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ON THE METHOD OF CORRECT DETERMINATION OF EIGENVALUES OF A TRUNCATED HAMILTONIAN MATRIX ON THE EXAMPLE OF A MORSE OSCILLATOR

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A method of precise determination of the eigenvalues of energies of the molecular Hamiltonian based on high-order perturbation theory has been developed and implemented for a diatomic molecule. The proposed method makes it possible not only to obtain the energy values, but also to estimate the accuracy of their prediction and the applicability limits for the employed model. Numerical calculations have been performed for the extended Morse oscillator with corrections for the potential functions up to the sixth power of the Morse coordinate. The results obtained are compared with the results of calculation for the model of the truncated Hamiltonian matrix. The possibilities of application of the method are analyzed compared to other approaches to the determination of the potential functions for polyatomic molecules.

Keywords: intramolecular potential function, Morse oscillator, eigenvalues of the molecular Hamiltonian.

INTRODUCTION

The problem of determining the intramolecular potential function (IPF) of a molecule (generally, polyatomic) is one of the most urgent modern problems of chemical physics, since quantitative information on the IPF of molecules provides the basis for solving numerous purely academic and applied problems. Because of the limited volume of publications, it is impossible to present a comprehensive review on the current state of the art of this problem. We note only that this problem has been considered for many decades and still remains urgent owing to its complexity not only (and not so much) because of the lack of methods and models (the theoretical basis) of its solution, but also because of the possibilities of its practical implementation (computational power of computers). Bearing in mind a constant growth of resources (first of all, random access memory and computational rate) of modern computers, the constant increase in accuracy of the so-called *ab initio* calculations [1–6] is not surprising. However, it should be noted that the results of even the most accurate calculations are only *points* in the multidimensional spatial internuclear distances and angles between the bonds. To realize on this basis the intramolecular potential function, a Hamiltonian model (a model of the potential function) with the parameters defined by fitting to *ab initio* calculated points and experimental data is necessary first of all. Moreover, even the most accurate model does not yet guarantee the correct determination of the sought-after intramolecular function for the simple reason that the final result depends directly on the method of determining the model parameters. Here it is possible to mention: 1) various modifications of perturbation theory [7–12], 2) classical variational method of quantum mechanics [13–15], and 3) construction and subsequent diagonalization of the Hamiltonian matrix in the basis of infinitely-dimensional functions according to the general principles of quantum mechanics [13–15]. The last method requires (for its practical implementation) truncation of the constructed (generally infinitely dimensional) matrices to reasonable dimensions with allowance for the capabilities of the employed computers. It should also be taken into account that in the process of determining the model Hamiltonian

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parameters, in any case it is necessary to use the variational procedure; for this reason, the construction of a high-dimensional matrix and its subsequent diagonalization are multiply repeated. This imposes certain restrictions on the dimensions of such matrices. From our point of view, at present the repeated construction (100–1000 iterations) and diagonalization of matrices with dimensions $n\cdot(10^4–10^5)$ are already impossible owing to huge computational time. It should be borne in mind that according to the principles of quantum mechanics [13–15], both the classical variational approach and the use of the *truncated* matrices permit a correct description of only some examined states (for example, in approach (3) it is possible to consider as those no more than the third of the lowest states taken into account in the construction of the state matrix). Obviously, these conditions are more than favorable for a study of diatomic molecules for a description of their real spectra corresponding up to several tens excited vibrational states. However, they become inacceptable for polyatomic molecules.

Main objectives of the present work are the development and practical implementation of the computational scheme which permits correct determination of the eigenvalues of the Hamiltonian.

