Computational Chemistry & Classical Molecular Dynamics

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Lecture – 11
Numerical Methods: Analysis of Errors

Welcome to this next lecture, computational chemistry course. So what we have done so far, we have discussed several aspects of programming, elementary statements of programming, do loops, if statements, dimension statements which refer to array variables and several other aspects and we were able to execute these programs. So after we execute it some very simple programs, we also discussed functions and subroutines.

The user functions and subroutines are, it allows your main program to be very simple and uncluttered and all the smaller tasks of something like say you want to calculate an integral or you want to invert a matrix or you want to solve an equation, you want to calculate a new function, all these objects are done by your subprograms or subroutines. So main program looks very clean.

Different subroutines and functions will do different tasks and the entire thing can be arranged in a nice structure.

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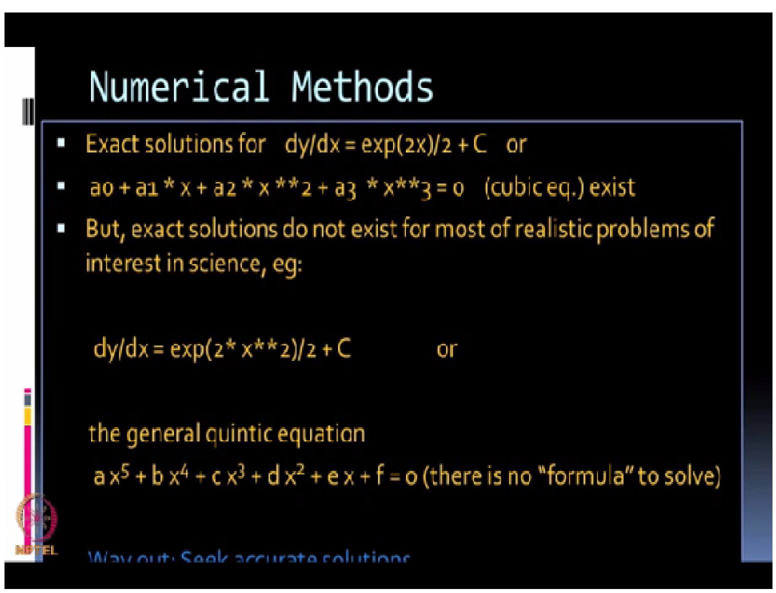

So that is what the whole thing about programming. Now we want to apply these to several problems in chemistry. So before we apply these to chemistry, we want to see what are the numerical methods that are useful in doing these calculations. Now before even going to numerical methods, let us see why we need numerical methods in the first place. So let us take these 2 examples.

One is this differential equation, dy/dx=exponential of 2x/2+C. So this is the differential equation and it has a solution. You can integrate exponential of 2x. You can easily integrate that and you will get a value. So you have an exact integral as a solution to this differential equation. Or you consider the second example. The second example is a cubic equation. What is a cubic equation?

a0+a1*x+a2*x square, this double star means square. This is the Fortran language. x**2 means x raise to second power, +a3*x**3, that is x raise to third power, so this is the cubic equation. What is a cubic equation? You have x up to the third power, a0+a1*x+a2*x square, this is my Fortran language for the square of a function, a3*x**, see that means a3*x cube, so this is a cubic equation.

So solution to this cubic equation exists. Just as you have a quadratic equation, ax square+bx+c, for that quadratic equation, you know that the solutions are -b+ or - b square-4ac/2a. So just as there are solutions to a quadratic equation, there are exact solution to a cubic equation. So whenever there are exact solutions, there is no problem but fortunately or unfortunately, exact solutions do not exist for most of the realistic problems of interest in science.

Just to take an example, there is an exact solution for the earth and the sun moving together but for the earth, sun and the moon moving together, there is no exact solution. Now why do we have to go to such a complicated problem? Take an extremely simple problem like this, dy/dx=e to the 2x square/2+C. Even for this very simple differential equation, it is not e to the 2x but it is e to the 2x square, okay.

For such a differential equation, there is no exact solution. Now consider this quintic equation, what is a quintic equation? Quintic equation is an equation where x to the 5 is there. So this is an equation where unlike the cubic equation above or the quadratic equation. Quadratic equation is, x to the 4 power. For the quadratic, cubic and quartic, there are exact solution but for the quintic equation, a to the x5+bx to the power 4+cx to the 3, dx square, e*x+f=0, there is no formula to solve this equation.

