) in [41]) the Radau coordinates are simple sums of Δr_N coordinates with coefficients depending on the nuclear masses. At the same time, as is seen from Eq. (12), the suggested coordinates, R_N : (a) depend on different orders of not only the stretching coordinates, Δr_N , but on the bending coordinates, as well, (b) even the simplest coefficients, f_i^N , in Eq. (12) depend not only on the nuclear masses but on the equilibrium interbond angle, α_e , and on the ambiguous parameter, $\sin\gamma$, (see Appendix B).

$$T_1 = -\frac{\hbar^2}{2\mu_1} \frac{\partial^2}{\partial R_1^2} - \frac{\hbar^2}{2\mu_3} \frac{\partial^2}{\partial R_3^2} - \frac{\hbar^2}{2} \frac{\partial^2}{\partial R_2^2}. \quad (10)$$

Here, μ_N ($N = 1, 3$) has the meaning of a reduced mass of a fragment, XY_N , with:

$$\mu_1 = \mu_3 = 2(C_1^1 - C_3^1)^{-2}. \quad (11)$$

From Eq. (6) (see also footnote 2) it follows that the units of the C_λ^N -coefficients is $\text{g}^{-1/2}$. It follows that the units of μ_N is g. From Eqs. (8,9) it also follows that the new coordinates, R_1 and R_3 , have units of cm, and the units of the coordinate R_2 is $\text{g}^{1/2} \times \text{cm}$.

The second part, T_2 , of the kinetic operator, T , in Eq. (5) is considerably smaller than the main part, T_1 , and it can be transformed without difficulties to the new set of coordinates.

Let us look now at the potential function, V , in Eq. (4). Taking into account Eqs. (6)–(8), it is possible to express the following relations between the Δr , $\Delta \alpha$, and R_λ coordinates:

$$\Delta r_N = R_N + F_N(R_1, R_2, R_3) \equiv R_N + \sum_\lambda f_\lambda^N R_\lambda + \sum_{\lambda\mu} f_{\lambda\mu}^N R_\lambda R_\mu + \dots, \quad (12)$$

and

$$\begin{aligned} \Delta \alpha &= C_2 R_2 + F(R_1, R_2, R_3) \\ &\equiv C_2 R_2 + \sum_\lambda f_\lambda R_\lambda + \sum_{\lambda\mu} f_{\lambda\mu} R_\lambda R_\mu + \dots; \end{aligned} \quad (13)$$

where $F_N(R_1, R_2, R_3)$ and $F(R_1, R_2, R_3)$ are small corrections of the first terms and the absolute values of the coefficients f_{\dots} in Eqs. (12,13) are decreasing quickly with increasing order of the coordinates R_i in the right hand side of those equations. In principle, all the coefficients, f_{\dots}^N , in Eqs. (12,13) can be obtained in analytical form on the basis of the equations in Appendix A; however, even the simplest of them are so cumbersome that it is not suitable to keep them in analytical form. For this reason we used the numerical representation of all f_{\dots}^N coefficients and, only for illustration, one of the most simple coefficients, f_3^1 , is presented in Appendix B.

In practice, after such a transformation of coordinates, the properties of the potential function, $V(R_1, R_2, R_3)$, of a molecule do not differ from the properties of the potential function discussed in case (b) above. This implies that it is very suitable for application in the procedure of construction of the Hamiltonian matrix and its further diagonalization. At the same time, the key point of the considered approach, the exact kinetic operator, T_1 , of a molecule is extremely simple and completely included into the zero-order operator, H_0 .

Moreover, let us introduce one more set of coordinates, and turn now from the coordinates R_1 and R_3 to Morse-type coordinates:

$$y_N = 1 - \exp(-a_N R_N). \quad (14)$$

By analogy with the usual Morse coordinates

$$y'_N = 1 - \exp(-a \Delta r_N), \quad (15)$$

we introduced in Eq. (14) a parameter, a_N , which would coincide with the parameter a of Eq. (15) if the coordinates R_N would coincide with Δr_N . However, because the coordinates R_N slightly differ from Δr_N (see Eq. (12)), the values of a_N must be slightly different from the value of a . We now make the reciprocal transformation of Eq. (14):

$$R_N = \frac{1}{a_N} \sum_{p \geq 1} \frac{1}{p} y_N^p. \quad (16)$$

Then the potential function $V(y_1, R_2, y_3)$ can be written as

$$V = V_0 + V_1(y_1, y_3) + V_2(R_2) + V_3(y_1, R_2, y_3), \quad (17)$$

where V_0 is the main zero-order term defined as:

$$V_0 = D(y_1^2 + y_3^2) + \frac{(2\pi c \omega_2)^2}{2} R_2^2 \quad (18)$$

($a_1 = a_3$ because of equivalence of the bonds $X - Y_1$ and $X - Y_2$);

$$\begin{aligned} V_1(y_1, y_3) &= \frac{1}{6} a_{111} (y_1^3 + y_3^3) + \frac{1}{24} a_{1111} (y_1^4 + y_3^4) \\ &+ a_{13} y_1 y_3 + \frac{1}{2} a_{113} (y_1^2 y_3 + y_1 y_3^2) \\ &+ \frac{1}{4} a_{1133} y_1^2 y_3^2 + \frac{1}{6} a_{1113} (y_1^3 y_3 + y_1 y_3^3) + \dots; \end{aligned} \quad (19)$$

$$V_2(R_2) = \frac{1}{6} a_{222} R_2^3 + \frac{1}{24} a_{2222} R_2^4 + \dots; \quad (20)$$

and

$$\begin{aligned} V_3(y_1, R_2, y_3) &= a_{12} (y_1 + y_3) R_2 + \frac{1}{2} a_{112} (y_1^2 + y_3^2) R_2 + \frac{1}{2} a_{122} (y_1 + y_3) R_2^2 \\ &+ a_{123} y_1 y_3 R_2 + \frac{1}{6} a_{1112} (y_1^3 + y_3^3) R_2 + \frac{1}{4} a_{1122} (y_1^2 + y_3^2) R_2^2 \\ &+ \frac{1}{6} a_{1222} (y_1 + y_3) R_2^3 + \frac{1}{2} a_{1123} (y_1^2 y_3 + y_1 y_3^2) R_2 \\ &+ \frac{1}{2} a_{1223} y_1 y_3 R_2^2 + \dots \end{aligned} \quad (21)$$

In Eqs. (18)–(21) all the parameters, D, \dots, a_{1223} , etc., can be easily expressed as functions of the parameters of the initial expression in Eq. (4).

As a result of all of the above, one can see from Eqs. (10) and (18) that the main zero-order part, H_0 , of the molecular Hamiltonian is a simple sum of two Morse-type oscillators for the stretching type coordinates, R_1 and R_3 , and of a harmonic oscillator for the bending type coordinate, R_2 :

$$H_0 = \sum_{N=1,3} \left(-\frac{\hbar^2}{2\mu_N} \frac{\partial^2}{\partial R_N^2} + D y_N^2 \right) + \left(-\frac{\hbar^2}{2} \frac{\partial^2}{\partial R_2^2} + \frac{(2\pi c \omega_2)^2}{2} R_2^2 \right). \quad (22)$$

All the other terms both in the potential function, Eqs. (19)–(21), and in the operator, T_2 (Eq. (4)), can be considered as small corrections to the main zero-order Hamiltonian in Eq. (22). It is important that in the present approach (contrary to the approach (b) discussed above) there are no contributions from the T_1 operator, with the exception of the zero-order part in Eq. (22).

The solution of the Schrödinger equation with the Hamiltonian in Eq. (22) is well known (see, e.g., Refs. [42–44]). In this case, the eigenvalues of the harmonic oscillator have the form:

$$E_\nu / hc = \omega_2 \left(\nu + \frac{1}{2} \right) \quad (23)$$

and the eigenvalues of the Morse-oscillator have the form

$$E_n = \frac{2D}{k} \left(n + \frac{1}{2} \right) - \frac{D}{k^2} \left(n + \frac{1}{2} \right)^2; \quad (24)$$

where $k = \frac{\sqrt{2\mu D}}{ah}$. The corresponding eigenfunctions are the known Hermitian polynomials, [42], and the Morse functions, [43,44]. The eigenvalues and eigenfunctions obtained in this way allow us to construct the matrix of the whole molecular Hamiltonian without any difficulties. Moreover, as comparative analysis shows, which was made for different types of molecules on the basis of approach (c) and of the above discussed approaches (a) and (b), in our case, the ratios between the diagonal and nondiagonal elements of the whole Hamiltonian matrices have more appropriate values for the possibility of a successful reduction of these matrices. This implies that the set of basic functions that in our case are the eigen-

functions of the zero-order Hamiltonian in Eq. (22), are closely adapted to the set of eigenfunctions of the whole Hamiltonian, H , in Eq. (3).

