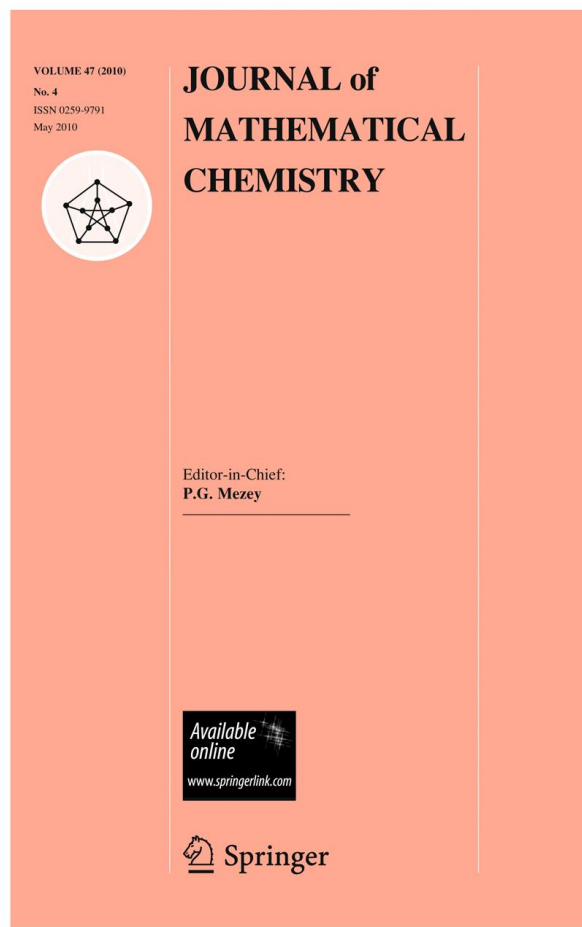


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A treatment of the torsional wave equation with an internal rotation constant depending on a torsional angle via point canonical transformation

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Abstract A numerical method using a canonical point transformation has been developed for determining the energy levels of the internal rotation of asymmetric rotors. An internal rotation constant is assumed to be a function of a torsional angle.

Keywords Internal rotation · Angle-dependent moment of inertia · Periodic potentials · Point canonical transformations

1 Introduction

Internal rotation occurs in a molecule in which one group of atoms (a rotor) can rotate about another group (a rigid frame) through considerable angles. This rotation is restricted by a potential barrier that turns it into hindered rotation. The hindered rotation with s equivalent internal configurations is described in terms of wave equation in which the internal rotation constant F is independent of the torsional angle ϕ if the potential barrier has a threefold or higher symmetry [1–5]. Rigorous methods are available that can be used to solve this problem numerically [3, 5–7]. For example, Hamiltonian matrix elements can be readily calculated in terms of the basis of wave functions corresponding to a free rotation. This matrix can be then diagonalized to get the spectrum of eigenvalues [5, 7]. One leading term can be often left in a potential energy given in the form of a series to derive the wave equation similar to the Mathieu equation [1–5], which allows an analytical treatment of the problem [8–12]. When the potential barrier has no threefold or higher symmetry, the stable equilibrium configurations cease to be equivalent and molecules can exist as a mixture of rotational

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isomers. The internal rotation constant will have different values for different molecule conformations. Thus, $F(\phi)$ becomes a torsional angle function in the case of asymmetric rotors. There are several approaches to this problem. In the simplest case, a mean F_{av} can be used instead of $F(\phi)$ if the range of deviations in ϕ is negligible [7, 13]. When the barrier is high enough, the internal motion is represented by small torsional vibrations, at least, at its bottom. In this case, energy levels are reasonable to calculate assuming that F depends on molecule conformation and is independent of ϕ for a given conformation [6, 14]. Recent developments in ab initio techniques are now available to treat a small molecule such as H_2O_2 in the full set of its internal degrees of freedom [15, 16]. Nevertheless, calculations of the required hindered rotor state energies using ab initio methods are very time consuming and they are limited to low levels of excitations.

In the present work, we introduce a new angular variable by a nonlinear coordinate transformation to derive the wave equation in which the influence of the variable $F(\phi)$ is eliminated by adding additional terms to the potential function and redefining ϕ . This transformation belongs to the class of canonical point transformations [17–19] (and earlier references cited therein). Mathematically, this task is equivalent to the problem of position-dependent mass in the one-dimensional Schrödinger equation.