MODEL OF A MOLECULE AND VIBRATIONAL ENERGY SPECTRUM

Note that the problems of correctness and accuracy of results of *ab initio* calculations and correctness of the model used for a description of the IPF *points* obtained by *ab initio* calculations are not discussed here (it is assumed that those and others are quite physical and adequate). As a model of a diatomic molecule, we consider the perturbed Morse oscillator [16]

$$\hat{H} = -\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2} + Dy^2 + a_3 y^3 + a_4 y^4 + \cdots, \tag{1}$$

where $y = 1 - e^{-a(r-r_e)}$ is the coordinate, a is the Morse parameter, and D is the dissociation energy. Strictly speaking, the total number of functions in the Morse oscillator model is limited; therefore, the basis of the Morse functions is incomplete [17, 18]. However, for the present work, as follows from considerations below, the given circumstance is not an obstacle. The problem can be solved, for example, using the results obtained in [18].

As in the general problem of determining the eigenvalues of the Hamiltonian given by Eq. (1) and of comparative analysis presented below, the first step is the construction of the Hamiltonian matrix given by Eq. (1). To solve this problem, we use the results obtained in [19], where the eigenvalues of the molecular Hamiltonian for the model of the unperturbed Morse oscillator and the nonzero matrix elements in powers of the coordinate y were obtained in the form:

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

(the characteristic number of bounded states is $k = \sqrt{2\mu D}/a\hbar$),

$$\langle n|y|n\rangle = \langle n|y^2|n\rangle = \frac{1}{k}\left(n + \frac{1}{2}\right), \tag{3}$$

$$\langle n|y^3|n\rangle = \frac{3}{2k^2}\left(n + \frac{1}{2}\right)^2 - \frac{1}{8k^2} - \frac{n}{4k^3}(2n^2 + 3n + 1), \tag{4}$$

$$\langle n|y^4|n\rangle = \frac{3}{2k^2}\left(n + \frac{1}{2}\right)^2 + \frac{1}{8k^2} - \frac{n}{4k^3}(2n^2 + 3n + 3) - \frac{1}{4k^3}, \tag{5}$$

$$\left\langle m|y|n\right\rangle = \left\langle n|y|m\right\rangle = -\frac{1}{2ak}\left(m|n\right), \tag{6}$$

$$\left\langle m\left|y^2\right|n\right\rangle = \left\langle n\left|y^2\right|m\right\rangle = \left[\frac{1}{2ak}(j-1) - \frac{1}{4ak^2}j(2n+j+1)\right]\left(m|n\right), \tag{7}$$

$$\begin{gathered}\left\langle m\left|y^3\right|n\right\rangle = \left\langle n\left|y^3\right|m\right\rangle \\ = \left[-\frac{1}{4ak}(j-1)(j-2) + \frac{1}{8ak^2}(j-2)(2j+1)(2n+j+1)\right]\left(m|n\right),\end{gathered} \tag{8}$$

$$\begin{gathered}\left\langle m\left|y^4\right|n\right\rangle = \left\langle n\left|y^4\right|m\right\rangle \\ = \left[\frac{1}{12ak}(j-1)(j-2)(j-3) - \frac{1}{8ak^2}(j-1)(j^2-3j-2)(2n+j+1)\right]\left(m|n\right),\end{gathered} \tag{9}$$

and the multiplier

$$\left(m|n\right) = (-1)^j a\sqrt{\frac{(2k-2m-1)(2k-2n-1)m!\Gamma(2k-m)}{n!\Gamma(2k-n)}} \tag{10}$$

is defined for $m > n$ and $j = m - n$. With allowance for formulas (3)–(10), Hamiltonian matrix (1) can be easily constructed. However, a question arises on the parameters $a_3, a_4, \ldots$ entering the Hamiltonian. In principle, to perform a comparative analysis, it is sufficient to take reasonable values of all these parameters. We here use the parameters of the real HCl molecule borrowed from [20] and recalculated into the parameters of model (1).

