Comparative Study of Two Approaches for Solving the Torsional Schrödinger Equation: Fourier Grid Hamiltonian Method and Hamiltonian Diagonalization Method

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***Abstract*—In this study, we have compared the computational performance of two methods implemented to solve the Schrödinger equation for intramolecular torsional motions. The first approach is the Fourier grid Hamiltonian (FGH) operator method, which is based on fragmentation of the total torsional Hamiltonian into kinetic energy part, which is diagonal in momentum representation, and the potential energy part, diagonal in coordinate representation. The second approach is the standard diagonalization technique, based on variational principle of quantum mechanics. Torsional energy eigenvalues are further used to compute the torsional correlation times in the framework of BPP (Bloembergen-Purcell-Pound) approach. The results show that diagonalization technique performs much faster than the FGH algorithm. Besides that, the convergence of eigenvalues with the number of basis functions appears to be achieved faster with Hamiltonian diagonalization**

Keywords*—torsional Shcödinger equation, Fourier Grid Hamiltonian method, diagonalization technique, computational performance

I. Introduction

Solution of the torsional Schrödinger equation is a problem that arises in many areas of contemporary science and technology, and is therefore a rather relevant computational task. If one wants to treat rigorously (*i.e.* quantum-mechanically) the intramolecular hindered rotations of particular atomic groups, it is necessary to go beyond the classical approximation in treating such motions. For example, in case of molecular systems which are potential candidates for molecular switches or transistors, one of the possible mechanisms that underlay the switching behavior is the conformational transition between two (or in principle, even more) possible conformations in the considered molecule. The potential energy function $V(\varphi)$ for this motion is often conveniently represented as Fourier series expansion, which allows one to easily account for the inherent symmetry of intramolecular motion:

$$V(\varphi) = V_0 + \sum_{n=1}^{\infty}[V_n \cos(n\varphi) + V'_n \sin(n\varphi)] \qquad (1)$$

The corresponding torsional Hamiltonian is:

$$\hat{H}_{\text{torsion}} = -\frac{\hbar^2}{2I_\varphi}\frac{\partial^2}{\partial\varphi^2} + V(\varphi) \qquad (2)$$

In the last equation, φ is the torsional variable (angle), I is the moment of inertia corresponding to the motion considered, while ($\hbar$ being Planck's constant). In principle, the torsional transitions may occur as a result of classical "over the barrier" flip, by intrawell transitions (between different states within the same well of the potential), and due to tunneling between adjacent wells. Accounting for all these types of torsional transitions is essential if one wants to describe the actual realization and functioning of a molecular device under realistic conditions. To achieve this aim, however, one has to solve the torsional Schrödinger equation as a first step. In the present study, we consider a solution of such equation for a realistic molecular system.

The goal of our research is to find the computational performance of the Fourier Grid Hamiltonian method and standard diagonalization technique of the Hamiltonian matrix to solve the Schrödinger equation for intramolecular torsional motions. The Fourier Grid Hamiltonian method is diagonal in momentum representation, and the potential energy part, diagonal in coordinate representation. The transformation between the two representations is achieved via Fourier transformation algorithm using a suitably chosen grid of points.

In a case of the standard diagonalization technique, the Hamiltonian operator is written in matrix representation within a suitably chosen basis set, consisting of the free rotor wave functions. The Hamiltonian matrix is further diagonalized, giving energy eigenvalues and eigenfunctions.

When applying the Fourier Grid Hamiltonian operator method, the dependence of computational performance and the convergence of obtained torsional energy levels on the number of grid points used are analyzed, while when applying the standard diagonalization technique, the dependence of

computational effectiveness and the convergence of obtained torsional energy levels on the number of basis functions is studied. Special attention was paid to the high-energy bound levels (close to the torsional barrier) and their convergence in both cases.

The paper is organized as follows. The related work is given in Section 2. The methods for solving the torsional Schrödinger equation are described in Section 3. Section 4 presents the experiments and results of the experiments for measuring the computational effectiveness of the applied methods. The conclusion and future work are exposed in Section 5.

II. Related Work

Solution of the torsional Schrödinger equation has been a research subject for several authors. Turovtsev et al. [1] find the characteristics of the internal rotation based on the solution of the torsion Schrödinger equation. They solved the one-dimensional torsional Schrödinger equation with a general periodic potential and found the relations for the calculation of eigenvalues and eigenfunctions of the Hamiltonian of internal rotational motion in molecules in the basis of plane waves. In [2], the authors present a numerical method for solving the approximate Schrödinger equation (SE) for a single internal motion. They pay special attention to computer programs for calculations and their applications to torsional studies in areas of spectroscopy, thermodynamics, and reaction rates.