3. Application to axially symmetric XY_3 and ZXY_3 molecules with three equivalent bonds

In the preceding Section the $XY_2(C_{2v})$ type molecule was considered. However, an analogous consideration can be adopted for any type of polyatomic molecules having a set of equivalent bonds such as X–Y in the XY_2 molecule. The key point in the suggested approach is the proper choice of the coefficients $\alpha_{\lambda\mu}$ in Eq. (8). In this case, the coefficients $\alpha_{\lambda\mu}$ should be chosen in such a way, firstly, not to destroy the simple form of the operator, T_1 , and, secondly, to provide the validity of the coordinate transformations of the type of Eqs. (12,13). Fortunately, as the analysis shows, the symmetry of the molecules leads to such relations between the C_λ^N - and C_λ -type coefficients in Eqs. (6,7) that the above required conditions may be satisfied for many polyatomic molecules (not only with two, but also with more equivalent bonds).

In this section we discuss the introduction of the corresponding coordinates for four-atomic $YX_3(C_{3v})$ and five-atomic $ZYX_3(C_{3v})$ type molecules that have three equivalent bonds. Because the corresponding analytical formulas for the analogous $f_{\lambda,\mu}^N$ -coefficients of Eqs. (12,13) are complicated (nevertheless, they always can be derived on the basis of the relations from Appendix A), we will explain the introduction of the R_λ coordinates in the case considered on the examples of four-atomic PH_3 and AsH_3 and five-atomic CH_3D and CHD_3 molecules (see, Fig. 2).

Analogous to the H_2S molecule, discussed in the previous Section, the C_λ^N coefficients can be numerically calculated for any of those molecules. They are presented in Table A2 of Appendix A. Here, generalizing the notation, $\lambda = 1$ denotes the symmetric stretching mode and $\lambda = 2$ and 3 denote the doubly degenerated stretching mode. Additionally, $\lambda = 4$ denotes the Y–Z vibration in deuterated methane species. Other λ -values indicate bending modes. As earlier for the H_2S molecule, it is possible to see that the symmetry of all the considered molecules leads to a set of relations between the values of the C_λ^N coefficients. In particular:

$$C_1^1 = C_1^2 = C_1^3 = c; C_2^1 = -2C_2^2 = -2C_2^3 \approx \pm\sqrt{2}C_1^1 = \pm\sqrt{2}c;$$

$$C_3^1 = 0; C_3^2 = -C_3^3 \approx C_1^1\sqrt{\frac{3}{2}} = \mp c\sqrt{\frac{3}{2}}.$$

It is possible to show that if one introduces a new set of vibrational coordinates with the help of Eq. (8) then both the above discussed key conditions will be satisfied if the nonzero coefficients, $\alpha_{\lambda\mu}$, are chosen in the following form :

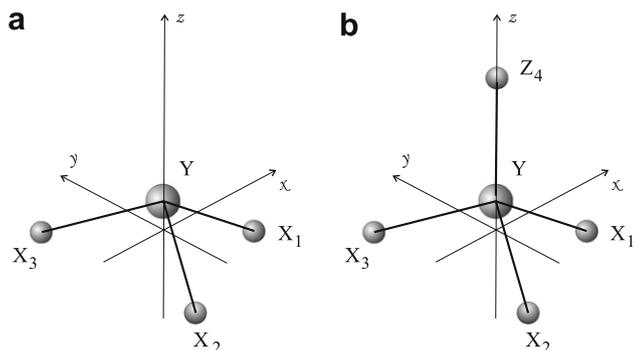


Fig. 2. Structure of the $XY_3(C_{3v})$ and $ZXY_3(C_{3v})$ molecules.

$$\alpha_{11} = \alpha_{12} = \alpha_{13} = \left(C_1^1 \mp \sqrt{2}C_2^2 \pm \sqrt{\frac{3}{2}}C_3^3 \right)^{-1} = a \approx \frac{1}{3c};$$

$$\alpha_{22} = \alpha_{23} = -\frac{1}{2}\alpha_{21} = \frac{1}{\sqrt{2}}\alpha_{11};$$

$$\alpha_{31} = 0; \alpha_{32} = -\alpha_{33} = \sqrt{\frac{3}{2}}C_1^1;$$

and, additionally for the CH_3D/CHD_3 molecules, $\alpha_{44} = 1/C_4^4$. Coefficients, $\alpha_{\lambda\lambda} = 1$ ($\lambda = 4-6$ for XH_3 and $\lambda = 5-9$ for CH_3D/CHD_3), and all the other coefficients, $\alpha_{\lambda\mu} = 0$.

It is easy to show that:

(a) As in the case of the molecule with two equivalent bonds, the introduced coordinates will transform the main part, T_1 , of the “kinetic” operator from Eq. (5) to the exact and very simple expression:

$$T_1 = -\sum_{i=1}^3 \frac{\hbar^2}{2\mu_i} \frac{\partial^2}{\partial R_i^2} - \sum_{j=4}^6 \frac{\hbar^2}{2} \frac{\partial^2}{\partial R_j^2};$$

where

$$\mu_1 = \mu_2 = \mu_3 = 3 \left(C_1^1 + \sqrt{2}C_2^2 - \sqrt{\frac{3}{2}}C_3^3 \right)^{-2}.$$

(b) The relationship between the coordinates, $\Delta r/\Delta\alpha$, on the one hand, and the introduced coordinates, R_i , on the other hand, will have exactly the same form as Eqs. (12,13). Of course, the coefficients $f_{\lambda,\mu}$ in this case will be different, but all of the deductions of Section 2 concerning their relative values will be valid in the considered case as well. It means that everything said in the preceding Section will be valid in the considered cases.

Eq. (26) is valid for the four-atomic XY_3 molecule. From the above discussion, it is not difficult to see that for the five-atomic CH_3D/CHD_3 (or, in the general case, ZXY_3 axially symmetric) molecule the “kinetic” operator can be transformed to the exact expression:

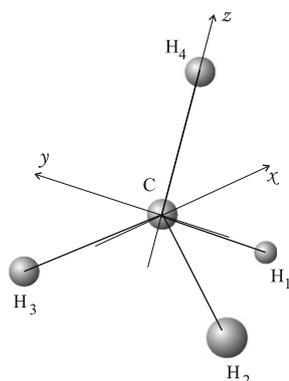
$$T_1 = -\frac{\hbar^2}{2\mu_Y} \sum_{i=1}^3 \frac{\partial^2}{\partial R_i^2} - \frac{\hbar^2}{2\mu_Z} \frac{\partial^2}{\partial R_4^2} - \sum_{j=5}^9 \frac{\hbar^2}{2} \frac{\partial^2}{\partial R_j^2};$$

where μ_Y has the same form as μ_i in Eq. (27) and $\mu_Z = (C_4^4)^{-2}$.

Exactly the same scheme of introduction of the R_i coordinates can be realized for the asymmetric isotopic species of the considered four- and five-atomic molecules. We will not discuss the corresponding mathematical manipulations and will mention only that the α -coefficients in the general equation (Eq. (8)) will have exactly the same form as values in Eq. (9) both for the pair of equivalent bonds in the XY_2'/XY_2 molecules and for the two pairs of equivalent bonds in the CH_2D_2 type molecule. The corresponding “kinetic” operators, T_1 , effective masses, μ_i , analogous to Eqs. (12,13), and the potential functions (analogous to Eqs. (17)–(21)) can also be derived very easily.

4. Application to the five-atomic XY_4 molecule with four equivalent bonds

We will consider molecules with four equivalent bonds using the CH_4 molecule (Fig. 3) as an illustration. In this case analytical formulas for the C_λ^N coefficients have a very complicated form and, as in the preceding Sections, we use their numerical values for analysis. In any case, the presence of symmetry and of four equivalent bonds leads to the following relations between the C_λ^N coefficients (for the CH_4 molecule the values of the corresponding coefficients are given in column 6 of Table A2):


 Fig. 3. Structure of the $XY_4 (T_d)$ molecule.

$$\begin{aligned} C_1^1 &= C_1^2 = C_1^3 = C_1^4; \\ C_2^1 &= -C_3^1 = -C_4^1 = -C_2^2 = C_3^2 = -C_4^2 \\ &= -C_2^3 = -C_3^3 = C_4^3 = C_2^4 = C_3^4 = C_4^4; \\ C_1^1 &\approx C_4^1. \end{aligned} \quad (29)$$

In this case, the corresponding α -coefficients in the general formula, Eq. (8), should be taken as:

$$\begin{aligned} \alpha_{11} &= \alpha_{12} = \alpha_{13} = \alpha_{14} = \alpha_{21} = -\alpha_{22} = -\alpha_{23} = \alpha_{24} \\ &= -\alpha_{31} = \alpha_{32} = -\alpha_{33} = \alpha_{34} = -\alpha_{41} = -\alpha_{42} = \alpha_{43} = \alpha_{44} \\ &= (C_1^1 + 3C_4^1)^{-1}; \\ \alpha_{\lambda\lambda} &= 1, \lambda = 5, 6, 7, 8, 9. \end{aligned} \quad (30)$$

All other $\alpha_{\lambda\mu}$ elements should be taken to be equal to zero.

