

High order finite difference algorithms for solving the Schrödinger equation in molecular dynamics

Raul Guantes and Stavros C. Farantos^{a)}

Institute of Electronic Structure and Laser, Foundation for Research and Technology-Hellas, Iraklion, Crete, 711 10, Greece

(Received 20 May 1999; accepted 20 September 1999)

The view of considering global Pseudospectral methods (Sinc and Fourier) as the infinite order limit of local finite difference methods, and vice versa, finite difference as a certain sum acceleration of the pseudospectral methods is exploited to investigate high order finite difference algorithms for solving the Schrödinger equation in molecular dynamics. A Morse type potential for iodine molecule is used to compare the eigenenergies obtained by a Sinc Pseudospectral method and a high order finite difference approximation of the action of the kinetic energy operator on the wave function. Two-dimensional and three-dimensional model potentials are employed to compare spectra obtained by fast Fourier transform techniques and variable order finite difference. It is shown that it is not needed to employ very high order approximations of finite differences to reach the numerical accuracy of pseudospectral techniques. This, in addition to the fact that for complex configuration geometries and high dimensionality, local methods require less memory and are faster than pseudospectral methods, put finite difference among the effective algorithms for solving the Schrödinger equation in realistic molecular systems. © 1999 American Institute of Physics. [S0021-9606(99)30147-1]

I. INTRODUCTION

Our understanding of basic molecular phenomena is strongly based on our ability to successfully simulate such processes. In this respect, the solution of the Schrödinger equation for realistic molecular systems constitutes the aim of quantum molecular dynamics and the way to obtain reliable quantitative predictions. However, very useful physical insight can be gained from the use of a causal time dependent picture where for instance the path of a molecular encounter or a vibrational motion can be traced in configuration space. Therefore, much effort has been directed toward the development of methods which combine classical description with quantum corrections. Accurate wave packet propagation, together with knowledge of the proper classical orbits of the system, is one of the most complete views that we can have for a molecular process because exact numerical results are supplemented by a very clear physical picture. Such a program is accomplished by locating families of periodic orbits which then can be used to assign initial conditions for the wave packets.^{1,2}

Grid methods for the solution of the Schrödinger equation are nowadays one of the most powerful and exploited tools both for the time independent [here mainly known as discrete variable representation (DVR)] and time dependent pictures. Concerning the latter, it was the introduction of the Fourier pseudospectral (PS) method which provided the necessary accuracy and computational efficiency to compete with the traditional variational techniques and to make feasible the task (for an excellent review see Ref. 3). In the time

dependent picture or wave packet propagation, the wave packet is advanced in time by an evolution operator which, if the Hamiltonian \hat{H} is time independent, is an exponential function $\hat{U}(t; \hat{H}) = e^{-i\hat{H}t/\hbar}$ (from now on we take $\hbar = 1$). This can be approximated by, for instance, a polynomial expansion.⁴ The basic operation is therefore reduced to the evaluation of the action of the Hamiltonian operator onto the wave packet, $\hat{H}\Psi$. In long time propagation this operation has to be repeated many times, and thus, its efficiency will generally determine the computational cost of the problem. In practice, the wave function is often discretized in a grid using a collocation method and the Hamiltonian operator is represented by a matrix. If we considered only local operators this matrix would be diagonal, but the Hamiltonian includes the kinetic energy operator which is nonlocal in the coordinate domain. If the number of collocation points in each coordinate α is n_α , the Hamiltonian matrix will contain of the order of $N \times n$ nonzero elements, where N is the total number of collocation points $N = \prod_\alpha n_\alpha$ and $n = \sum_\alpha n_\alpha$.

In the time independent picture one is concerned with the diagonalization of the Hamiltonian matrix constructed in the same way to obtain the eigenvalues and eigenvectors. Usually, an iterative procedure such as the Lanczos method and variants⁵ is used for efficient diagonalization, which again involves products of the Hamiltonian matrix with vectors as the basic step. It is clear that important computational savings are possible when the Hamiltonian matrix is sparse or its action on the wave function can be calculated efficiently.

A way to increase significantly the sparsity of the Hamiltonian matrix is by the use of *local* methods. Here, local means that the action of the kinetic energy operator (or the

^{a)}Also at Department of Chemistry, University of Crete, Iraklion 711 10, Crete, Greece

Laplacian) on the wave function is approximated by using only local information or neighboring grid points. Although the derivative of a function is a local property, the wave function is defined on the whole configuration space and a piecewise representation of a function by a local polynomial approximation, generally, converges more slowly than a spectral representation. In this work we want to investigate this convergence in problems of molecular dynamics, and compare the numerical effort and accuracy of global and local methods. We will exploit some recent advances in finite difference algorithms which allow us to make a systematic comparison.

In Sec. II we will review briefly global pseudospectral (PS) methods and local finite difference (FD) schemes by using a very general formulation which puts them on the same footing. The relation between both approaches is discussed in two aspects, i.e., how one can obtain certain PS methods taking the infinite order limit of FD and, more importantly, how FD schemes can be obtained by applying a given acceleration scheme to these PS methods. These different points of view will allow us to gain much insight on the nature of both approaches and on what is the best use that we can give them for the applications we have in mind. A simple one-dimensional system, namely the vibrational levels of the I_2 molecule, is investigated in Sec. III to show the numerical convergence of FD to a Sinc PS method. In Sec. IV we will implement high order FD for the solution of the time dependent Schrödinger equation in two- and three-dimensional model problems, obtaining correlation functions and spectra from wave packet propagation, and comparing numerical accuracy and computational cost with the well established Fourier method. Conclusions and directions to future work concerning the improvement of local methods are given in Sec. V.

