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Six-dimensional tunneling dynamics of internal rotation in hydrogen peroxide molecule and its isotopomers

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The six-dimensional torsion-vibration Hamiltonian of the H_2O_2 molecule and its H/D- and $^{18}O/^{16}O$-isotopomers is derived. The Hamiltonian includes the kinetic energy operator, which depends on the tunneling coordinate, and the potential energy surface represented as a quartic polynomial with respect to the small-amplitude transverse coordinates. Parameters of the Hamiltonian were obtained from DFT calculations of the equilibrium geometries, eigenvectors, and eigenfrequencies of normal vibrations at the stationary points corresponding to the ground state and both the *cis*- and *trans*-transition states, carried out with the B3LYP density functional and 6-311+G(2d,p) basis set. The quantum dynamics problem is solved using the perturbative instanton approach generalized for the excited states situated above the barrier top. Vibration-tunneling spectra are calculated for the ground state and low-lying excited states with energies below 2000 cm^{-1}. Strong kinematic and squeezed potential couplings between the large-amplitude torsional motion and bending modes are shown to be responsible for the vibration-assisted tunneling and for the dependence of tunneling splittings on the quantum numbers of small-amplitude transverse vibrations. Mode-specific isotope effects are predicted.

Key words: multidimensional tunneling, tunneling splittings, hydrogen peroxide, vibration-tunneling spectra.

The perturbative instanton approach (PIA)[1—9] is specially intended for quantitative description of multidimensional tunneling dynamics of molecules and reaction complexes beyond the conventional minimum energy path (MEP)[10—12] or linear reaction path[13—15] approximations in which the multidimensional Hamiltonian is replaced by the effective one-dimensional (1D) Hamiltonian. The PIA is based on the instanton formalism[15,16] proposed for solving the deep tunneling problem. Unlike traditionally used semiclassical methods, this approach allows construction of globally uniform vibrational wave functions for the ground and low-lying excited states in the classically forbidden region. Yet another advantage of the PIA is that the solution of the quantum dynamics problem does not require a great body of information. The parameters needed for recon-

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Table 1. Equilibrium geometric parameters and energies of stationary configurations (V) of H_2O_2 molecule at the potential energy minimum (I) and in the *trans*- (II) and *cis*-transition states (III)

Method	R_{OO}/Å			R_{OH}/Å			H—O—O angle/deg			φ*,	V/cm^{-1}		Reference
	I	*II*	*III*	*I*	*II*	*III*	*I*	*II*	*III*	*I*	*II*	*III*	
Experiment	1.464	—	—	0.965	—	—	99.4	—	—	111.9	387.1	2563	26
MP2 TZ2P+f	1.454	1.465	1.462	0.967	0.966	0.967	99.5	97.9	104.1	114.5	342	2684	17
GVB+1+2QC	1.462	1.472	1.471	0.964	0.963	0.963	99.6	98.3	104.1	113.4	371	2582	18
CCSD(T) cc-pVQZ	1.453	1.464	1.463	0.963	0.962	0.963	99.91	98.31	104.1	112.5	377	2545	28, 29
MP4SDQ 6-311+G(2dp)	1.452	1.463	1.461	0.966	0.965	0.966	100.1	98.6	104.6	115.7	394	2209	**
DFT B3LYP cc-pVTZ	1.452	1.463	1.461	0.965	0.965	0.965	100.4	98.8	104.9	114.0	329	2578	19
DFT B3LYP 6-311+G(2dp)	1.451	1.462	1.461	0.968	0.967	0.968	100.5	98.9	105.1	115.8	377	2797	**

* Listed are the values of the H—O—O—H dihedral angle given in degrees.
** This work.

structing the Hamiltonian are the electronic energy, equilibrium geometry, and the eigenvectors and eigenfrequencies of normal vibrations at the stationary points of the potential energy surface (PES). All of them can be obtained from quantum-chemical calculations.

In this work, we used the PIA for calculations of the vibration-tunneling spectra of hydrogen peroxide molecule and its isotopomers. The reasons for the choice of H_2O_2 molecule are as follows: (i) this is the simplest molecule in which internal rotation occurs; (ii) information obtained from quantum-chemical calculations (see above) is sufficient for constructing the Hamiltonian with nearly the same number of parameters as those used in the known high-level quantum-chemical calculations[17—20] of the PES (see below); (iii) the barrier to the *trans*-transition state of H_2O_2 molecule is so low that the excited states of all transverse vibrations are situated above the barrier top; these highly excited states have not been considered in the framework of the PIA as yet; and (iv) the molecule is characterized by large anharmonicity of transverse vibrations, which has not also been taken into account in the previously reported studies. These features are to some extent typical of the reaction complexes of most of simple chemical reactions and indicate the necessity of generalization of the PIA. The vibration-tunneling spectrum of H_2O_2 molecule is convenient to use for evaluation of the generalized PIA. In addition, persistent interest in the vibration-tunneling spectrum of this molecule is related to global problems of atmosphere monitoring.

Thorough experimental and theoretical studies of the vibration-tunneling spectra of H_2O_2 and its isotopomers[21—25] allowed establishment of the geometries and normal frequencies of two stable configurations with a H—O—O—H dihedral angle of $\pm\phi_0$; the energies of inequivalent *cis*- and *trans*-transition states with a dihedral angle of 0 and 180°, respectively; and tunneling splittings in the ground and low-lying excited states of the torsional and most of transverse vibrations. Tables 1 and 2 list the experimental[26] bond lengths, bond angles, and normal frequencies and a number of corresponding data sets obtained from high-level quantum-chemical calculations (see also Refs. 17—20).

