Numerical Integration of the Wavefunction in FEM

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Abstract

Although numerous techniques for calculating stationary states of the schrödinger equation are well known to physicist, computationally stable methods of numerical integration to determine the time evolution of wave functions are less well understood. This paper intends to introduce a few theoretical means of time evolving the schrödinger equation and exploring the results of similar calculations.

1 General Approach

It is our objective to derive a general solution to the time dependent schrödinger equation (1).

$$i\hbar\frac{\partial}{\partial t}\psi = \hat{H}\psi \tag{1}$$

Where here $\hat{H}$ is the hamiltonian operator (2) defining the system.

$$\hat{H} = \frac{-\hbar^2}{2m}\nabla^2 - V \tag{2}$$

Given this, solutions to the time dependent SE can be found by first defining a time evolution operator $T(\hat{H}, t)$ which propagates the wavefunction ψ forward in time such that

$$T(\hat{H}, t)\psi_0 = \psi_t \tag{3}$$

Analyzing equation (3) shows an arbitrary solution to the TDSE requires knowledge of the wavefunctions initial state ψ_0 which is then time evolved by the time evolution operator $T(\hat{H}, t)$. The initial wavefunction ψ_0 can be found as a solution to the time independent schrödinger equation (4). Numerous techniques exist to solve this problem both analytically and numerically already, however, it is the FEM approach of [1] which will be emphasized here.

$$\hat{H}\psi = E\psi \tag{4}$$

Given solutions to the time independent SE, only the time evolution operator remains undefined. It is immediately clear from (1) that one solution for the time evolution operator is

$$T(\hat{H}, t) = e^{-it\hat{H}/\hbar} \tag{5}$$

These results are well understood and in an effort to develop an efficient explicit numerical integration technique our efforts will focus on exploring the time evolution operator.

2 Operator Expansion

The basic task is here to expand the time evolution operator such that the wavefunction can be iteratively solved for at successive timesteps. Adopting the notation $\psi_n = \psi(t = n\Delta t)$ we now have

$$\psi_{n+1} = T\psi_n = e^{-it\hat{H}/\hbar}\psi_n \tag{6}$$

An obvious first approach would be to attempt a power series expansion of the form

$$e^x = \sum_{n=0}^{\infty} \frac{x^n}{n!} \tag{7}$$

while keeping only the first few terms. Keeping the first two terms in the expansion yields the relationship

$$\psi_{n+1} = (1 - \frac{i}{\hbar}\Delta t\hat{H})\psi_n \tag{8}$$

Where the constant $\hbar$ has been normalized to one. This scheme, although easily implemented, is no longer a unitary transformation and accurate only to first order. A similar thought process can be used to generate the crank nicholson scheme in which the ψ_n term is eliminated [2].

$$e^{i\Delta t\hat{H}/\hbar}\psi_{n+1} = e^{-i\Delta t\hat{H}/\hbar}\psi_{n-1} \tag{9}$$

and

$$(1 + \frac{i}{\hbar}\Delta t\hat{H})\psi_{n+1} = (1 - \frac{i}{\hbar}\Delta t\hat{H})\psi_{n-1} \tag{10}$$

This assumes the potential and therefore the Hamiltonian are not themselves time varying, in which case the Hamiltonian operator would also need to be subscripted by time. Numerous authors including A. Askar [2] and A. Goldberg [4] proceed at this point to expand the Hamiltonian using a finite differences approach, however, given the inherent advantages of FEM, detailed elsewhere,

and the relative ease of performing matrix multiplication on sparse matrices we here prefer leaving these expressions in terms of the Hamiltonian operator.

Askar, building on the Crank Nicholson method in [2] proposed an alternative approach taking the difference between ψ_{n+1} and ψ_{n-1} [2].

$$\psi_{n+1} - \psi_{n-1} = (e^{-i\Delta t\hat{H}/\hbar} - e^{i\Delta t\hat{H}/\hbar})\psi_n \tag{11}$$

Again, using a first order approximation of the exponential yields an integration of the form

$$\psi_{n+1} = -2i\Delta t\hat{H}\psi_n + \psi_{n-1} \tag{12}$$

This approximation is accurate to order $O(\Delta x^4)$ for finite differences, is stable, and can be scaled to arbitrary dimensions. However, due to the nature of the approximation, this explicit scheme is not unitary, does not include time varying potentials, and as always, greater accuracy would be preferred. Goldberg proposed to instead apply a unitary approximation for $e^{-i\Delta t\hat{H}}$ with it's Cayley form, accurate to order $O(\Delta t^2)$ [4].

