Computational Methods - Lesson 7 (Luxembourg, 28.10.2020)

Partial Differential equations II

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1. The Schrödinger equation

In quantum Mechanics[1,2] the state of a given system is described through a complex 'wave function' $\Psi(x,t)$ whose square modulus gives the probability of finding the system at time t in the interval $(x, x+dx)$:

$$\Pi(x,t)dx = |\Psi(x,t)|^2\, dx \tag{1}$$

that satisfies the normalization condition

$$\int_{-\infty}^{\infty} \Pi(x,t)dx = 1. \tag{2}$$

The time-dependent Schrödinger equation[1,2] defines the evolution of the wave function in time

$$i\hbar\frac{\partial\Psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\Psi(x,t)}{\partial x^2} + V(x)\Psi(x,t) \tag{3}$$

where $\hbar$ is the reduced Planck constant and $V(x)$ is an external potential that constraints its motion. The physical observables are given as mean values of the operators over the wave functions

$$\langle A\rangle = \int_{-\infty}^{\infty} \Psi^*(x,t)\hat{A}\Psi(x,t)dx. \tag{4}$$

By separating the spatial and time variables, we can rewrite the general solution as

$$\Psi(x,t) = \psi(x)e^{-i\frac{E}{\hbar}t} \tag{5}$$

which represents the state of a particle with energy E. The spatial wave function $\psi(x)$ satisfies the time independent Schrödinger's equation

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2} + V(x)\psi(x) = E\psi(x), \tag{6}$$

which is the eigenvalue-eigenvector equation

$$\hat{H}\psi(x) = E\psi(x) \tag{7}$$

for the hermitian Hamiltonian operator

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x). \tag{8}$$

This equation admits a series of discreet solutions (eigenfunctions of the Hamiltonian) $\psi_n(x)$ with corresponding energy values (eigenvalues of the Hamiltonian) E_n that satisfy the boundary conditions depending on $V(x)$. The general solution of the time-dependent Schrödinger equation will be a linear combination of the infinite time-independent eigenvectors each multiplied by a phase that depends on the corresponding eigenvalue

$$\Psi(x,t) = \sum_{n=1}^{\infty} c_n\psi_n(x)e^{-i\frac{E_n}{\hbar}t} \tag{9}$$

whose coefficients are defined as the overlap between the nth eigenfunction and the initial state $\Psi(x,0)$ of the system

$$c_n = \int_{-\infty}^{+\infty} \psi_n^*(x)\Psi(x,0)dx. \tag{10}$$

1.1. Schrödinger equation for the free particle. In the case in which the potential energy is absent $V(x) = 0$ the time-independent Schrödinger equation becomes

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2} = E\psi(x) \tag{11}$$

which has a general solution of the form

$$\psi_k(x) = Ae^{ikx} \tag{12}$$

where A is a constant, and k is the wave vector defined by the energy value

$$E = \frac{\hbar^2 k^2}{2m}. \tag{13}$$

The solution is thus a plane-wave with a wave vector k and energy $E > 0$ with a continuous spectrum. The constant A should be determined through the normalization condition of the wave function which cannot be imposed if the particle moves in an infinite interval.

1.2. Schrödinger equation in an infinite potential well. Let us suppose that the potential energy is defined as

$$V(x) = \begin{cases} +\infty & x \leq -L \\ V_0 & -L < x < L \\ +\infty & x \geq L \end{cases} \tag{14}$$

so that the wave function will exist only inside the open interval $(-L, L)$ and the general solution will have to satisfy the boundary conditions of $\psi(\pm L) = 0$. Because of the parity of the potential operator we can define two different classes of solutions, with even

$$\psi_k(x) = \frac{A}{2}\left(e^{ikx} + e^{-ikx}\right) = A\cos(kx). \tag{15}$$

or odd

$$\psi_k(x) = \frac{A}{2i}\left(e^{ikx} - e^{-ikx}\right) = A\sin(kx), \tag{16}$$

parity. By imposing the boundary conditions $\psi(\pm L) = 0$ we have that for the for the even solutions

$$k_n = \frac{(2n-1)\pi}{2L} \quad \text{with} \quad n = \pm 1, \pm 2, \ldots. \tag{17}$$

and the energy levels will be given by:

$$E_n = \frac{\hbar(2n-1)^2\pi^2}{8mL^2}. \tag{18}$$

The value of the constant A is obtained by imposing the normalization condition, so that

$$A^{-2} = \int_{-L}^{L}\cos^2(kx)dx = L + \frac{\sin(2k_n)}{2k_n} = L \tag{19}$$