The results of *ab initio* quantum-chemical calculations[27—29] are in good agreement with the experimental data. A six-dimensional PES for the ground electronic

Table 2. Experimental frequencies of normal vibrations of $H_2{}^{16}O_2$, $H_2{}^{18}O_2$, $D_2{}^{16}O_2$, $H^{16}O^{18}OH$, and $H^{16}O^{16}OD$ molecules in stationary configurations and those obtained from B3LYP/6-311+G(2d,p) calculations

Vibration*		ν/cm^{-1}			
		Experiment[18]	Minimum	Transition state	
				trans	*cis*
ν^s(OH)	(ν_1)	3599	3769	3797	3796
		—	3756	3784	3784
		2667	2748	2769	2766
		—	3756	3787	3790
		—	3769	3801	3775
δ^s(HOO)	(ν_2)	1387	1448	1534	1327
		—	1441	1524	1327
		1028	1062	1138	940
		—	1444	1528	1327
		—	1392	1429	1400
ν(OO)	(ν_3)	875	946	946	933
		—	892	891	879
		869	944	942	930
		—	919	918	906
		—	945	943	932
$\tau(HO)_2$	(ν_4)	—	395	320i	613i
		—	393	319i	610i
		—	289	234i	455i
		—	394	320i	611i
		—	346	280i	540i
ν^{as}(OH)	(ν_5)	3611	3768	3804	3753
		—	3756	3792	3741
		2661	2744	2769	2736
		—	3769	3802	3746
		—	2746	2770	2751
δ^{as}(HOO)	(ν_6)	1265	1323	1246	1449
		—	1316	1241	1435
		947	978	906	1105
		—	1320	1243	1442
		—	1014	984	1011

* Notations of vibrations: ν is stretching, δ is bending, τ is torsional, s is symmetric, and as is antisymmetric vibration.

state of the molecule was constructed[17—20] using the symmetrized changes in the equilibrium bond lengths and bond angles as the internal coordinates of small-amplitude vibrations and the cosine of the H—O—O—H dihedral angle as the curvilinear tunneling coordinate:

$$s_1 = R_{OO} - R_{OO}{}^0,\ s_2 = (R_{OH} - R_{OH}{}^0)_{sym},$$
$$s_3 = (R_{OH} - R_{OH}{}^0)_{anti},\ s_4 = (\theta_{HOO} - \theta_{HOO}{}^0)_{sym},$$
$$s_5 = (\theta_{HOO} - \theta_{HOO}{}^0)_{anti},\ s_6 = \cos\phi. \qquad (1)$$

The PES was approximated by a series

$$V = V_\phi + \sum_{m,k} F_{mk}\, s_k\cos(m\phi) + \frac{1}{2}\sum_{m,k,k'} F_{mkk'}\, s_k s_{k'}\cos(m\phi) + {} $$
$$+ \frac{1}{6}\sum_{m,k,k',k''} F_{mkk'k''}\, s_k s_{k'} s_{k''}\cos(m\phi) + \frac{1}{2}\sum_{kk'} f_{kk'}\, s_k s_{k'} + {}$$
$$+ \frac{1}{6}\sum_{kk'k''} f_{kk'k''}\, s_k s_{k'} s_{k''} + \frac{1}{24}\sum_{kk'k''k'''} f_{kk'k''k'''} s_k s_{k'} s_{k''} s_{k'''}, \qquad (2)$$

where the 1D-potential had the form

$$V_\phi = \sum_m F_m \cos(m\phi). \qquad (3)$$

The second sum in expression (2) describes the s-dependent couplings of the tunneling coordinate with transverse coordinates and the next two terms proportional to s^2 and s^3 respectively describe the dependence of the frequencies and anharmonicities of transverse vibrations on ϕ. Other sums define the ϕ-independent anharmonicity of vibrations.

Reconstruction of a PES was reported,[17] the expression for which contained six coefficients in the expansion (3) and two Fourier coefficients for each ϕs-coupling. The same number of parameters was used in reconstructing another PES.[18] Since the coordinates defined by expressions (1) differ from normal coordinates, the force and kinematic matrices written in these coordinates are nondiagonal and the solution of the dynamics problem requires additional approximations. In particular, a variational procedure with a restricted basis set of separable trial functions[30] was used.[17] This approach holds if the trial functions are close to the eigenfunctions, *i.e.*, in the weak coupling approximation. Calculations in the adiabatic approximation, in which the true reaction path is replaced by the MEP,[10—12,15] have also been reported.[18] This approximation can be used for calculations of H_2O_2 molecule since the frequency of torsional vibration is several times lower than the frequencies of all transverse vibrations. In the high-frequency limit, the above-mentioned ϕs-couplings are taken into account by using a specific form of the 1D-Hamiltonian, in which the effective mass depends on ϕ and the adiabatic potential includes changes in the frequencies and anharmonicities of transverse vibrations along the reaction path. Tunneling splittings calculated in the above-mentioned studies are in excellent agreement with the experimental data. The reaction path Hamiltonian (RPH) formalism was used[20] in combination with more accurate quantum-chemical calculations. Close values of tunneling splittings were also obtained[19] from calculations by the quantum diffusion Monte Carlo method.[31]

Symmetry of the Hamiltonian

In the ground state and in the *trans*- and *cis*-transition states the H_2O_2 molecule belongs to the C_2, C_{2h} and C_{2v} point groups of symmetry, respectively. The isodynamic group of a non-rigid molecule,[32] $G_4{}^+ = C_2 \otimes C_{2h}$, includes the C_2 point group for an arbitrary value of the dihedral angle and the group of internal operations, C_{2h}, as subgroups. The correlation diagram of irreducible representations of the point groups and the isodynamic group is shown in Fig. 1. The trigonometric functions of the dihedral angle ϕ belong to the following representations

$$\sin(0.5\phi) \in A.A_{2g},\ \cos(0.5\phi) \in A.A_{2u},$$
$$\sin\phi \in A.A_{1u},\ \cos\phi \in A.A_{1g}. \qquad (4)$$

Since the vibrations, which are totally symmetric in both transition states ($Q(\phi) = Q(-\phi) = Q(2\pi - \phi) = Q(2\pi + \phi)$), can belong only to the $A.A_{1g}$ representation in $G_4{}^+$, the Fourier expansion for the coordinates of the totally symmetric vibrations contains only the terms proportional to $\cos(m\phi)$:

$$Q_k = Q_k{}^{(0)} + \sum_m a_{km}\cos(m\phi).$$

If the reactive coordinates $\{Y_k\}$ are chosen in such a way that they coincide with the normal coordinates $\{Q_k\}$ at one of the stationary points,[3,5] the ϕY-couplings correspond to those terms of the Hamiltonian that are proportional to $\cos(m\phi)$. Antisymmetric vibrations belong to the $B.A_{1u}$ representation in $G_4{}^+$, so that the expressions for the ϕY-couplings contain no odd powers of transverse coordinates. Taking into account the fact