2 The method

A one-dimensional wave equation with an angle-dependent internal rotation constant is of the form [16, 20]

$$-\frac{d}{d\phi} \left[F(\phi) \frac{d\Psi(\phi)}{d\phi} \right] = [E - V(\phi)] \Psi(\phi), \quad (1)$$

where $V(\phi)$ is the potential function. Actually, the solution of this differential equation yields the torsional eigenvalues E and eigenfunctions $\Psi(\phi)$. However, the dependence of F on ϕ strongly complicates the problem. Our approach is in many ways similar to that proposed in [17–19]. In order to derive a simpler equation, we introduce the transformation $\phi \rightarrow \alpha$ through a mapping function $\alpha = f(\phi)$ and rewrite the wave function as

$$\Psi(\phi) = g(\phi) \tilde{\Psi}[f(\phi)], \quad (2)$$

where the unknowns $f(\phi)$ and $g(\phi)$ should be determined. Substituting this expression into Eq. (1), we get the transformed wave equation

$$\begin{aligned} & -F(f')^2 \frac{d^2 \tilde{\Psi}}{d\alpha^2} - \left(F' f' + 2F f' \frac{g'}{g} + F f'' \right) \frac{d\tilde{\Psi}}{d\alpha} \\ & = \left[E - V(\phi) + F' \frac{g'}{g} + F \frac{g''}{g} \right] \tilde{\Psi}, \end{aligned} \quad (3)$$

where the prime denotes differentiation with respect to ϕ . Determine now the function $f(\phi)$ from the equation

$$\frac{df}{d\phi} = \left[\frac{F_{\text{av}}}{F(\phi)} \right]^{\frac{1}{2}}, \quad (4)$$

where F_{av} is a constant. The general solution of Eq. (4) is

$$\alpha = f(\phi) = f(\phi_0) + \int_{\phi_0}^{\phi} \left[\frac{F_{\text{av}}}{F(x)} \right]^{\frac{1}{2}} dx, \quad (5)$$

In the following, we make the particular choice $f(\phi_0) = \phi_0$ due to a periodicity of this function. The term in front of the first derivative can be made vanish if function $g(\phi)$ is taken as

$$g(\phi) = \left[\frac{F_c}{F(\phi)} \right]^{\frac{1}{4}} \quad (6)$$

Hence, Eq. (2) at $\phi = \phi_0$ provides

$$\Psi(\phi_0) = \left[\frac{F_c}{F(\phi_0)} \right]^{\frac{1}{4}} \tilde{\Psi}(\phi_0) \quad (7)$$

For a periodic function $F(\phi)$ with period 2π in ϕ , it is necessary to assume that $F_c = F(\phi_0)$ for the initial wave function and the transformed one to coincide at $\phi_0 = 0$ and 2π .

Then, we rewrite again Eq. (3) to get

$$-F_{\text{av}} \frac{d^2 \tilde{\Psi}(\alpha)}{d\alpha^2} = [E - V_{\text{eff}}(\alpha)] \tilde{\Psi}(\alpha), \quad (8)$$

where

$$V_{\text{eff}}(\alpha) = \tilde{V} \left[f^{-1}(\alpha) \right] \quad (9)$$

and

$$\tilde{V}(\phi) = V(\phi) + \frac{1}{4} \frac{d^2 F}{d\phi^2} - \frac{1}{16F(\phi)} \left(\frac{dF}{d\phi} \right)^2 \quad (10)$$

Here $f^{-1}(\alpha)$ is an inverse function for $\alpha = f(\phi)$. It is worth noting that the eigenvalues of Eq. (8) will be the eigenvalues of Eq. (1). We call the old potential $V(\phi)$ as the reference potential and the new potential $\tilde{V}(\phi)$ as the target potential. Thus, using

Eqs. (5) and (6) we transformed our reference problem into the target problem with the effective potential $V_{\text{eff}}(\alpha)$.