Again, it is easy to show that the “kinetic” operator, T_1 , in this case has an exact and simple form:

$$T_1 = -\frac{\hbar^2}{2\mu} \sum_{i=1}^4 \frac{\partial^2}{\partial R_i^2} - \sum_{j=5}^9 \frac{\hbar^2}{2} \frac{\partial^2}{\partial R_j^2}; \quad (31)$$

where

$$\mu = 4(C_1^1 + 3C_4^1)^{-2} \quad (32)$$

5. Reduction of a Hamiltonian matrix of large dimension

The coordinate representation suggested in the preceding Sections allows one to represent the molecular Hamiltonian in a form that provides a possibility to make a diagonalization of the Hamiltonian matrix, in principle, of arbitrary dimension on the basis of perturbation theory. In this Section we present (without details of the procedure of their determination) formulas that can be obtained on the basis of the well known Van Vleck transformation (see, for example, Ref. [45]). We discuss the general algorithm of the procedure of diagonalization of large-dimensional Hamiltonian matrices and the expected accuracy of the obtained results. Of course, the scheme that is based on the perturbation theory gives only an approximation to the “exact” molecular PES. However, under conditions when the direct diagonalization does not allow us to obtain any result at all, even approximate results obtained in the framework of the perturbation calculations are suitable.⁵

⁵ It is necessary to mention that a very similar perturbation scheme was used earlier in vibrational–rotational calculations in the works by S. Brodersen with co-authors (see, e.g., Refs. [46,47] and references therein).

Let us assume that the nondiagonal matrix elements of the Hamiltonian matrix are considerably smaller than the diagonal elements (as it can be seen from the above discussion, the coordinate representation suggested in Sections 2–4 can be considered as a reasonable basis for this assumption). Without loss of generality, we can assume that the diagonal matrix elements, h_{ii} , are the values of order κ^0 and the nondiagonal elements, $h_{ij}(i \neq j)$, are of order κ^1 (κ is a small parameter whose value, as it will be seen from the discussion below, can be changed depending on the peculiarities of the problem). In this case it is possible to show that using only one Van Vleck transformation:

$$b_{ij} = (G_1^+ H G_1)_{ij}; \quad (33)$$

with the unitary operator, $G_1 = \exp(ig_1)$, allows one to transform the large-dimensional initial matrix, H , to a new matrix, B , with the elements b_{ij} as in Eq. (33), which satisfies a set of important properties:

(1) Matrix B can be divided into a set of sub-blocks. Out-of-block elements of the transformed matrix, B , are of order κ^2 .

(2) Diagonal elements of the sub-blocks can be calculated (taking into account the third-order correction) with the general formula:

$$\begin{aligned} b_{ii} &= h_{ii} + \sum_{k \notin \Omega_i} \frac{h_{ik} h_{ki}}{h_{ii} - h_{kk}} + \sum_{k, l \notin \Omega_i} \frac{h_{ik} h_{kl} h_{li}}{(h_{ii} - h_{kk})(h_{ii} - h_{ll})} \\ &\quad (k \neq l) \\ &\quad - \sum_{m \in \Omega_i (m \neq i)} \frac{h_{im} h_{mk} h_{ki}}{(h_{mm} - h_{kk})(h_{ii} - h_{kk})} \dots + O(\kappa^4). \end{aligned} \quad (34)$$

Here, $\Omega(i)$ is the space of all states interacting with the state $|i\rangle$. Analogously, the nondiagonal matrix elements, b_{ij} , of the sub-blocks are obtained by the formulas (the states $|i\rangle$ and $|j\rangle$ belong to the same space, $\Omega(i)$):

$$\begin{aligned} b_{ij} &= h_{ij} + \frac{1}{2} \sum_{k \notin \Omega_i} h_{ik} h_{kj} \left(\frac{1}{h_{ii} - h_{kk}} + \frac{1}{h_{jj} - h_{kk}} \right) \\ &\quad + \sum_{k, l \notin \Omega_i} \frac{h_{ik} h_{kl} h_{lj}}{(h_{ii} - h_{kk})(h_{jj} - h_{ll})} \\ &\quad (k \neq l) \\ &\quad - \frac{1}{2} \sum_{k \notin \Omega_i} \frac{h_{im} h_{mk} h_{kj}}{(h_{ij} - h_{kk})(h_{mm} - h_{kk})} \\ &\quad m \in \Omega_i (m \neq i) \\ &\quad - \frac{1}{2} \sum_{k \notin \Omega_i} \frac{h_{jm} h_{mk} h_{ki}}{(h_{ii} - h_{kk})(h_{mm} - h_{kk})} \dots + O(\kappa^4). \end{aligned} \quad (35)$$

Both Eqs. (34) and (35) are valid with an accuracy of order κ^3 .

(3) It is possible to show that using the second Van Vleck transformation:

$$\tilde{b}_{kl} = (\exp(-ig_2) B \exp(ig_2))_{kl}; \quad (36)$$

where $g_2 \sim \kappa^2$, will give corrections of order κ^4 only, both to the diagonal and nondiagonal elements of the sub-blocks. It provides the possibility to claim (if one neglects the out-of-block elements of the B matrix) that the differences between the eigenvalues of the sub-matrices of the B matrix, on the one hand, and the eigenvalues of the initial Hamiltonian, on the other hand, can be estimated as being of order κ^4 .

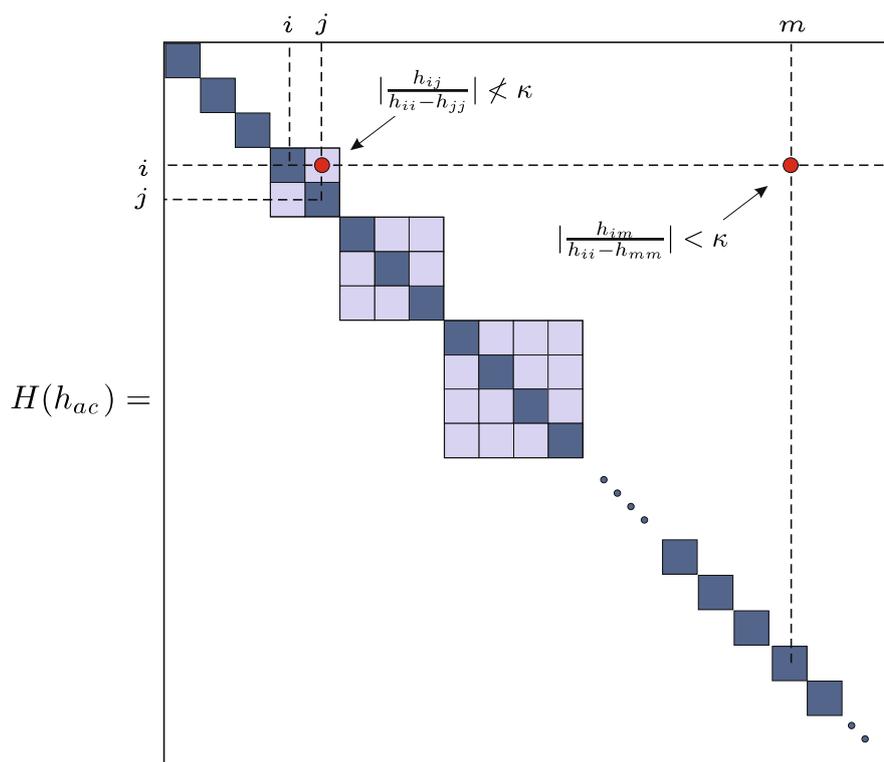


Fig. 4. Scheme of the Hamiltonian matrix reduction after check-up of the condition in Eq. (37).

(4) It can be shown that the quantitative criteria for the possibility to reduce the initial Hamiltonian matrix to a set of sub-matrices are determined by the following conditions:

(a) If the nondiagonal element, h_{ij} , of the initial Hamiltonian matrix does not satisfy the condition:

$$\frac{h_{ij}}{h_{ii} - h_{jj}} < \kappa, \quad (37)$$

then the states, $|i\rangle$ and $|j\rangle$, should be combined into one block (see Fig. 4).

(b) If the out-of-block elements of the transformed matrix, B , does not satisfy the condition:

$$b_{ik} = \sum_{j \in \Omega(i)} \frac{h_{ij}h_{jk}}{h_{kk} - h_{ij}} + \sum_{\substack{l \notin \Omega_i; \\ l \notin \Omega_k}} \frac{h_{il}h_{lk}}{2} \left(\frac{1}{h_{kk} - h_{ll}} + \frac{1}{h_{ii} - h_{ll}} \right) < \kappa^2 \quad (38)$$

($i \in \Omega(i); k \notin \Omega(i)$), then the two corresponding sub-blocks should be combined into one extra-block (see Fig. 5). In this case, all matrix elements of this new block should be calculated in accordance with Eqs. (34) and (35).