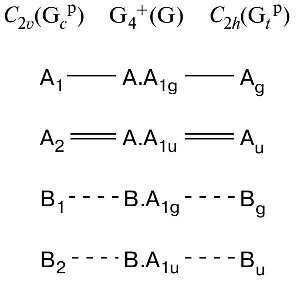

Fig. 1. Correlation diagram of irreducible representations of the point symmetry groups for the ground state (C_2) and *trans*- (C_{2h}) and *cis*- transition states (C_{2v}) of H_2O_2 molecule and the isodynamic group $G_4{}^+$. Solid lines connect irreducible representations for totally symmetric vibrations with G-couplings, double solid lines connect those for torsional vibration, and dashed lines connect irreducible representations for antisymmetric vibrations with Sq-couplings.

that in the region of the *trans*-barrier the potential can be described by a linear coordinate, transverse ϕY-couplings can be classified[1,3,5] in three groups, namely, linear (L), gated (G), and totally symmetric or squeezed (Sq) couplings. For convenience, hereafter the Y-coordinates with the corresponding types of potential couplings will also be referred to as L-, G-, and Sq-coordinates. The PESs of H_2O_2 molecule and its symmetric isotopomers include the tunneling (torsional) coordinate, three G-vibrations, and two Sq-vibrations. For asymmetric isotopomers HDO_2 and $H^{18}O^{16}OH$, all the five transverse coordinates are coupled by G-couplings.

A 1D-potential, the shape of which depends on parameter b, can be approximated by a sum:

$$V_{1D}(\phi) = \frac{1}{2}\sum_{k=2}^{6} V_k \left(\frac{b + \cos\phi}{b - 1}\right)^k . \tag{5}$$

Unlike conventional Fourier expansion, even the first term of the sum ($k = 2$) in expression (5) allows a rather accurate description of the potential with two barriers of different heights owing to the shape parameter b. In the dimensionless coordinates, the length is measured in units of the distance between the potential minima, while the potential is measured in units of γ^2, where γ is the semiclassical parameter defined as follows

$$\gamma = I\Omega_0/\hbar, \tag{6}$$

where Ω_0 is the frequency at the minimum of the 1D-potential and I is the moment of inertia. The γ value is found simultaneously with the coefficients V_k provided that $V_2 = 1$. Let us choose the coordinates coinciding with the normal coordinates of the *trans*-transition state with real frequencies as reactive transverse coordinates $\{Y_k\}$. In what follows we will use the conventional numbering of vibrations with abbreviated notations corresponding to the types of ϕY-couplings, namely, symmetric G-vibrations $\nu_1 > \nu_2 > \nu_3$, torsional vibration ν_4, and antisymmetric Sq-vibrations $\nu_5 > \nu_6$, *i.e.*, $k = 1$, 2, 3, 5, and 6 while the index of the torsional vibration ($k = 4$) is omitted. Now, we can write for the PES

$$\begin{aligned} V(\phi,\{Y_k\}) = V_{1D}(\phi) &+ \sum_{k}^{\mathrm{G,Sq}} \frac{\omega_k^2}{2} Y_k^2 + \\ &+ \sum_{k,m}^{\mathrm{G}} C_k^{(m)} (b + \cos\phi)^m Y_k + \sum_{k,m}^{\mathrm{G,Sq}} \alpha_{kk}^{(m)} (b + \cos\phi)^m Y_k^2 + \\ &+ \frac{1}{2} \sum_{k \neq k',m}^{\mathrm{G,Sq}} \alpha_{kk'}^{(m)} (1 + \cos\phi)^m Y_k Y_{k'}, \end{aligned} \tag{7}$$

where ω_k are the dimensionless frequencies of transverse vibrations divided by the frequency of torsional vibration; $C_k{}^{(m)}$ and $\alpha_{kk}{}^{(m)}$ are the constants of G- and Sq-couplings, respectively; and $\alpha_{kk'}{}^{(m)}$ are the cross-coupling constants. The indices $m = 1, 2$ appear in the terms proportional to $(b + \cos\phi)^m$ or $(1 + \cos\phi)^m$. For cross-couplings of the G- and Sq-coordinates, $\alpha_{kk'}{}^{(m)} = 0$. The form of the PES given by expression (7) was chosen so that the force F-matrix be diagonal in the *trans*-transition state ($\phi = \pi$).

The use of reactive coordinates[3] and expansion (7) for representing the PES has some advantages over the expansions (2) and (3). First, this allows reduction of the number of coupling constants from symmetry considerations. Second, close relation of the reactive coordinates to the normal vibrations allows the ϕ-dependent kinematic matrix to be calculated and the basis set of separable harmonic oscillator functions to be used as initial approximation in solving the dynamics problem. In the next Section, we will show that knowledge of the equilibrium geometry, eigenvectors, and eigenfrequencies of normal vibrations at three stationary points of the PES (these data are obtained from quantum-chemical calculations) allow determination of two coefficients in the sums over $m = 1, 2$.

For the kinetic energy $\hat{T}$ operator be totally symmetric, the products of the momenta p_k and $p_{k'}$ and the corresponding Fourier components must belong to the $A.A_{1g}$ representation. The momenta conjugate to the ϕ-, G-, and Sq-coordinates belong to the $A.A_{1g}$, $A.A_{1u}$, and $B.A_{1g}$ representations, respectively. Let us write the classical kinetic energy T for symmetric isotopomers in such a way that the kinematic matrix be a unit matrix for the *trans*-transition state ($\mathbf{G}(\phi = \pi) = \hat{1}$):

$$\begin{aligned} T = \frac{p_\phi^2}{2} &+ \sum_{k}^{\mathrm{G,Sq}} \frac{p_k^2}{2} + \sum_{m} \frac{g^{(m)}}{2} (1 + \cos\phi)^m p_\phi^2 + \\ &+ \sum_{k,k',m}^{\mathrm{G,Sq}} \frac{g_{kk'}^{(m)}}{2} (1 + \cos\phi)^m p_k p_{k'} + \sum_{k}^{\mathrm{G}} \frac{g_k}{2} \sin\phi\, p_\phi p_k, \end{aligned} \tag{8}$$

where p_ϕ, p_k are the momenta conjugate to the torsional and transverse coordinates, respectively; $g^{(m)}$ and $g_{kk'}{}^{(m)}$ are the coefficients in the expansions of the elements of the kinematic matrix in powers of $(1 + \cos\phi)^m$, $m = 1, 2$; and g_k are the constants of kinematic ϕG-couplings. For the terms containing the momenta conjugate to different-type coordinates (the G-coordinate and Sq-coordinate), we get $g_{kk'}{}^{(m)} = 0$. Thus, the Hamiltonian of H_2O_2 molecule written in the form of relationships (5)—(8) has 58 parameters.