Not only there is no formula to solve this equation, there is no formula to solve equations of higher power then x to the 5. So even these polynomial equation, if you want to find the roots of these equations, there is no exact formula. So when there are no exact formulae, then you are forced to use what are called numerical methods. So numerical methods are really techniques which you can use to find approximate solutions to complex problems and the good thing is that whatever solutions you can get, you can try to make them as accurate as you want.

You can improve the accuracy of the methods. For example, I you have a quintic equation, you can get 5 solutions to that equation numerically, although it is not an exact formula. What is an exact formula? Exact formula is say quadratic equation. The solution is in terms of a, b, c. So what would be an exact formula for a quintic equation? A solution in terms of a, b, c, d, e, f.

So although there is no exact formula in terms of a, b, c, d, e, f; you can numerically come up with these 5 solutions to say fifth decimal place accuracy, eighth decimal place accuracy, fifteenth decimal place accuracy. So if you can get a solution up to fifteen decimal places accuracy, then that is more than sufficient for most of the situations.

Of course, you might require solutions to the thirtieth place in accuracy, that is also possible. You can extend numerical method to higher and higher accuracy. Of course, you will need better and better computers, faster and faster computers to do that. So numerical methods are an alternative to analytical methods. Analytical methods are basically exact solutions.

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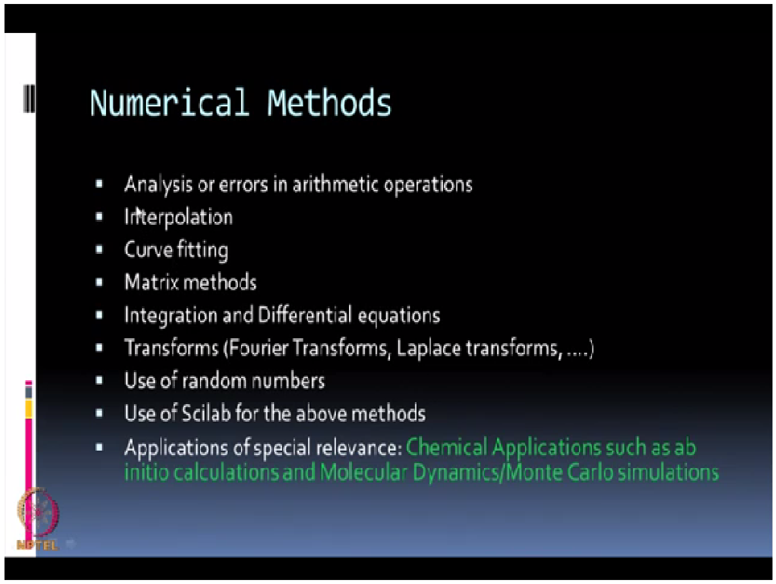

So now let us see what are some of the techniques that are used in numerical methods. The first thing would be analysis of errors in arithmetic operations, because as I said in numerical methods, you can calculate a number up to a given accuracy. So beyond that particular accuracy, it will not be accurate. So I need to know what is the error in my final result. So error analysis becomes an extremely important technique to understand how good my solution is.

So this is one of the things we will discuss today a little bit. Then there is a method called interpolation. Then curve fitting, then matrix methods. So suppose I have a 5*5 matrix or a 10*10 matrix, it is always, although I have a formula for the inverse of a matrix. To actually calculate the inverse, I will need a determinant and calculating a determinant is a very invert task because it involves a large number of operations.

So again we will need numerical methods. For example, suppose you want to calculate a 13*13 determinant. So I have asked many people how long it takes to calculate a 13*13 determinant by hand without using a computer? So today I will leave this as an exercise. Next time, you see whether my answer agrees with your answer, okay. What is the question? How long will it take you to calculate a 13*13 determinant, that is a determinant of a matrix which is 13 rows and 13 columns by hand without using a computer and without using a calculator?

Let us see if my answer agrees with you. So this will also need numerical methods. Then integration and differential equations. We already saw in the last slide that some differential equations have no exact solution. So I will need a numerical method to do it and there are many many integrals for which there are no exact formulae. So there also I will use a numerical method.

Then there are many things called Transforms like Fourier Transforms, Laplace transforms. All these things are extremely useful in numerical methods. So they are basically analytical expressions but you will note, you will need numerical methods to calculate them accurately. Then random numbers, these are very useful in several problems. Random numbers are also numbers for which you will need numerical methods to estimate them.