II. THEORY: GLOBAL VERSUS LOCAL METHODS

A. Pseudospectral methods

Pseudospectral methods are traditionally introduced as *global* approximations to the true solution of a partial differential equation $\mathcal{D}(u)=f$, where \mathcal{D} is a differential operator, in the expansion form:

$$u(x) \approx u_N(x) = \sum_{j=1}^N a_j \phi_{N,j}(x). \quad (1)$$

$\{\phi_{N,j}(x)\}$ is a smooth basis of analytic functions in the domain of interest which satisfies the appropriate boundary conditions. Then, once the class of basis functions have been chosen, the remaining problem is to determine the coefficients a_j . The general collocation method consists of enforcing the approximate solution to be exact on a set of N grid points, i.e., the equation $\mathcal{D}(u_N)=f$ is satisfied at a given set of collocation points $\{x_j, 1 \leq j \leq N\}$. The main requirements for the basis functions are that approximations $\sum_{j=1}^N a_j \phi_{N,j}(x)$ must converge rapidly to the true solution with the order of approximation N , and that, given the coefficients a_j , the determination of $b_{k,j}^{(m)}$, such that

$$\left. \frac{d^m}{dx^m} \left(\sum_{j=1}^N a_j \phi_{N,j}(x) \right) \right|_{x=x_k} = \sum_{j=1}^N b_{k,j}^{(m)} \phi_{N,j}(x_k), \quad (2)$$

should be efficient. Also, it must be possible to convert quickly between the coefficients a_j and the values of the sum $u_N(x_k)$ at the set of collocation points. Equation (2) for all x_k can be expressed as a matrix-vector multiplication

$$\frac{d^m u_N(x)}{dx^m} = \mathbf{D}^m \cdot \mathbf{t}, \quad (3)$$

where the *differentiation matrix* \mathbf{D}^m contains the coefficients necessary for calculating the m th derivative at the collocation points and \mathbf{t} is the column vector of dimension N containing the basis functions.

For periodic problems trigonometric expansions satisfy all the above requirements (the efficiency due to the use of the FFT algorithm), while for nonperiodic problems a very successful type of basis functions is orthogonal polynomials of Jacobi type, with Chebychev and Legendre as the most important special cases (see the discussion in Ref. 6). Here we will concentrate on two widely used PS methods: the Fourier method, mainly employed in the solution of the time dependent Schrödinger equation,³ and the Sinc method, very much applied in the context of the DVR.⁷ Both methods are closely related. Indeed, they give the same numerical accuracy as we will see below.

In the Fourier PS method, orthogonal basis functions of the type

$$\phi_{N,j}(x) = e^{i2\pi jx/L}, \quad j = -N/2, \dots, 0, \dots, (N/2-1), \quad (4)$$

are chosen, leading to N equally spaced collocation points, $x_k = k\Delta x$, ($k=1, \dots, N$), and $L = N\Delta x$. The expansion coefficients a_j are then the discrete Fourier expansion coefficients

$$a_j = \frac{1}{N} \sum_{k=1}^N u(x_k) e^{-i2\pi jx_k/L}, \quad (5)$$

and, when this method is applied to the Schrödinger equation, the coefficients have the physical interpretation of the amplitude of the wave function in momentum space. The last requirements of computational efficiency are then satisfied by use of the FFT algorithm for Eq. (5). Since Fourier functions are eigenfunctions of the differentiation matrix (DM) with eigenvalues $(i2\pi j/L)^m$, this matrix is automatically determined and matrix-vector multiplication can be implemented by FFT too.

A very general formulation of the approximation problem is obtained by using *cardinal basis functions*. If the basis functions $\phi_{N,j}(x)$ in Eq. (1) satisfy

$$\phi_{N,j}(x_k) = \delta_{j,k}, \quad 1 \leq j, k \leq N, \quad (6)$$

they are called cardinal basis functions and the coefficients in Eq. (1) are given simply by the values of the function u at the collocation points x_k . Loosely speaking, different cardinal basis functions correspond to different representations of the Kronecker delta function and will have different properties.

The approximation of the derivative of a function $u_N(x)$ at the collocation points can now be expressed as

$$\left. \frac{d^m u_N(x)}{dx^m} \right|_{x=x_k} = \sum_{j=1}^N b_{k,j}^{(m)} u_N(x_j), \quad (7)$$

which is again a matrix-vector multiplication. The advantage of such an approach is that the coefficients $b_{k,j}^{(m)}$ can be calculated analytically by taking the derivatives of the corresponding basis functions.

A cardinal basis function widely used in interpolation theory is the Sinc function,⁸ defined as $\text{Sinc}(x) \equiv \sin(\pi x)/\pi x$. The Sinc function can be naturally generated from the Fourier basis discussed above, because it can be considered as the Fourier transform of a Fourier basis function in momentum space (see for instance Ref. 9):

$$\text{Sinc}[(x-x_j)] = \int_{-\infty}^{\infty} e^{-ipx} \tilde{\phi}_{N,j}(p) dp, \quad (8)$$

where

$$\tilde{\phi}_{N,j}(p) = \begin{cases} e^{i2\pi x_j p} & |p| < \pi \\ 0 & |p| > \pi \end{cases}. \quad (9)$$

Note that the optimum grid for interpolation with Sinc functions must also be equi-spaced and centered, $x_j = j\Delta x$, ($j=0, \pm 1, \pm 2, \dots, \pm N/2$). By the properties of the Fourier transform, we see that the discrete version of Eq. (8) above will span all the momenta up to the value $p_{\max} = \pi/\Delta x$ and therefore Fourier and Sinc pseudospectral methods are completely equivalent in accuracy. The coefficients $b_{k,j}^{(m)}$ which give the approximation to the m th derivative can be obtained by analytically differentiating the Sinc function, $\text{Sinc}[(x-x_j)/\Delta x]$. For the second derivative, which is the case of interest for the kinetic energy term in the Schrödinger equation, the coefficients read:

$$b_{k,j}^{(2)} = \begin{cases} \frac{2(-1)^{j+1}}{j^2 \Delta x^2} & j = \pm 1, \pm 2, \dots \\ -\frac{\pi^2}{3\Delta x^2} & j = 0 \end{cases}. \quad (10)$$

Note that these coefficients decay as $\mathcal{O}(1/j^2)$. In common physical applications we want our wave function to decay exponentially with j (for instance it can initially be a Gaussian wave packet), i.e., we want the boundary conditions $u(x \rightarrow \infty) = 0$ to be satisfied. Therefore, the derivative sum, Eq. (7), will differ from the infinite series by an amount which decreases exponentially with the order N , since contributions of $u(x_j)$ for large j will be negligible. We can effectively compute the derivative with the accuracy of the full infinite series if N is sufficiently large. The ‘‘sufficient’’ value of N to reach the pseudospectral limit of course depends on the problem we are investigating. In quantum molecular dynamics, the number of grid points (number of terms in the expansion) one should use for a sufficient sampling of the phase space volume is given by the requirement of ‘‘one point per Planck cell,’’³ which leads to a relation

between the grid spacing and the maximum value of the wave number k ($p = k\hbar$) we want to represent:

$$\Delta x = \frac{\pi}{|k_{\max}|}. \quad (11)$$

This is precisely the same relation arising in the Sinc or the Fourier PS methods as discussed above. The maximum momentum can be obtained from physical considerations, since we want in general our wave function to be zero at sufficiently distant points of the grid, $\Psi(x_{\max}) = 0$, and we calculate the potential energy at $x = x_{\max}$ and the momentum as $|p_{\max}| = \sqrt{2mV(x_{\max})}$.