Determination of parameters of the Hamiltonian

To determine the coefficients at the lowest Fourier components in relationships (6)—(8), is it sufficient to use the quantum-chemical data obtained only for stationary points.[3,5] Since the eigenvectors of normal vibrations have not been reported earlier,[17—20] we performed calculations for H_2O_2 molecule and its isotopomers at the MP2 and MP4SDQ levels of theory and using the DFT approach with the B3LYP density functional. All calculations were carried out using the Gaussian-94 program package[33] with the 6-311+G(2d,p) basis set. Augmentation of the basis set with polarization functions to describe the d-AO of oxygen and p-AO of hydrogen is due to the necessity[34] (see also Ref. 35) of taking into account the ϕ-dependent electron correlations on the bonding and antibonding MOs composed of the oxygen AOs.[19] The results of our calculations are listed in Tables 1 and 2 and can be compared with the experimental data.

The calculated equilibrium geometry is in agreement with the experimentally measured structural parameters[26] and the results of calculations by other methods. It should be noted that if the Hamiltonian is constructed in dimensionless variables, the previously discussed[22,26] scatter of experimental and calculated ϕ_0 values between 111° and 120° has little effect on the γ value. Because of this, the B3LYP/6-311+(2d,p) calculations appear to be reasonably accurate. As can be seen from the data listed in Table 2, the frequencies calculated by all the above-mentioned methods are 1.05 to 1.08 times higher than the experimental frequencies. However, the ratios of transverse frequencies to the torsional frequency required for calculating the tunneling splittings are nearly the same. The heights of the *trans*- and *cis*-barriers are also close to the experimental values, except for V_{cis} obtained from MP2 calculations. Since calculations carried out at the MP4SDQ level of theory and in the framework of DFT approach with the B3LYP density functional led to the same values of the parameters of the Hamiltonian and tunneling splittings, hereafter we use the results obtained from B3LYP calculations.

Since the Hamiltonian of H_2O_2 molecule contains no terms with L-couplings, the reactive coordinates ϕ and $\{Y_k\}$ coincide with the normal coordinates of the *trans*-transition state ($\phi = \pi$), in which the tunneling motion is separable. The *cis*- and *trans*-barrier heights are equal to the energy differences between the corresponding transition state and ground state provided that the dihedral angle in the transition state is π (*cis*-) and 0° (*trans*-) and the geometry of the transition state is exactly the same as that of the ground state. According to our calculations, the barrier heights are $V_{1D}{}^{trans} = 421$ cm^{-1} and $V_{1D}{}^{cis} = 3192$ cm^{-1}. The frequencies at stationary points of the 1D-potential were found from calculations of the second derivatives of the potential, which corresponded to small variations of the dihedral angle in the vicinity of the points $\phi = 0$, ϕ_0, and π at $\{Y_k\} = 0$. Using the calculated frequencies, barrier heights, and the equivalent moments of inertia for internal rotation in the *trans*-transition state ($0.763 \cdot 10^{-40}$ g cm^{-2} for H_2O_2, $H^{18}O^{16}OH$, and $H_2{}^{18}O_2$; $1.018 \cdot 10^{-40}$ g cm^{-2} for HDO_2; and $1.527 \cdot 10^{-40}$ g cm^{-2} for D_2O_2), one can calculate the parameter γ defined by relationship (6), and five coefficients of the Fourier expansion for the 1D-potential (5). The 1D-potential given by expression (5), the adiabatic potential (along the MEP), and a scheme of the torsional energy levels are shown in Fig. 2.

The potential L-coupling and G-coupling constants are linearly related to the displacements ΔY_k in the transition state with respect to the standard configuration in the ground state.[1–5] Since there are two transition states, we can determine two coupling constants ($m = 1, 2$) for each of the two gated vibrations for the PES given by expression (7):

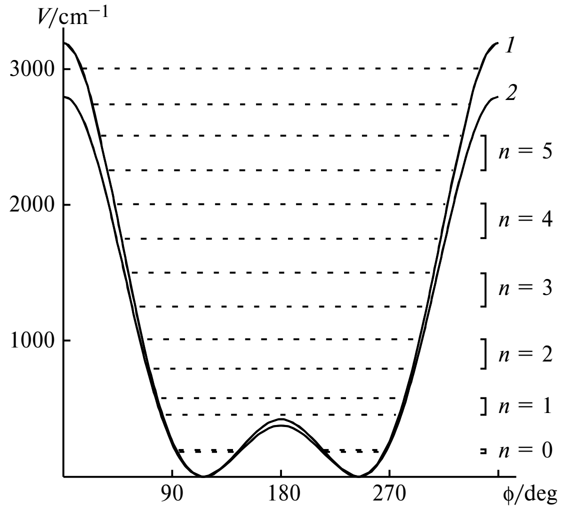

Fig. 2. One-dimensional (*1*) and adiabatic (*2*) barriers to internal rotation in H_2O_2 molecule. The torsional vibrational levels in the 1D-potential are shown by dashed lines.

$$\Delta Y_k{}^{cis} = -[(1 + b)/\omega_k{}^2][C_k{}^{(1)} + C_k{}^{(2)}(1 + b)],$$
$$\Delta Y_k{}^{trans} = [(1 - b)/\omega_k{}^2][C_k{}^{(1)} - C_k{}^{(2)}(1 - b)]. \quad (9)$$

The Sq-coupling constants, $\alpha_{kk}{}^{(m)}$, are related to the changes in the frequencies at stationary points of the potential by the relationships:

$$(\omega_k{}^{cis})^2 = \omega_k{}^2 + 2(1 + b)[\alpha_{kk'}^{(1)} + \alpha_{kk'}^{(2)}(1 + b)],$$
$$(\omega_k{}^{trans})^2 = \omega_k{}^2 - 2(1 - b)[\alpha_{kk'}^{(1)} - \alpha_{kk'}^{(2)}(1 - b)], \quad (10)$$

where ω_k, $\omega_k{}^{cis}$, and $\omega_k{}^{trans}$ are the dimensionless frequencies in the ground state and in the *cis*- and *trans*-transition states, respectively, which are defined as follows

$$\omega_k = (\Omega_k/\Omega_0)\sqrt{1 - b^2}, \quad (11)$$

where Ω_k and Ω_0 are the frequencies for the Y_k and ϕ coordinates. Since in the *trans*-transition state the kinematic matrix becomes a unit matrix, the kinematic coupling constants are found by solving the system of equations for the other two stationary points at which the **G**-matrices have the form

$$\mathbf{G}^0 = \tilde{\mathbf{S}}^0\mathbf{S}^0, \qquad \mathbf{G}^{cis} = \tilde{\mathbf{S}}^{cis}\mathbf{S}^{cis}, \quad (12)$$

where $\mathbf{S}^0$ and $\mathbf{S}^{cis}$ are the matrices relating the normal coordinates at the three stationary points:

$$\mathbf{Q}^{trans} = \mathbf{S}^0\mathbf{Q}^0, \qquad \mathbf{Q}^{trans} = \mathbf{S}^{cis}\mathbf{Q}^{cis}. \quad (13)$$