A comparison of the methods for solving the vibrational Schrödinger equation is given in [3]. The authors apply three numerical methods to compute the anharmonic OH stretching vibrational frequencies of the free and aqueous hydroxide ion on the basis of one-dimensional vibrational potential energies: simple Hamiltonian matrix diagonalization technique, based on representation of the vibrational potential in Simons-Parr-Finlan (SPF) coordinates, Numerov algorithm and Fourier grid Hamiltonian method (FGH). According to their research, the diagonalization technique performs remarkably well in a very wide range of frequencies and frequency shifts (up to 300 cm1) and FGH method, showed a very good performance, exhibits more significant (and nonuniform) discrepancies with the Numerov algorithm, even for rather modest frequency shifts.

III. Methods for Solving the Torsional Schrödinger Equation

A. Fourier Grid Hamiltonian Method

The Fourier grid Hamiltonian (FGH) method is a special case of a discrete variable representation method (DVR) described in [4] [5]. The FGH method generates the wavefunctions of the Hamiltonian operator as amplitudes of the wave function on the grid points. It is simple because the wavefucntions are not given as a basis functions or as a linear combination [6]. Discretization is achieved when the continuous range of the coordinates values x is replaced by a grid of discrete values x_i. The uniform grid x_i is defined as:

$$x_i = i\Delta x \tag{3}$$

where Δx is the uniform spacing between the grid points.

The state function (property of a system which depends only on the current state of the system) $|\psi\rangle$ can be given as a vector on a discretized grid of points in coordinate space represented as:

$$|\psi\rangle = \psi^x = \sum_i |x_i\rangle \cdot \Delta x \cdot \psi(x_i) = \sum |x_i\rangle \cdot \Delta x \cdot \psi_x^i \tag{4}$$

where $|x_i\rangle$ are basis functions or in momentum space represented as:

$$|\psi\rangle = \psi^k = \sum_i |k_i\rangle \cdot \Delta k \cdot \psi(k_i) = \sum |k_i\rangle \cdot \Delta k \cdot \psi_k^i \tag{5}$$

where Δk is the reciprocal grid size in momentum space and it is defined as:

$$\Delta k = \frac{2\Pi}{N\Delta x} \tag{6}$$

and $N\Delta x$ is the total length of the coordinate space covered by the grid. The grid points are evenly distributed about $k = 0$ which is the central point in the momentum space [3] [6].

The transformation from one to other representation is performed by using the Fourier transform technique (FTT) that decomposes a function of time (signal) into the frequencies that it is made of [7]. Transformation between the two representations can be written as:

$$\psi^k = U * \psi^x \tag{7}$$

where U is an unitary matrix.

We also have to define a column vector matrix ϕ_n where each element is 0 except the unity element in the n-th row:

$$\phi_n = \begin{pmatrix} 0 \\ 0 \\ \vdots \\ 1 \\ \vdots \\ 0 \\ 0 \end{pmatrix} - \text{n-th row} \tag{8}$$

The $n_t h$ column of the Hamiltionan matrix can be represented as follows by implementing a forward and reverse FFT:

$$H_{in} = [(U^{-1}TU + V)\phi_n]_i \tag{9}$$

where T and V are the diagonal kinetic energy and potential energy $[V(x_i)]$ matrices. The complete Hamiltionian matrix H can be generated by repeating this process for all possible N vectors ϕ_n.

B. Standard Diagonalization Technique Method

Schrödinger equation can be solved by using the standard matrix diagonalization technique. In this case, the wavefunction is represented as a finite set of basis functions. The eigenfunctions and eigenvalues are found from the diagonalization of the Hamiltonian matrix [8].

The Schrödinger equation can be written in the following form [9]:

$$\hat{H}\psi(q) = E\psi(q) \tag{10}$$

where $\hat{H}$ is the Hamiltonian operator, $\psi(q)$ are eigenfunctions and E are eigenvalues of $\hat{H}$. This equation is solved by finding the eigenvalues and eigenfunctions of the Hamiltonian operator.