B. Finite difference methods

Finite difference methods are related to interpolation using Lagrange polynomials. Now our cardinal basis functions can be chosen to have the general form:^{10,11}

$$\phi_{N,j}(x) = \frac{1}{c_j} \alpha(x) \frac{\omega_N(x)}{x-x_j}, \quad 1 \leq j \leq N, \quad (12)$$

where $\alpha(x)$ is an analytic function in the real domain and $\omega_N(x) = \prod_{k=1}^N (x-x_k)$. The coefficients c_j are chosen so that Eq. (6) is satisfied, i.e.,

$$c_j = \alpha(x_j) \omega'_N(x_j), \quad 1 \leq j \leq N. \quad (13)$$

The simplest choice, $\alpha(x) = 1$, corresponds to polynomial interpolation. For a general grid x_k , $k=1, \dots, N$, the functions $\phi_{N,j}(x)$ are the Lagrange interpolating polynomials. In the case that $x_1 = -1$ and $x_N = 1$, and the other x_k are the zeros of some orthogonal polynomial, these basis functions will produce orthogonal polynomial collocation methods [for instance, if we choose the interpolation points at $x_k = \cos(k\pi/N)$ it gives the Chebychev method]. Other choices of $\alpha(x)$ will produce other methods: for example, $\alpha(x) = e^{-x}$ is the Hermite collocation method, or if $\alpha(x)$ is a rational function we have a rational function collocation method. Also note that the Sinc method described in the previous subsection corresponds to a similar general form for $\phi_{N,j}(x)$ but with $\omega_N(x) = \sin(\pi(x-x_j)/\Delta x)$ and $\alpha(x) = 1$.

To approximate the derivatives, i.e., to calculate the coefficients $b_{k,j}^{(m)}$ in Eq. (7), we can proceed in the same way taking analytical derivatives of the corresponding interpolating polynomials. Explicit expressions for first and second derivatives have been given.¹² For Lagrange polynomial basis functions, instead of using the analytical expressions we found it preferable to employ an algorithm proposed by Fornberg.^{6,13} Fornberg was able to find recurrence relations for the derivatives of the Lagrange polynomials to obtain the coefficients for any order of derivative and arbitrarily spaced grids in a computationally very efficient way (only four arithmetic operations for each coefficient). This algorithm then provides a very fast generation of the Hamiltonian matrix for any type of grid and order of approximation (degree of the Lagrange polynomial). The systematic way with which one can vary the order and the great flexibility in defining the grid points will prove to be quite advantageous.

Note also that, because the interpolating polynomial of

minimal degree is unique, differentiation [Eq. (7)], is exact if $u_N(x)$ is a polynomial of degree N or less.

C. Relations between FD and PS methods

That PS and FD approaches must be related can be seen intuitively from the fact that PS methods also provide the

$$\phi_{M,j}(x) = \frac{(x+M) \cdot (x+M-1) \cdots (x-j+1) \cdot (x-j-1) \cdots (x-M)}{(j+M) \cdot (j+M-1) \cdots (1) \cdot (-1) \cdots (j-M)}. \quad (14)$$

Starting from the central factors, this can be rearranged as the product $\prod_{k=1}^M (1 - (x-j)^2/k^2)$, which in the limit $M \rightarrow \infty$ becomes

$$\lim_{M \rightarrow \infty} \phi_{M,j}(x) = \prod_{k=1}^{\infty} \left(1 - \frac{(x-j)^2}{k^2} \right) = \frac{\sin[\pi(x-j)]}{\pi(x-j)}. \quad (15)$$

Therefore, the infinite order limit of FD gives a PS method with Sinc functions as the expansion basis functions.^{14,15} This has also been noted by Colbert and Miller⁷ in the context of a discrete variable representation for the calculation of reaction probabilities.

To understand better the character of both approaches, we turn to the example of the time dependent Schrödinger equation:

$$i \frac{\partial \Psi(x)}{\partial t} = \hat{T}\Psi(x) + \hat{V}\Psi(x). \quad (16)$$

The application of the kinetic energy operator at a given collocation point is

$$\hat{T}\Psi(x_j) = -\frac{1}{2m} \left. \frac{\partial^2 \Psi(x)}{\partial x^2} \right|_{x=x_j}. \quad (17)$$

If we use a Fourier basis for the expansion of the wave function as in Eq. (4), the kinetic energy operator will be

$$\hat{T}\Psi(x_j) = -\frac{1}{2m} \sum_{k=-N/2}^{N/2-1} \left(\frac{i2\pi k}{L} \right)^2 a_k e^{i2\pi k x_j/L}. \quad (18)$$

The spectrum in momentum space of the kinetic energy operator is obtained by taking the Fourier transform and that gives

$$\tilde{T}(k) = \frac{1}{2m} \frac{4\pi^2}{N^2 \Delta x^2} \sum_{k=-N/2}^{N/2-1} k^2 a_k. \quad (19)$$

We know that the operation on a component of the wave function in momentum space is

$$\hat{T}\tilde{\Psi}(k) = \frac{\hat{p}^2}{2m} \tilde{\Psi}(k) = \frac{k^2}{2m} a_k. \quad (20)$$

Thus, we see that all momenta until the value $|k_{\max}| = \pi/\Delta x$ are represented, by virtue of the sampling theorem.