The essence of the aforementioned analysis in this work consists in the following. For the HCl molecule (according to the theory of the Morse oscillator [16–19]), 24 vibrational states are located below the dissociation threshold. As a consequence, the maximum dimensions of the Hamiltonian matrix in this model are 24 × 24. The twenty four eigenvalues of Hamiltonian (1) in this model are determined by diagonalization of the matrix, and we call them *exact* energy values. It is obvious that for real problem, the Hamiltonian matrix has infinite dimensions, and important questions arise: Where the matrix should be truncated to solve the problem? What is the accuracy of the energy values obtained with this truncated matrix? And to what extent can we believe the predictions obtained based on this truncated matrix? Hence, a correct solution can be obtained only for the lower states of the system, and even energy values of the lower states depend strongly on the number of states taken into account in the matrix. Figure 1 shows plots of the dependence of the energies of the vibrational states for the model Hamiltonian of the HCl molecule studied in this work on the number of states taken into account in the matrix (the convergence to the exact value).

For example, it can be seen that with allowance for ten states, more or less correct are only five lower states. For the diatomic molecules (as already indicated above), this circumstance is not critical, since the number of the employed states can always be increased. However, if we consider only 10 main states per one vibrational degree of freedom, even for the smallest polyatomic molecules we obtain at least 10^3 lines and columns in the matrix. For a four-atomic molecule, the dimensions of the matrix will already be ($10^6 \times 10^6$), etc. (in this case, it becomes practically impossible to solve the problem, not mentioning the molecules with a greater number of atoms).

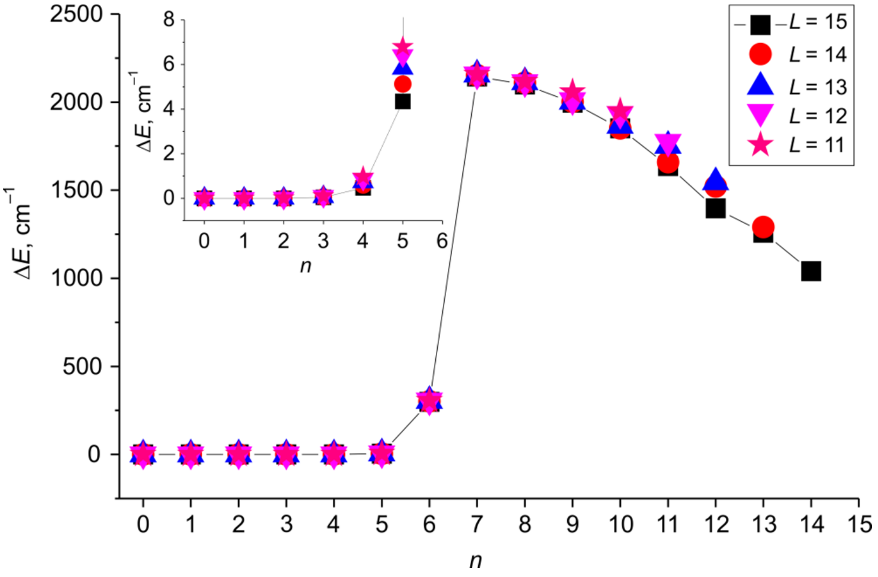

Fig. 1. Deviations of the energy values obtained by diagonalization of the truncated matrices (the figures indicate the dimensions) from the *exact* values obtained by diagonalization of the full-dimensional 24 × 24 matrix.

METHOD OF DETERMINING THE EIGENVALUES

In this work, we propose sufficiently simple and more exact procedure of determining the eigenvalues of the Hamiltonian matrix based on the analogy to the operator theory of perturbations in the matrix construction [10–12] that can be easily generalized to polyatomic molecules. Let us assume that using this or that model Hamiltonian, we construct the matrix H_{ij} for which the condition

$$H_{ii} >> H_{ij} \tag{11}$$

is satisfied, that is, the non-diagonal elements are much less than the diagonal ones (without loss of generality, it is possible to consider that H_{ij} ($i \neq j$) are values of the order k with respect to the values of H_{ii} (here κ is a small parameter). We take advantage of the transformation

$$\tilde{H} = G^{+} H G \tag{12}$$

with the operator G small compared to the unit unitary operator. It can be represented in the form

$$G = \exp\left(i \sum_{n=1}^{\infty} g_n (\kappa^n) \right) = 1 + i \sum_{n=1}^{\infty} g_n + \frac{1}{2} \left(i \sum_{n=1}^{\infty} g_n \right)^2 + \cdots, \tag{13}$$