If we split the function $\psi(q)$ in basis functions, we can write the $\psi(q)$ as:

$$\psi(q) = \sum_n a_n \varphi_n(q) \tag{11}$$

and if we replace the $\psi(q)$ in the eq. 10:

$$\hat{H}\sum_n a_n \varphi_n(q) = E\sum_n a_n \varphi_n(q) \tag{12}$$

Hamiltonian operator is a linear operator and it can be embedded in the sum:

$$\sum_n a_n(\hat{H}\varphi_n(q)) = E\sum_n a_n \varphi_n(q) \tag{13}$$

If (13) is multiplied scalarly by $\varphi_m^*(q)$ and integrated by q, then we get the following:

$$\sum_n a_n \int \varphi_m^*(q)\hat{H}\varphi_n(q)\mathrm{d}q = \sum_n a_n E \int \varphi_m^*(q)\varphi_n(q)\mathrm{d}q \tag{14}$$

$$\int \varphi_m^*(q)\hat{H}\varphi_n(q)\mathrm{d}q = H_{mn} \tag{15}$$

$$\int \varphi_m^*(q)\varphi_n(q)\mathrm{d}q = \delta_{mn} \tag{16}$$

If we substitute in (14), we have:

$$\sum_n a_n H_{mn} - \sum_n a_n E\delta_{mn} = 0 \tag{17}$$

Equation (17) can be written in the following form:

$$\sum_n a_n(H_{mn} - E\delta_{mn}) = 0 \tag{18}$$

where H_{mn} is the matrix element of the Hamiltonian operator $\hat{H}$.

An homogeneous algebraic system of equations is defined by (18). It has a nontrivial solution if its determinant is equal to zero:

$$|H_{mn} - E\delta_{mn}| = 0 \tag{19}$$

Equation (19) is a polynomial whose roots are the possible values of E. Thus, the eigenvalues of $\hat{H}$ are roots of (19). The eigenfunction, which corresponds to a given eigenvalue is determined such that the given eigenvalues is inserted in (17). Thus, the system of coefficients a_n is determined ant that helps to find the corresponding eigenfunction.

The elements H_{mn} determined by (15) are called matrix elements of the Hamiltonian operator $\hat{H}$ in the basis functions $\varphi_n(q)$ and they constitute the matrix $[H]$:

$$[H] = \begin{bmatrix} H_{11} & H_{12} & \dots & H_{1n} & \dots \\ H_{21} & H_{22} & \dots & H_{2n} & \dots \\ \dots & \dots & \dots & \dots & \dots \\ H_{n1} & H_{n2} & \dots & H_{nn} & \dots \\ \dots & \dots & \dots & \dots & \dots \end{bmatrix} \tag{20}$$

From (12), it follows that the functions $\psi(q)$ have a corresponding column vector:

$$\psi(q) \rightarrow \begin{bmatrix} a_1 \\ a_2 \\ \dots \\ a_n \\ \dots \end{bmatrix} \tag{21}$$

If the matrix $[H]$ is diagonal, then its diagonal elements determine the eigenvalues of the operator $\hat{H}$.

IV. Experiments and Results

A. Testing environment

The testing of these two different approaches for solving the torsional Schrödinger equation was performed by using the Fourier Grid Hamiltonian 1D Program (FGH1D) [10] and Basis-set Expansion solver for 1-Dimensional Schrödinger equation (BEx1D) [11].

The FGH1D program calculates the energy levels (eigenvalues) and wavefunctions (eigenvectors) for a given one-dimensional potential. It solves the Shrödinger equation variationally by using the Fourier Grid Hamiltonian method which is described in the subsection III-A. This method uses a basis set of delta functions and it requires an even number of grid points (basis functions). The accuracy increases with increasing the number of grid points. The most computationally intensive part is the matrix diagonaization. We used the option $cos(nx)$ potential which is useful for describing torsional rotations. The range is set automatically to be 0 to $2p(p-1)/p$ where p is the number of grid points, x is an angle in radians and the moment of inertia (in our case 22.84588830778) is expressed in amu * Å^2 (Å=Ångströms, 1Å = 10^{-10} m, amu = atomic mass unit.

The BEx1D program is a package of calculation tools for finding eigenstates and partition functions of intramolecular nuclear motions, for which harmonic oscillator approximation is inadequate. We used the bx1HRsol file which is Schrödinger-equation eigen-problem solver for a intramolecular one-dimensional hindered Rotation on a Fourier series potential. The basis functions used by bx1HRsol are the free-rotor eigen functions. We only had to change the number of basis functions maxAbsQN which is the maximum absolute J. For example, if maxAbsQN= 50, the program will use

101 basis functions in total from $J = -50$ to $+50$. Another parameter that we have specified is the rotational constant (rotConst) which in our case was set to 0.738488849 cm^{-1}.

Both programs were run under the Windows operating system on a single node computer with Intel Core 2 Duo processor with speed of 2.26 GHz.