For definiteness, we consider the case where the asymmetric rotor and rigid frame have at least a plane of symmetry. As a result, $V(\phi)$ and $F(\phi)$ will be even functions and the effective potential will also be an even function. Let us represent $V(\phi)$ in the standard form

$$V(\phi) = \frac{1}{2} \sum_{m=1}^{\infty} V_m [1 - \cos(m\phi)] \quad (11)$$

A similar expansion can be written for the effective potential

$$V_{\text{eff}}(\alpha) = \tilde{V}(0) + \frac{1}{2} \sum_{m=1}^{\infty} (V_{\text{eff}})_m [1 - \cos(m\alpha)], \quad (12)$$

where the expansion coefficients are given by the expression

$$(V_{\text{eff}})_m = -\frac{2}{\pi} \int_0^{2\pi} \tilde{V} [f^{-1}(\alpha)] \cos(m\alpha) d\alpha \quad (13)$$

The equation giving the zeroth order Fourier component leads to

$$\frac{1}{\pi} \int_0^{2\pi} \left\{ \tilde{V} [f^{-1}(\alpha)] - \tilde{V}(0) \right\} d\alpha = \sum_{m=1}^{\infty} (V_{\text{eff}})_m \quad (14)$$

For further advance, the constant F_{av} should acquire an explicit physical meaning. We determine F_{av} using the periodicity property of the wave functions $\Psi(\phi)$ and $\tilde{\Psi}(\phi)$. The periodicity of these functions yields the periodicity of function $f(\phi)$ with the same period. To put it differently, if $f(\phi_0) = \phi_0$ then $f(\phi_0 + 2\pi)$ should be equal to $\phi_0 + 2\pi$. Hence,

$$\frac{1}{2\pi} \int_{\phi_0}^{\phi_0+2\pi} \left[\frac{F_{\text{av}}}{F(\phi)} \right]^{\frac{1}{2}} d\phi = \frac{1}{2\pi} \int_0^{2\pi} \left[\frac{F_{\text{av}}}{F(\phi)} \right]^{\frac{1}{2}} d\phi = 1 \quad (15)$$

Using Eq. (15), one obtains

$$F_{\text{av}} = \left[\frac{1}{2\pi} \int_0^{2\pi} \frac{d\phi}{\sqrt{F(\phi)}} \right]^{-2} \quad (16)$$

This definition specifies the mean or effective internal rotation constant that appears in Eq. (8). For definiteness sake, we assume that $\phi_0 = 0$.

Energy levels can be calculated using the wave functions of free internal rotation as the basis eigenfunctions (for details, see [7]). The energy eigenvalues are determined by numerical diagonalization of Hamiltonian with the matrix elements

$$H_{kk'} = \begin{cases} k^2 F_{\text{av}} + \tilde{V}(0) + \sum_{m=1}^{\infty} \frac{(V_{\text{eff}})_m}{2}, & k = k' \\ -\frac{(V_{\text{eff}})_{|k-k'|}}{4}, & k \neq k' \end{cases} \quad (17)$$

Note that the eigenvalues of this matrix will be the eigenvalues of Eq. (1). In these computations, it should be seen that each subsequent eigenvalue exceeds the preceding one. In numerical calculations, the question always arises: how many terms should be retained in the infinite series (12)? The answer is clear from Eq. (14). We can calculate the left-hand side of Eq. (14) to within certain accuracy. A comparison with the right-hand side can be used then to estimate the finite number of terms that should be left to attain the same accuracy.

3 Approximate solution

For the potential barrier with the symmetry lower than the threefold one, the angular dependence of $F(\phi)$ can be represented as a Fourier series [21,22]

$$F(\phi) = F_0 + \sum_{k=1}^{\infty} F_k \cos(k\phi) \quad (18)$$

We substitute this relation into Eq. (5) and retain the first-order terms with respect to small ratios F_k/F_{av} fixed at $k \geq 1$. Thus, we get

$$\alpha = \phi + \frac{F_{\text{av}} - F_0}{2F_{\text{av}}} \phi - \sum_{k=1}^{\infty} \frac{F_k}{2kF_{\text{av}}} \sin(k\phi) \quad (19)$$