exact derivatives of the interpolation polynomial passing through the collocation points. We can be more specific and take the limit $N \rightarrow \infty$ of the Lagrange interpolating polynomial. Consider an equi-spaced grid around $x=0$ with spacing $\Delta x=1$ extended over $N=2M+1$ grid points. The Lagrange polynomial will be:

Now, if we use cardinal basis functions like Sinc functions or Lagrange polynomials, we have an approximation to the kinetic energy operator given by Eq. (7), therefore

$$\hat{T}\Psi(x_k) = -\frac{1}{2m} \sum_{j=-N/2}^{N/2-1} b_{k,j}^{(2)} \Psi(x_j). \quad (21)$$

Taking into account that $x_j = x_k + j\Delta x$, and using the fact that the Fourier transform of a translated function $\Psi(x + \Delta x)$ is

$$e^{ik\Delta x} \tilde{\Psi}(k), \quad (22)$$

we obtain the spectrum in momentum space

$$\tilde{T}(k) = -\frac{1}{2m} \sum_{j=-N/2}^{N/2-1} b_{k,j}^{(2)} e^{ikj\Delta x} \tilde{\Psi}(k). \quad (23)$$

For simplicity we will consider a uniform grid with N an odd number of grid points. Then, we have

$$\tilde{T}(k) = -\frac{1}{2m} \left(b_{k,0}^{(2)} + 2 \sum_{j=1}^M b_{k,j}^{(2)} \cos(kj\Delta x) \right) \tilde{\Psi}(k), \quad (24)$$

where $N=2M+1$. The coefficients in the cosine series expansion are the FD weights in case we use Lagrange polynomials or the weights given by Eq. (10) for Sinc functions. We want to find the coefficients that give a good approximation to the kinetic energy operator. Since we know that the exact spectrum in momentum representation is given by Eq. (20), we require that the trigonometric expansion of k^2 between $[-k_{\max}, k_{\max}]$ equals the series expansion in Eq. (24). The trigonometric expansion for k^2 is:

$$k^2 = \frac{k_{\max}^2}{3} + \sum_{j=1}^{\infty} \frac{(-1)^j (2k_{\max})^2 \cos(\pi j k/k_{\max})}{(\pi j)^2}. \quad (25)$$

Comparing with Eq. (24) we immediately see that

$$b_{k,0}^{(2)} = \frac{k_{\max}^2}{3},$$

$$b_{k,j}^{(2)} = \frac{2(-1)^{j+1} k_{\max}^2}{\pi^2 j^2}. \quad (26)$$

If we identify the maximum momentum with the grid spacing as in the Fourier or Sinc approaches, i.e., $k_{\max} = \pi/\Delta x$, we find exactly the infinite order coefficients given in Eq.

(10). Thus, the trigonometric expansion provides another method for evaluating the coefficients of any derivative.

The infinite order coefficients of a FD approach or equivalently the Sinc DVR expansion coefficients [Eq. (10)] decrease only as $\mathcal{O}(1/j^2)$ and therefore the approximating series to the derivative of the wave function converge slowly if $\Psi(x)$ is of the same order of magnitude as the coefficients [i.e., we are above the aliasing limit,¹⁶ Eq. (11)]. This means that truncation of the Sinc PS method using less points than the needed from the relation Eq. (11) will give very poor results. If we want to improve the convergence of the trigonometric series in order to be able to use less terms (less grid points) in the approximation, we should use an acceleration scheme, which in turn implies to multiply the terms in the series by some acceleration weights. A classical example is the Euler's transformation.¹⁷

We can consider the series Eq. (24) above as the special case, $z=1$, of the general alternating series:

$$S_M = \sum_{j=0}^M a_j z^j, \quad (27)$$

with

$$\begin{aligned} a_0 &= b_{k,0}^{(2)} \\ a_j &= b_{k,j}^{(2)} \cos(kj\Delta x), \end{aligned} \quad (28)$$

where $b_{k,j}^{(2)}$ are the Sinc weights defined in Eq. (10) (note that they alternate in sign). Alternating series are ideal candidates for linear acceleration techniques.^{18,19} Boyd has shown that the M th order finite difference approximation is equivalent to the accelerated series:¹⁹

$$S_M^{\text{FD}} = \sum_{j=0}^M c_{M,j} a_j z^j, \quad (29)$$

with acceleration weights

$$\begin{aligned} c_{M,0} &= (6/\pi^2) \left\{ \sum_{j=1}^M 1/j^2 \right\} \\ c_{M,j} &= (M!)^2 / [(M-j)!(M+j)!], \quad j=1, \dots, M. \end{aligned} \quad (30)$$

Here we stress two facts: first, the above acceleration weights can be shown to satisfy the required mathematical properties to be a robust and well behaved acceleration scheme, therefore, we expect high order FD to improve uniformly the convergence of the trigonometric series expansion. That this is indeed the case will be shown in the next section. Second, it can be demonstrated that accelerating the trigonometric series in this way corresponds to choosing the coefficients in Eq. (24), so that the Taylor expansion of the truncated trigonometric series coincides with k^2 to the highest degree.¹⁴ Thus, FD is going to improve the accuracy of the spectrum mainly at lower values of the momentum.

III. APPLICATION TO IODINE MOLECULE

We applied both methods, PS and high order FD, to find the eigenvalues of the one dimensional Schrödinger equation for the vibrational motion of the I_2 molecule. The potential is a Morse oscillator:

$$V(x) = D[e^{-2ax} - 2e^{-ax}] + D, \quad (31)$$

where $D=0.0224$ a.u. and $\alpha=0.9374$ a.u. The model is analytically solvable²⁰ using confluent hypergeometric functions, and the exact expression for the eigenvalues is

$$E_n = \kappa \left[n + \frac{1}{2} - \frac{1}{\beta} \left(n + \frac{1}{2} \right)^2 \right], \quad (32)$$

with $\kappa=5.741\,837\,286 \times 10^{-4}$ a.u. and $\beta=156.047\,612\,535$. The reduced mass for the I_2 is $\mu=119\,406$ a.u. This system has recently been studied computationally by Wei *et al.*²¹ as a test case for another local method, the Lagrange distributed approximating functionals, introduced by the authors. This is in fact a FD scheme (approximation by Lagrange polynomials) with weights multiplied by rapidly decreasing Gaussian functions to improve further the convergence.

