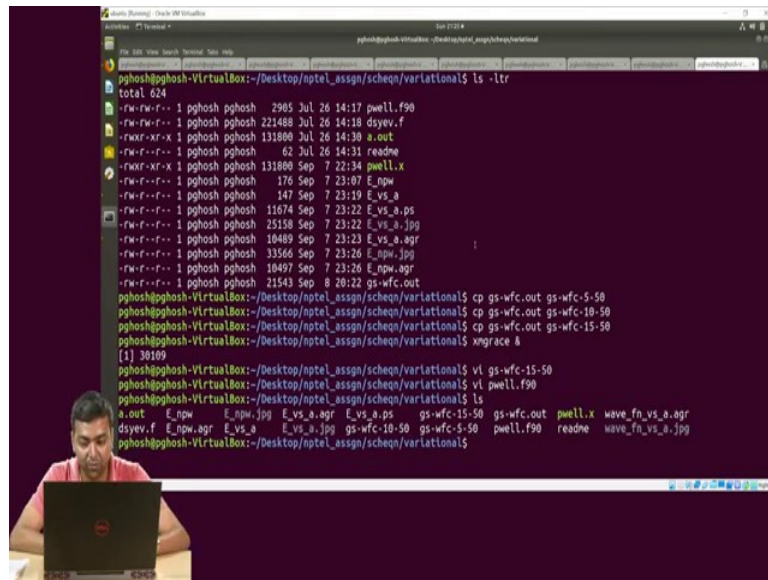


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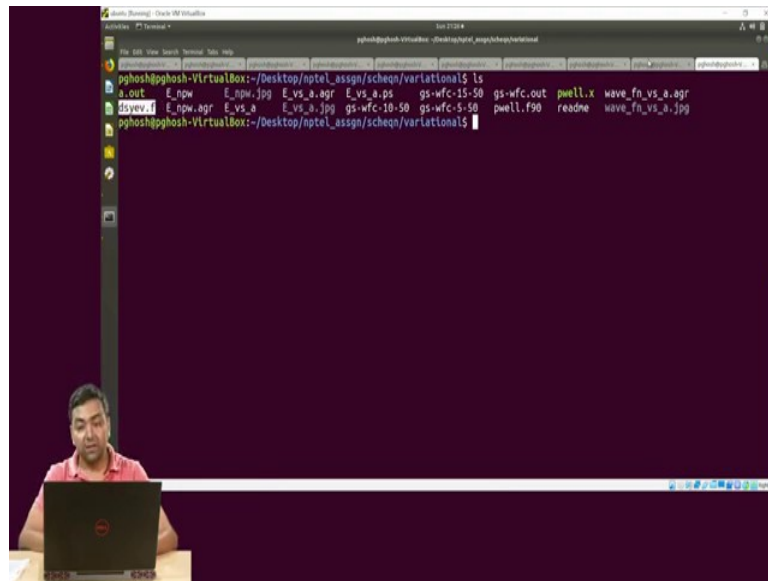
**Lecture – 45**  
**Differential Equation for Quantum Mechanical Problems: Variational Principle**  
**Part 05**

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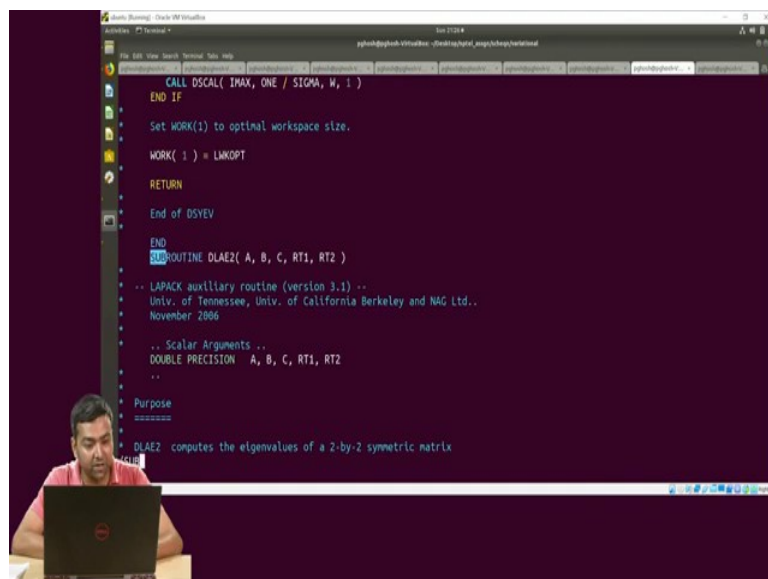
So, now we have we need to use two problems. One is this... let me just clear this.