In summary, the following scheme of analysis may be proposed for the problem of molecular PES determination:

- (1) On the basis of the model suggested in Sections 2–4, the elements, h_{mn} , of the Hamiltonian matrix should be calculated.
- (2) The validity of the conditions in Eqs. (37) and (38) should be checked and, on that basis, submatrices of the transformed matrix, B , should be identified.
- (3) Matrix elements of the diagonal sub-matrices should be determined in accordance with Eq. (34) (diagonal elements b_{ii}) and Eq. (35) (nondiagonal elements b_{ij}), and then submatrices should be directly diagonalized.

As was mentioned above, the accuracy of the discussed calculation scheme is estimated as κ^4 . If one is not satisfied with this accu-

racy of calculations, the accuracy can be increased in two ways. On the one hand, the second transformation in Eq. (36) can be made. Obviously, this transformation will simultaneously decrease absolute values of the out-of-block matrix elements, and will provide elements of the diagonal submatrices by corresponding corrections.

On the other hand, the second way to increase the accuracy of the calculations can be achieved even without the second unitary transformation. To provide this, one can simply decrease the value of the small parameter, κ , in Eqs. (37) and (38). Indeed, let us assume that the diagonal elements, h_{ii} , in the initial Hamiltonian matrix have values in the range of 5000–10,000 cm^{-1} and $\kappa = \frac{1}{7}$. In this case, the errors in the eigenvalues, E_i , obtained from the discussed procedure are expected to be $(5000 - 10,000) \times \kappa^4 = (5000 - 10,000) \times 4 \times 10^{-4} \text{ cm}^{-1}$. However, if we assume that $\kappa = \frac{1}{10}$, then the errors in the eigenvalues, E_i , are expected to be four times smaller, $(5000 - 10,000) \times 1 \times 10^{-4} \text{ cm}^{-1}$. Of course, in the second case, the conditions for fulfillment of Eqs. (37) and (38) are stricter than in the first case. As a consequence, the initial Hamiltonian matrix is divided into submatrices of larger dimension than in the first case. Finally, the choice in favor of the first or the second way depends on the problem considered.

To check the validity of the above discussed scheme, we performed some diagonalization tests of the Hamiltonian matrix of dimension approximately $10,000 \times 10,000$. The Hamiltonian matrix of the H_2S molecule was constructed in accordance with the model of Section 2. Different combinations of $f_{i...j}$ parameters were used for such testing calculations. In all of the considered cases, the obtained matrix was directly diagonalized and, on the other hand, the calculation procedure discussed in this section was used for its diagonalization. In the result of all testing calculations, the differences in eigenvalues obtained by the two different methods were not larger than $0.3\text{--}0.6 \text{ cm}^{-1}$. It can be considered as a more than satisfactory correspondence if one recalls that the discussion of the present paper is in the frame of the Born–Oppenheimer approximation.

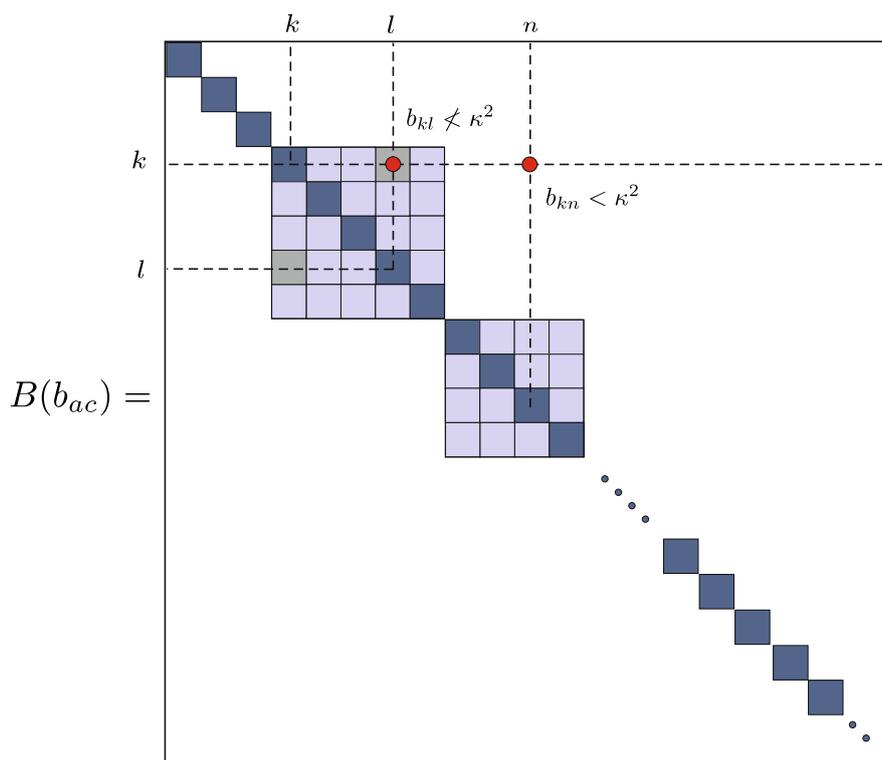


Fig. 5. Scheme of the Hamiltonian matrix reduction after check-up of the condition in Eq. (38).

6. Three-atomic (hydrogen sulfide) and four-atomic (formaldehyde) molecules as an illustration

To check the efficiency of the proposed approach in comparison with traditional methods of PES determination, we made some model calculations for the three-atomic H_2S and four-atomic H_2CO molecules.

(a) *Three – atomic molecule.* For such a test, 141 band centers with $\nu_{\text{bend.}}^{\text{max.}} = 4$ and $n_{\text{stretch.}}^{\text{max.}} = 7$ from Ref. [29] were used in our model as initial data. The use of only six parameters in our model (namely D , a , a_{13} , ω_2 , a_{122} , and a_{1122}) allowed us to reproduce all 141 band centers of the H_2S molecule with a root mean square deviation, $\text{rms} = 0.69 \text{ cm}^{-1}$. This result is more than satisfactory if one takes into account that our model is constructed in the frame of the Born–Oppenheimer approximation, and deviations from this approximation for molecules like hydrogen sulfide may reach the order of $0.5\text{--}2.0 \text{ cm}^{-1}$. An analogous fit of the same number, 141, of $D_2\text{S}$ band centers from the same Ref. [29] with the same six parameters gave even better results with a $\text{rms} = 0.58 \text{ cm}^{-1}$. Test calculations of this kind show that the proposed model allows one to produce results that are, at least, not worse than ones obtained with considerably more complicated methods.

As one more illustration of the possibilities and efficiency of the discussed approach we consider below the problem of the determination of the real intramolecular potential function for the hydrogen sulfide molecule. In this case, because the proposed approach allows for the use of experimental information about all isotopic species of a molecule, we jointly considered three main isotopic species of hydrogen sulfide, H_2S , $D_2\text{S}$, and HDS . The obtained results are compared with analogous previous results from Refs. [29] and [48–51]. In this case we would like to remark that in the testing calculations presented below we did not have the goal to produce PES parameters better than the very accurate results obtained for hydrogen sulfide, for example, in Refs. [49] and/or [51]. In those two papers, special efforts (adiabatic and nonadiabatic corrections, inclusion of repulsion

terms, large number of fitted parameters, etc.) have been made with the goal to achieve a highly accurate reproduction of known experimental data. It should be kept in mind that in those cases three-atomic molecules were considered for which the methods of PES-determination known in literature are very efficient. In our case we suggest an approximate method, whose accuracy is comparable with the values of corrections caused by adiabatic corrections. At the same time, as it follows from the above discussion, there are no obstacles for applications of the suggested method to molecules with more than three to four atoms (in particular, in Refs. [32,33] and [52] the suggested method is applied to the determination of the methane PES on the basis of highly accurate experimental data about more than 200 band centers of the CH_2D_2 , CH_3D , and CHD_3 methane isotopic species).

One more minor remark should be made in the context of the discussed PES calculation for hydrogen sulfide. One of its isotopic species (namely, HDS) has no equivalent bonds. For this reason, in accordance with the main strategy of the discussed approach, the $\alpha_{\lambda\nu}$ coefficients in Eq. (8) should be taken for the HDS molecule as $\alpha_{\lambda\nu} = 0$ for $\lambda \neq \nu$, $\alpha_{22} = 1$, $\alpha_{11} = 1/C_1^1$, and $\alpha_{33} = 1/C_3^3$.

From Refs. [53–67], we used 88 band centers of the three isotopic species as initial experimental data. Obtained from the fit is a set of 16 parameters of the potential function from Eq. (4) presented in Table 1 together with their 1σ statistical confidence intervals. Two remarks should be made here. Firstly, in accordance with the general discussion, we separately varied the a -parameters both for different species, and for different bonds of the HDS species. Secondly, we used one parameter, y_{11122} , from Eq. (21) additionally to the force parameters, f_{\dots} , of the potential function in the form of Eq. (4). This parameter was introduced in order to obtain a better description of the highly excited states of the H_2S species. Of course, the y_{11122} parameter can be expressed as a function of the f_{\dots} -parameters of the potential function in Eq. (4). However, the number of f_{\dots} -parameters on which the y_{11122} depends on is so large that we preferred to keep y_{11122} in its original form.

Table 1
Potential energy parameters for hydrogen sulfide^a.