Thus, we can determine two coefficients for each Fourier expansion, except for the g_k coefficients, since the corresponding Fourier components (sinϕ) are equal to zero at two stationary points. The cross-coupling constants, $\alpha_{kk'}{}^{(m)}$, can be found by solving the system of equations[5]

$$\alpha_{kk'}^{(1)}\ (1-b)+\alpha_{kk'}^{(2)}\ (1-b)^2=$$
$$=-\omega_k{}^2\delta_{kk'}+\sum_{i=1}^{6}\omega_i{}^2\left(S_{ik}^{0}\right)^{-1}\left(S_{ik'}^{0}\right)^{-1},$$

$$2\,\alpha_{kk'}^{(1)}+4\,\alpha_{kk'}^{(2)}=$$
$$=-\left(\omega_k^{cis}\right)^2\delta_{kk'}+\sum_{i=1}^{6}\left(\omega_i^{cis}\right)^2\left(S_{ik}^{cis}\right)^{-1}\left(S_{ik'}^{cis}\right)^{-1}. \quad (14)$$

According to our calculations, the adiabatic *trans*- and *cis*-barriers are 44.6 and 394.3 cm^{-1} (or 42 and 376 cm^{-1}, see Ref. 18) lower than the corresponding 1D-barriers. For the PES given by expression (7) the "lowering factors" for the adiabatic barriers compared to 1D-barriers have the form

$$\left\{1+\sum_{k}^{G}\left[C_k^{(1)}(\mp 1+b)+C_k^{(2)}(\mp 1+b)^2\right]^2\omega_k^{-2}\right\}^{-1},$$

and correspond to a decrease in the *trans*- and *cis*-barrier heights by 49.0 cm^{-1} and 361.7 cm^{-1}, respectively, provided that the G-coupling constants are known. This comparison characterizes the extent to which relationship (7) containing no anharmonicity corrections for transverse vibrations can approximate the PES.

The changes in intrinsic coordinates (1) in the case of motion along the MEP found earlier[18] and those calculated in this work are shown in Fig. 3. Though the absolute values of R_{OO} and θ_{OOH} differ, on the average, by 0.01 Å and 0.88°, respectively, the corresponding curves nearly coincide. An analogous matching is also observed for the changes in the transverse frequencies (Fig. 4). Since the PES is determined by the differences between the geometric parameters and frequencies at the stationary points rather than by their absolute values, the characteristics of the PES given by expressions (5)—(7) found using the results of B3LYP/6-311+g(2d,p) calculations differ only slightly from those obtained previously.[17,18]

Relationships (5)—(8) contain no corrections for ϕ-independent anharmonicity of transverse vibrations. Though the corrections to the action on the extreme tunneling trajectory (ETT), which are due to this type of anharmonicity, are infinitesimals of higher orders as

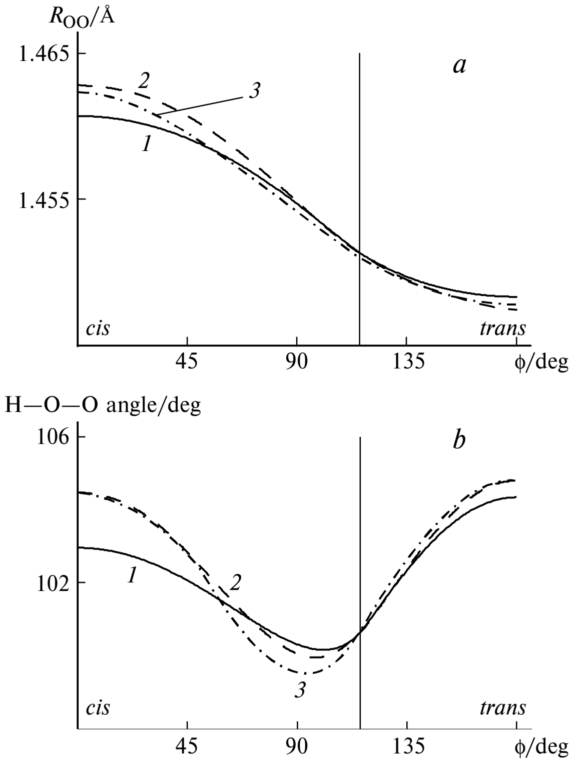

Fig. 3. Changes in the bond length (*a*) and bond angle (*b*) in H_2O_2 molecule calculated in this work for internal rotation corresponding to the motion along the extreme tunneling trajectory (*1*) and minimum energy path (*2*) and the results of calculations[18] for the motion along the minimum energy path (*3*).

