SOLVING THE TIME-DEPENDENT SCHROEDINGER EQUATION

Throughout these notes I will use Dirac's bra and ket notation, and though the wave function depends on one or more spatial coordinates, this dependence will NOT be explicitly indicated.

We are interested in solving the time-dependent Schroedinger equation,

$$i\hbar \frac{\partial |\Psi>}{\partial t} = \hat{H}| \Psi>.$$

This is an initial value problem: given $|\Psi(t=0)>$, we want to find the wave function $|\Psi(t)>$ at a later time t. Formally at least, we could solve this equation IF the Hamiltonian does NOT explicitly depend on time, by separating the variables (ignoring the finesse required since H is an operator). Rearranging the Schroedinger equation gives

$$\frac{d|\Psi>}{|\Psi>} = -i\frac{\hat{H}}{\hbar}dt.$$

Integrating from t=0 to a later time t, we obtain

$$\ln |\Psi(t)> - \ln |\Psi(0)> = -\frac{i\hat{H}t}{\hbar}.$$

Exponentiating on both sides of this equation gives (being mindful now of the fact that H is an operator),

$$|\Psi(t)\rangle = e^{-i\hat{H}t/\hbar} |\Psi(0)\rangle.$$

The exponential operator preceding $|\Psi(0)\rangle$ in this equation is called the PROPAGATOR because application of $\exp\left(-i\hat{H}t/\hbar\right)$ on $|\Psi(0)\rangle$ produces $|\Psi(t)\rangle$, i.e., it propagates $|\Psi(0)\rangle$ forward to time t.

However, practical implementation of this scheme for obtaining the time-evolved wave function is not exactly straightforward since the propagator involves the exponential of the Hamiltonian which of course is some function of the operators $\hat{p}$ and $\hat{x}$ which do NOT commute. The standard way in which this equation was routinely solved for many years was to use a basis set expansion, i.e., the initial wave function $|\Psi(0)\rangle$ is represented as a linear combination (superposition) of the stationary state energy eigenfunctions which are the solutions of

$$\hat{H}|\psi_n\rangle = E_n |\psi_n\rangle.$$

Then $|\Psi(0)\rangle$ can be constructed as

$$|\Psi(0)> = \sum_n c_n |\psi_n>,$$

where $c_n = <\psi_n|\Psi(0)>$. The time-evolved wave function is then

$$|\Psi(t)> = e^{-i\hat{H}t/\hbar} \sum_n c_n |\psi_n>.$$

Since the $\{|\psi_n>\}$ are eigenfunctions of the Hamiltonian operator, the effect of the propagator on $|\Psi(0)>$ can be easily evaluated [since when $\hat{O}f = o\,f$, $g(\hat{O})f = g(o)f$] to give

$$|\Psi(t)> = \sum_n c_n\, e^{-iE_n t/\hbar} |\psi_n>.$$

If you have already solved the corresponding stationary state problem, the propagation then consists of doing the integrals (either numerically or analytically) needed to evaluate the $\{c_n\}$, and evaluating some sufficiently large but finite number (n_{max}) of terms in the sum such that

$$\sum_n^{n_{max}} |c_n|^2 = 1$$

to within some acceptably small difference. Historically this method developed earliest because numerical techniques for solving the stationary state eigenvalue problem were developed early on since such problems are of great practical importance in physical applications. One nice feature of this method is that one can jump as far ahead in time as one wants to get $|\Psi(t)>$ without having to calculate $|\Psi(t')>$ at all times t' such that $0 < t' < t$. The drawback to this method is that often hundreds of eigenfunctions may be needed to obtain a converged expansion, so that an eigenvalue problem of very large dimension may need to be solved. In recent years numerical methods have been developed that try to deal directly with the partial differential equation that is the time-dependent Schroedinger equation. For example, in one spatial dimension

$$i\hbar \frac{\partial |\Psi>}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2 |\Psi>}{\partial x^2} + V(x)|\Psi>.$$

Then one approach (pioneered in the 1950's) is to convert this partial differential equation into a set of algebraic equations by replacing the time and spatial derivatives by one of their finite difference approximations. If the time derivative is replaced by a 2-point central difference approximation and the spatial derivative is replaced by a 3-point central difference approximation, i.e.,

$$\frac{\partial |\Psi(t)>}{\partial t} \approx \frac{|\Psi(t+\Delta t)> - |\Psi(t-\Delta t)>}{2\Delta t}$$

and

$$\frac{\partial^2 |\Psi(x)>}{\partial x^2} \approx \frac{|\Psi(x+\Delta x)> -2|\Psi(x)> + |\Psi(x-\Delta x)>}{(\Delta x)^2},$$

a conditionally stable explicit finite difference algorithm for solving the time-dependent Schroedinger equation can be obtained. Notice though that we have used rather crude finite difference approximations; as a result an extraordinarily large number of grid points and time steps are required to get good accuracy. Due to its high computational demands this method which was used extensively until the 1980's is no longer the method of choice.