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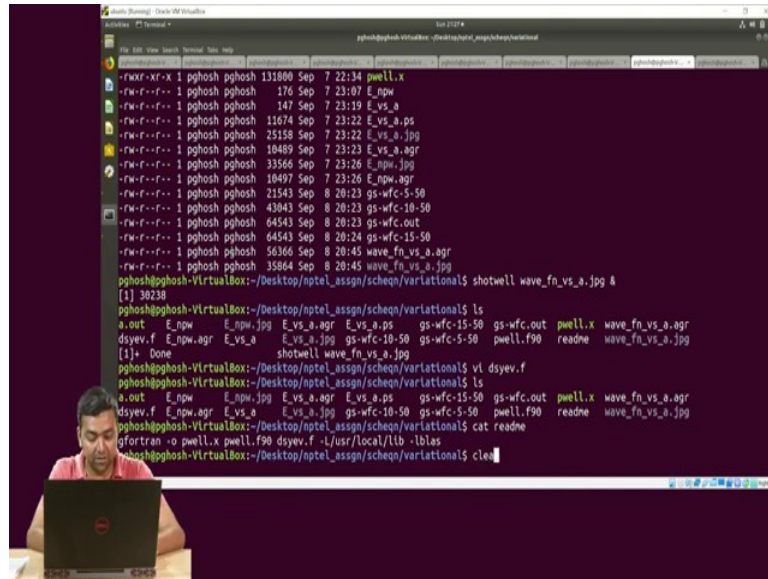
So, if I do ls, so, my relevant files are these ones which is my main program and then this one which is my the Fortran subroutine which are the part of the lab excel routine which does the diagonalization. So, now in remember in order to compile this program this particular subroutine this dy dsyev this remain requires some other subroutines also, let me see where it is written.

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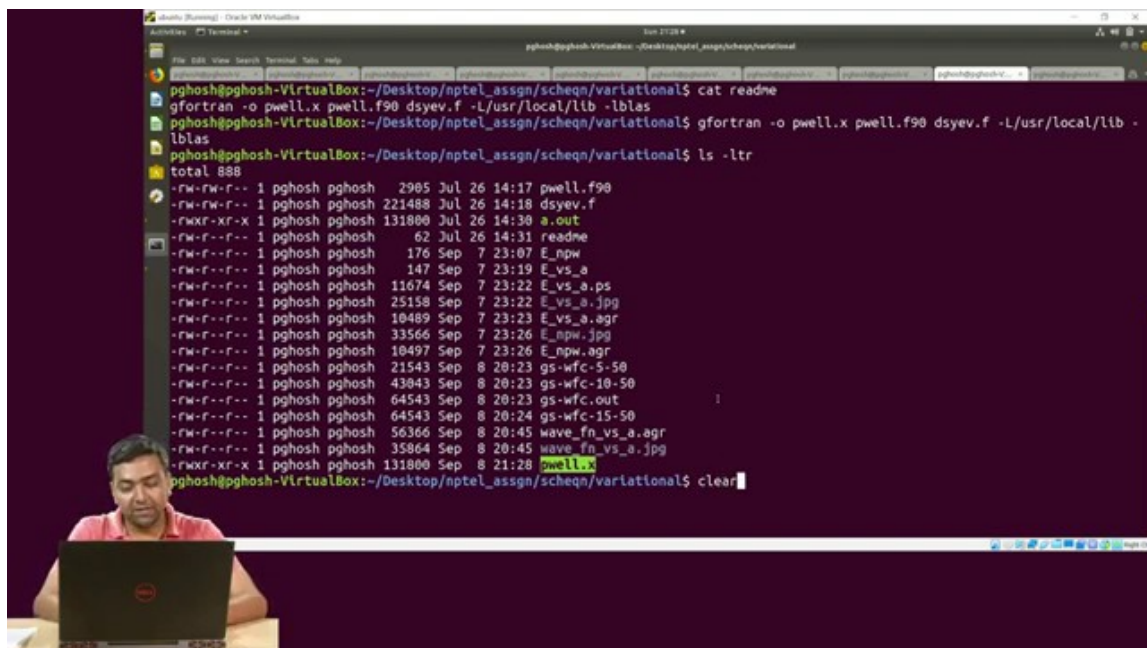
So, see for example, here it requires this particular subroutine and if I go down it will require another subroutine and so on and so forth.