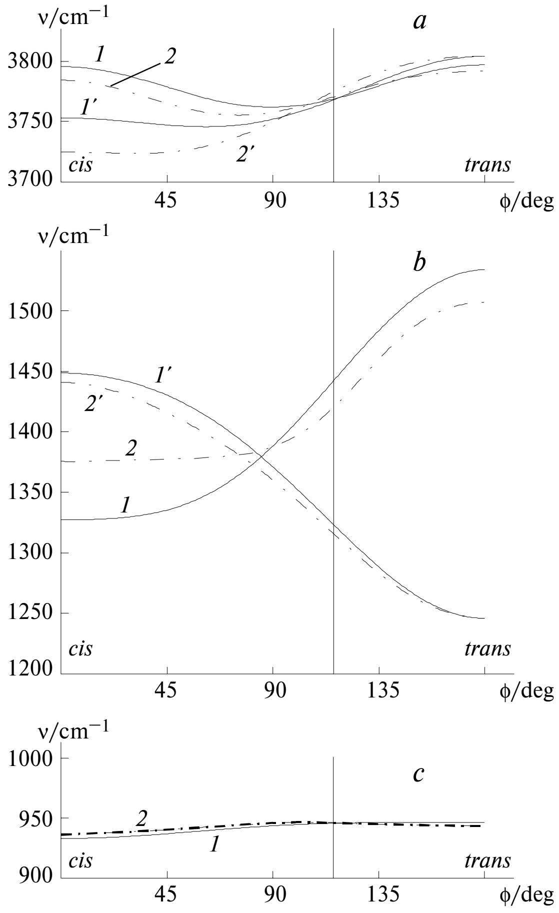

Fig. 4. Changes in the transverse frequencies of symmetric (*1*, *2*) and antisymmetric (*1′*, *2′*) vibrations of H_2O_2 molecule calculated for the motion along the minimum energy path in the adiabatic approximation[18] (*1*, *1′*) and using the PIA (*2*, *2′*): OH stretching vibrations (*a*), HOO bending vibrations (*b*), and OO stretching vibrations (*c*).

compared to the interactions taken into account by formulas (5)—(8), we performed calculations using the third-and fourth-order anharmonicity corrections[18] for the PES given by expression (7). The difference between the results of calculations with inclusion of anharmonicity corrections and experimental frequencies of transverse vibrations does not exceed 45 cm^{-1}. Changes in the frequencies due to the anharmonicity are also taken into account when solving the transport equation (TE).

Let us list the salient features of the vibrational Hamiltonian of H_2O_2 molecule. The potential and kinematic couplings proportional to cosϕ are strong, whereas the couplings proportional to cos(2ϕ) are weak. G-Couplings with the symmetric HOO bending vibration and OO stretching vibration as well as Sq-couplings with both bending vibrations and antisymmetric OH stretching vibration are also strong. Substitution of heavy atoms has no effect on the potential coupling constants, but decreases the frequency at the minimum of 1D-potential and, hence, the quasi-classical parameter γ. Scaling of the parameters of the Hamiltonian due to an increase in γ by a factor of ~1.47 also takes place upon H/D substitution. The diagonal kinematic couplings characterize the ν_2, ν_3, and ν_6 vibrations. The kinematic couplings and off-diagonal Sq-couplings are weak.

Perturbative solution of quasi-classical equations

Analysis of the tunneling dynamics of internal rotation in H_2O_2 molecule performed in this work differs from that reported earlier[1—9] in that in this case we succeeded in extending the framework of the PIA to the case of a complex shape of the 1D-potential and anharmonic transverse vibrations. If the unperturbed Hamiltonian contains no terms with ϕY-couplings and ϕ-dependent YY'-couplings ($C_k{}^{(m)} = 0$, $\alpha_{kk'}{}^{(m)} = 0$) but, at the same time, contains the terms responsible for the "diagonal" anharmonicity with respect to the displacements from the minimum, the eigenfunctions of the basis set are separable:

$$\Psi^{(0)}_{n\{n_k\}} = \Phi^{(0)}_n(\phi - \phi_0)\prod_k \Theta^{(0)}_{\{n_k\}}\left(Y_k - Y_k^{(0)}\right), \qquad (15)$$

where $\Phi_n{}^{(0)}(\phi - \phi^0)$ and $\Theta_{\{nk\}}{}^{(0)}(Y_k - Y_k{}^{(0)})$ are the eigenfunctions of the $V_{1D}(\phi)$ potential and anharmonic potentials for transverse coordinates, respectively, and n and n_k are the quantum numbers of the torsional vibration and transverse vibrations, respectively (n, $n_k = 0, 1, 2...$). These eigenfunctions are found using numerical diagonalization of the matrices of the 1D-Hamiltonians in an appropriate basis set of orthonormalized functions (*e.g.*, in the basis set of harmonic oscillator functions or Fourier components). The minimum number of the eigenfunctions is chosen in such a way that the eigenvalues be independent of the size of the basis set; usually, this number is at most 100. Calculations of the nonseparable action are reduced to perturbative solution of linearized Hamilton—Jacobi equations (HJE) with ϕY-couplings and ϕ-dependent YY'-couplings in the first, second, and third order with respect to the coupling constants. This universal procedure is the same as that described earlier.[5,7] When solving the HJE, the necessary number of terms in the perturbative expansion is determined by the coupling constants. For H_2O_2 molecule, it is sufficient to use the second-order perturbative expansion.

We now turn to the problem of solving the TE. The eigenfunctions appeared in expression (15) can be written in the semiclassical form:

$$\begin{aligned}\Phi_n{}^{(0)} &= A_n{}^{(0)}(\phi)\exp[-\gamma W_0(\phi)],\\ \Theta_{n_k}{}^{(0)} &= A_{n_k}{}^{(0)}(Y_k)\exp[-\gamma W_{0k}(Y_k)],\end{aligned} \qquad (16)$$

where W_0 and W_{0k} are the solutions of the 1D-HJE. Using these solutions and the 1D-eigenfunctions described above, one can calculate the zero-order prefactors

$$A^{(0)}_{n\{n_k\}} = A^{(0)}_n \prod_k A^{(0)}_{n_k} \qquad (17)$$

and find the solution of the TE in the form of expansion over the basis set of eigenfunctions (15). The first-order prefactors are calculated using the relationship

$$A^{(1)}_{n\{n_k\}} = A^{(0)}_{n\{n_k\}} + \sum_{n'\{n_{k'}\}} a_{n\{n_k\}n'\{n_{k'}\}} A^{(0)}_{n'\{n_{k'}\}}\,. \qquad (18)$$