An alternative class of methods adopts the strategy of replacing the cumbersome and troublesome exact propagator by a more manageable BUT APPROXIMATE propagator. In the method developed by Feit and Fleck in the 1980's, known as the **split operator method**, the exact propagator

$$\exp\left[-i\left(\hat{p}^2/2m + V(x)\right)\Delta t\right]$$

is replaced by

$$\exp\left\{\frac{-i\hat{p}^2\Delta t}{4m}\right\}\exp\{-iV(x)\Delta t\}\ \exp\left\{\frac{-i\hat{p}^2\Delta t}{4m}\right\}.$$

This replacement is of course not exact since $\hat{p}$ and $V(x)$ do not commute, BUT the error associated with this approximation $[O((\Delta t)^3)]$ can be made acceptably small if Δt is chosen sufficiently small.

How has this replacement of the exact propagator by the so-called split operator propagator helped to make the problem more tractable? In this approximation

$$|\Psi(\Delta t)> \approx \exp\left\{\frac{-i\hat{p}^2\Delta t}{4m}\right\}\exp\{-iV(x)\Delta t\}\ \exp\left\{\frac{-i\hat{p}^2\Delta t}{4m}\right\}|\Psi(0)>$$

.

What one does now is take advantage of the fact that there is a complementary representation of $|\Psi(0)>$ in momentum space. In other words, there is a momentum space wave function $|\Phi(p)>$ that corresponds to the coordinate space wave function $|\Psi(x)>$. To obtain this momentum space wave function, one must perform an integral transformation known as the Fourier transform. In atomic units ($\hbar = 1$),

$$|\Phi(p)> = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} |\Psi(x)> e^{-ipx}\, dx\,.$$

Now in this representation, the exponential operator involving the momentum is just a simple multiplicative operator, so that the product

$$\exp\left\{-\frac{i\hat{p}^2\Delta t}{4m}\right\} |\Phi(p)> \equiv |\Phi'(p)>$$

is readily evaluated. One now Fourier transforms back to the coordinate representation since the next term in the split operator approximation will again be a simple multiplicative operator in this representation. To get there we must perform the inverse Fourier transform, i.e., we must calculate

$$|\Psi'(x)> = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} |\Phi'(p)> e^{ipx}\, dp\,.$$

We then multiply by $\exp\{-iV(x)\Delta t\}$ to obtain a result we can call $|\Psi''(x)>$. Finally the effect of the last term in the split operator approximation will again be very simple to evaluate if we convert $|\Psi''(x)\rangle$ to its momentum representation $|\Phi''(p)\rangle$. We then evaluate the product

$$\exp\left\{-\frac{i\hat{p}^2\Delta t}{4m}\right\}|\Phi''(p)\rangle$$

to obtain the momentum space representation of the wave function at $t = \Delta t$. One then repeats this process N times to determine the wave function at $t = N\Delta t$. If one wishes to "see" (visualize) the wave function in coordinate space at any point in **time**, an additional Fourier transform must be performed. The power of this method relies upon the development in the 1950's of a rapid method for performing Fourier transforms of discretized data known as the Cooley-Tukey Fast Fourier Transform (FFT). The split operator method is unconditionally stable and distinctly more accurate (for the same number of grid points and time step) than the explicit finite difference method discussed above.

Chebychev Polynomial Method

In this method the propagator is expanded in a series. This expansion is based on the following basic result

$$\exp(iRX) = \sum_n A_n(R)T_n(X)$$

for X in the range –1 to 1, and where $T_n(X)$ is a Chebychev Polynomial of order n and

$$A_n(R) = (2 - \delta_{n,0}) i^n J_n(R),$$

where $J_n(R)$ is the regular Bessel function of order n. To use the expansion to represent the propagator the Hamiltonian must be scaled so that energies are between –1 and 1. Thus

$$H_{norm} = \frac{H - H_{ave}}{\Delta H}$$

where $H_{ave} = (E_{max} + E_{min})/2$ and $\Delta H = (E_{max} - E_{min})/2$ where E_{max} and E_{min} are maximum and minimum values of the eigenvalues of H. (These are not known always and estimates must be made.) Thus,

$$\exp(-iHt/\hbar) = \sum_n A_n\left(\frac{\Delta E t}{2\hbar}\right) T_n(H_{norm})$$

And, the Chebychev polynomials satisfy a simple recursion relationship, i.e.,

$$T_{n+1}(x) = 2x T_n(x) - T_{n-1}(x); T_0 = 1, T_1 = x.$$

More details to follow

References

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