A measure of basis efficiency at solving the Schrödinger torsion equation. Reaching the variational limit

A N Belov¹, V V Turovtsev², Yu A Fedina³ and Yu D Orlov¹

¹Tver State University, 33 Zhelyabova, Tver, Russia, 170100
²Tver State Medical University, 4 Sovetskaya, Tver, Russia, 170100
³EAHS DCSD 1701 Mountain Industrial Blvd, Stone Mountain, GA, 30083, USA

E-mail: belov.an@tversu.ru

Abstract. The procedure of the numerical solution of the Schrödinger torsion equation in matrix form in the planar wave basis set was considered. The concept of the largest level number that has reached the variation limit for a given number of basis functions was introduced as a quantitative measure of the basis efficiency. The rate of convergence to reliable values of levels and transitions has been studied. The problem of the maximum possible energy level number computed with the required accuracy for a given basis size has been solved. It was demonstrated that the number of levels that have reached the variational limit has linear relationship with the number of basis functions, and the angular slope coefficients of such dependencies are quite close to each other and equal to roughly 0.96. This allows prediction of the accuracy of the calculation method and conscious choice of the basis power.

1. Introduction

The spectroscopic and thermodynamic properties of compounds in quantum mechanics are studied within the scope of the model of motion separation where large-amplitude intramolecular motions make a significant contribution [1]. Usually, they are isolated from the oscillatory motion and considered separately. The greatest attention among these movements is paid to internal rotation. The internal rotation of the fragments of the molecule relative to each other is described by the Schrödinger torsion equation [2].

\[
\left( -\frac{d}{d\phi} F(\phi) \frac{d}{d\phi} + V(\phi) \right) \Psi = E \Psi
\]  

(1)

where \( V(\phi) \) is the potential, and \( F(\phi) \) is the structural function of the internal rotation. Solution (1) enables finding the probability amplitude \( \Psi(\phi) \) and torsion energy levels \( E \). The functions \( V(\phi) \) and \( F(\phi) \) are given in a table form for the problems of quantum mechanics of molecules, therefore, the initial calculation points \( V(\phi) \) and \( F(\phi) \) in (1) are approximated by some finite-dimensional basis set. The number of initial points imposes certain restrictions on the number of variable parameters and the approximation discrepancy. A segment of the trigonometric Fourier series is used in most calculations but the application of an “extended” basis set with additional degrees of freedom, however, is more efficient. For example, in [3], the approximation of the torsion potential and structural function in the basis set of Mathieu functions is substantiated.

Solution (1) is usually represented as an expansion in the corresponding complex-valued basis \( \{ U_n \} \)

\[
\Psi = \sum_{n=-\infty}^{\infty} \psi_n U_n,
\]  

(2)
where $\psi_m$ are the variable complex-valued coefficients. The basis size in reality is restricted based on the task requirements and the resource consumption of the calculations and the index $n$ runs over a series of integers $-N \leq n \leq N$ so the number of basis functions in $\{U_n\}$ is $M = 2N + 1$. Thus, the problem is solved for a limited set $\{U_n\}$

$$\sum_{n=-N}^{N} H_{mn} \psi_n = E_m \psi_m$$

(3)

on eigenvalues and eigenvectors of the matrix of the Hamiltonian $H_{mn}$, containing $M$ rows and columns.

The main question in solving problem (1) considering (2) and (3) is the selection of the most effective basis set that is determined by the *smallest* $M$ required to obtain the energy of the $m^{th}$ level with a given accuracy. The second question can be formulated as follows: how many reliable energy levels $m_{max}$ (accounting for a reasonable number of significant digits in the values of $E_m$) will provide the calculation of the eigenvalues of the Hamiltonian matrix (3) for the selected basis size $\{U_n\}$. It’s obvious that the use of large bases (large matrices $H_{mn}$) ensures obtaining a larger number of $E_m$ with the required accuracy while this quantity may be excessive in solving several applied problems. For instance, computation and diagonalization of very large matrices $H_{mn}$ is not necessary to determine levels located near the lower edge of the spectrum. In turn, an increase in basis (2) leads to a significant and sometimes an excessive number of mathematical operations, an increase in the computing time, etc. This matter becomes particularly relevant when studying molecules with several torsion rotations and using multidimensional potential energy surfaces where the non-optimal choice of the number $N$ for basis (2) can make the calculation simply unfeasible due to the requirements for memory capacity, error accumulation, the time spent, etc.

2. Evaluation for reaching the variational limit

The variational method is widely used in quantum mechanics, for example, at the Schrödinger equation solution [4, 5]. Moreover, the accuracy of the solution depends on the trial function choice. Quantitative efficiency evaluation of using the basis set on which the trial function is presented will be given below. We introduce some criteria to perform this.