Expression (18) contains both the low-lying ($E_{n\{nk\}}{}^{(0)} < V^{\#}$) and highly excited states ($E_{n\{nk\}}{}^{(0)} \geq V^{\#}$). Since the zero-order prefactors $A_n{}^{(0)}(\phi)$ and $A_{nk}{}^{(0)}(Y_k)$ are orthonormalized with the statistical weights exp($-\gamma W_0$) and exp($-\gamma W_{0k}$), respectively, the expansion coefficients have the form

$$a_{n\{n_k\}n'\{n_{k'}\}} = \frac{V_{n\{n_k\}n'\{n_{k'}\}} + R_{n\{n_k\}n'\{n_{k'}\}}}{E^{(0)}_{n\{n_k\}} - E^{(0)}_{n'\{n_{k'}\}}}, \qquad (19)$$

where

$$\begin{aligned}V_{n\{n_k\}n'\{n_{k'}\}} &= \gamma C\left\langle \Phi^{(0)}_{n\{n_k\}}\middle| V_1 \middle| \Phi^{(0)}_{n'\{n_{k'}\}}\right\rangle,\\ R_{n\{n_k\}n'\{n_{k'}\}} &= C\left\langle \Phi^{(0)}_{n\{n_k\}}\middle| \nabla w_1 \nabla + 0.5\Delta w_1 \middle| \Phi^{(0)}_{n'\{n_{k'}\}}\right\rangle,\end{aligned} \qquad (20)$$

and V_1 is the nonseparable part of the Hamiltonian, which is considered as perturbation, and w_1 is the first-order action, which obeys the equation $\nabla W_0 \nabla w_1 = V_1$. This perturbative procedure converges if

$$\sum_k (C_k{}^2/\omega_k{}^2) \leq 1, \qquad (21)$$

whereas the conventional perturbative procedure converges at much weaker couplings, $\gamma^2\sum_k (C_k{}^2/\omega_k{}^2) \leq 1$. An increase in the radius of convergence is due to the fact that the exponent of the wave function of the order of γ^1 is found from the solution of the HJE, whereas the prefactor, which of the order of γ^0, is found as an expansion in terms of the eigenfunctions. After deriving semiclassical wave functions, tunneling splittings can be calculated using the Lifshitz—Herring formula as the probability flow through the dividing surface:

$$\Delta_{n\{nk\}} = \frac{\hbar\Omega}{\gamma}\int \Phi_{n\{n_k\}}\nabla\Phi_{n\{n_k\}}\Big|_{\phi=\phi^{\#}} \mathrm{d}\{Y_k\}. \tag{22}$$

Tunneling dynamics

The ETT was found by numerical integration of the equations of motion. The deviations of the ETT from the MEP are shown in Fig. 3. The inclusion of corrections to the action on the ETT leads to an increase in the tunneling splitting by a factor of 1.31 as compared to the 1D action owing to the assistance of three G-vibrations (ν_1—ν_3). The higher the frequencies of the G-vibrations, the more pronounced their effect.[2,8] Since the MEP corresponds to the high-frequency limit for the transverse vibrations, replacement of the ETT by the MEP leads to overestimation of the tunneling splittings (by 6.5% for H_2O_2 molecule). The appearance of the Franck—Condon factors for the transverse vibrations is due to changes in their frequencies along the ETT (see Fig. 4). The Franck—Condon factors are responsible for the dependence of the tunneling splittings on the quantum numbers of transverse vibrations, which is described by the formula

$$\Delta_{0...nk...}/\Delta_{0...0...} \approx \exp\left\{\left[2n_k/(1+\omega_k)\right]\left[\alpha_k^{(1)} - \alpha_k^{(2)}(1-b)\right]\right\}. \tag{23}$$

Replacement of the ETT by the MEP leads to errors (5 to 10%) in determination of the values of the Franck—Condon factors for transverse vibrations in the ground state. Though the errors in both the action and pre-exponential factors partly cancel each other, the accuracy of calculations of the tunneling splitting in the vibrational-adiabatic approximation for the ground state of H_2O_2 molecule is ~5%.

The basis set of the 1D-functions used in this work included eight functions for the tunneling coordinate and two or three functions for each transverse coordinate. This allowed all vibrational states with the energies up to the height of the *cis*-barrier to be taken into account. We found that further extension of the basis set has no effect on the accuracy of calculations of tunneling splittings. The major advantage of the PIA consists of the possibility of solving the quantum dynamics problem in a restricted basis set of quasi-classical functions owing to the fact that the matrix elements of the interactions between the low-lying excited states of transverse vibrations (*i.e.*, the excited states localized in the potential wells) and highly excited torsional states exponentially decrease as the energy increases.[7]

The tunneling splittings of the ground state and all first excited vibrational states of H_2O_2 molecule and its isotopomers are listed in Table 3. The results obtained in this work coincide within the limits of experimental error with the experimental data and supplement them with the data for those IR bands that have not been studied as yet. They are also in agreement with the results of calculations in the vibrational-adiabatic approximation[17—20] (within the accuracy of the corresponding computational procedure, 5%). It should be emphasized that the use of the PIA allowed one to calculate the tunneling splitting of the ν_6 band in the spectrum of HOOD molecule (earlier,[20] this was impossible owing to resonance between the ν_6 and ν_4 vibrations). Comparison of the calculated vibration-tunneling spectrum with the experimental data (Table 4) shows that the use of the Hamiltonian constructed in this work

Table 3. Tunneling splittings (cm^{-1}) of vibration-tunneling levels of H_2O_2, HOOD, D_2O_2, $H_2{}^{18}O_2$, and $H^{16}O^{18}OH$ molecules

Level	H_2O_2				HOOD			D_2O_2			$H_2{}^{18}O_2$	$H^{16}O^{18}OH$
	Experiment[22,24]	RPH[18]*	RPH[20]**	PIA	Experiment[22]	RPH[20]**	PIA	Experiment[22]	RPH[20]**	PIA	PIA	PIA
0	11.44	11.24	11.0/11.1	11.37	5.8	5.6/6.6	5.72	1.9	1.9/1.9	1.93	11.30	11.32
$1\nu_4$	116.3	—	120/119	116.7	82.6	82.6/82.9	81.3	42.3	43.6/44.0	43.7	116.1	116.2
$2\nu_4$	206.4	—	—	204.7	167.7	—	177.3	141.4	—	140.2	204.3	204.1
$3\nu_4$	234	—	—	228.3	—	—	208.1	—	—	189.2	234.1	233.7
$1\nu_1$	9.1	10.24	7.4/7.4	9.42	—	2.6/3.8	4.50	—	1.2/1.2	1.44	9.58	10.19
$2\nu_1$	—	—	—	7.88	—	—	3.53	—	—	1.19	8.07	9.12
$1\nu_2$	6.2	6.25	6.1/5.0	6.32	—	7.7/4.2	4.31	—	1.6/0.7	0.93	6.85	6.84
$2\nu_2$	—	—	—	2.70	—	—	3.24	—	—	0.52	2.89	2.93
$1\nu_3$	11.6	11.61	11.1/10.8	11.78	—	5.6/5.4	5.79	—	1.8/1.7	1.78	11.60	11.62
$2\nu_3$	—	—	—	13.23	—	—	5.86	—	—	1.81	13.00	13.04
$1\nu_5$	8.2	8.73	7.6/8.4	8.78	—	3.8/4.2	4.80	—	6.2/1.4	1.36	8.95	8.43
$2\nu_5$	—	—	—	6.82	—	—	4.03	—	—	1.05	7.10	6.27
$1\nu_6$	20.5	19.28	20.8/21.8	19.92	—	15.9/8.4	8.11	—	4.5/4.6	4.42	18.58	18.73
$2\nu_6$	—	—	—	30.86	—	—	10.05	—	—	8.47	29.11	29.49

* Calculated using the reaction path Hamiltonian formalism.