and $A = \sqrt{\frac{1}{L}}$. For the of odd solutions for which $\psi(x) = -\psi(-x)$, by imposing the same boundary conditions we have that

$$k_n = \frac{\pi n}{2L} \quad \text{with} \quad n = \pm 1, \pm 2, \ldots \tag{20}$$

with eigenvalues

$$E_n = \frac{\hbar^2 n^2\pi^2}{2mL^2}. \tag{21}$$

And again from the normalization condition we will obtain the value of the A constant

$$A^{-2} = \int_{-L}^{L}\sin^2(kx)dx = \int_{-L}^{L}[1-\cos^2(kx)]dx = 2L - \int_{-L}^{L}\cos^2(kx)dx = L - \frac{\sin(2k_n)}{2k_n} = L, \tag{22}$$

again equal to $A = \sqrt{1/L}$

1.3. Numerical solution through the 'shooting' method. Since the time independent Schrödinger equation is a second order ordinary differential equation in the position, in order to solve it numerically we can apply the different algorithms used for the classical harmonic oscillator. For example, by rewriting the equation as

$$\frac{\partial^2\psi(x)}{\partial x^2} = -\frac{2m}{\hbar^2}\left[E - V(x)\right]\psi(x), \tag{23}$$

decomposing it in the linear system of coupled first order ordinary differential equations

$$\begin{cases} \frac{\partial}{\partial x}\psi'(x) = -\frac{2m}{\hbar^2}\left[E - V(x)\right]\psi(x) \\ \frac{\partial}{\partial x}\psi(x) = \psi'(x) \end{cases} \tag{24}$$

we can integrate it through the Euler-Cromer method, by introducing the space discretization Δx

$$\begin{cases} \psi'(x+\Delta x) = \psi'(x) - \frac{2m}{\hbar^2}\left[E - V(x)\right]\psi(x)\Delta x \\ \psi(x+\Delta x) = \psi(x) + \psi'(x+\Delta x)\Delta x \end{cases} . \tag{25}$$

During the integration procedure the value of the energy E is kept as a parameter of the evolution. Now, since the potential is even in the position variable x we can have both symmetric and antisymmetric solutions and these can be selected through the choice of the boundaries at $x = 0$ in fact, by setting

$$\psi(0) = 0 \qquad \left.\frac{\partial\psi(x)}{\partial x}\right|_{x=0} = 1 \tag{26}$$

we are choosing an antisymmetric solution (odd wavefunctions) while by setting

$$\psi(0) = 1 \qquad \left.\frac{\partial\psi(x)}{\partial x}\right|_{x=0} = 0 \tag{27}$$

we are choosing the symmetric ones (even wavefunctions).
Now, in principle, the value of the energy E for a given eigenvalue is not known, we only know that all the solutions must be the functions that evolving from $\psi(0)$ converge to the boundary condition $\psi(L) = 0$, and that this happens only if E is an eigenvalue so that the integrated state is an eigenfunction of the Hamiltonian. One possibility thus, is to 'shoot' the integration from 0 to L for different values of the energy E until we get closer to the solution, and this is the idea behind the 'shooting method'.
In the case of the infinite potential well, the eigenvalues are $E_n > 0$. If we start from $E = 0$ we integrate the constant solution in the box since the second term in the first Euler-Cromer equation, that gives the first derivative of $\psi(x)$, is always zero and the derivative is a constant along the integration.
We thus have that for $E = 0$ the even solution will give $\psi(L) = 1.0$ and for the odd one we will have $\psi(L) = L$.
As E increases, suppose $E + n\Delta E$ with $n = 0, 1, 2, 3, 4, \ldots$, the value of the integrated function in L decreases so that $\psi(L; E) > \psi(L; E + \Delta E) > \psi(L; E + 2\Delta E)$ until it crosses the value for which $\psi(L; E_0) = 0$, that is, the energy is $E < E_0$, where E_0 is the ground state for a certain parity. When the eigenvalue is crossed the wave function in L changes sign, that is $\psi(L; E+n\Delta E)\psi(L; E+(n+1)\Delta E) < 0$. If the change of sign occurs we can thus invert the direction of the variation of the energy and diminish the step by a factor $\alpha < 1$, *ie* $\Delta E = -\alpha\Delta E$, so that the integration restarts now getting nearer from the correct eigenfunction from below the correct energy $E_0 > E$.
This procedure can be repeated until the estimation of the eigenvalue has not reached a certain accuracy.