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So, these subroutines are part of the BLAS library. So, you need to have a pre installed BLAS in your machine in order to compile this code and the way the compilation is done is in the following way. So, again I am using gfortran as my compiler. So, let me just clear the screen.

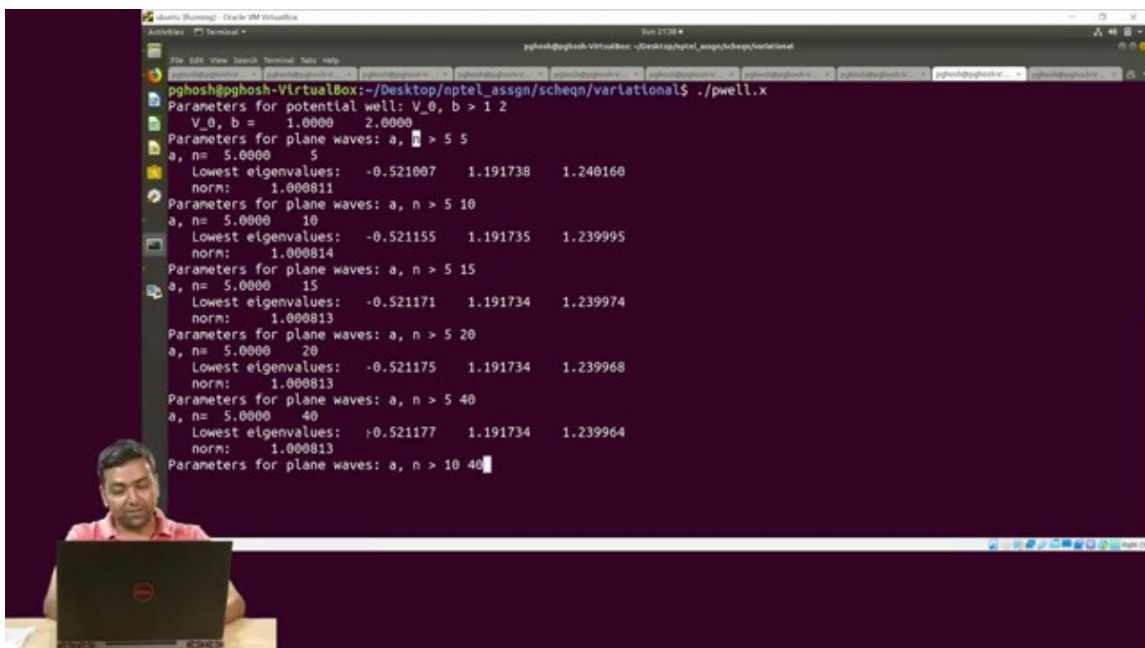
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So, I am using gfortran as my; so, gfortran is my compiler. So I write gfortran minus o the compiled output is stored in this file pwell dot x, then the name of the main program which I want to compile name of the subroutine which I am I will be using to diagonalize this matrix and this particular subroutine needs to be linked to your blas library. So, that is done in the following way. So, minus L is the command and then minus L and then you have to still where the compiler where this blas library is.

So, in my machine it is stored in slash user slash local slash lib and then you link that particular. So, you go to that particular directory and then link the blas and then you compile it. So, my compilation is done and this is the output file it has produced where the executable is.