Then most of the things that are mentioned here, we will try to use our programming skills to calculate most of these things but often our programs, since we are all learning at the beginning, we will not be as good as a professional program. So there are many softwares, examples Scilab, they allow you to do all these operations in a very effective, accurate and fast manner. So we should also know how to use available external software to do these operations and the advantage of Scilab is that it is free.

You can just download it for free and most of the calculations, you need to do in life, Scilab will allow you to do it very effectively. So we will also have a 3 or 4 lectures on how to use Scilab for all the numerical methods that are listed here. So that is the Scilab. Then what are applications of special relevance for us? We want to do chemical calculations. See ab initio methods allow you to calculate structure of molecules.

Then this particular course we will not do too much of ab initio methods. That we can take up in another course but this course, we will do programming, it will do numerical methods and it will also do classical molecular dynamics and Monte Carlo simulations. That we will do as applications of this course towards the later part of this course. So today, I will now let us start with this concept of interpolation or before that, let us do this error analysis. So what is the meaning of error analysis?

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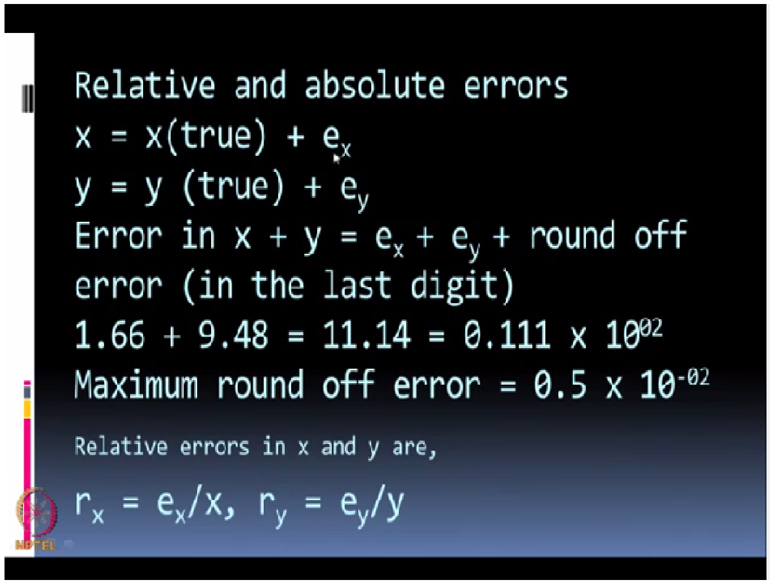

Whenever you measure any quantity, experimentally when you measure, there is a true value of this quantity but there will always be some error. This error could be because your instrument is not accurate enough or this error could be when you make a measurement, there is a human error, there is an instrumentation error, there is a random error. So whatever we measure, it will never be its perfect value but a value with some error.

For example, velocity of light is a quantity which is measured very accurately. So you can measure this quantity, let us say up to the eleventh decimal place, but there will be some error in the twelfth decimal place. The same is true for several physical quantities. For example, the mass of an electron. You may know the mass of an electron up to say tenth digit, twelfth digit but you will never know the exact value because any measuring device will have certain error in that.

So any value, physical quantity, will have its true value+some error. So suppose I have x which has a true value+some error and I have a y which has a true value+some error, I would like to know what is the error when I add x+y. Now why do I need to find this error? Because in calculations, in computers, we will be doing several operations, multiplications, additions, so if there are already errors in my individual physical quantities, the final quantity I calculate, there will be some errors in that too.

So it is very necessary that I have a good idea of what the error would be. So what I want to do here? I want to calculate the error in x+y. So what will be the error in x+y? It will be the error in ex which is already an error in x. There will be an error ey+a round off error. So what is a round off error. Often in the last digit, you round off that object. So since you round off, there will be some round off error in the last object.

Let us take this example. I have this number, 1.66. To that number, I want to add 9.48 and the sum of that is 11.14. Now suppose I want to write it with only 2 places after the decimal. If I want to have only 2 places of the decimal, the third things will have no place in that. So the round off error in this particular number will be 0.5*10-2. So there is always a round off error which occurs in the last digit and the error would be 0.5*the number of digits that are here.

So in this case, the maximum round of error will be 0.5*10 raise to -2. So this is the round off error when I have 2 numbers. When I have 100 numbers? That will be even larger round off error. So now let us see, what are relative errors now. These are absolute errors. Relative error would be? rx is the relative error in x that is given by ex/x. Now relative error in y will be ey/y. So that is a relative error. Not an absolute error.