Parameter	Value
1	2
$a^H/\text{Å}^{-1b}$	1.71729 (896)
$a^D/\text{Å}^{-1b}$	1.75556 (904)
$a_{HDS}^H/\text{Å}^{-1b}$	1.9554 (648)
$a_{HDS}^D/\text{Å}^{-1b}$	1.42589 (805)
$f_{rr}/\text{aJ Å}^{-2}$	4.2860587(924)
$f_{rr'}/\text{aJ Å}^{-2}$	-0.233600 (740)
$f_{rz}/\text{aJ Å}^{-1}$	0.10217 (661)
f_{zz}/aJ	0.758639 (636)
$f_{rrr}/\text{aJ Å}^{-3}$	-20.6047 (839)
$f_{rr'r'}/\text{aJ Å}^{-2}$	-1.0400 (457)
$f_{rrz}/\text{aJ Å}^{-1}$	-0.61012 (912)
f_{zzz}/aJ	0.21301 (741)
$f_{rrrr}/\text{aJ Å}^{-4}$	71.091 (849)
$f_{rrrr'}/\text{aJ Å}^{-4}$	0.38381 (759)
$f_{rrzz}/\text{aJ Å}^{-2}$	0.44713 (672)
$y_{11122}/\text{cm}^{-1c}$	0.03414(747)
$r_e/\text{Å}^d$	1.3356
α_{el}/deg^d	92.12

^a Uncertainties in parentheses are one standard errors.
^b Parameters a for the H₂S and D₂S species are denoted as a^H and a^D , respectively. Analogous parameters a associated with S–H and S–D bonds in the HDS molecule are denoted as a_{HDS}^H and a_{HDS}^D , respectively.
^c The y_{11122} is the extra coefficient from Eq. (21) which was used for the H₂S molecule only. In this case it is assumed that numerical calculations were made with dimensionless coordinate R_2 .
^d Constrained to the value from Ref. [29].

It should be mentioned that the values of the potential parameters obtained from the fit correlate more than satisfactorily with the values of the corresponding sets of parameters known in the literature (see, for example, the above mentioned [29], [48–51]).

Columns 2 of Tables 2–4 present values of the experimental band centers of the three isotopic species of hydrogen sulfide. References for Table 2 are given in column 3. The quality of the fit is illustrated by column 4 in Table 2 and by columns 3 in Tables 3 and 4. These columns present differences, $\Delta = \nu_{exp.} - \nu_{calc.}$, between experimental energy levels and ones calculated with the parameters given in column 2 of Table 1. Because the present fit was made in the frame of the Born–Oppenheimer approximation, these values of Δ express a more than satisfactory result of our approach. For illustration, columns 5–7 of Table 2, columns 4–5 of Table 3, and column 4 of Table 4 present analogous results from [29] and [48–50]. One can see reasonable, even good, correlations between all sets of calculated values.⁶

The last remark that we would like to make here is that one of the most important consequences of the approach suggested in Section 2 is the possibility to present a large-dimensional Hamiltonian matrix in a quasi-diagonal form. In its turn, this allows us to divide a large matrix into a set of matrices of considerably smaller dimension. As a consequence, it provides the possibility to strongly reduce the calculation time. In particular, the above discussed procedure applied to the three hydrogen sulfide isotopic species took us about 30 min of calculations with an ordinary lap-top, which is a significant decrease in the calculation time compared to analogous calculations by traditional methods even using supercomputers.

(b) *Four – atomic molecule.* As an illustration of the application of the above discussed approach to a more complicated molecular

⁶ In Ref. [49] the PES parameters have been determined on the basis of experimental band centers of only one H₂S isotopic species. Moreover, the breakdown of the Born–Oppenheimer approximation was taken into account. As a consequence, all values of the differences, $\Delta = \nu_{exp.} - \nu_{calc.}$, in column 7 of Table 2 are smaller than in our case.

Table 2
Band centers of the H₂S molecule (in cm⁻¹).

Band	Value	Ref.	Δ , our	Δ , [29]	Δ , [48]	Δ , [49]	Δ , [50]
1	2	3	4	5	6	7	8
ν_2	1182.5769	[53]	0.41	-0.6	0.14	-0.33	-8.82
$2\nu_2$	2353.9655	[54]	0.02	-1.0	0.14	-0.19	-21.43
ν_1	2614.4074	[54]	0.61	0.2	-0.25	0.02	-5.64
ν_3	2628.4552	[54]	-0.59	0.4	-0.10	-0.34	-2.19
$3\nu_2$	3513.7909	[55]	-0.50	-1.6	0.62	0.05	-38.51
$\nu_1 + \nu_2$	3779.1667	[55]	1.44	1.3	0.12	0.13	-15.78
$\nu_2 + \nu_3$	3789.2693	[55]	-0.50	0.0	-0.39	0.08	-10.88
$4\nu_2$	4661.6770	[56]	-0.36	-2.8	2.20	0.11	-60.32
$\nu_1 + 2\nu_2$	4932.6992	[56]	1.21	3.0	-0.21	0.35	-29.95
$2\nu_2 + \nu_3$	4939.1044	[56]	-0.68	0.2	-0.72	0.44	-23.35
$2\nu_1$	5144.9862	[56]	0.61	0.6	-0.53	-0.31	-7.77
$\nu_1 + \nu_3$	5147.2205	[56]	-1.47	0.5	0.10	-0.05	-6.78
$2\nu_3$	5243.1014	[56]	-0.19	-0.3	-0.28	-0.43	-7.34
$5\nu_2$	5797.2372	[57]	1.09		5.41	0.61	-87.26
$\nu_1 + 3\nu_2$	6074.5824	[57]	0.15	5.0	0.08	-0.11	-48.57
$3\nu_2 + \nu_3$	6077.5942	[57]	-0.46	0.7	-0.46	-0.34	-39.96
$2\nu_1 + \nu_2$	6288.1456	[57]	1.29	1.3	-0.22	0.25	-18.58
$\nu_1 + \nu_2 + \nu_3$	6289.1741	[57]	-0.96	0.9	0.18	0.47	-17.93
$\nu_2 + 2\nu_3$	6385.1381	[57]	0.32	1.0	-0.75		-17.53
$2\nu_1 + 2\nu_2$	7419.9184	[58]	0.90	3.3	-0.11		-32.98
$\nu_1 + 2\nu_2 + \nu_3$	7420.0930	[58]	-1.07	2.1	0.17	0.46	-32.91
$3\nu_1$	7576.3833	[58]	-0.09	1.0	-0.07	-0.04	-8.96
$2\nu_1 + \nu_3$	7576.5466	[58]	-0.59	1.0	0.13	0.06	-8.86
$\nu_1 + 2\nu_3$	7752.2638	[58]	-1.71	-1.3	-0.14	-0.39	-14.29
$3\nu_3$	7779.3208	[58]	0.92	-0.7	-0.28	-0.48	-7.97
$3\nu_1 + \nu_2$	8697.142	[59]	-0.24	0.5	0.56	0.39	-22.56
$2\nu_1 + \nu_2 + \nu_3$	8697.155	[59]	-0.56	0.5	0.68	0.44	-22.55
$2\nu_1 + 4\nu_2$	9647.167	[60]	-0.27	7.3	2.10		-74.66
$\nu_1 + 4\nu_2 + \nu_3$	9647.167	[60]	-0.41	7.3	2.10		-76.00
$2\nu_1 + 2\nu_2 + \nu_3$	9806.667	[60]	-0.78	2.3	1.31		-39.93
$3\nu_1 + 2\nu_2$	9806.773	[60]	-0.70	2.4	1.27		-39.83
$3\nu_1 + \nu_3$	9911.023	[60]	0.27	1.3	0.27	0.32	-9.80
$4\nu_1$	9911.023	[60]	0.39	1.3	0.25	0.33	-9.50
$4\nu_1 + \nu_2$	11008.696	[61]	-0.56	1.9		-0.18	-27.02
$3\nu_1 + \nu_2 + \nu_3$	11008.696	[61]	0.66	1.9		-0.17	-27.02
$\nu_1 + 3\nu_2 + 2\nu_3$	11097.161	[61]	0.51	-0.4			-65.66
$5\nu_1$	12149.458	[62]	1.51	-0.3			-9.45
$4\nu_1 + \nu_3$	12149.458	[62]	1.49	-0.3			-9.45
$3\nu_1 + 2\nu_3$	12524.637	[63]	0.47	-1.6			-15.14
$2\nu_1 + 3\nu_3$	12525.214	[63]	-1.05	-1.6			-14.80
$6\nu_1$	14284.705	[64]	0.72	6.0			-15.82
$5\nu_1 + \nu_3$	14284.705	[64]	0.68	6.0			-15.82
$5\nu_1 + 2\nu_2$	14291.122	[64]	0.49	-20.2			-52.53
$4\nu_1 + 2\nu_2 + \nu_3$	14291.122	[64]	0.49	-20.3			-52.53
$7\nu_1$	16334.162	[65]	-1.09	6.7			-11.23
$6\nu_1 + \nu_3$	16334.162	[65]	-1.09	6.7			-11.23

system we discuss here the four-atomic formaldehyde molecule. Because we speak only about the illustration of the efficiency of the derived approach, we will use the potential function of the H₂CO molecule in the form of Eqs. (17)–(21) (not in the form of Eq. (4)), which are suitable for consideration of separate isotopic species of a molecule. The problem of determination of the intramolecular potential function of the formaldehyde molecule on the basis of experimental information about all of its isotopic species will be considered in detail in a forthcoming paper [68].⁷

Because the H₂CO molecule has six vibrational coordinates: (1) two equivalent H–C stretching vibrations; (2) one C=O stretching vibration; (3) two equivalent H–C–O in-plane bending vibrations; and (4) one out-of-plane (H–C–H)–O variable, the discussion of Section 2 is totally valid for the considered situation. In this case, the “kinetic” part of the vibrational Hamiltonian will have the form:

⁷ As was mentioned above, in Ref. [52] the suggested method is applied to the determination of the PES of more complicated five-atomic methane molecule.