The variational limit of the $m^{th}$ energy level is the quantity $E_{m}^{\infty}$ that the $m^{th}$ eigenvalue of the Hamiltonian matrix approaches with an infinite increase in the number of basis functions

$$E_{m}^{\infty} = \lim_{M \to \infty} E_{m}^{(M)}.$$  

(4)

In practice, when computing the energy of a specific level $E_{m}$, it’s pointless to increase basis (2) over a certain value $M_{\text{max}}$ because when using experimental data as “input quantities”, the accuracy $E_{m}^{(M)}$ cannot be higher than their accuracy and the numerical values of energy should always be rounded to significant digits (reliable digits of the input quantities). The significant digits $E_{m}^{(M)}$ at the lower $m$ levels stop changing when the basis size is higher and if the number of significant digits in $E_{m}^{(M)}$ corresponds to the experimental results, then it can be concluded that the basis of the size $M_{\text{max}}$ enabled the accuracy of $m$ levels specified by the input parameters and the actual values $E_{m}^{(M_{\text{max}})}$ have reached the variational limit.

In other words, the real variational limit of the $m^{th}$ energy level exists

$$E_{m}^{M_{\text{max}}} = \lim_{M \to M_{\text{max}}} E_{m}^{(M)}.$$  

(5)

The measure of reaching the variational limit in computer algorithms can be the value

$$\epsilon_{m}^{M,k} = E_{m}^{(2(N+k)+1)} - E_{m}^{(2N+1)},$$  

(6)

representing the energy difference of the level $m$ of the initial calculation when adding $k$ basic functions (which corresponds to adding $2k$ rows/columns to the Hamiltonian matrix) in (3).

The Rayleigh – Ritz variational procedure [5-7] always leads to the fact that energies below a certain level will change insignificantly or their significant figures will not change at all with an increase of the Hamiltonian matrix size. If $M = M_{\text{max}}$ in (6) is assumed to be quite large and extends beyond the limits of available computing capabilities, then we can set a small value $\epsilon_{0}$ such that approaching some $M$

$$\epsilon_{m}^{M,k} \leq \epsilon_{0}.$$  

(7)
Selection $\varepsilon_0$ depends on further application of $E_{\text{sn}}$. It affirms from the experiment that it is enough to specify $\varepsilon_0$ with the order of tenths of a cm$^{-1}$ (the dimension of the points $V(\varphi)$ and $F(\varphi)$, as a rule, is given in cm$^{-1}$). If relation (7) is satisfied, such a level $m$ will be defined as a level that has reached the variational limit. Considering the case when $m = 0$ has a particular interest (the variational limit for the zero level) and the dependence $m_{\text{max}}$ (the number of the highest level that reached the variational limit for a given $\varepsilon_0$) on the number of basis functions $M$.

Some of the few studies related to the question of the variational limit of the Hamiltonian matrix although without introducing a rigorous mathematical description are [6, 8–10]. So in [8] the energy levels for H$_2$O molecule were compared depending on the sizes of the Morse and harmonic bases when solving anharmonic problems. In [9] the convergence of various level values for the CO$_2$ molecule was studied depending on the size of the basis set. In [10] an example of the convergence of the first three overtones C–H vibrations of the HCN molecule with a change in the number of basis functions for the “intrinsic” and “extended” basis is given. It was demonstrated that convergence has monotone nonlinear pattern.

The review performed above allows the use of $m_{\text{max}}$ as a quantitative measure of the effectiveness of the chosen basis in this problem. The goal of the present work is to establish the type and parameters of the dependence of the number of levels that have reached the variational limit ($m_{\text{max}}$) on the size of the basis $2N + 1$ in the variational solution of the Schrödinger equation.

3. Variational limit for torsion energy levels

The concepts and rules discussed above were examined using ethanol, methacrolein (CH$_2$=C(CH$_3$)–COH) and the FC*HC$_3$H$_7$ radical as an example. The choice of ethanol is justified by a significant amount of collected experimental data on spectroscopy which is in good agreement with theoretical calculations [11–14]. The methacrolein molecule is an example of a more complex molecule that has symmetry elements and has been sufficiently studied theoretically and experimentally [15]. The third molecule FC*HC$_3$H$_7$ is an asymmetric radical with rotation of the FCH fragment with a potential function referenced in [16]. Thus, the examples used enable us to demonstrate the difference in the behaviour of the variational limits $m_{\text{max}}$ when the torsion energy levels in symmetric and asymmetric compounds are calculated.

As usual, the structural function $F(\varphi)$ and potential $V(\varphi)$ of internal rotation are approximated by trigonometric series for the symmetric (8.1), (8.2) and asymmetric (8.3), (8.4) cases

\[
F(\varphi) = F_0 + \sum_k F_k \cos(k\varphi),
\]

\[
V(\varphi) = \frac{1}{2} \sum_n V_n (1 - \cos n\varphi),
\]

\[
F(\varphi) = F_0 + \sum_k F'_k \cos(k\varphi) + \sum_k F''_k \sin(k\varphi),
\]

\[
V(\varphi) = V_0 + \sum_k V'_k \cos(k\varphi) + \sum_k V''_k \sin(k\varphi).
\]

Torsion energy levels of the considered compounds were determined in the basis of planar waves [17, 18] for a different number of basis functions $\{U_n\}$. Figures 1–5 display the convergence of some torsion levels and their corresponding transitions based on the size of the basis (2) for selected molecules. The parameters for all dependencies are set as follow $\varepsilon = 0.1$ cm$^{-1}$ and the step $k = 1$ (7). The results of calculations of the zero level energy of ethanol in various conformations based on the number of basis functions are presented in figure 1.