So now these relative errors will be useful when I calculate the product of numbers.

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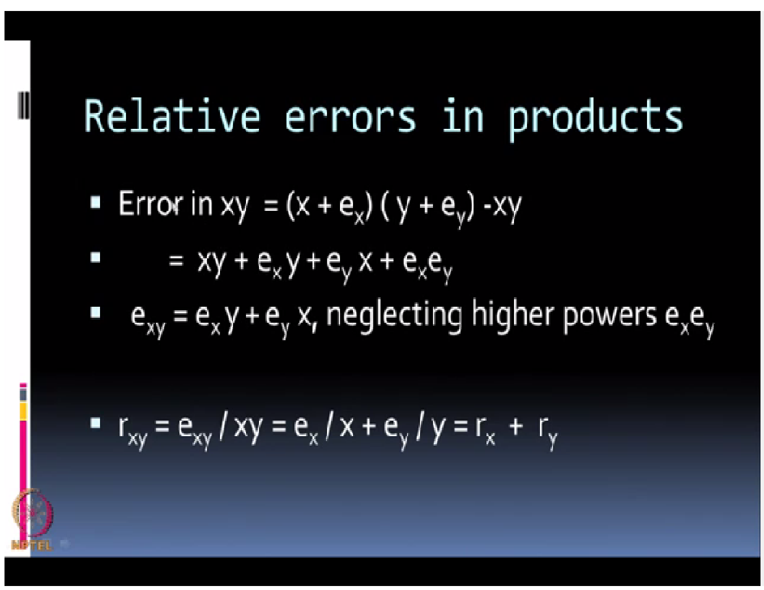

So let us go to the next one. I want to find the relative error in the products now. Now instead of a sum of x+y, suppose I take the product xy. xy will be, the product would be x+ex, because ex is the error in x, multiplied by y+ey-xy. This is my maximum possible error in the product. So I expand this. When I expand, I have xy ex*y, then ey*x+exey, because now this xy will cancel with this xy.

The total error would be, okay this xy will cancel with the original value of xy. So the error in the product will be exy*eyx. I have neglected exey because ex is already small, ey is already small. The product will be much much smaller than either of them. So it will be a much smaller order of magnitude than either x, either ex or ey, so I neglect. So we now want to express this error in exy as a relative error.

So I will divide exy/xy, so that will be my relative error in xy, that will be exy/xy, that is my relative error, that is I multiply, I divide this by xy, divide ex*y/xy, so what I get is? ex/x. Divide eyx/xy, so I will get ey/y. So the relative error in the xy would be relative error in x+relative error in y. When I add 2 objects, the absolute error is the sum of the absolute error. When I multiply 2 objects, the relative error is the sum of the relative errors.

So now we know how to calculate the relative error in a sum, relative error in a product. So suppose my program involves 5000 multiplications and 30,000 additions, so I can estimate the maximum possible error in all these operations. This I will need because once I know the maximum possible error, then I know whether to trust my final result or not. Suppose my final result is 2.2 and the maximum error in this is 3.2, then there is not so much meaning to this 2.2.

But suppose 2.2 as my result and my error is 0.0033, then I can trust my 2.2 with great deal of confidence. So therefore, there is a need always to keep track of how many operations you did in the calculations and what is the maximum possible error. And one good thing is that, although there are errors in addition and multiplications, many of these errors cancel. It is that if I have 1000 operations, the error, round error in these 1000 operations is not necessarily 1000 times the round off error in each one.

So there is lot of random cancellations in these errors. So your final errors are distributed in what is called a Gaussian distribution. At a later time in this course, we will consider these distributions but the purpose of introducing errors right at the very beginning of numerical methods is to tell you that these are important and we should keep in mind that the final result that you get, there is an error in that and I should be able to assess what is the error. So the next task that we will consider is called an interpolation, okay.