Table 3
Band centers of the D₂S molecule (in cm⁻¹)^a.

Band	Value	Δ, our	Δ, [29]	Δ, [48]
1	2	3	4	5
v ₂	855.40416	0.34	-0.4	-0.02
v ₁	1896.43154	0.38	-0.5	0.58
v ₃	1910.18375	-0.23	0.3	0.05
3v ₂	2549.07336	0.29	-0.4	-0.33
v ₁ + v ₂	2742.66570	0.86	-0.2	0.33
v ₂ + v ₃	2754.45192	0.03	0.1	-0.26
2v ₂ + v ₃	3593.12888	0.23	-0.3	-0.72
2v ₁	3753.470	-0.63	-0.7	0.67
v ₁ + v ₃	3757.45948	-0.38	-0.1	0.85
2v ₃	3809.154	0.01	-0.4	0.36
v ₁ + 3v ₂	4417.95894	0.44	1.7	-0.56
3v ₂ + v ₃	4426.08293	0.58	0.9	-1.08
2v ₁ + v ₂	4589.226	0.56	-0.2	0.36
v ₁ + v ₂ + v ₃	4592.18104	-0.34	0.0	0.45
v ₂ + 2v ₃	4643.477	0.40	0.1	-0.08
v ₁ + 2v ₂ + v ₃	5421.3007	-0.53	0.9	-0.11
3v ₁	5560.15	0.11	-0.5	1.00
2v ₁ + v ₃	5560.74	-0.14	-0.4	1.14
v ₁ + 2v ₃	5647.13	-1.43	-1.9	1.64
3v ₃	5672.89	0.82	-0.9	0.15
3v ₁ + v ₂	6384.63	-0.47	-0.4	0.75
2v ₁ + v ₂ + v ₃	6384.99	-0.71	-0.3	0.87

^a Experimental band centers from Ref. [66].

Table 4
Band centers of the HDS molecule (in cm⁻¹)^a.

Band	Value	Δ, our	Δ, [48]
1	2	3	4
v ₂	1032.71556	0.19	0.06
v ₁	1902.85624	0.01	0.15
2v ₂	2056.96580	-0.36	0.10
v ₃	2621.45594	0.17	-0.33
v ₁ + v ₂	2924.97773	-0.14	0.10
3v ₂	3072.49232	-0.70	0.52
v ₂ + v ₃	3634.33224	0.73	-1.14
2v ₁	3756.32989	-0.28	0.31
v ₁ + 2v ₂	3938.63701	-0.60	0.03
v ₁ + v ₃	4522.65030	0.85	-0.55
2v ₂ + v ₃	4638.86437	-2.09	-1.78
2v ₁ + v ₂	4767.69431	-1.83	-0.59
2v ₃	5147.35539	0.13	-0.61
v ₁ + v ₂ + v ₃	5525.26664	2.16	-1.01
3v ₁	5560.54225	-0.87	0.59
v ₂ + 2v ₃	6139.73928	2.54	1.56
v ₁ + 2v ₃	7047.15309	0.83	-0.73
2v ₂ + 2v ₃	7123.89641	-1.29	-2.36
3v ₃	7577.84009	-0.04	-0.38
v ₂ + 3v ₃	8548.90007	0.94	-1.28

^a Experimental band centers from Ref. [67].

$$T_1 = - \sum_{i=1,5} \frac{\hbar^2}{2\mu_{C-H}} \frac{\partial^2}{\partial R_i^2} - \frac{\hbar^2}{2\mu_{C-O}} \frac{\partial^2}{\partial R_2^2} - \sum_{j=3,4,6} \frac{\hbar^2}{2} \frac{\partial^2}{\partial R_j^2}. \quad (39)$$

In Eq. (39) indices 1 and 5 belong to the C–H stretches, index 2 belongs to the C–O stretch, indices 3 and 6, and 4 belong to in-plane and out-of-plane deformations, respectively. All the values here correspond to the values introduced in Section 2. The coordinates R_2 , R_3 , and a combination $R_1 + R_5$ are totally symmetric (A_1). Coordinate R_4 is of B_1 symmetry and coordinate R_6 and the combination $R_1 - R_5$ are transformed in accordance with the B_2 irreducible representation of the C_{2v} symmetry group. Taking into account the symmetry properties, the potential function of the type of Eqs. (17)–(21) can be easily constructed. For our testing calculations the cubic part of the potential function is not suitable, and we present here only its quadratic, quartic, and sextic parts:

$$V = V_0 + V_1(y_1, y_5, y_2) + V_2(R_3, R_4, R_6) + V_3(y_1, y_5, y_2; R_3, R_4, R_6); \quad (40)$$

where

$$V_0 = D_{H-C}(y_1^2 + y_5^2) + D_{C-O}y_2^2 + \sum_i \frac{(2\pi c\omega_i)^2}{2} R_i^2, \quad (41)$$

$$V_1(y_1, y_5, y_2) = \frac{1}{24} a_{1111}(y_1^4 + y_5^4) + \frac{1}{4} a_{1155} y_1^2 y_5^2 + \frac{1}{6} a_{1115} y_1 y_5 (y_1^2 + y_5^2) + \frac{1}{24} a_{2222} y_2^4 + \frac{1}{6} a_{1112} (y_1^3 + y_5^3) y_2 + \frac{1}{2} a_{1152} y_1 y_5 (y_1 + y_5) y_2 + \frac{1}{4} a_{1122} (y_1^2 + y_5^2) y_2^2 + \frac{1}{2} a_{1522} y_1 y_5 y_2^2 + \frac{1}{6} a_{1222} (y_1 + y_5) y_2^3 + \frac{1}{48} a_{12222} (y_1^2 + y_5^2) y_2^4 + \frac{1}{24} a_{152222} y_1 y_5 y_2^4 + \dots, \quad (42)$$

$$V_2(R_3, R_4, R_6) = \frac{1}{24} \sum_{i=3,4,6} a_{iii} R_i^4 + \frac{1}{4} \sum_{ij>i}^{3,4,6} a_{ijij} R_i^2 R_j^2 + \frac{1}{6!} \sum_{i=3,4,6} a_{iiii} R_i^6 + \frac{1}{48} \sum_{ij=3,4,6} a_{ijij} R_i^4 R_j^2 + \dots, \quad (43)$$

and

$$V_3(y_1, y_5, y_2; R_3, R_4, R_6) = \frac{1}{48} \sum_{i=3,4,6} a_{11iii} (y_1^2 + y_5^2) R_i^4 + \frac{1}{8} \sum_{ij>i}^{3,4,6} a_{11ijij} (y_1^2 + y_5^2) R_i^2 R_j^2 + \frac{1}{24} \sum_{i=3,4,6} a_{15iii} y_1 y_5 R_i^4 + \frac{1}{4} \sum_{ij>i}^{3,4,6} a_{15ijij} y_1 y_5 R_i^2 R_j^2 + \frac{1}{8} \sum_{i=3,4,6} a_{1122ii} (y_1^2 + y_5^2) y_2^2 R_i^2 + \frac{1}{4} \sum_{i=3,4,6} a_{1522ii} y_1 y_5 y_2^2 R_i^2 + \frac{1}{48} \sum_{i=3,4,6} a_{22iiii} (y_1^2 + y_5^2) R_i^4 + \frac{1}{8} \sum_{ij>i}^{3,4,6} a_{22ijij} y_2^2 R_i^2 R_j^2 + \frac{1}{48} \sum_{i=3,4,6} a_{2222ii} R_i^4 R_i^2 + \dots \quad (44)$$

To realize the above derived method of the PES determination it is necessary to have initial experimental data for the vibrational band centers. In the present case we use 279 vibrational band centers from Ref. [69], most of which have been obtained from dispersed fluorescence spectra with an accuracy of 1.0–2.0 cm⁻¹. In