where g_n are the Hermitian operators of the order of smallness κ^n. This circumstance allows us to represent G in the form of the Hausdorff series [13]. We now substitute Eq. (13) into Eq. (12) and consider that all three operator multipliers in the right-hand side represent the sum of terms of different orders of smallness. As a consequence, the operator $\tilde{H}$ in the left-hand site is also the sum of terms of different orders of smallness. Thus, in order that Eq. (12)

was correct, it is necessary and sufficient to level the terms of different orders of smallness in the right- and left-hand sites. As a consequence, we obtain

$$\tilde{H}_{ij}(\kappa^0) = H_{ij}(\kappa^0) \equiv H_{ij}\delta_{ij}, \tag{14}$$

$$\tilde{H}_{mm}(\kappa^0) = H_{mm}$$

for the zero order of smallness,

$$\tilde{H}_{ij}(\kappa^1) = (G^+HG)_{ij}(\kappa^1)$$

$$= \sum_{k,l} G^+_{ik} H_{kl} G_{lj}(\kappa^1) = \sum_{k,l} \delta_{ik}(H_{kk}\delta_{kl})\langle l|ig_1|j\rangle - \sum_{k,l}\langle l|ig_1|k\rangle(H_{kk}\delta_{kl})\delta_{lj} + \sum_{\substack{k\\ l\neq k}} \delta_{ik}H_{kl}\delta_{lj}, \tag{15}$$

$$\tilde{H}_{mm}(\kappa^1) = 0 \tag{16}$$

for the first order of smallness,

$$\tilde{H}_{mm}(\kappa^2) = \sum_{l\neq m} \frac{A_{ml}A_{lm}}{(A_{mm} - A_{ll})} \tag{17}$$

for the second order of smallness,

$$\tilde{H}_{mm}(\kappa^3) = \sum_{\substack{n\neq m\\ l\neq n,m}} \frac{A_{mn}A_{nl}A_{lm}}{(A_{mm} - A_{nn})(A_{mm} - A_{ll})} \tag{18}$$

for the third order of of smallness,

$$\tilde{H}_{mm}(\kappa^4) = \sum_{\substack{k,l,n\neq m\\ l\neq k,n}} \frac{A_{mk}A_{kl}A_{\mathrm{ln}}A_{nm}}{(A_{mm} - A_{kk})(A_{mm} - A_{ll})(A_{mm} - A_{nn})}$$
$$- \sum_{l,n\neq m} \frac{A_{ml}A_{lm}A_{\mathrm{mn}}A_{nm}}{2(A_{mm} - A_{ll})(A_{mm} - A_{nn})}\left(\frac{1}{A_{mm} - A_{ll}} + \frac{1}{A_{mm} - A_{nn}}\right) \tag{19}$$

for the fourth order of smallness (the procedure can be continued to refine further the eigenvalues of the Hamiltonian).

Since the unitary operator G is arbitrary, it is possible to choose from a set of unitary operators such the part $i(g_1)$ of which, according to formula (15), will nullify values of all non-diagonal elements of $\tilde{H}_{ij}(\kappa^1)$ of the order κ^1, the part $i(g_2)$, according to formula (15), will nullify values of all non-diagonal matrix elements $\tilde{H}_{ij}(\kappa^2)$ of the order κ^2, etc. Obviously, the diagonal elements with accuracies κ^1 and κ^2 will coincide with the eigenvalues of the initial matrix (the eigenvalues of the Hamiltonian). From the above discussed, the advantage of this approach is understandable over the simple diagonalization of the truncated Hamiltonian matrix: 1) this approach allows one to use *non-truncated* full matrix; 2) its applicability limits for a specific model of the molecule can be easily estimated; 3) its application for the excited states yields more correct results compared to the *truncated* matrix.