1.4. Time-dependent Schrödinger equation. Let us now consider the time-dependent Schrödinger equation that describes the evolution of a wave packet. Let us assume that at the initial time $t_0 = 0$ the wave function is a normalized Gaussian of variance ω^2 and mean value x_0:

$$\Psi(x, 0) = \left(\frac{1}{2\pi\omega^2}\right)^{1/4} e^{-\frac{(x-x_0)^2}{4\omega^2}}. \tag{28}$$

It is easy to verify that this function is normalized[1] and that the mean value of the quantity $(x-x_0)$, *ie* $\int_{-\infty}^{\infty}\Psi^*(x,0)(x-x_0)\Psi(x,0)dx = 0$, is null, since the square of the Gaussian is an even function, while $(x - x_0)$ is odd.

[1] Compute the integral $\int_{-\infty}^{\infty}|\Psi(x,0)|^2dx = 1$

If we now consider the momentum operator $\hat{p} = -i\hbar\frac{\partial}{\partial x}$, its mean value on the initial state will be

$$\langle p\rangle = -i\hbar\int_{-\infty}^{\infty}\Psi^*(x,0)\frac{\partial}{\partial x}\Psi(x,0)dx = \frac{i\hbar}{2\omega^2}\int_{-\infty}^{\infty}\Psi^*(x,0)(x-x_0)\Psi(x,0)dx = 0, \tag{29}$$

again null, which means that the initial momentum of the wave packet is zero.
In order to give an initial impulse we can modify the initial condition multiplying it by a phase $e^{ik_0(x-x_0)}$

$$\Psi(x,0) = \left(\frac{1}{2\pi\omega^2}\right)^{1/4} e^{-\frac{(x-x_0)^2}{4\omega^2}} e^{ik_0(x-x_0)} \tag{30}$$

so that it will still have zero mean value, but with initial momentum $\langle p\rangle = \hbar k_0$:

$$\langle p\rangle = -i\hbar\int_{-\infty}^{\infty}\Psi^*(x,0)\frac{\partial}{\partial x}\Psi(x,0)dx = i\hbar\int_{-\infty}^{\infty}\Psi^*(x,0)\left(\frac{x-x_0}{2\omega^2} - ik_0\right)\Psi(x,0)dx = \hbar k_0. \tag{31}$$

The energy of this initial state will then be equal to $E_0 = \frac{\hbar k_0^2}{2m}$.

1.5. Euler discretization of the time-dependent Schrödinger equation. As seen for the diffusion equation, let us proceed to apply the simplest Euler discretization to the time dependent equation in the following way

$$i\hbar\frac{\Psi(x,t+\Delta t)-\Psi(x,t)}{\Delta t} = -\frac{\hbar^2}{2m}\frac{\Psi(x+\Delta x,t)+\Psi(x-\Delta x,t)-2\Psi(x,t)}{\Delta x^2} \tag{32}$$

from which we have that

$$\Psi(x,t+\Delta t) = \Psi(x,t) + \frac{i\hbar\Delta t}{2m\Delta x^2}\left[\Psi(x+\Delta x,t)+\Psi(x-\Delta x,t)-2\Psi(x,t)\right]. \tag{33}$$

In order to study the stability we apply again the von Neumann method considering a solution of the type $\Psi(x,t) = \tau(t)e^{ikx}$ that substituted inside the algorithmic solution leaves us with

$$\tau(t+\Delta t)e^{ikx} = \tau(t)\left\{e^{ikx} + \frac{i\hbar\Delta t}{2m\Delta x^2}e^{ikx}\left[e^{ik\Delta x}+e^{-ik\Delta x}-2\right]\right\} \tag{34}$$

from which we have that

$$\begin{aligned}\frac{\tau(t+\Delta t)}{\tau(t)} &= 1 + \frac{i\hbar\Delta t}{2m\Delta x^2}\left[e^{ik\Delta x}+e^{-ik\Delta x}-2\right] = \\ &= 1 - \frac{i\hbar\Delta t}{m\Delta x^2}\left[1-\cos(k\Delta x)\right] = 1 - \frac{i\hbar\Delta t}{m\Delta x^2}2\sin^2(\frac{k\Delta x}{2}).\end{aligned} \tag{35}$$

In order for the solution to be stable, the modulus (and thus also the square modulus) has to be lower then 1, that is

$$\left|\frac{\tau(t+\Delta t)}{\tau(t)}\right|^2 = 1 + \left(\frac{2\hbar\Delta t}{m\Delta x^2}\sin^2(\frac{k\Delta x}{2})\right)^2 \geq 1 \tag{36}$$

which is always false since the second term is always positive. This corresponds to a loss of normalization in the initial function. In quantum Mechanics the square modulus of the wave function is a density probability of finding the particle in a certain position. If we imagine the particle in a box, with no external impulses the density of the particle is conserved and thus the normalization must remain equal to 1. In the Euler approach this does not happen and the normalization lowers as time progresses making the physical interpretation of the solution slightly difficult. For this reason the Euler algorithm cannot be used and some other methods have to be applied.