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```
pgghosh@pgghosh-VirtualBox:~/Desktop/nptel_assgn/scheqn/variational$ ./pwell.x
Parameters for potential well: V_0, b > 1 2
V_0, b = 1.0000 2.0000
Parameters for plane waves: a, n > 5 5
a, n = 5.0000 5
Lowest eigenvalues: -0.521007 1.191738 1.240160
norm: 1.000811
Parameters for plane waves: a, n > 5 10
a, n = 5.0000 10
Lowest eigenvalues: -0.521155 1.191735 1.239995
norm: 1.000814
Parameters for plane waves: a, n > 5 15
a, n = 5.0000 15
Lowest eigenvalues: -0.521171 1.191734 1.239974
norm: 1.000813
Parameters for plane waves: a, n > 5 20
a, n = 5.0000 20
Lowest eigenvalues: -0.521175 1.191734 1.239968
norm: 1.000813
Parameters for plane waves: a, n > 5 40
a, n = 5.0000 40
Lowest eigenvalues: -0.521177 1.191734 1.239964
norm: 1.000813
Parameters for plane waves: a, n > 10 40
```

Now, let us run this and see what we get. So, if I run it; so first of all it asked me for these parameters for this potential well that is V 0 and b.

So, let me choose V 0 to be 1 and my b to be 2. So, the depth of my potential is minus 1 and the width is 2. So, if we do that, so the code reads in and then prints out these values then it asks me the parameters for the plane waves that is a the periodicity and n which determines the number of plane waves. So, let me start with a small value of a and let me start with say a small value of number of plane waves that is this 5 n 5.

So, now if you see here, it does the job and then it prints out the lowest eigenvalues. So, let us look at the lowest eigenvalue 3 eigen values. So, what you see is that the lowest eigenvalue is minus 0.52, then the next one is 1.19 and then the next one is 1.24. So, if you remember the potential which I am using that is a attractive potential. So, we should have at least one bound state. So, and that is what; so what from our solutions what we see is that we can we are getting one bound state and then there are two unbound states here.

So, now let us see how the values of this wave eigenvalues change if we increase the  $n$  that is the number of plane waves. So, remember when I am choosing here  $n$  equals to 5 here when I am giving an input  $n$  equals to 5 the number of plane waves is actually 11 ok. So, let me keep the width, the periodicity of my plane waves to be same, but instead of 5 let me go to 10 say.

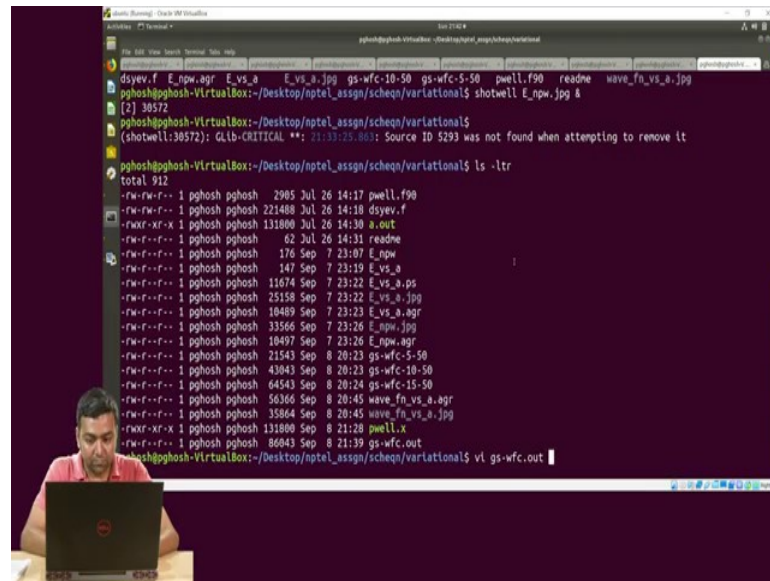
So,  $n$  value I go to 10. So, what it means is that I have 21 plane waves now and if I run my code, so, you see the eigenvalues are changing. So, the new eigenvalues which I get is minus 5 0.521155 which is lower than this particular eigen value which I get when I use 11 plane waves here.

If I reduce it, increase the number of plane waves further and do it, so then I see that my eigen value is the ground state, the lowest energy eigen value it reduces further and if I go to say 20 then you see there is still a slight reduction here. So, the question is, is this the correct behaviour which we expect.

So, to understand this ok, but before we go to that questions so, another thing which I have like to point out is that see for all the cases the norm of the potential norm of the wave function is always 1, its approximately very close to 1.

So, what I have done here is ok. So, now, let us try to understand the behaviour of my potential behaviour of my energy eigenvalues that is this quantities here as a function of the number of plane waves.