B. Results

The computational performances of the used programs are obtained by measuring the time required for the program execution for a different number of basis functions (grid points). The maximum number of basis functions when using the BEx1D program is 3001 (maxAbsQN= 1500) and the maximum number of grid points when using the FGH1D program is 710. The execution times (in seconds) of the programs are shown in the fig. 1. The x-axis denotes the number of grid points or basis functions. The y-axis denotes the execution time in seconds.

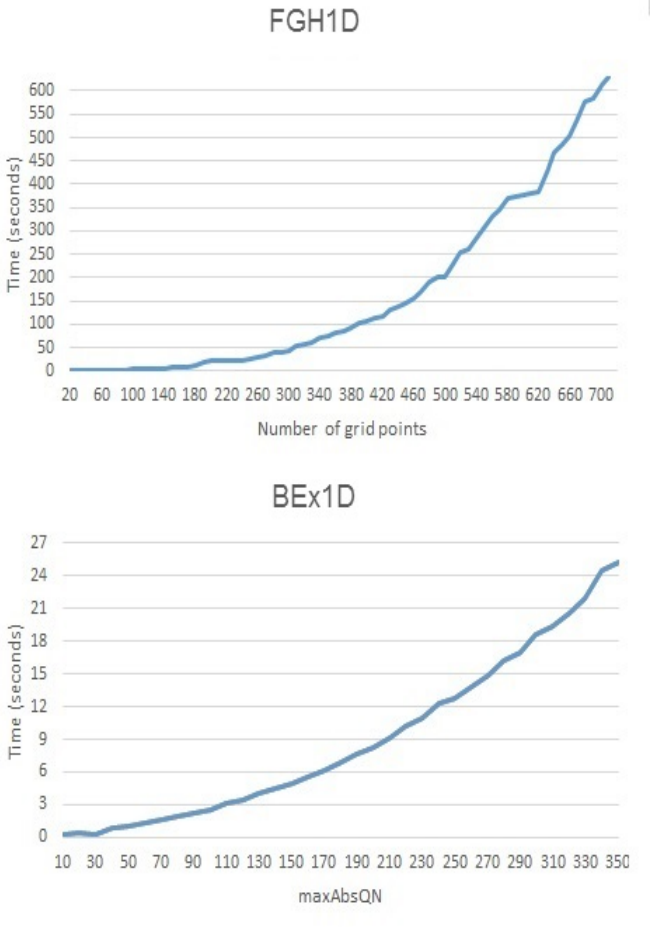

Fig. 1. Comparison of the execution times of BEx1D (up) and FGH1D program (down)

The execution times of the BEx1D program, starting for 101 (maxAbsQN= 50) to 3001(maxAbsQN= 1500) basis functions are shown in fig. 2.

The convergence with an error of 1% relative to the converged one has been achieved with the FGH1D method for 102 grid points. In the case of diagonalization technique, on the other hand, such convergence is achieved with 47 basis functions.

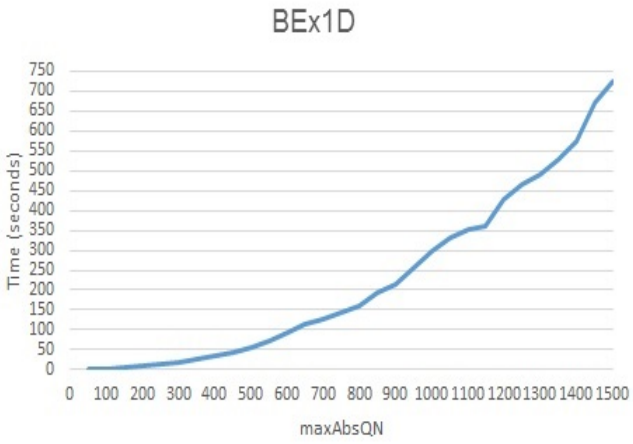

Fig. 2. Execution times of BEx1D program

V. Conclusion and Future Work

In conclusion, we can summarize the results of the present work as follows. Making an analogy between the number of grid points used to discretize the operators in the FGH1D methodology and the number of basis functions in diagonalization technique, one can see from Fig. 1 and Fig. 2 that the diagonalization technique performs much faster than the FGH1D algorithm. Besides that, the convergence of eigenvalues with the number of basis functions appears to be achieved faster with Hamiltonian diagonalization in the basis of free-rotor wavefunctions than by discretization technique. Further improvements of both techniques are certainly possible from a purely computational viewpoint, either by implementing more efficient large matrix diagonalization parallel algorithms and more efficient Fourier transformation algorithms that allow transition from coordinate to momentum basis in FGH technique.

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