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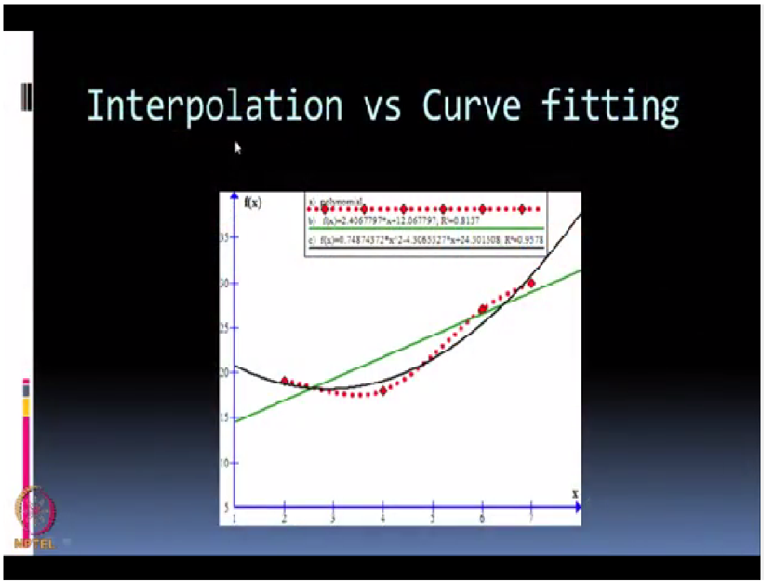

Interpolation is a method where if I have a data points, so here on the screen, I have given 4 values of data points. These red diamonds are my data points. This is the first data point second data point, third data point and fourth data point. What an interpolation does? Interpolation connects these points through some function, through some smooth function. So remember that I do not know the value of this function at all points other than these 4 points.

All I know is that I know these 4 points, so I want to draw a smooth curve which goes through that point. So what is the advantage of this smooth curve. Suppose now my x values are between 1 and 7 or 1 and 8, y values are between 10 and let us say 40 or 50, so this is my function. So suppose I need the value of the function when x=3. When x=3, I have not measured that object. So a good estimate would be the dotted line that is drawn here.

So interpolation allows me to estimate values of the function at points which are not measured between the starting point and the ending point. Interpolation is to find the value of the function at points in between. Now suppose I want the function not at 7 but at 8, that will be called extrapolation. So usually when I extrapolate, there will be much greater error in extrapolation than in interpolation.

Because what is the point in interpolation? If I have some point here, the neighbouring points give me a good idea of what the function is going to look like. Whereas when I extrapolate, since I do not know what is the value of the function beyond that point or if I want to extrapolate on the lower side, suppose I want the value at 0.5, I have no idea what the function looks like at 1 or -1, so errors in extrapolations are usually much greater.

So interpolation is an extremely useful thing. Now what are the uses of interpolation? Suppose I want the derivative of this function, at any point in this region. I can get a derivative. If I want the integral of this function, I can get an integral. So many operations that I want to do with this data, I can do with this interpolating curve. So how to interpolate is a problem of interpolation.

So what we will take up shortly. Now before we go further, we also want to talk about curve fitting. You know many times when I have lots and lots of data points, you have these 4 data points, I want to fit that through a curve. What is the simplest curve that I know of? Straight line is the simplest curve that I know of. So suppose I draw this green line. Green line is so called best fitting line through these points.

The best fitting line does not necessarily pass through those points, but it is a best linear representation of this data. So the green line is the best fit. So I have also given you some equation for that fit here. There is an equation for that line. So you can look up that equation for that green line. The second fit would be this black line. You see this black line. Black line is the best quadratic fit to my data. It is a quadratic function.

Line is a linear function. The curve is a quadratic function. The best quadratic fit through the function is this black line and notice that in a fitting function, the function need not pass from my original data points. Whereas when I interpolate, everything passes through those data points. So when I have a given set of data, I can go for interpolation or I can go for curve fitting. Which one

I shall use? Depending upon my requirement, okay.

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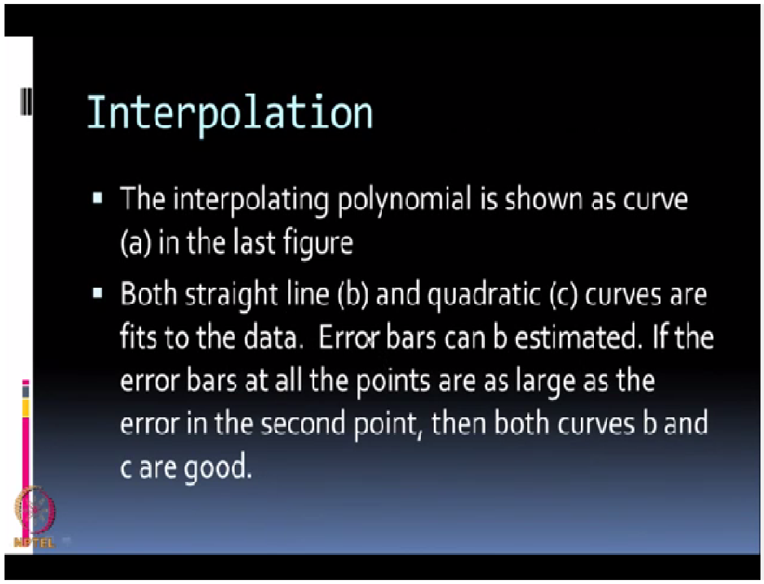