(Refer Slide Time: 06:17)



```
dsyev.f E_npw.agr E_vs_a E_vs_a.jpg gs-wfc-10-50 gs-wfc-5-50 pwell.f90 readne wave_fn_vs_a.jpg
pghosh@pghosh-VirtualBox:~/Desktop/nptel_assgn/scheqn/variational$ shotwell E_npw.jpg &
[2] 38572
pghosh@pghosh-VirtualBox:~/Desktop/nptel_assgn/scheqn/variational$
(shotwell:38572): Glib-CRITICAL **: 21:33:25.863: Source ID 5293 was not found when attempting to remove it
pghosh@pghosh-VirtualBox:~/Desktop/nptel_assgn/scheqn/variational$ ls -ltr
total 912
-rw-rw-r-- 1 pghosh pghosh 2985 Jul 26 14:17 pwell.f90
-rw-rw-r-- 1 pghosh pghosh 221488 Jul 26 14:18 dsyev.f
-rwxr-xr-x 1 pghosh pghosh 131880 Jul 26 14:30 a.out
-rw-rw-r-- 1 pghosh pghosh 62 Jul 26 14:31 readne
-rw-rw-r-- 1 pghosh pghosh 176 Sep 7 23:07 E_npw
-rw-rw-r-- 1 pghosh pghosh 147 Sep 7 23:19 E_vs_a
-rw-rw-r-- 1 pghosh pghosh 11674 Sep 7 23:22 E_vs_a.ps
-rw-rw-r-- 1 pghosh pghosh 25158 Sep 7 23:22 E_vs_a.jpg
-rw-rw-r-- 1 pghosh pghosh 10489 Sep 7 23:23 E_vs_a.agr
-rw-rw-r-- 1 pghosh pghosh 33566 Sep 7 23:26 E_npw.jpg
-rw-rw-r-- 1 pghosh pghosh 10497 Sep 7 23:26 E_npw.agr
-rw-rw-r-- 1 pghosh pghosh 21543 Sep 8 20:23 gs-wfc-5-50
-rw-rw-r-- 1 pghosh pghosh 43843 Sep 8 20:23 gs-wfc-10-50
-rw-rw-r-- 1 pghosh pghosh 64543 Sep 8 20:24 gs-wfc-15-50
-rw-rw-r-- 1 pghosh pghosh 56366 Sep 8 20:45 wave_fn_vs_a.agr
-rw-rw-r-- 1 pghosh pghosh 35844 Sep 8 20:45 wave_fn_vs_a.jpg
-rwxr-xr-x 1 pghosh pghosh 131880 Sep 8 21:28 pwell.x
-rw-rw-r-- 1 pghosh pghosh 86643 Sep 8 21:39 gs-wfc.out
pghosh@pghosh-VirtualBox:~/Desktop/nptel_assgn/scheqn/variational$ vi gs-wfc.out
```

So, let I have taken this data and then plotted it and let me just show you the result.

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So, what I have done is I have varied the number of plane waves starting from value which is 11 to a of value which is 51 and I have plotted the energy as a function of the number of plane waves.

So, you see as we go to higher and higher plane values of this plane waves my energy goes down and then gradually the differences between energy say for example, in this case with 21 and 31 this difference is smaller than say for example, 11 and 21 and as we

go to higher and higher plane waves this energy difference gradually goes down, it dies down.

So, the question is why are we getting this type of a behaviour. Remember what the basic principles of quantum mechanics that we have used in order to develop this method. So, this is based on a variational principle. So, what variational principle says that the more and more number of wave functions you use in your expansion of the wave functions that is more and more parameters you have that my parameters of the coefficients the closer and closer to the actual ground state you will go.

So, what it means is that the energy whatever energy eigenvalue I compute or whatever energy of my system I compute that will always be higher than the actual ground state energy. So, when you add more and more number of bases in your plane in your wave function expansion in this case we are doing a plane wave expansion of the wave function. So, you will slowly go towards the ground state that means, your energy will slowly, the total energy will slowly go down and in the limit where it is converged then you will not see any significant change in energy.

