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Improved methods for mapped grids: Applied to highly excited vibrational states of diatomic molecules

S. Kallush *, R. Kosloff

The Fritz Haber Research Center, The Hebrew University of Jerusalem, Jerusalem 91904, Israel

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Abstract

The origin of an artifact known as the appearance of *ghost states* in mapped Fourier grid methods is investigated. It was found that the ghost states can be attributed to under sampling of the high momentum components which are folded from the inner to the outer region of the potential to create the ghosts. The effect was corrected by addition of a complex potential at the outer region. The exterior complex potential was shown to shift the ghost states to the continuum part of the spectrum in a controllable way. The various methods to improve the mapped grid method are discussed in this context, and the use of zero boundary conditions is shown to be not essential.

1. Introduction

The computational cost of a quantum calculation crucially depends on the size of the Hilbert space N used for the simulation. Dynamical calculations can be made to scale semi linearly with the number N ($O(N\log N)$) directly for propagation methods, or as $O(N^3)$ for methods based on diagonalization [1]. Practically, N becomes the number of grid points required to converge the calculation. Efficient computational methods tend to minimize the number N as much as possible. The idea is to limit the representation to points where the probability amplitude of the wavefunction is above a certain threshold value. A preestimation of the number of grid points can be obtained by examining the representation boundaries in phase space. Once an upper limit for the energy in the calculation is established, the phase space volume contained in this energy shell can be calculated from the Hamiltonian. In one dimension the minimum number of points N is the phase pace volume $\mathscr{V}$ divided by $\hbar$, $N_{\min} = \frac{\mathscr{V}}{\hbar}$ [2]. Outside the energy shell the wavefunction will decay exponentially fast and some sampling points are required to represent the evanescent part of the wavefunction. As a result the actual number of points required to achieve exponential convergence is larger than $N_{\min} = \frac{\mathscr{V}}{h}$ [2,3]. In addition, sampling considerations increase further the number of grid points. For example, a uniform grid has a rectangular shape in phase space. The boundaries of such a grid have to be set to contain the extreme points of the energy shell. If the shape of the energy shell is convoluted most of the phase space area of the rectangular representation is waisted. This leads to a lower sampling efficiency $\eta = \frac{N_{\text{Min}}}{N} \ll 1$. The problem is particularly acute in the field of ultracold scattering and photoassociation. A very small grid spacing is required to represent the maximum momentum the colliding atoms acquire when they approach each other. On the other hand, the grid has to be extended to extremely large distances in order to describe the very long De-Broglie wavelength of the cold atoms in free space. The sampling efficiency can be as low as $\eta \approx 10^{-4}$.

A solution to the grid optimization problem was suggested by Fatal et al. [4] which introduced a mapping function from a uniform to a non-uniform grid. Such a grid has a denser sampling at points with higher momentum values. As a result, the sampling correlates position with momentum. An important addition to the mapping procedure

* Corresponding author.
E-mail address: kallush@fh.huji.ac.il (S. Kallush).

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was developed by Kokoouline et al. [5] suggesting the use of a semiclassical mapping function. The idea is to relate the local grid spacing to the inverse of the classical momentum corresponding to the value of the energy shell at that point. An improvement of the sampling to account for regions where the semi-classical approximation is not valid was suggested by Nest and Meyer [6]. Since its introduction the semiclassical procedure has been extensively used in the field of ultracold molecules [7]. For example calculating the last bound levels of alkali diatomic molecules as well as in simulating photoassociation of ultracold atom pairs [8,9]. The mapping procedure enabled accurate calculation of these processes which was not possible before.

Despite this success, a troubling artifact appeared and was termed *ghost* states [10]. The signature of these states showed unphysical energy states embedded in the physical spectrum of bound states. Most of the amplitude of the ghost was at large interatomic distances. The exact origin of the ghost states has never been fully understood. It was found that the use of fixed boundary conditions that vanish at the end of the grid eliminate some of the ghost states. This enforcement of zero boundary conditions is restrictive. Moreover, it sets constraints on the number of grid points to contain exact integer number of periods, a limitation which does not necessarily relate directly to the system under consideration.

In this Letter we characterize in more details the ghost states and suggest an explanation of their origin. We show also that a complex scaling of the potential, namely, the addition of imaginary boundary conditions to the potential can be used as a simple and natural solution to the removal of ghost states.