We used a total number of 80 grid points to discretize the Schrödinger equation with uniform spacing in the interval of $[-0.8, 2.0]$. From the values of the potential energy, we see that the maximum eigenvalue we can properly reproduce is $n \approx 30$, and the optimum grid spacing is 0.0515. Note, that with 80 grid points we have a spacing $\Delta x=0.035$ and we are well below the aliasing limit for the representative eigenvalues. The time independent Schrödinger equation is solved as usually²² by employing an expansion of the wave function in basis functions which are orthogonal for different grid points, so that the potential energy matrix is diagonal:

$$V_{i,j} = \delta_{i,j} V(x_i), \quad (33)$$

and the kinetic energy matrix has the form

$$T_{j,i} = -\frac{1}{2m} \sum_{k=1}^M b_{M,k}^{(2)} \delta_{|i-j|,k} = -\frac{1}{2m} b_{M,|i-j|}^{(2)}. \quad (34)$$

Here, the coefficients $b_{M,k}^{(2)}$ are either the infinite order coefficients, Eq. (10), or the FD weights, which can be obtained in closed form by multiplying Eq. (10) with the acceleration weights given by Eq. (30). In this study the weights in FD approximation are computed by using Fornberg's algorithm.⁶ In the case that M , the order of approximation, is equal to the number of total grid points, we obtain the usual Sinc DVR method.

In Fig. 1 we present the fractional error ($E_{\text{approx.}}/E_{\text{exact}} - 1$) for the eigenvalues $n=5, 15$ and 25 as a function of the order of the approximation M . The Hamiltonian matrix was diagonalized using a routine from the IMSL mathematical library which is a hybrid of LR and QR algorithms. The order of approximation increases up to a value where the error becomes constant, so that the numerical error for the eigenvalues is mainly due to the diagonalization routine and not in the approximation of kinetic energy operator.

As is clearly seen, even for the largest eigenvalue we do not need to use the full number of grid points to achieve the pseudospectral accuracy. In fact, for the eigenvalue $n=25$ the pseudospectral limit is reached using $M=27$, while for the Sinc method we should use at least $M=68$. We also note that for the usual Sinc DVR scheme the Hamiltonian matrix in one dimension would be a dense matrix, while FD pro-

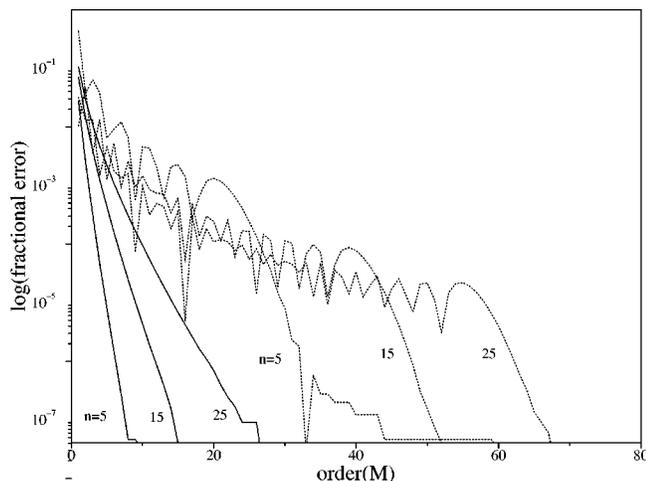


FIG. 1. The logarithm of the fractional error in the vibrational eigenenergies ($E_{\text{approx.}}/E_{\text{exact}} - 1$) of I_2 molecule versus the order of FD and Sinc DVR approximations. The vibrational levels $n=5$, 15 and 25 are examined using FD coefficients (solid lines) and infinite order coefficients (dashed lines). In the finite difference method centered equi-spaced grids are used ($N=2M+1$).

vides a banded matrix with at most $2M+1$ nonzero elements in each row. It is obvious that the sparsity of the Hamiltonian matrix will increase in higher dimensions, making a significant difference in computational cost between a FD approach and a DVR scheme.

IV. MULTIDIMENSIONAL WAVE PACKET PROPAGATION WITH FD

In quantum molecular dynamics simulations, since the introduction of the Fourier method, the two main problems which make its implementation difficult in many realistic molecules are the complexity of the quantum phase space displayed by such molecules and its high dimensionality which causes the numerical effort and the computer memory requirements to be too large for the current computers. Part of the difficulties come from the fact that the choice of the grid is very restrictive in PS methods with fast transforms for matrix-vector multiplication (we must use a uniform grid with a number of grid points equal to a power of a specific number for the Fourier method, or the grid points must be chosen as the zeros of the Chebychev polynomials for the Chebychev technique).

Apart from the wasted configuration space sampling, care must also be taken when the potential energy surface (PES) has a complicated topography. The Fourier approach imposes periodic boundary conditions, but in many situations, like vibrational spectroscopy, the topic we are mainly concerned with, the correct boundary condition, is that the wave function vanishes at the boundaries of the grid (for radial coordinates). Thus, in many occasions one has to resort to the use of complex absorbing potentials²³ or to employ other tricks such as fast sine transforms²⁴ which *a priori* satisfy the box boundary conditions. A very convenient way to impose these conditions, which also reduce appreciably the size of the grid, is to use a cutoff value of the potential, V_c , as a criterion to choose the grid points, i.e., we discard

all those grid points x_i for which $V(x_i) > V_c$.⁷ Then, the wave function will be negligibly small for those configurations with energy near V_c . It is here where the FD method can be most useful, since it has complete flexibility in the generation of the grid. One could of course use the Sinc PS method in case we still use a uniform grid, but then the Hamiltonian matrix is not very sparse and no fast transform exists to calculate the Laplacian of the wave function.