So now let us review what we did. In interpolating polynomial was shown in the last figure, okay. So since there are 4 points, through 4 points, you can draw a cubic polynomial. Through 2 points, you can draw a unique line. Through 3 points, I can draw a unique quadratic function. Through 3 points, I can draw a unique cubic polynomial. 4 points, there is a cubic polynomial that was shown as the red fit in the last slide.

Now the straight line and the quadratic curves are fits to the data. So when they are fits to the data, so you see that I can estimate now errors. Suppose this I have a quadratic function, red one is the actual value. The error is roughly of the width between the point and the curve. So this can be taken as the width. These are all called error bars. At the second point, the error bar is of the order of, so it is 15, 20. If this is 5 units, there error is of the order of 2 units.

Here also the error is of 2 units. But the straight line fit has a much greater error because at the middle point, the difference between the green curve and the red curve is almost of the order of 5 units. So this is a very large error. So the linear function has a large error. The quadratic function has less error. So errors can be represented as error bars on these curves.

We have not actually shown the bars but you can easily calculate depending on the distance. You can estimate the error bars. If the error bars at all the points are as large as the error in the second point, then if the actual data has lot of errors, then the fitting curves may be okay. But if the errors are very small, then the fitted functions are very poor, okay.

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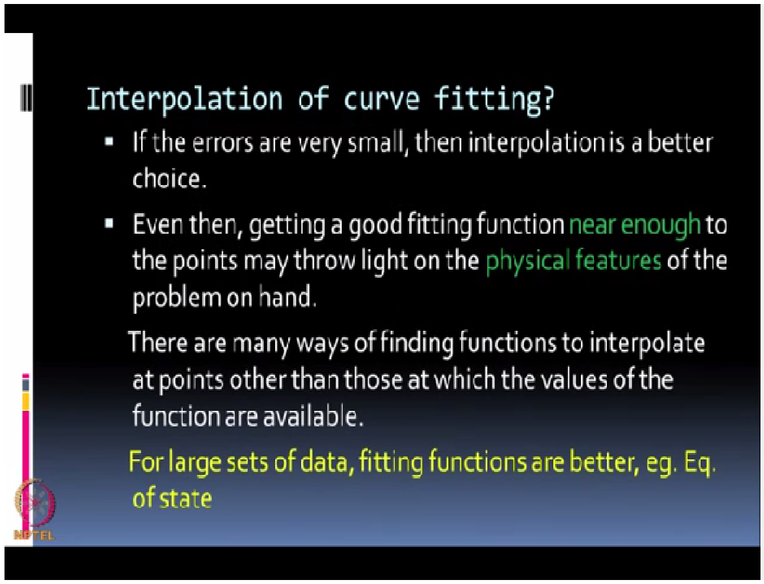

So usually with some experience, you will be able to know when you can use the interpolation, when you can use curve fitting. So this particular slides give an example. So if the errors are very small, then interpolation is a better choice because if I am very sure of my data, every point is a very important point, then neighbouring points should follow value of this point at a given point.

So therefore, small errors interpolation is very good, okay. But even though, interpolation is very good, now what is the advantage of a fitting function? Suppose you have fitting function, then it may throw some information about the actual physical process. For example, there is a famous story that Newton wanted to know what is the law of gravitation. We all know that it is gm1m2/r square.

The actual value he got was not 1/r square but 1/r to the 1.98. But Newton was a very clever man. He said 1.98 cannot be the law of gravitation. There must be some error in my data. So my gravitational force will be gm1m2/r square. Now we all know that gravitational law is r square, but if you experimentally want to find out that power, you may not exactly get the value of 2 but you will get a close to the value of 2.

So fitting functions can really give you physical features of a problem in hand. Now there are many ways of finding functions to interpolate at points other than those at which the functions are available. So we will consider several ways of finding these interpolating function as we go along. But as a general comment, I can say that if you have a very large set of data, fitting functions are much better.