Note that the ratio $(F_{\text{av}} - F_0)/2F_{\text{av}}$ will be of the second-order smallness with respect to F_k/F_{av} and this term can be omitted. Within the same accuracy, we find

$$\phi = f^{-1}(\alpha) = \alpha + \sum_{k=1}^{\infty} \frac{F_k}{2kF_{\text{av}}} \sin(k\alpha) \quad (20)$$

Expanding the potential function $V[f^{-1}(\alpha)] = V(\alpha + \Delta\alpha)$ in a power series of $\Delta\alpha$, from Eq. (13) we immediately obtain

$$(V_{\text{eff}})_m = V_m + \frac{m^2 F_m}{2} - \sum_{k=1}^{\infty} \frac{F_k}{4kF_{\text{av}}} [(m+k)V_{m+k} - (m-k)V_{m-k}] \quad (21)$$

In the first order with respect to F_k/F_{av} , the term proportional to $(F')^2$ makes no contribution to this expression. Usually, there are the finite number (M) of the potential

Table 1 Rotational constants (F) and potential coefficients (V) for n -butane (all values in cm^{-1}). F_m and V_m are taken from [21]. $F_{\text{av}} = 1.6213 \text{ cm}^{-1}$

m	F_m	V_m	\tilde{V}_m	$(V_{\text{eff}})_m^{\text{exact}}$	$(V_{\text{eff}})_m^{\text{appr}}$
0	1.623	1,431	1,431	1,427.3	1,427.9
1	-0.0774	242	241.9607	231.5448	231.8993
2	0.0420	43	43.0840	80.3804	80.7874
3	-0.00789	1,148	1148.0	1,148.2	1,149.6
4	0.00204	40	40.0159	0.6951	-0.5670
5	-0.000469	-6	-6.0057	1.3777	0.6432
6	0.000113	-36	-35.9980	-36.7863	-36.5152
7			0.0000	2.6791	2.6863
8				-0.8270	-0.7243
9				0.1548	0.0929
10				-0.0351	-0.0161
11				0.0080	0.0030
12				-0.0019	-0.0006

coefficients V_m and the finite number ($K + 1$) of the rotational constants F_k . Then m runs through the values $1 \leq m \leq M + K$ in Eq. (21). Substituting the potential coefficients from (21) into the right-hand side of Eq. (14), we can estimate a reliability of approximation (21) with a finite number of terms. Thus, Eq. (21) allows one to calculate the expansion coefficients of the effective potential using the available Fourier coefficients V_m and F_k .

4 Results

As a rule, the effect of a variation F with ϕ is not too large for many molecules. Thus, we can restrict ourselves to this case choosing the n -butane molecule as an example. In n -butane, the asymmetric rotor has a plane of symmetry, which leads to an even parity of the potential function and allows it to be represented in a standard form of Eq. (11). The potential function governing the conformational interchange in n -butane has been more than once considered in the literature from both experimental and theoretical points of view [21, 22]. We have used the potential coefficients from [21] to set the reference potential for purposes of calculating the Fourier coefficients of the effective potential. The numerically exact $(V_{\text{eff}})_m$ values were calculated from Eq. (13) and the approximate values were found from Eq. (21). These values are listed in Table 1. The Fourier coefficients of the target potential are presented for comparison.

The numerical diagonalization of matrix $H_{kk'}$ provides the necessary energy levels arising below the potential barrier in n -butane. The method incorporates the lowest 200 energy levels; however, more levels can easily be included if needed. Table 2 summarizes the calculated values for the energy levels lying well below the *cis* barrier ($1,384 \text{ cm}^{-1}$). There is a close agreement between the numerically exact and

Table 2 Calculated energy levels of torsional motion (in cm^{-1}) for n -butane

Near the bottom of a barrier			Near the top of a barrier		
n	E_n^{exact}	E_n^{appr}	n	E_n^{exact}	E_n^{appr}
0	62.112	62.078	27	1,134	1,134
1	185.16	185.06	28	1,137	1,136
2	295.47	294.75	29	1,209	1,209
3	295.47	294.75	30	1,214	1,215
4	305.69	305.53	31	1,218	1,219
5	411.89	411.39	32	1,268	1,269
6	411.89	411.39	33	1,285	1,285
7	423.43	423.21	34	1,296	1,296
8	525.81	525.51	35	1,331	1,331
9	525.81	525.21	36	1,347	1,348
10	538.09	537.83	37	1,378	1,379

approximate E_n values. The energy levels for the *trans* conformation are nondegenerate. Because of the existence of two potential wells in the *gauche* conformation, the energy levels appear to be double degenerate. Above $1,000\text{ cm}^{-1}$ the degeneracy is lifted. It also shows that energy separations near the barrier top depend non-monotonically on the quantum number n owing to a complex form of the barrier and a change of internal motion from torsional oscillations to free rotation.