1.6. Visscher discretization of the time-dependent Schrödinger equation. An alternative discretization is that of Visscher[3] for which the real and immaginary parts of the wave function are separated

$$\Psi(x,t) = R(x,t) + iI(x,t) \tag{37}$$

so that the full time-dependent Schrödinger equation can be separated in a system of coupled differential equations

$$\begin{cases} \hbar \frac{\partial R(x,t)}{\partial t} = \hat{H} I(x,t) \\ \hbar \frac{\partial I(x,t)}{\partial t} = -\hat{H} R(x,t) \end{cases} \tag{38}$$

By using a shifted 'Runge-Kutta like' discretization for the two parts, we can write the algorithmic solution of the system as

$$\begin{cases} \hbar \frac{R(x,t+\Delta t) - R(x,t)}{\Delta t} = \hat{H} I(x, t + \frac{\Delta t}{2}) \\ \hbar \frac{I(x,t+\frac{3}{2}\Delta t) - I(x,t+\frac{1}{2}\Delta t)}{\Delta t} = -\hat{H} R(x,t) \end{cases} \tag{39}$$

from which we have

$$\begin{cases} R(x, t + \Delta t) = R(x,t) + \frac{\Delta t}{\hbar} \hat{H} I(x, t + \frac{\Delta t}{2}) \\ I(x, t + \frac{3}{2}\Delta t) = I(x, t + \frac{1}{2}\Delta t) - \frac{\Delta t}{\hbar} \hat{H} R(x,t). \end{cases} \tag{40}$$

It can be shown that this algorithm is of second order in the time step, and that the norm is conserved. Moreover it can be at least shown that the algorithm is locally stable[3] (that is considering the local value of the potential as finite) if

$$-\frac{2\hbar}{\Delta t} \leq V \leq \frac{2\hbar}{\Delta t} - \frac{2\hbar^2}{m^2 \Delta x^2}. \tag{41}$$

Finally we have to recall that, since the algorithm is shifted, in order to start it is required to have the values of the functions $R(x,0)$ and $I(x, \frac{\Delta t}{2})$. In order to initialize the algorithm we thus need the compute the immaginary part at 'half' the time of the real part's integration step, and to do so we can rewrite the Euler-like variation of the wave packet's mean as

$$x - x_0 \to x - x_0 - \frac{\langle p \rangle}{m} \frac{\Delta t}{2} = x - x_0 - \frac{\hbar k_0}{m2} \Delta t \tag{42}$$

and the evolution of the initial phase as

$$i k_0 (x - x_0) \to i k_0 (x - x_0) - i \frac{E}{\hbar} \frac{\Delta t}{2} = i k_0 (x - x_0) - i \frac{\hbar k_0^2}{2m} \frac{\Delta t}{2}. \tag{43}$$

Through these shifts the Gaussian wave packet at time $t_0 + \frac{\Delta t}{2}$ will be written as

$$\Psi(x, \frac{\Delta}{2}) = \left(\frac{1}{2\pi\omega^2} \right)^{1/4} e^{-\frac{(x - x_0 - \frac{\hbar k_0}{m^2} \Delta t)^2}{4\omega^2}} e^{i k_0 (x - x_0)} e^{-i \frac{\hbar k_0^2}{2m} \frac{\Delta t}{2}} \tag{44}$$

and its immaginary part will be

$$I(x, \frac{\Delta}{2}) = \left(\frac{1}{2\pi\omega^2} \right)^{1/4} e^{-\frac{(x - x_0 - \frac{\hbar k_0}{m^2} \Delta t)^2}{4\omega^2}} \sin\left(k_0 (x - x_0) - \frac{\hbar k_0^2}{2m} \frac{\Delta t}{2} \right). \tag{45}$$

References

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(2) Cohen-Tannoudji, C.; Diu, B.; Laloe, F. *Quantum Mechanics, Volume 1*; 1986; Vol. 1.

(3) Visscher, P. B. A fast explicit algorithm for the time-dependent Schrödinger equation. *Comput. Phys.* **1991**, *5*, 596–598.