$$e^{-i\Delta t\hat{H}} \approx \frac{(1 - \frac{1}{2}i\Delta t\hat{H})}{(1 + \frac{1}{2}i\Delta t\hat{H})} \tag{13}$$

This then yields an integration of the form

$$(1 + \frac{1}{2}i\Delta t\hat{H})\psi_{n+1} = (1 - \frac{1}{2}i\Delta t\hat{H})\psi_n \tag{14}$$

However, combining Askars approach with that of the Cayley form generates an alternative scheme where equation (11) now takes the form

$$\psi_{n+1} - \psi_{n-1} = (\frac{1 - \frac{1}{2}i\Delta t\hat{H}_n}{1 + \frac{1}{2}i\Delta t\hat{H}_n} - \frac{1 + \frac{1}{2}i\Delta t\hat{H}_{n-1}}{1 - \frac{1}{2}i\Delta t\hat{H}_{n-1}})\psi_n \tag{15}$$

Here the Hamiltonian is allowed to vary in time. This expression has the distinct advantage of being unitary and can further be simplified significantly both for the time varying and independent Hamiltonian.

$$\psi_{n+1} - \psi_{n-1} = (\frac{4}{i\Delta t\hat{H}_n + 2} + \frac{4}{i\Delta t\hat{H}_{n-1} - 2})\psi_n \tag{16}$$

In the case of a time independent Hamiltonian this corresponds to

$$\psi_{n+1} = \psi_{n-1} - \frac{2i\Delta t\hat{H}}{1 + \frac{1}{4}\Delta t^2\hat{H}^2}\psi_n \tag{17}$$

A binomial expansion can now be applied to the denominator of the ψ_n term yielding

$$\psi_{n+1} = \psi_{n-1} - 2i\Delta t\hat{H}(1 - \frac{1}{4}\Delta t^2\hat{H}^2 + ...)\psi_n \tag{18}$$

Keeping only the first term in this expansion returns the Askar result of a 1st order expansion of the time evolution operator, however, this expansion converges much faster being in powers of $\Delta t^2 \hat{H}^2$. Applying a similar binomial expansion in the more general time dependent Hamiltonian case yields a similar result wherein

$$\psi_{n+1} = \psi_{n-1} + i\Delta t(\hat{H}_{n-1} - \hat{H}_n + ...)\psi_n \tag{19}$$

Unfortunately applying the expansion again means the integration scheme is no longer unitary but provided sufficient terms in the expansion still yields useful results.

3 Other Formulations

Work by C. Bottcher followed a similar approach to solve the time-dependent Schrödinger equation for collisions between H^+ and C^{+6} with H [5]. In this scheme a single charged particle was launched with constant velocity v on a straight line trajectory with impact parameter b. The Hamiltonian was expressed in a rotating frame in terms of the two dimensional coordinates ρ and ϕ such that

$$H = H_{rot} + H_{cor} \tag{20}$$

Where H_{rot} is the axially symmetric Hamiltonian and H_{cor} contains all angular terms, ϕ. H_{rot} was then expressed as a sum of kinetic and potential terms such that

$$H_{rot} = T_\rho + T_z + V(\rho, z) \tag{21}$$

The Peaceman-Rachford propagator was used as the time evolution operator.

$$\psi(t+\tau) = L_\rho^{-1} L_g^{-1} L_g^* L_\rho^* \psi(t) \tag{22}$$

where

$$L_w = 1 + \frac{1}{2} i\tau (T_w + \frac{1}{2} V), w = \rho, z. \tag{23}$$

Following this prescription, Bottcher was able to generate density plots (figure 1) corresponding to the negative log of the squared wavefunction by iteratively performing numeric integrations with various initial kinetic energies and impact parameters.

Alternative formulations have exploited Arnoldi type iterative solutions where the propogation operator $e^{-i\hat{H}\Delta t/\hbar}$ is expressed in terms of a matrix of vectors Q which span a Krylov subspace [6].