The outline of this Letter is as follows: in Section 2 we will describe shortly the mapped Fourier grid method, following Refs. [5,10]. Section 3 will investigate the features of the ghost states and will try to deduce explanation of their origin. In Section 4 we will show the usefulness of an addition of an exterior complex potential in removing these states from the spectrum. Section 5 will conclude and summarize the discussion.

2. The mapped fourier grid method

The purpose of the mapping procedure is to find the most efficient grid representation for the Hamiltonian of the form:

$$\widehat{\mathbf{H}} = \widehat{\mathbf{T}} + \widehat{\mathbf{V}} \tag{1}$$

where $\widehat{\mathbf{H}}, \widehat{\mathbf{T}}$ and $\widehat{\mathbf{V}}$ are the Hermitian Hamiltonian, kinetic and potential energy operators. A *uniform* Fourier grid will be built according to the following steps:

1. The energy space of the problem $E_{\max}$ and $E_{\min}$ is estimated. Typically $E_{\min}$ is the bottom of the attractive potential and $E_{\max}$ is the maximum kinetic energy of the colliding pair to be represented on the grid.
2. Using $E_{\max}$ and a semiclassical estimation of tunneling $R_{\min}$ is determined. $R_{\max}$ is determined to include all the interval needed to represent the last bound state. The grid interval becomes $L_R = R_{\max} - R_{\min}$.
3. By estimating the maximal kinetic energy $T_{\max} = E_{\max} - V_{\min}$, the maximal possible semiclassical momentum is calculated $p_{\max} = \sqrt{2mT_{\max}}$, where m is the reduced mass of the pair. The corresponding grid in momentum space has to comply with $|p| \leqslant p_{\max}$, so that $L_p = 2p_{\max}$.
4. Each volume in phase space at the size of $\hbar$ should hold at least one grid point. The number of grid points to support the system will be than given by: $N\hbar = L_R L_p$.
5. Distribute the N grid points equally on the grid (each grid point at the middle of a segment).

The operator $\widehat{\mathbf{V}}$ in this coordinate representation is diagonal. The kinetic energy operator $\widehat{\mathbf{T}}$ can be evaluated either numerically by bidirectional FFT, or analytically as :

$$\widehat{\mathbf{T}}_{i,i} = \frac{\pi^2}{mL_R^2}\frac{N^2+2}{6} \tag{2}$$

$$\widehat{\mathbf{T}}_{i\neq j} = \frac{\pi^2}{mL_R^2}\frac{(-1)^{i-j}}{\sin^2[(i-j)\pi/N]} \tag{3}$$

assuming an even number of grid points. For the case of odd number of points see [11]. For large grids the numerical application of $\widehat{\mathbf{T}}$ is more efficient since it scales as $O(N\log N)$ compared with $O(N^3)$ for applying Eq. (3) while the accuracy of the two is comparable.

An important feature of the uniform Fourier grid method is that the considerations for choosing the grid are *global*. Each of the grid points can support the largest possible momentum required. This over-estimation is reduced significantly by using a Mapped Fourier Grid. The algorithm for building a mapped Fourier grid is the following:

1. Use the same grid length in coordinates L_R as was determined in the uniform Fourier grid method.
2. Beginning from the inner grid point $R_{\min}$, integrate the local classical action up to β to get R_1:

$$\beta = \left(\frac{2m}{\pi^2}\right)^{\frac{1}{2}} \int_{R_{\min}}^{R_1} \sqrt{E_{\text{add}} - V(r)}\,\mathrm{d}r. \tag{4}$$

   E_{add} is given by the maximal asymptotic kinetic energy to be represented on the grid, usually with small additional energy to allow the extension of the grid to classically forbidden zones. The parameter $\beta \leqslant 1$ serves as an estimation for the local volume coverage in phase space. Smaller values of β will distribute more points on the grid, while for $\beta = 1$ the minimal classical estimation for the needed phase space density of the points is taken.
3. Continue to integrate the action from R_1 to get R_2, R_3 etc. to the end of the physical grid, with $R_N = R_{\max}$.
4. The length of the *mapped* grid L_x is given by $\beta(N-1)$.