For example, suppose you want to know the equation of state, you have measured pressure at different volumes of the system. You have 100s of data for pressure, 100s of data for volume. So in interpolating function would be a very complicated function. Instead of that if I had just that a polynomial function like PV=nRT+BP+CP square, you have all seen this virial equations of state.

They are either quadratic, cubic, or quartic equations. So if I have nice fitting equations, it is always good to have a good fitting function for a large set of data. So fitting functions are always useful and the other advantage of a fitting function is that you do not have to have large number of tables of data. So instead of having pressure versus volume for every gas that we know under the sun, we just go for the equation of state for a gas which contains entire information about its pressure-volume behaviour. So many situations, large sets of data, fitting functions are better.

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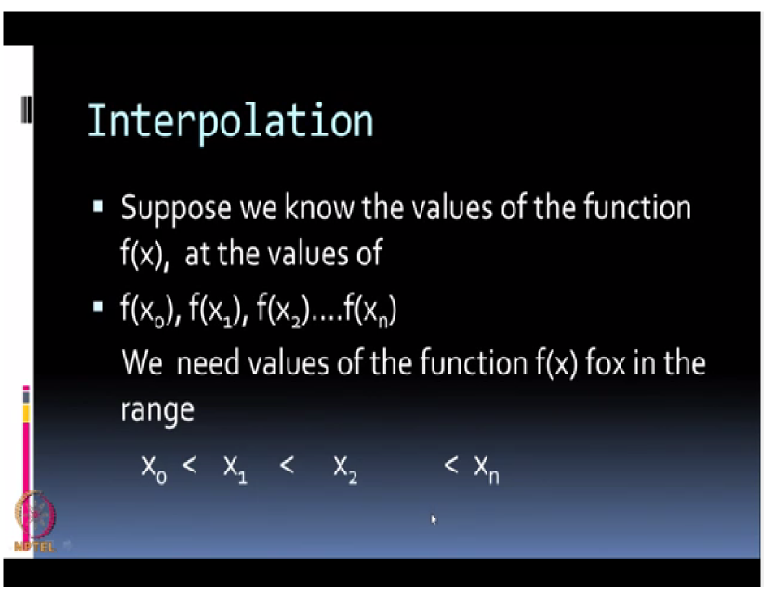

Now let me go to the concept of interpolation. This is what I will continue in detail in the next class. So this time what I want to do is to let us say, define the problem for interpolation and how I can get functions for that interpolation, okay. So what is the problem of interpolation? I have my data points, x0, x1, x2, x3 up to xn. So normally, we start counting from 0, 1, 2, up to n. So when I count from 0 1 2 3 up to n, I have n+1 data points.

I have n+1 values of x and at each one of those n+1 values, I have already determined the function, fx0, fx1, fx2. So I have n+1 values of x and n+1 value of the function. So what I need to do now? I need to know the value of function x for x in the range. So I know the value of x0, I know the value at x1, x2. In between I do not know.

In between x1 and x2, I do not know. In between x2 and x3, I do not know. So the interpolating function should give me the values in between the data points that are measured. So that is the problem of interpolation. So the question is how I can determine a function to interpolate between these 2 points?

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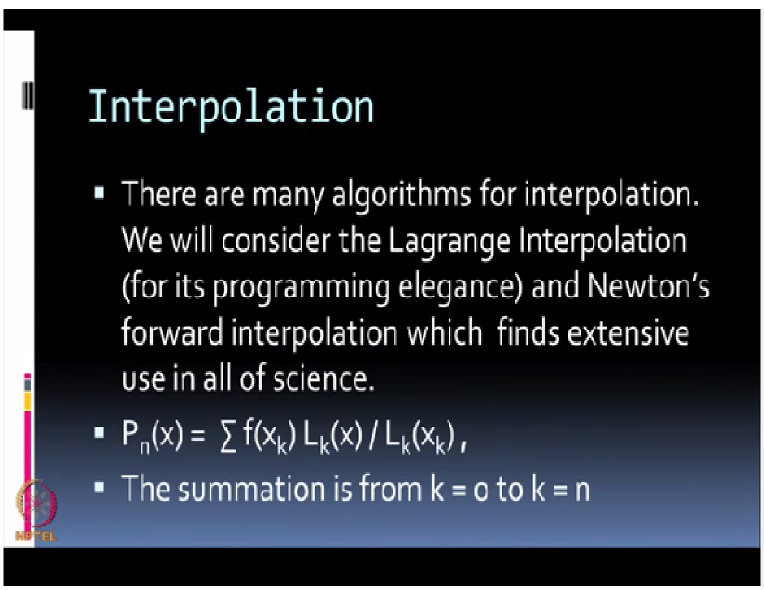