Table 5
Potential parameters for the H₂CO molecule.^a

Parameter	Value	Parameter	Value
1	2	1	2
$a_{H-C}/\text{\AA}^{-1}$	1.964 (50)	a_{3333}/aJ	-0.000030 (14)
$a_{C-O}/\text{\AA}^{-1}$	1.985 (22)	a_{3344}/aJ	0.000026 (23)
D_{H-C}/aJ	0.60496 (71)	a_{3355}/aJ	-0.00503 (96)
D_{C-O}/aJ	1.71507 (84)	a_{3366}/aJ	-0.000490 (49)
ω_3/cm^{-1}	1533.5 (49)	a_{4444}/aJ	0.00000 (38)
ω_4/cm^{-1}	1178.3 (12)	a_{4455}/aJ	-0.00312 (62)
ω_6/cm^{-1}	1258.7 (40)	a_{4466}/aJ	0.000222 (53)
a_{1111}/aJ	0.140 (37)	a_{5555}/aJ	0.141 (15)
a_{1122}/aJ	-0.442 (65)	a_{5566}/aJ	0.00057 (20)
a_{1133}/aJ	-0.00503 (53)	a_{6666}/aJ	-0.000026 (12)
a_{1144}/aJ	-0.00306 (32)	a_{333344}/aJ	0.000002 (2)
a_{1155}/aJ	-0.1057 (86)	a_{333366}/aJ	0.000025 (11)
a_{2233}/aJ	-0.0126 (33)	a_{334466}/aJ	-0.000131 (14)
a_{2244}/aJ	-0.01333 (82)	a_{336666}/aJ	-0.000011 (10)
a_{2255}/aJ	-0.443 (78)	a_{444444}/aJ	-0.000032 (10)
a_{2266}/aJ	0.00710 (58)	a_{444466}/aJ	-0.000012 (3)
$r_{C-H}^e/\text{\AA}^b$	1.1033		
$r_{C-O}^e/\text{\AA}^b$	1.2096		
α_e/deg^b	116.19		

^a Uncertainties in parentheses are one standard errors.

^b Constrained to the value from Ref. [3].

this case, for experimental band centers the maximum values of the vibrational quantum numbers are $\nu_4^{\max} = 10$, $\nu_2^{\max} = 6$, $\nu_3^{\max} = 3$, $\nu_6^{\max} = 5$, and $\nu_7^{\max} = \nu_2^{\max} = 2$.

The fit procedure with the above mentioned 279 experimental band centers leads to the set of 35 parameters (they are presented in Table 5) that reproduce the initial experimental data with a rms deviation of 1.8 cm^{-1} , which is comparable with the experimental uncertainties.

7. Conclusion

As a summary of the discussion in the present contribution we conclude that the very simple suggested Hamiltonian model, which creates a good basis for the construction and subsequent diagonalization of large matrices, allows us to considerably simplify the realization of the procedure of determination of the PES in comparison with more cumbersome standard methods. It gives results that are not worse than those given by other methods for three- and four-atomic molecules and opens the possibility for a successful solution of analogous problems for molecules with a larger number of atoms.

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Appendix 1

For the XY_2 (C_{2v}) molecule (see, Fig. 1) the relationship between the bond lengths, r_N ($N = 1, 3$), and the interbond angles, α , on the one hand, and the coordinates, Q_i , on the other hand, have the following form:

$$r_N \equiv r_{2-N} = \left\{ \sum_{\beta} (r_{2\beta} - r_{N\beta})^2 \right\}^{1/2} \quad (45)$$

and

$$\cos \alpha = \frac{\sum_{\beta} r_{1\beta} r_{3\beta}}{r_1 r_3}; \quad (46)$$

where $r_{N\beta}$ are the instantaneous Cartesian coordinates of the nuclei. In this case, it is possible to obtain the following formulas for the coefficients, C_{λ}^N , $C_{\lambda\mu}^N$, and $C_{\lambda\mu\nu}^N$ from Eq. (6):

$$C_{\lambda}^N = \frac{1}{r_e} \sum_{\beta} (r_{N\beta}^e - r_{2\beta}^e) (m_N^{-1/2} l_{N\beta\lambda} - m_2^{-1/2} l_{2\beta\lambda}), \quad (47)$$

$$C_{\lambda\mu}^N = \frac{1}{r_e} (b_{\lambda\mu}^N - C_{\lambda}^N C_{\mu}^N), \quad (48)$$

$$C_{\lambda\mu\nu}^N = \frac{1}{r_e^2} (3C_{\lambda}^N C_{\mu}^N C_{\nu}^N - C_{\lambda}^N b_{\mu\nu}^N - C_{\mu}^N b_{\lambda\nu}^N - C_{\nu}^N b_{\lambda\mu}^N); \quad (49)$$

where

$$b_{\lambda\mu}^N = \sum_{\beta} (m_N^{-1/2} l_{N\beta\lambda} - m_2^{-1/2} l_{2\beta\lambda}) (m_N^{-1/2} l_{N\beta\mu} - m_2^{-1/2} l_{2\beta\mu}). \quad (50)$$

Here, m_N ($N = 1, 3$) is the mass of the nucleus, Y_N , m_2 is the mass of the nucleus, X, r_e is the equilibrium bond length, and $r_{N\beta}^e$ and $r_{2\beta}^e$ ($\beta = x, y, z$) are the equilibrium Cartesian coordinates of the nuclei in the molecular fixed coordinate system. The dimensions of the coefficients C_{λ}^N are: $[C_{\lambda}^N] = \text{g}^{-1/2}$, $[C_{\lambda\mu}^N] = \text{g}^{-1} \text{cm}^{-1}$, and $[C_{\lambda\mu\nu}^N] = \text{g}^{-3/2} \text{cm}^{-2}$.

Analogously, for the coefficients, C_{λ} , $C_{\lambda\mu}$, and $C_{\lambda\mu\nu}$, one can obtain from Eq. (7):

$$C_{\lambda} = \frac{1}{\sin \alpha_e} \frac{1}{r_e} \{ j^{13} (C_{\lambda}^1 + C_{\lambda}^3) - A_{\lambda}^{13} \}; \quad (51)$$

where we denote

$$j^{13} = \frac{1}{r_e^2} \sum_{\beta} (r_{1\beta}^e - r_{2\beta}^e) (r_{3\beta}^e - r_{2\beta}^e), \quad (52)$$

$$A_{\lambda}^{13} = \frac{1}{r_e} \sum_{\beta} \left\{ (m_1^{-1/2} l_{1\beta\lambda} - m_2^{-1/2} l_{2\beta\lambda}) (r_{3\beta}^e - r_{2\beta}^e) + (m_3^{-1/2} l_{3\beta\lambda} - m_2^{-1/2} l_{2\beta\lambda}) (r_{1\beta}^e - r_{2\beta}^e) \right\}, \quad (53)$$

and α_e is the value of the equilibrium interbond angle.

Higher order coefficients, $C_{\lambda\mu}$ and $C_{\lambda\mu\nu}$, have considerably more complicated forms:

$$C_{\lambda\mu} = -\frac{1}{\sin \alpha_e} P_{\lambda\mu}^{13} - \frac{\cos \alpha_e}{\sin^3 \alpha_e} P_{\lambda}^{13} P_{\mu}^{13} \quad (54)$$

and

$$C_{\lambda\mu\nu} = -\frac{1}{\sin \alpha_e} P_{\lambda\mu\nu}^{13} - \frac{\cos \alpha_e}{\sin^3 \alpha_e} (P_{\lambda}^{13} P_{\mu\nu}^{13} + P_{\mu}^{13} P_{\lambda\nu}^{13} + P_{\nu}^{13} P_{\lambda\mu}^{13}) - \frac{1 + 2 \cos^2 \alpha_e}{\sin^5 \alpha_e} P_{\lambda}^{13} P_{\mu}^{13} P_{\nu}^{13}; \quad (55)$$

where

$$P_{\lambda}^{13} = \frac{1}{r_e} A_{\lambda}^{13} + r_e^2 j^{13} F_{\lambda}^{13}, \quad (56)$$

$$P_{\lambda\mu}^{13} = \frac{1}{r_e^2} b_{\lambda\mu}^{13} + r_e (A_{\lambda}^{13} F_{\mu}^{13} + A_{\mu}^{13} F_{\lambda}^{13}) + r_e^2 j^{13} F_{\lambda\mu}^{13}, \quad (57)$$

and

$$P_{\lambda\mu\nu}^{13} = (b_{\lambda\mu\nu}^{13} + b_{\lambda\nu}^{13} F_{\mu}^{13} + b_{\mu\nu}^{13} F_{\lambda}^{13}) + r_e (A_{\lambda}^{13} F_{\mu\nu}^{13} + A_{\mu}^{13} F_{\lambda\nu}^{13} + A_{\nu}^{13} F_{\lambda\mu}^{13}) + r_e^2 F_{\lambda\mu\nu}^{13}, \quad (58)$$

with

$$b_{\lambda\mu}^{13} = \sum_{\beta} \left\{ (m_1^{-1/2} l_{1\beta\lambda} - m_2^{-1/2} l_{2\beta\lambda}) (m_3^{-1/2} l_{3\beta\mu} - m_2^{-1/2} l_{2\beta\mu}) \right\}, \quad (59)$$

Table A1

Numerical values of the first and second order C-coefficients for the H_2S molecule.