5 Conclusions

In the present work, we have applied the approach based on the canonical point transformation for hindered asymmetric rotors with the angle-dependent internal rotation constant. The numerical method developed can be used to calculate the energy levels of torsional motion for almost any periodic potential. As with any numerical method, there are many parameters that can be varied to enhance the accuracy of calculations. Just one of them is used in our method; it consists only in the number of necessary levels. The key equations of the method are Eqs. (13), (16) and (17) that give implicitly hindered rotor state energies. In the first stage, it is necessary to determine the target potential from the reference potential and to calculate then effective potential parameters using a mapping function. Perturbation approximation (21) that requires small deviations of the internal rotation constant from its mean value is sufficient in most cases of real molecules. The second stage includes the Hamiltonian matrix diagonalization. The problem of finding the eigenvalues of the symmetric matrix with a few diagonals with identical elements along each diagonal is very simple for numerical calculations, and may be solved with modest computer aids.

References

1. H.H. Nielsen, *Phys. Rev.* **40**, 445 (1932)
2. J.S. Koehler, D.M. Dennison, *Phys. Rev.* **57**, 1006 (1940)
3. K.S. Pitzer, W.D. Gwinn, *J. Chem. Phys.* **10**, 428 (1942)
4. C.C. Lin, J.D. Swalen, *Rev. Mod. Phys.* **31**, 841 (1959)
5. J.L. Wood, *Trans. Faraday Soc.* **62**, 1411 (1966)
6. V. Van Speybroeck, D. Van Neck, M. Waroquier, S. Wauters, M. Saeys, G.B. Marin, *J. Phys. Chem. A* **104**, 10939 (2000)
7. B.A. Ellingson, V.A. Lynch, S.L. Mielke, D.G. Truhlar, *J. Chem. Phys.* **125**, 084305 (2006)
8. D.G. Truhlar, *J. Comput. Chem.* **12**, 266 (1991)
9. R.B. McClurg, R.C. Flagan, W.A. Goddard, *J. Chem. Phys.* **106**, 6675 (1997)
10. W. Witschel, C. Hartwigsen, *Chem. Phys. Lett.* **273**, 304 (1997)
11. J.R. Barker, C.N. Shovlin, *Chem. Phys. Lett.* **383**, 203 (2004)
12. M.L. Strekalov, *Chem. Phys.* **355**, 62 (2009)
13. K.S. Pitzer, *J. Chem. Phys.* **14**, 239 (1946)
14. P. Vansteenkiste, V. Van Speybroeck, G.B. Marin, M. Waroquier, *J. Phys. Chem. A* **107**, 3139 (2003)
15. B. Fehrensens, D. Luckhaus, M. Quack, *Chem. Phys.* **338**, 90 (2007)
16. A.C.P. Bitencourt, M. Ragni, G.S. Maciel, V. Aquilanti, F.V. Prudente, *J. Chem. Phys.* **129**, 154316 (2008)
17. C. Tezcan, R. Sever, *J. Math. Chem.* **42**, 387 (2007)
18. M. Aktaş, R. Sever, *J. Math. Chem.* **43**, 92 (2008)
19. C.-S. Jia, L.-Z. Yi, Y. Sun, *J. Math. Chem.* **43**, 435 (2008)
20. A. Bauder, E. Mathier, R. Meyer, M. Ribeaud, H.H. Günthard, *Mol. Phys.* **15**, 597 (1968)
21. W.A. Herrebout, B.J. van der Veken, A. Wang, J.R. Durig, *J. Phys. Chem.* **99**, 578 (1995)
22. G.D. Smith, R.L. Jaffe, *J. Phys. Chem.* **100**, 18718 (1996)