The purpose of this section is to show that high order FDs can be used for accurate numerical propagation of wave packets even for very long times. As expected from the simple system treated in the previous section, a numerical accuracy similar to that of the Fourier method can be obtained using sparse differentiation matrices. Moreover, due to this fact and the possibility of easily optimizing the grid in the way described above, for three or more dimensions the method requires appreciably less computational resources than the FFT. Before proceeding to the discussion of the two- and three-dimensional examples, we wish to make a few technical remarks: unless we intend to use dynamically changing grids, the differentiation matrix (Hamiltonian operator) is generated only at the beginning of the calculation and used when needed for the time propagation. Because of the efficiency of the algorithm described by Fornberg¹³ the generation of the differentiation matrix is very fast, so this algorithm could also be used with adaptive or dynamically changing grids. Moreover, we do not need to store the zero elements of the differentiation matrix and this also reduces appreciably the storage requirements in the computer memory, a point which is crucial in high-dimensional systems.

A. The 2D Contopoulos–Barbanis potential

We will study a two-dimensional system employed in several investigations in the past,²⁵ mainly in the connection between classical and quantum dynamics. One of us²⁶ carried out extensive studies of the periodic orbit structure of this system and its relation to quantum mechanics. The system is described by the Hamiltonian:

$$H = \frac{1}{2}(p_x^2 + p_y^2) + \frac{1}{2}(\omega_x^2 x^2 + \omega_y^2 y^2) - \epsilon x^2 y, \quad (35)$$

where the parameters are $\omega_x^2 = 0.9$, $\omega_y^2 = 1.6$, and $\epsilon = 0.08$. The time dependent Schrödinger equation, Eq. (16), was numerically solved using a Chebychev expansion⁴ for the propagation in time, while the action of the Hamiltonian operator on the wave function was evaluated with the FFT method and with matrix-vector multiplication using FD, in order to study the convergence and compare the computation times. The resulting vibrational spectrum was obtained as usual with the Fourier transform of the autocorrelation function of the wave packet

$$I(E) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \exp(iEt) \langle \phi(\mathbf{x}, 0) | \phi(\mathbf{x}, t) \rangle dt. \quad (36)$$

We propagated a Gaussian wave packet initially localized on a 1:2 resonance periodic orbit at a high energy ($E = 23$ a.u., see Fig. 12b in Ref. 26). It is interesting to plot the wave packet in configuration space and compare the solution of Schrödinger equation using the two methods. In both

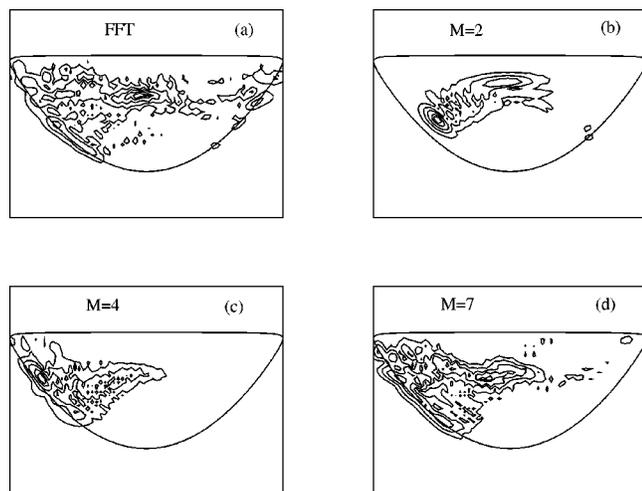


FIG. 2. Snapshots of the wave packet at $t=28$ a.u. (1/4 of total propagation time) with a rectangular grid and 64 grid points in each dimension. (a) FFT method; (b) FD with $M=2$ (second order); (c) FD 4th order; (d) FD 7th order.

cases we used a rectangular grid with 64 points in each dimension, and $\Delta x=0.3175$. We wanted to obtain a high resolution for the spectrum ($\Delta E \approx 0.056$), and thus, we propagated the wave packet for 1024 time steps. At $t=1/4$ of the total time we took a snapshot of the wave function. In Fig. 2(a) we show the wave function obtained with the FFT method (the potential energy contour is superimposed on the same plot at the mean energy of the wave packet). In Figs. 2(b), 2(c) and 2(d) we show the same wave packet obtained with a second, fourth and seventh order finite difference approximation, respectively. From Fig. 2 we can see that convergence of the wave function is approached with the FD method, even for a wave packet quite spread in configuration space. Finer details reproduced by even higher order FD approximations, however, will not affect very much the spectrum, since, this is an average of the propagated wave function over the configuration space. The resulting spectra are shown in Fig. 3 (here we omit the second order FD for the sake of clarity, although the comparison is very poor as expected). Even with order $M=7$, the only appreciable difference is in the intensities at high energies.

We recall that, a FD approximation is equivalent to a Taylor expansion series of the kinetic energy spectrum, therefore, in the limit of $\Delta x \rightarrow 0$ we recover the exact spectrum irrespectively of the order of the approximation. It is worthwhile to investigate then how the FD converges to the Fourier method as we increase the order as well as we decrease the grid spacing. We examine the differences of the central eigenvalue ($E=22.18$) from that obtained with the FFT method with 64 points in each dimension. When this difference is less than the resolution in the power spectrum the results are considered identical. Of course, for higher eigenvalues we should increase further the order or decrease the grid spacing to converge to the desired resolution, but the general behavior is seen in Fig. 4 where we used 64, 80, 100 and 120 points ($\Delta x=0.3175, 0.2532, 0.2020$ and 0.1681 , respectively). It is seen that convergence in both directions is quite fast, although it is computationally cheaper to increase

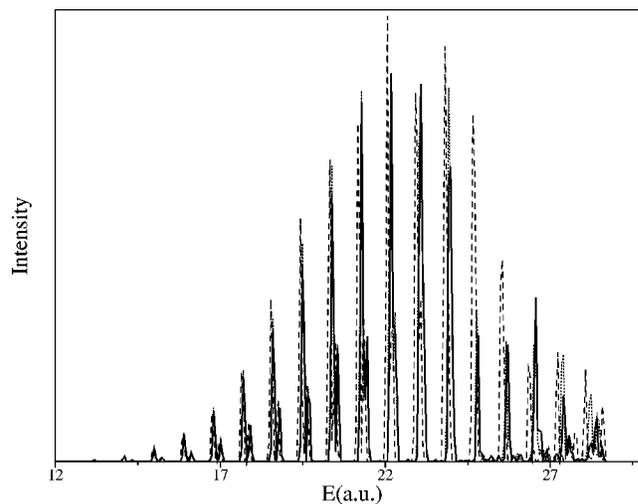


FIG. 3. Power spectra obtained from the correlation function of the wave packet shown in Fig. 2. FFT (solid line), FD 4th order (dashed line) and FD 7th order (dotted line).

the order of the approximation and take less grid points than to increase the number of grid points (by increasing the order by one we should add two more grid points to evaluate the Laplacian, but we should increase N by about 20 points at low order to get the same reduction in the error).