TABLES 1. Energy Values Obtained by Direct Diagonalization of Matrices of the Indicated Dimensions in Comparison with the Result Obtained by Application of the Scheme Given by Eqs. (12)–(19)

n	*L* = 24	*L* = 20	*L* = 10	*L* = 5	PT2	PT3	PT4
1	2	3	4	5	6	7	8
0	1480.225	1480.225	1480.225	1480.225	1480.225	1480.225	1480.225
1	4365.005	4365.005	4365.005	4365.005	4365.008	4365.005	4365.005
2	7142.623	7142.623	7142.630	7142.643	7142.627	7142.625	7142.622
3	9811.957	9811.961	9812.074	9813.752	9811.933	9811.994	9811.944
4	12371.248	12371.289	12372.306	12378.781	12371.030	12371.584	12371.086
5	14815.381	14816.245	14822.321		14814.966	14817.881	14814.306
6	16854.732	17132.751	17160.941		17128.723	17038.984	16994.460

Without intermediate calculations, we present the results obtained using procedures (12)–(19) for contributions of the lower states to the eigenvalues of Hamiltonian (1) and the corresponding results for the unitary operator G that allowed us to implement this procedure. In this case, we consider that in accordance with quantum mechanics (for example, see [13]), to determine the contributions to energy up to the order of smallness κ^{2n}, it is sufficient to know the eigenfunctions (in our case, the unitary operator *G*) to within the accuracy κ^{n}. As a result of calculations from formulas (12)–(19), for the operator G it was obtained that: 1) it can be assigned in the matrix form and 2) to determine the operator G, it is sufficient to know the matrix elements of the operators ig_n entering in it:

$$(ig_1)_{mn} = \frac{A_{mn}}{(A_{nn} - A_{mm})}, \tag{20}$$

$$(ig_2)_{mn} = \frac{1}{(A_{nn} - A_{mm})} \sum_{l \neq m,n} \frac{A_{ml} A_{\mathrm{ln}}}{2} \left(\frac{1}{A_{nn} - A_{ll}} + \frac{1}{A_{mm} - A_{ll}} \right). \tag{21}$$

Equations (16)–(19) allow the eigenvalues of the Hamiltonian matrix to be determined up to the fourth order of smallness. Because of the limited volume of the work, it is impossible to present contributions of higher orders of smallness.

As an example of application of the results obtained and for their comparison with the results obtained by diagonalization of the *truncated* matrix, we now consider the HCl molecule. The corresponding parameters of the Hamiltonian obtained by recalculation of the potential parameters from [20] are D = 35747.2 cm^{-1}, $a = 1.90102 \cdot 10^{9}$ cm^{-1}, $\rho = 1.298 \cdot 10^{-8}$ cm, a_3 = 1452.6 cm^{-1}, and a_4 = 241.32 cm^{-1}. We limited ourselves to six lower vibrational states sufficient for a comparative analysis.

The second column in Table 1 contains the *exact* values of the vibrational energy obtained by diagonalization of the *full* Hamiltonian matrix ((24×24) in our test calculation). Results of calculations with the *truncated* (20, 10, and 5 dimensional) matrix are presented in columns 3–5. Results of calculations by the scheme proposed in this work are shown in columns 6–8. As can be seen from columns 6–8, the energy values obtained by the proposed method are in better agreement with the exact values. With allowance for the corrections of higher order of smallness, a better agreement can be obtained.

CONCLUSIONS

The method of determining the eigenvalues of the molecular Hamiltonian which demonstrates the best convergence to the *exact* energy values compared to the energy values obtained by diagonalization of the *truncated* Hamiltonian matrix has been proposed, which is critical for investigation of polyatomic molecules. Compared to the application of the *truncated* matrices, the proposed method allowed us to consider contributions from non-diagonal elements disregarded in the incomplete set of the basic functions. The approach has also the advantages associated with resource consumption, since it has no restrictions on the dimensions of the initial matrix and obviates the necessity of its numerical diagonalization. The efficiency of the developed approach was demonstrated on the example of the diatomic molecule and can be important for solving direct and inverse problems for polyatomic molecules.

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