$$e^{-i\hat{H}\Delta t/\hbar} = Q e^{-ih\Delta t/\hbar} Q^\dagger \tag{24}$$

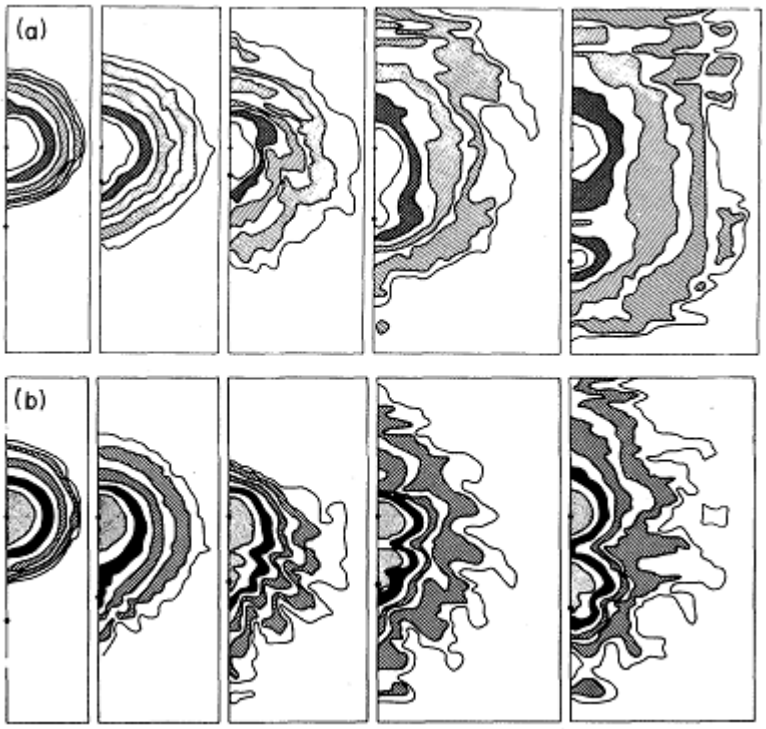

Figure 1: Contour density plots at times 3.75, 7.35, 10.75, 14.55, and 18.15 for H^+ + H (top) and C^{+6} + H collisions. [5]

The vectors Q can be solved iteratively via a gram-schmidt process where $Q_0 = \psi/|\psi|$ and Q_k is found by orthonormalizing the vector HQ_{k-1} with respect to the previous vecotrs Q. Finally the matrix h is the krylov subspace Hamiltonian

$$h = Q^\dagger H Q \tag{25}$$

or simply H in the space spanned by the vectors $Q_0, Q_1, ...Q_n$. This is advantageous as the new operator h accurately represents the Hamiltonian to order n, it is still smaller than the global Hamiltonian, usually by a large margin. According to work by Smyth this formulation is at least twice as efficient as a similar Taylor series and because the computational difficulty scales linearly with n this ratio improves with higher order approximations. This process was used to determine the ground state of helium among other initial states as can be seen in figure 2.

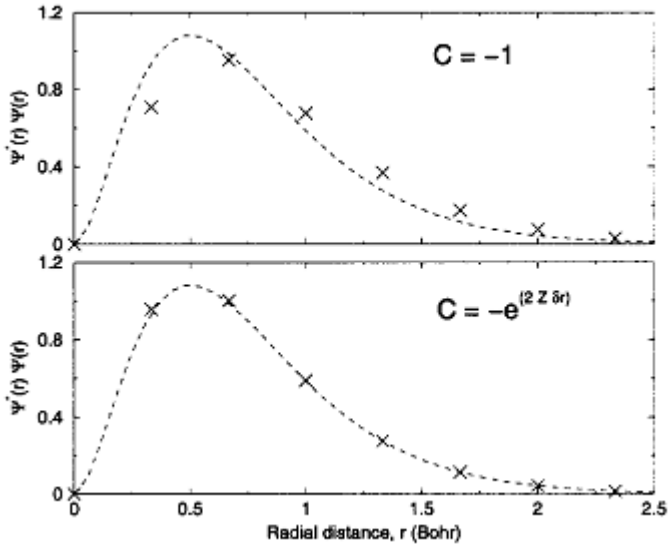

Figure 2: Dashed line is the expected functional form of the helium ground state wavefunction with X's being the calculated values at each lattice point with spacing $dr = 1/3$ bohr radius [6].

4 Conclusion

The basics of time integration within the context of quantum Mechanics revolves principally upon the manner in which the time evolution operator T is evaluated. The most obvious expansion of the operator $T = e^{-it\hat{H}}$ is that of a power series expansion, however, more complicated type calculations which maintain the unitarity of the operation can be instead used. The Cayley form of the exponential was used to explore the time evolution operator both in the case of a time varying and time independent potential and it was shown that this approximation, to first order, equivalent to the Crank Nicholson method proposed by Askar. However, this new expansion being in powers of Δt^2 converges more quickly for small time steps.

Similar type FEM calculations were also performed by Bottcher to determine the behavior of ion collisions between H^+ and H as well as C^{+6} and H. While more advanced expansions involving vectors spanning the krylov subspace of the Hamiltonian have been used to determine ground states of various systems to very high degrees of accuracy. Although there exist numerous numerical integrators ranging enormously in complexity such schemes have been used to make accurate predictions both of analytically known results and in a predictive capacity.

References

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