B. The 3D Contopoulos–Barbanis potential

Now, we extend the model potential to three dimensions,

$$V(x,y,z) = \frac{1}{2}(\omega_x^2 x^2 + \omega_y^2 y^2 + \omega_z^2 z^2) - \epsilon x^2 y - \eta x^2 z. \quad (37)$$

The additional parameters have the values $\omega_z^2=0.4$ and $\eta=0.01$.²⁷ The initial Gaussian wave packet is put on a periodic orbit which is a 1:2:2 resonance among the three degrees of freedom. The family of this periodic orbits turns from stable to complex unstable. The same potential was used by one of us²⁷ to study quantum mechanically the phenomenon of complex instability, which was also found in

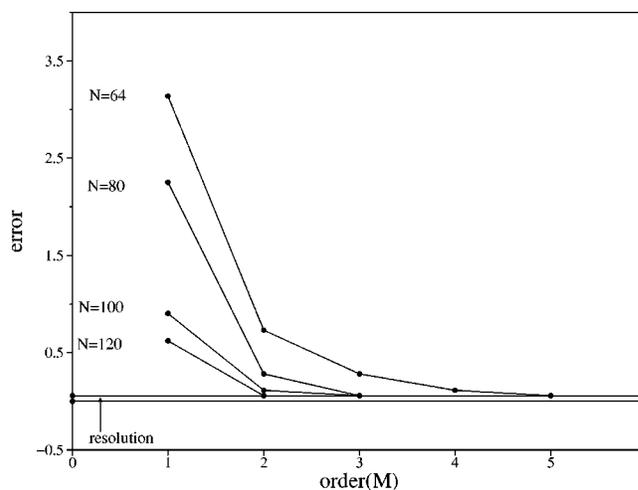


FIG. 4. Differences in energy with respect to the central eigenvalue ($E=22.18$) in the FFT spectrum of Fig. 3 as a function of the order of approximation. Rectangular grids with 64, 80, 100 and 120 points were used.

TABLE I. The total number of grid points (N) and CPU times in minutes (\prime) and seconds ($''$) for propagating a 3D wave packet with FFT and variable order (M) finite difference approximations. The number of grid points necessary to compute the derivatives in the FD method is $2M+1$, equispaced and centered at each grid point. Optimized grid is that in which the selected grid points correspond to potential values less than the cutoff value, $V_c=15$ a.u. The computations were carried out with a PC Pentium II at 450 MHz and memory of 512 MBytes.

Rectangular grid (N)	Optimized grid	Order (M)	CPU-Time	FFT
32 256	15 972	3	43' 3''	Converged
		5	64' 54''	
		7	88' 4''	
		9	160' 28''	
65 536	33 180	2	95' 46''	674' 4''
		3	216' 46''	
		5	285' 39''	
		7	288' 56''	
115 200	59 214	1	149' 14''	Converged
		2	248' 5''	
		3	289' 30''	
		5	468' 20''	

molecules such as HCN and acetylene.²⁸ We will use the same initial conditions for the wave packet as those used in Ref. 27.

Here, we are interested in comparing both numerical methods (FFT and FD) from the computational point of view, and in studying the application of optimized grids to the time dependent Schrödinger equation. We chose a potential cutoff value of $V_c=15$ a.u. after doing some test calculations to verify that this value provides the proper boundary conditions for the wave function in the range of energies in which we are interested. Even if in this simple model the topography of the potential is not complicated (it is like two harmonic oscillators weakly coupled) the reduction in the number of grid points is significant. As seen from Table I, it is about a factor of 2, which, combined with the sparsity of the differentiation matrix, allows us to reduce the computation time by about a factor of 3. Here, we used for the FFT a rectangular grid with the edges tangent to the potential cutoff value, and convergence means that even the highest values of the spectrum are reproduced to the accuracy of the spectral resolution which in this case is 0.038 a.u.

V. CONCLUSIONS

We have investigated the implementation of high order FD methods to solve simple models of molecular potentials for the time independent and time dependent Schrödinger equation. In the past, FD was mainly considered at low order²⁹ which of course gave poor results when it was compared with a PS scheme. However, investigations of some high order FD calculations have appeared in the literature³⁰ such as the calculations of eigenvalues. Here, we emphasize two facts: first, thanks to the algorithm developed by Fornberg,¹³ FD weights are easily obtained recurrently for any order and any grid spacings, without the necessity of solving any set of linear equations as previously. This sim-

plifies considerably the problem of constructing the Hamiltonian matrix in a DVR type calculation or the Hamiltonian operator for the time dependent problem. This also allowed us to check systematically the convergence, so that results can be obtained with any desired accuracy.

The common frame in which PS and local methods can be placed, starting from approximations to the solution of partial differential equations using cardinal basis functions, also allows us to explore the relations between the two methods. The ultimate reason why we do not need a very high order FD scheme to obtain the same accuracy as the Fourier or Sinc PS techniques is that FD can be seen as a robust sum acceleration procedure of the Sinc PS method.¹⁹ This was shown by a simple one-dimensional example in Sec. III. In the previous section we demonstrated the usefulness of high order FD applied to quantum molecular dynamics problems, with a considerable reduction in the computation time in the 3D case.

FD have additional advantages, like the sparsity of the Hamiltonian matrix. They are very easily vectorizable and ideal for parallel computation. Although we confined ourselves here to the use of uniform grids for comparison with the Fourier and Sinc methods, they can be used without any additional modification in irregularly spaced grids (we obtained preliminary results in the one-dimensional harmonic and Morse oscillators using different grid distributions). They can also be combined with different weight functions (like Gaussian windows, an approach that leads to wavelets³¹) to improve the convergence of the local methods. Although, high order FD works well for long time propagation, they could also be used in combination with filter diagonalization techniques,³² where only short time wave packet propagation is needed and we can decrease the order of the FD approximation without the sacrifice of accuracy.

