

Response to "Comment on 'High order finite difference algorithms for solving the Schrödinger equation in molecular dynamics'"

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In the preceding comment¹ Mazziotti refers to our first article on "High order finite difference algorithms for solving the Schrödinger equation in molecular dynamics,"² stating that we incorrectly classify the Lagrange distributed approximating functional (LDAF) method developed by Kouri and co-workers³ in the category of finite difference methods. In his original article, published in Chemical Physics Letters,⁴ Mazziotti described and applied to a Morse potential four known numerical methods for solving the Schrödinger equation. These are the truncated sinc, Boyd's Euler and finite difference sum acceleration methods,⁵ and LDAF.³ He collectively named them *spectral difference* methods.

On the other hand, the purpose of our article was mainly to investigate and compare finite difference schemes with pseudospectral methods, such as fast Fourier transforms (FFTs) and discrete variable representations (DVRs) for problems of chemical dynamics. We did not examine the LDAF method. However, we did classify grid methods as *global* (pseudospectral methods) where stencils with the total number of grid points are used for the computation of the derivatives and *local* (finite difference) where stencils with smaller size are employed. In this general scheme of classification we consider the LDAF method as *local*, since by weighting the basis functions (Lagrange interpolating polynomials or sinc) with Gaussian functions the derivatives are also computed with stencils of smaller size than the full grid.

In a series of articles Guantes and Farantos explored the finite difference (FD) techniques for solving the time dependent and time independent Schrödinger equation.^{2,6,7} This research project has been mainly motivated by the work of Fornberg,⁸ who has shown that high order finite difference approximations approach in a regular manner the accuracy of pseudospectral methods (PS), and by that of Boyd,⁵ who demonstrated that uniform FD can be considered as a certain acceleration scheme of the sinc cardinal series. In the first article² we examined the relation of high order finite difference approximations with the pseudospectral method based on sinc DVR. Three model potentials of one (1D), two (2D) and three (3D) dimensions were examined, whereas in a companion article the van der Waals system Ar₃ was studied.⁶

In a more recent article⁷ the high order FD method was applied to periodic variables with equispaced grid points related to Fourier pseudospectral method⁹ and nonuniform grid

distributions related to Chebyshev and Legendre PS methods. An application to SO₂ by employing a spectroscopic potential and using a variety of grid distributions (uniform and nonuniform) for the radial and angle variables was also presented.

By approximating the solution of a partial differential equation as an expansion in basis functions with the δ -Kronecker property (cardinal functions)

$$\Psi(x) \approx \sum_{k=1}^N \Psi(x_k) u_k(x), \quad (1)$$

a variety of different PS methods can be derived, better known in chemical physics literature as discrete variable representation (DVR),¹⁰ starting with an initial basis which does not possess the δ -Kronecker property known as finite basis representation.¹¹ Special classes of cardinal functions are Lagrange interpolating polynomials and sinc functions. Fourier functions can be transformed to a cardinal basis which consists of periodically repeated copies of the sinc functions.^{5,7}

In spite of the different classifications schemes, both research groups have demonstrated (Mazziotti for the Morse potential and Guantes and Farantos for 1D, 2D and 3D systems) that high order finite differences may obtain the accuracy of the pseudospectral methods. If this happens with smaller size stencils than the total grid, then finite difference results in sparse Hamiltonian matrices. However, the sparseness obtained in one dimension does not necessarily imply that FD will also lead in saving computer time in multidimensional problems. The DVR community treating multidimensional systems¹² has developed procedures for the optimum selection of the grid points and has learned to adapt the basis sets according to the studied system.

Furthermore, it is known⁹ that the convergence of the accelerated sinc series is highly nonuniform in wave number, giving very good accuracy for low values of the momentum but poor results for higher values (this is because FD can be considered as a Taylor expansion of the true spectrum around $k=0$, while a sinc series is a trigonometric expansion). Mazziotti compares different local schemes for only the first five eigenvalues of the Morse function. An accurate calculation of the large eigenvalues requires higher order finite difference approximations.

This can be seen in Fig. 1 of our first article.² The 25th eigenvalue of a Morse oscillator employs 55 points whereas the 15th eigenvalue only 31 points. The superiority of the finite difference method is demonstrated from the fact that the sinc DVR uses a larger grid space in order to achieve the same accuracy. If we want to keep the order of approximation in FD low, then we must increase the number of grid points, or equivalently to decrease the space interval, Δx . This is shown in Fig. 4 of the same article for a 2D model potential. The pseudospectral accuracy of one high energy eigenvalue ($E=22.18$) obtained by a FFT calculation can be achieved even with stencils of five grid points, but the total grid should be increased to 120 points.

Low order finite difference algorithms were the first which were applied in problems of quantum molecular dynamics.¹³ However, the introduction of the more accurate pseudospectral methods such as the FFT and DVR decreased the interest in finite differences. The previous examples show that, contrary to what was believed, finite difference can approximate the derivatives in the quantum mechanical equations of chemical dynamics accurately. Although the sparseness of the Hamiltonian matrix is one of the advantages in applying FD methods, this is not always the case. As it was said earlier, the calculation of high energy levels demands high order FD approximations. For small size total grids this may result in using the total grid stencil, thus the DVR limit. Presumably, this will be the case in high dimensional systems where large grids are prohibited. On the other hand, if we need to calculate highly excited vibrational levels we must use extended grids for the accurate representation of the wave functions. Then, a DVR calculation may be prohibited, whereas a FD approximation at low order is more feasible.

Fornberg with his research has shown that pseudospectral methods could be seen as limits of finite difference for-

mulas with the order of interpolating polynomials increasing. Irrespective of the extent of the sparseness in the Hamiltonian matrix, the introduction of the FD methods into chemical dynamics problems allows a systematic investigation for the convergence of the solutions with respect to the number of grid points and the order of approximation. The flexibility in choosing the grid points without any dependence on specific basis functions combined with Fornberg's algorithm for a fast generation of the weights enhances the advantages of finite difference methods. The exploration of new grid distributions, particularly in multidimensional systems, calls for more studies.¹⁴

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