Parameter	Value	Parameter	Value	Parameter	Value
$C_1^1/\text{amu}^{-1/2}$	0.714444	$C_{11}^1/\text{amu}^{-1}\text{Å}^{-1}$	0.000179	$C_{23}^3/\text{amu}^{-1}\text{Å}^{-1}$	-0.011663
$C_1^3/\text{amu}^{-1/2}$	0.714444	$C_{11}^3/\text{amu}^{-1}\text{Å}^{-1}$	0.000179	$C_{33}^1/\text{amu}^{-1}\text{Å}^{-1}$	0.000355
$C_{33}^1/\text{amu}^{-1/2}$	-0.715747	$C_{12}^1/\text{amu}^{-1}\text{Å}^{-1}$	-0.002619	$C_{33}^3/\text{amu}^{-1}\text{Å}^{-1}$	0.000355
$C_3^3/\text{amu}^{-1/2}$	0.715747	$C_{12}^3/\text{amu}^{-1}\text{Å}^{-1}$	-0.002619	$C_{11}^2/\text{amu}^{-1}\text{Å}^{-2}$	-0.007827
$C_{12}^1/\text{amu}^{-1/2}$	0.026651	$C_{13}^3/\text{amu}^{-1}\text{Å}^{-1}$	-0.000080	$C_{12}^2/\text{amu}^{-1}\text{Å}^{-2}$	0.572828
$C_2^3/\text{amu}^{-1/2}$	0.026651	$C_{13}^1/\text{amu}^{-1}\text{Å}^{-1}$	0.000080	$C_{13}^3/\text{amu}^{-1}\text{Å}^{-2}$	0.000000
$C_{11}^2/\text{amu}^{-1/2}\text{Å}^{-1}$	0.007318	$C_{22}^1/\text{amu}^{-1}\text{Å}^{-1}$	0.383436	$C_{22}^2/\text{amu}^{-1}\text{Å}^{-2}$	0.042748
$C_2^2/\text{amu}^{-1/2}\text{Å}^{-1}$	-1.071454	$C_{22}^3/\text{amu}^{-1}\text{Å}^{-1}$	0.383436	$C_{23}^2/\text{amu}^{-1}\text{Å}^{-2}$	0.000000
$C_3^2/\text{amu}^{-1/2}\text{Å}^{-1}$	0.000000	$C_{23}^1/\text{amu}^{-1}\text{Å}^{-1}$	0.011663	$C_{33}^2/\text{amu}^{-1}\text{Å}^{-2}$	-0.034921

$$F_{\lambda}^{13} = \frac{1}{r_e} (D_{\lambda}^1 + D_{\lambda}^3), \quad (60)$$

$$F_{\lambda\mu}^{13} = \frac{1}{r_e} (D_{\lambda\mu}^1 + D_{\lambda\mu}^3) + (D_{\lambda}^1 D_{\mu}^3 + D_{\mu}^1 D_{\lambda}^3), \quad (61)$$

$$F_{\lambda\mu\nu}^{13} = \frac{1}{r_e} (D_{\lambda\mu\nu}^1 + D_{\lambda\mu\nu}^3) + (D_{\lambda}^1 D_{\mu\nu}^3 + D_{\lambda}^3 D_{\mu\nu}^1 + D_{\mu}^1 D_{\lambda\nu}^3 + D_{\mu}^3 D_{\lambda\nu}^1 + D_{\nu}^1 D_{\lambda\mu}^3 + D_{\nu}^3 D_{\lambda\mu}^1), \quad (62)$$

and, for $N = 1, 3$:

$$D_{\lambda}^N = -\frac{1}{r_e^2} C_{\lambda}^N, \quad (63)$$

$$D_{\lambda\mu}^N = -\frac{1}{r_e^2} C_{\lambda\mu}^N + \frac{2}{r_e^3} C_{\lambda}^N C_{\mu}^N, \quad (64)$$

$$D_{\lambda\mu\nu}^N = -\frac{1}{r_e^2} C_{\lambda\mu\nu}^N + \frac{2}{r_e^3} (C_{\lambda}^N C_{\mu\nu}^N + C_{\mu}^N C_{\lambda\nu}^N + C_{\nu}^N C_{\lambda\mu}^N) - \frac{6}{r_e^4} C_{\lambda}^N C_{\mu}^N C_{\nu}^N. \quad (65)$$

The dimensions of coefficients C_{\dots} are: $[C_{\lambda}] = g^{-1/2} \text{ cm}^{-1}$, $[C_{\lambda\mu}] = g^{-1} \text{ cm}^{-2}$, and $[C_{\lambda\mu\nu}] = g^{-3/2} \text{ cm}^{-3}$.

The formulas we presented here, in spite of their difficulty, are simple enough in applications. It is important to note that the presence of symmetry in a molecule leads to the presence of symmetry in the C-coefficients as well. To illustrate this, Table A1 presents numerical values of the first- and second-order C-coefficients for the H_2S molecule. The values of the equilibrium parameters, r_e and α_e , necessary for the present calculations were taken from Ref. [29]. The transformation coefficients, $l_{N\beta\lambda}$, were obtained using the parameters f_{rr} , $f_{rr'}$, f_{rz} , and f_{zz} from Ref. [29]. The masses of nuclei H and S were taken from Ref. [39]. The symmetry of the C-coefficients can be clearly seen.

Appendix 2

Here, for illustration, we present in analytical form the main coefficients, f_{λ}^N ($N = 1, 2, \lambda = 1, 3$) (see Table A2), of Eq. (12). If we take into account the general equations of Appendix 1, it is possible to show that for these coefficients the following relations are valid:

$$f_1^1 = f_3^2 = 1 \quad (66)$$

Table A2

Numerical values (in $\text{amu}^{-1/2}$) of the first order C-coefficients for some axially symmetric molecules.^a

Parameter	Value				
	PH ₃	AsH ₃	CH ₃ D	CHD ₃	CH ₄
1	2	3	4	5	6
C_{λ}^1	-0.58259	-0.57799	-0.58211	-0.41568	0.49806
$C_{\lambda\mu}^1$	-0.58259	-0.57799	-0.58211	-0.41568	0.49806
$C_{\lambda\mu\nu}^1$	-0.58259	-0.57799	-0.58211	-0.41568	0.49806
C_{λ}^2	-0.82718	-0.63549	0.85723	0.63642	0.52488
$C_{\lambda\mu}^2$	0.41359	0.40945	-0.42862	-0.31821	-0.52488
$C_{\lambda\mu\nu}^2$	0.41359	0.40945	-0.42862	-0.31821	-0.52488
C_{λ}^3	0.00000	0.00000	0.00000	0.00000	-0.52488
$C_{\lambda\mu}^3$	0.71636	0.70919	-0.74239	-0.55115	0.52488
$C_{\lambda\mu\nu}^3$	-0.71636	-0.70919	0.74239	0.55115	-0.52488
C_{λ}^4			0.00000	0.00000	0.52488
$C_{\lambda\mu}^4$			-0.03211	0.04447	-0.52488
$C_{\lambda\mu\nu}^4$			-0.03211	0.04447	-0.52488
C_{λ}^5			-0.03211	0.04447	0.52488
$C_{\lambda\mu}^5$			-0.03211	0.04447	0.52488
$C_{\lambda\mu\nu}^5$			-0.03211	0.04447	0.52488
C_{λ}^6			-0.75617	-1.03592	0.52488

^a Only C_N^{λ} coefficients which are connected with the stretching vibrational modes and are important for the construction of the α -coefficients from Eqs. (25) and (30) are presented. The values of all the other C_N^{λ} coefficients are considerably smaller.

and

$$f_3^1 = f_1^2 = \frac{\cos \alpha_e \sin \gamma \sqrt{M+2m} + \sin \alpha_e \cos \gamma \sqrt{M} - \sqrt{M+2m} \sin^2 \alpha_e}{\cos \alpha_e \sin \gamma \sqrt{M+2m} + \sin \alpha_e \cos \gamma \sqrt{M} + \sqrt{M+2m} \sin^2 \alpha_e}. \quad (67)$$

All other coefficients in the general relations in Eq. (12) have considerably more complicated forms.

It is important that the $f_3^1 = f_1^2$ coefficients depend not only on the nuclear masses, but also on the value of the equilibrium interbond angle (α_e in Eq. (67) is half of the equilibrium interbond angle) and the ambiguity parameter, $\sin \gamma$. It is interesting to remark that for near local mode molecules (which satisfy the conditions, $M \gg m$, $\sin \alpha_e \approx 1/\sqrt{2}$, and $\sin \gamma \approx 1/\sqrt{2}$) the numerator of Eq. (61) is close to zero. In the general case, these conditions are not valid; however, the presence of the ambiguity parameter, $\sin \gamma$, in Eq. (67) allows one to minimize the values of the coefficients f_3^1 and f_1^2 .

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