** 6D-Harmonic approximation/harmonic approximation.

Table 4. Vibration-tunneling spectrum of H_2O_2 molecule

State*	Energy/cm^{-1}	
	Experiment[23,24]	PIA
0 (s)	0.0	0.0
0 (a)	11.44	11.37
$1\nu_4$ (s)	254.55	256.25
$1\nu_4$ (a)	370.89	372.98
$2\nu_4$ (s)	569.74	573.47
$2\nu_4$ (a)	776.11	778.23
$3\nu_4$ (s)	1000.88	999.81
$3\nu_4$ (a)	1235	1228.08
$1\nu_3$ (s)	865.94	860.04
$1\nu_3$ (a)	877.94	871.82
$1\nu_6$ (s)	1264.58	1267.15
$1\nu_6$ (a)	1285.12	1287.07
$1\nu_4 1\nu_6$ (s)	1504.87	1501.69
$1\nu_4 1\nu_6$ (a)	1648.37	1653.19
$2\nu_4 1\nu_6$ (s)	1853.63	1860.79
$2\nu_4 1\nu_6$ (a)	2072.44	2080.59
$1\nu_4 1\nu_3$ (s)	—	1112.16
$1\nu_4 1\nu_3$ (a)	—	1232.83
$2\nu_4 1\nu_3$ (s)	—	1434.46
$2\nu_4 1\nu_3$ (a)	—	1645.14

* The notations "s" and "as" correspond to symmetric and antisymmetric vibrations, respectively.

allows quantitative reproduction of the proper anharmonicity and cross-anharmonicity for all vibrations and their interaction with internal rotation.

For most energy levels the isotope effect is as small as the isotope shifts of the eigenfrequencies (see Table 2). The only exception are the excited states of the OH stretching vibrations ν_1 and ν_5, for which the splittings respectively increase and decrease by 12%. Anomalous isotope effect in the excited states of transverse vibrations an increase in tunneling splittings upon substitution of the light isotope by the heavy one) is typical of the multidimensional dynamics and is due to ϕY-interactions.[2,5] For H_2O_2 molecule, large anomalous isotope effect is due to the appearance of G-coupling and positive Sq-coupling upon the $^{18}O/^{16}O$ substitution. According to calculations, anomalous isotope effect should also be observed for the ν_6 vibration. This prediction can be checked experimentally since the IR spectrum of H_2O_2 in the region of this vibration has been studied in most detail.[23–25]

Results and Discussion

The most important outcome of our study is that the accuracy of calculations of the tunneling dynamics of small non-rigid molecules in the framework of the PIA depends on the accuracy of reconstruction of the Hamiltonian using the results of quantum-chemical calculations, since the accuracy of solution of the dynamics problem *per se* can always be increased (if necessary) by taking into account higher orders of perturbative expansion. The perturbative computational procedure is convergent if the condition (21) is satisfied, which holds for most non-rigid molecules. This represents the major advantage of the PIA over the variational methods and RPH formalism in which the accuracy of initial approximation is *a priori* unknown. Judging from the coincidence of the calculated geometric parameters, fundamental frequencies, and tunneling splittings with the corresponding experimental values, the use of the results obtained from quantum-chemical calculations provides the possibility of reconstructing the vibrational Hamiltonian of H_2O_2 molecule up to the energies of the order of ~2500 cm^{-1}.

Let us compare the applicability of the PIA and some other computational methods based on solution of the N-dimensional Schrödinger equation (N is the number of internal degrees of freedom) for calculations of tunneling splittings taking a PES with several minima as an example. Here, the set of numerical approaches includes diagonalization of the matrix of the Hamiltonian, variational procedure, and quantum diffusion Monte Carlo method.[31] All these methods are of limited utility in calculations of tunneling splittings owing to high computational cost. Since the tunneling splittings Δ_n are exponentially small, it is the need of obtaining the eigenvalues with an accuracy of $O(\Delta_n)$ that determines the size of the basis set required for diagonalization of the matrix of the Hamiltonian. In this case, the basis set is much larger than that required for calculations of vibrational frequencies of the molecules with one stable configuration; moreover, the size of the basis set increases as the height of the barrier between stable configurations increases.

As was mentioned above, diagonalization of the matrix of the 1D-Hamiltonian allows reproduction of tunneling splittings if the basis set contains ~10^2 oscillator functions. If the tunneling coordinate is strongly coupled with vibrations for which the displacements of the equilibrium positions in the transition state with respect to those in the ground state are comparable with the tunneling distance, a correct description of each transverse degree of freedom requires ~10 functions so that the total size of the basis set is ~10^N. Modern supercomputers can perform calculations only if $N \le 15$, *i.e.*, for molecules comprising less than seven atoms. Since the radius of convergence of the variational procedure applied to the excited states is nearly the same as that of conventional perturbative expansion, the computational cost of this procedure is comparable with the above-mentioned estimate. The quantum Monte Carlo method is specially intended for calculations of polyatomic molecules, but in this case the computational cost depends on both the PES steepness and presence of resonances.

Unlike these methods, the PIA allows calculations of tunneling splittings of the energy levels in the spectra of non-rigid polyatomic molecules at much lower computational cost. Solution of the dynamics problem is reduced to the perturbative solution of semiclassical equations. This requires calculations of (i) $\sim N^2$ integrals to describe the contributions of ϕY- and YY'-couplings to the action and (ii) nearly the same number of matrix elements in the rapidly converging expansion (18). The PIA also allows setting up the inverse problem of reconstructing the PES of a non-rigid molecule from its vibration-tunneling spectra and, thus, testing the accuracy of quantum-chemical calculations in the far forbidden regions of the configurational space.

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