The presented data shows that the energies of the lower torsion levels and the main transition reach the variational limit even at $M = 15$. This means that such a basis size is sufficient to calculate $E_{\text{sn}}$ and the main transition in ethanol with a required accuracy. The violation of the dependence monotony of the main transition is due to the splitting of two gauche levels, which are very close to the main level. This feature is due to the structure of the ethanol molecule and therefore is absent in the other two molecules considered here.
Figure 1. The dependence of the torsion energy levels values and the main transition of ethanol on the basis size.

Figure 2. The dependence of the energy values of torsion levels 24 and 25 and the transition 25→24 in ethanol on the size of the basis.

Figure 2 presents similar results for levels 24 and 25 and the corresponding transition. The variational limit of these levels is reached at approximately $M = 31$.

Figure 3 displays a pattern of energy convergence of the zero level, first torsion level, and the main transition in the methacrolein molecule. It is evident that the variational limit of the zero and first levels
is achieved at $M = 27$ and $M = 35$ respectively. The variational limit of the main transition is equal to the same of the first level (occur at the same $M$).

![Figure 3](image1.png)

**Figure 3.** Dependence of the torsion energy levels and the main transition for internal rotation in a methacrolein molecule on the basis size.

![Figure 4](image2.png)

**Figure 4.** The dependence of the energy values of torsion levels 24 and 25 and the transition 25→24 in methacrolein on the basis size.

The dependences similar to those in figure 2 showing the pattern of convergence of levels 24, 25 and the transition 25→24 to the variational limit for the methacrolein molecule are constricted in figure 4. The values $M$ required to reach vibrational limits of levels 24 and 25 vary significantly – 77 and 63 respectively.
Figure 5. Dependence of the values of torsion energy levels and the main transition upon rotation of the FCH fragment in the FC*H-C3H7 molecule on the basis size.

Figure 6. The dependence of the energy values of torsion levels 24 and 25 and the transition 25→24 upon rotation of the FCH fragment in the FC*H-C3H7 molecule on the basis size.

Reaching the variational limit of levels 24, 25 and the transition between them in the asymmetric compound FC*H-C3H7 is shown in figure 6.

According to the graphs, the rate of convergence of the torsion level energies to the variational limit in a symmetric molecule exceeds the same for an asymmetric one. The transition energies also decline with an increase in the basis set and reaching the variational limit occurs either at an equal convergence
of the level energies (the difference $E_{m+1}$ and $E_m$ is constant) or at the convergence of both levels. Moreover, the variational limits of transitions in high levels regions are reached faster than in low ones.

4. The dependence of an efficiency measure of using the basis on the number of basis functions
Let’s consider the question about the dependence of the number of levels $m_{\text{max}}$ that have reached the variational limit on the number of basis functions $M$ (i.e. how many reliable energy values are provided by the basis of the $2N + 1$ functions in expansion (2)) and the relationship among them. To clarify this, we will conduct a computational experiment for each molecule considered above – we will check the condition (7) for different basis sizes.

![Graph](image)

**Figure 7.** The dependence $m_{\text{max}}$ (the index of the highest level reaching the variational limit) on the basis size $M$ at $\varepsilon = 0.1$ cm$^{-1}$ and $k = 5$.

5. Conclusion
The results of the mentioned above calculations are revealed in figure 7. The number of basis functions $M$ was plotted along the abscissa axis and the number of reliable energy values $m_{\text{max}}$ was plotted along the ordinate axis satisfying the condition (7). Insignificant deviations from the linear approximation in the segment before $M = 101$ are observed for molecules with a complex internal structure. All three dependences are quite close to each other and are well described by linear regression when $M$ is greater than 101

$$m_{\text{max}} = \alpha M + b.$$  \tag{9}

It is clear that values of $M$ near zero do not make sense from the context of the problem. Linear regression (9) produces the following results: $m_{\text{max}} = 0.9237M - 6.6212$ for ethanol, $m_{\text{max}} = 0.9906M - 26.581$ for methacrolein, $m_{\text{max}} = 0.9592M - 29.525$ for the $\text{FC}^*\text{H}-\text{C}_3\text{H}_7$ molecule. It’s very important that the dependencies for symmetric and asymmetric molecules are characterized by a similar angular coefficient $\alpha$. The values of $\alpha$ are equal to 0.9237 for ethanol, 0.9906 for methacrolein and 0.9592 for the case of asymmetric rotation. The following examples enable the acceptance $\alpha \approx 0.96$. 
The linear dependence parameter $\alpha$ (9) serves as the summarizing indicator of the effectiveness of the applied method [3], its specific implementation in computer codes and the basis set (in this case [2]). Similar values of the coefficient $\alpha$ for different molecules permit us to answer the question – what basis size is required to obtain reliable values of torsion energy. Similar estimates can also be used to characterize the effectiveness of other sets of functions.

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