There are several methods are there. So one of the method is called a LaGrange Interpolation method. I will give the concept today and we will discuss the program in the next time. So this LaGrange interpolating polynomial, okay, it is very nice because to program it, is a very nice problem for programming. Very elegant; very nice. So the LaGrange interpolating polynomial determines your polynomial in terms of this function xk.

So what is my given set of data? xk and function of xk. So n+1 values of xk are known. And n+1 values of fxk are known. So then my polynomial is these values of xk, multiplied by a polynomial Lkx/a constant Lkxk. So what this polynomial does? It expresses the polynomial Pnx which is an interpolating polynomial in terms of known values of xk, multiplied by polynomials xk, polynomial Lkx,/constant Lkxk.

So what I will do, we will just tell you the formula for Lkx and Lkxk and close this lecture. The summation now k is again from 0 to n because there are n+1 values of fxk. So the summation is our all values of k going from 0 to n+1. So let us see what are the values of Lkx and Lkxk before we conclude.

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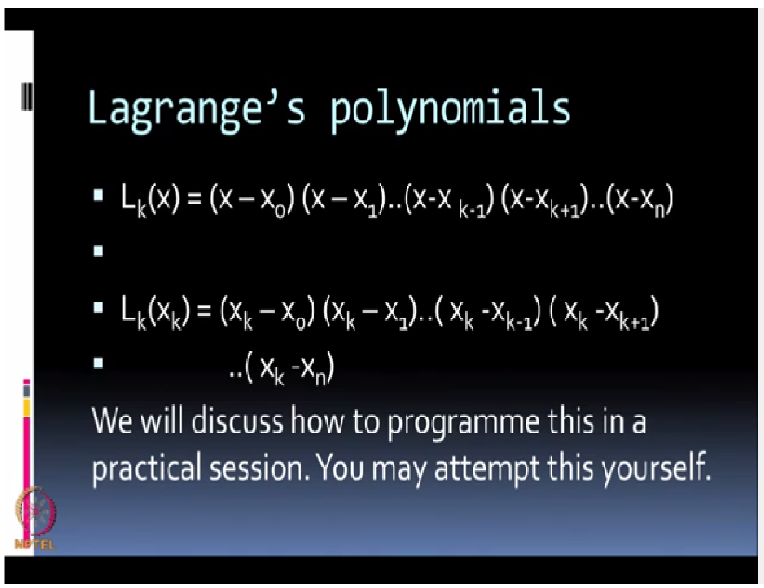

So these are my formulas. What is Lkx? Lkx is a polynomial, x-x0 x-x1 x-xk-1. There is no x-xk. If this is k, that x-xk is not there. x-xk-1 and x-xk+1 is there. Finally, x-xn. So this is an nth order polynomial. It has n factors except the x-xk factor. So what is Lkxk? Lkxk is again a product. This is not a polynomial because all these terms on the right hand side are known quantities. There is no variable here. xk-x0 xk-x1 xk-xk-1.

There is no xk-xk because xk-xk will be 0. So except the xk-xk terms are there, all other terms are there. So that is my Lkxk which is a numerical factor. Lkx is a polynomial, okay. So what is my LaGrange's polynomial? It is, I have given on the last slide. It is sum of fxk*Lkx/lkxk. So this is my polynomial function. So what we will do? We will discuss how to program this in a practical session.

I would want you to practice this yourself because if I have n factors, I am sure you can determine the polynomial Lkx at different values of x in the range between x0 and xn. So this is just a polynomial product of function. You know how to calculate the product of variables. You can do this in your own program. So what we have done today is that we summarized what we have learnt earlier about our programming up to the functions and subroutines.

Then we started discussing numerical methods. Why do we need numerical methods? Because there are no exact solution to most problems in science. So these numerical methods have several techniques interpolation, matrix method, finding roots of equation and so on. So as we go along in the next few lectures, we will discuss as many numerical methods as possible before we come up to the simulation using classical molecular dynamics. So I will conclude my lecture here today. Thank you.