Here, we treated simple models but in a companion paper we apply high order FD approximations to propagate wave packets and extract the eigenfunctions on a realistic molecular potential representing the inversion dynamics of Ar₃ van der Waals complex.³³ Work on higher than three-dimensional problems is in progress and will be published in the future.

ACKNOWLEDGMENT

R. Guantes gratefully acknowledges financial support from a European Union TMR grant (*FMRX'CT'97'0101*).

¹S. C. Farantos, *Int. Rev. Phys. Chem.* **15**, 345 (1996).

²S. C. Farantos, *Comput. Phys. Commun.* **108**, 240 (1998).

³R. Kosloff, in *Dynamics of Molecules and Chemical Reactions*, edited by R. E. Wyatt and J. Z. H. Zhang (Marcel Dekker, New York, 1996).

⁴R. Kosloff, *Annu. Rev. Phys. Chem.* **45**, 145 (1994).

⁵(a) C. Lanczos, *J. Res. Natl. Bur. Stand.* **45**, 58 (1950); (b) C. Jung and C. Leforestier, *J. Chem. Phys.* **102**, 8453 (1995); (c) R. E. Wyatt, *ibid.* **103**, 8433 (1995); (d) R. B. Lehoucq, D. C. Sorensen, and C. Yang, *Solution of Large Scale Eigenvalue Problems with Implicitly Restarted Arnoldi Methods* (SIAM, Philadelphia, 1998).

⁶B. Fornberg and D. M. Sloan, *Acta Numerica* **1994**, 203.

⁷D. T. Colbert and W. H. Miller, *J. Chem. Phys.* **96**, 1982 (1992).

⁸F. Stenger, *SIAM Rev.* **23**, 165 (1981).

⁹R. N. Bracewell, *The Fourier Transform and Its Applications* (McGraw Hill, New York, 1986).

- ¹⁰B. D. Welfert, SIAM (Soc. Ind. Appl. Math.) J. Numer. Anal. **34**, 1640 (1997).
- ¹¹C. Schwartz, J. Math. Phys. **26**, 411 (1985).
- ¹²A. Solomonoff and E. Turkel, J. Comp. Physics **81**, 239 (1989).
- ¹³B. Fornberg, Math. Comput. **51**, 699 (1988).
- ¹⁴B. Fornberg, SIAM (Soc. Ind. Appl. Math.) J. Numer. Anal. **27**, 904 (1990).
- ¹⁵B. Fornberg, *A Practical Guide to Pseudospectral Methods*, Cambridge in Applied and Computational Mathematics (Cambridge University Press, Cambridge, 1998), Vol. 1.
- ¹⁶W. H. Press, B. P. Flannery, S. A. Teukolsky and W. T. Vetterling, *Numerical Recipes* (Cambridge University Press, Cambridge, MA, 1986).
- ¹⁷J. Mathews and R. L. Walker, *Mathematical Methods of Physics* (Addison-Wesley, 1970), pp. 53–55.
- ¹⁸J. P. Boyd, J. Comp. Physics **103**, 243 (1992).
- ¹⁹J. P. Boyd, Comput. Methods Appl. Mech. Eng. **116**, 1 (1994).
- ²⁰I. I. Goldman and V. D. Krivchenkov, *Problems in Quantum Mechanics* (Dover, New York, 1993), pp. 217–218.
- ²¹G. W. Wei, D. S. Zhang, D. J. Kouri, and D. K. Hoffman, Phys. Rev. Lett. **79**, 775 (1997).
- ²²(a) J. V. Lill, G. A. Parker, and J. C. Light, Chem. Phys. Lett. **89**, 483 (1982); (b) J. C. Light, I. P. Hamilton, and J. V. Lill, J. Chem. Phys. **82**, 1400 (1985); (c) S. E. Choi and J. C. Light, *ibid.* **92**, 2129 (1990).
- ²³(a) C. Leforestier and R. E. Wyatt, Chem. Phys. Lett. **78**, 2334 (1983); (b) D. Neuhauser and M. Baer, J. Chem. Phys. **90**, 4351 (1989); (c) U. V. Riss and H. D. Meyer, J. Phys. B **28**, 1475 (1995).
- ²⁴M. Braun, S. A. Sofianos, D. G. Papageorgiou, and I. E. Lagaris, J. Comp. Physics **126**, 315 (1996).
- ²⁵(a) G. Contopoulos, Astron. J. **75**, 96 (1970); (b) M. J. Davis and E. J. Heller, J. Chem. Phys. **75**, 246 (1981); (c) R. C. Brown and R. E. Wyatt, *ibid.* **82**, 4777 (1984); (d) C. C. Martens and G. S. Ezra, *ibid.* **86**, 279 (1987).
- ²⁶M. Founargiotakis, S. C. Farantos, G. Contopoulos, and C. Polymilis, J. Chem. Phys. **91**, 1389 (1989).
- ²⁷G. Contopoulos, S. C. Farantos, H. Papadaki, and C. Polymilis, Phys. Rev. E **50**, 4399 (1994).
- ²⁸(a) S. C. Farantos and M. Founargiotakis, Chem. Phys. **142**, 345 (1990); (b) R. Prosmitti and S. C. Farantos, J. Chem. Phys. **103**, 3299 (1995).
- ²⁹(a) E. A. McCullough and R. E. Wyatt, J. Chem. Phys. **51**, 1253 (1969); (b) A. Askar and A. S. Cakmac, *ibid.* **68**, 2794 (1978).
- ³⁰G. C. Groenenboom and H. M. Buck, J. Chem. Phys. **92**, 4374 (1990).
- ³¹G. W. Wei, S. C. Althorpe, D. J. Kouri, and D. K. Hoffman, J. Chem. Phys. **108**, 7065 (1998).
- ³²(a) M. R. Wall and D. Neuhauser, J. Chem. Phys. **102**, 8011 (1995); (b) V. Mandelshtam and H. S. Taylor, *ibid.* **106**, 5085 (1997); (c) R. Chen and H. Guo, *ibid.* **105**, 1311 (1996).
- ³³R. Guantes, A. Nezis, and S. C. Farantos, J. Chem. Phys. **111**, 10836 (1999), following paper.