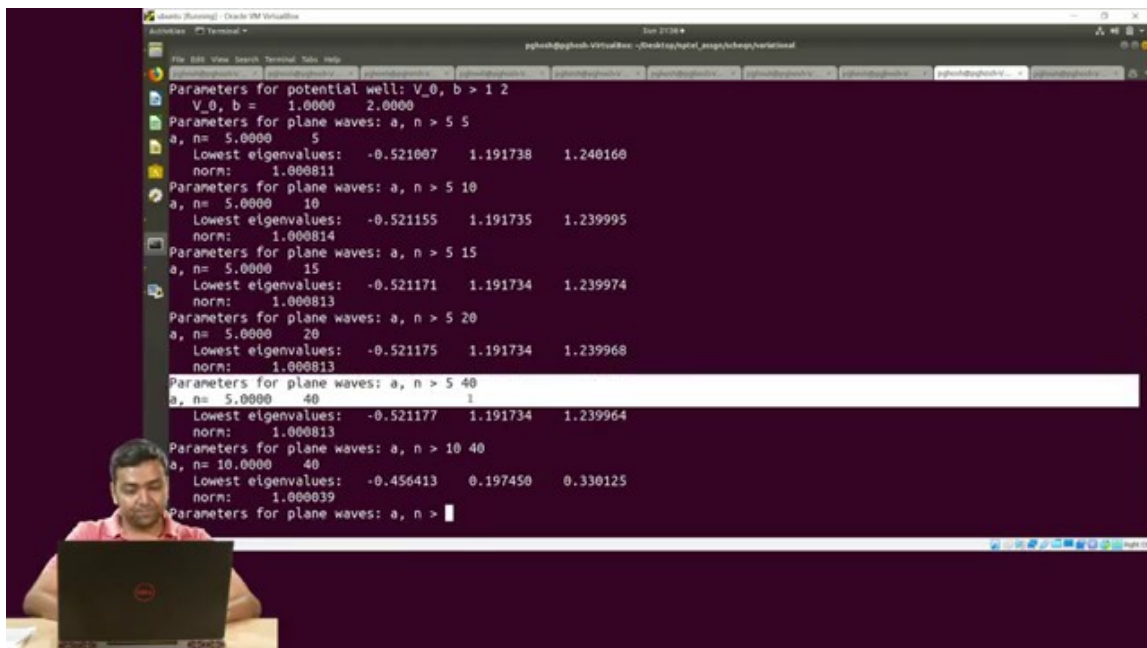
So, that is why as the function of the number of plane waves if the code if everything is correct, then you should always expect that your energy is energy should always go down. So, this is one thing and then the second thing which we would also like to check is how does the things change when you increase the periodicity of my of the plane wave. So, again I would before we see the results, so, I will just recollect what we have discussed regarding the periodicity of the plane waves.

So, because we are using these plane waves and we which has a finite periodicity, so, what we have is instead of just a single attractive square well potential we have periodic replicas of that ok. So, what it means is that now I am not simulating or doing the calculations for potential which is 0 everywhere except between minus  $p/2$  to plus  $p/2$  instead I am doing a calculations for a potential which has a nonzero value say at around so, minus  $b/2$  to plus  $b/2$  and then again a nonzero value from minus  $b/2$  plus  $a/2$  plus  $b/2$  plus  $a$ ; similarly a nonzero value from minus  $b/2$  minus  $a/2$  plus  $b/2$  plus  $b/a$ . So, these values these potentials which are fictitious potentials in our case because actual potential has nonzero value only between minus  $b/2$  and plus  $b/2$ . So, these are called periodic images.

So, the correct picture, so, when I will the periodicity of my plane waves that is this if this  $a$  is only when the  $a$  is infinitely large, then only the distance between the periodic images and the actual potential that will be large and I will be simulating a correct the actual potential. So, therefore, it is important to understand how my results will change as a function of this  $a$  value and what is a sufficiently large value of  $a$ .

So to do that what I will do is I will now rerun the code by changing the values of  $a$  that is this parameter with a fixed value of the number of plane waves. So, since from that figure which we had drawn which we had here, so, we see that it roughly converges say between 41 and 45 things do not change much. So, what I will do is I will just run the code with varying the value of  $a$ . So, I will start with  $a$  equals to 5 and my number of plane waves  $n$  value of  $n$  to be 40 and I will just run the code ok.

(Refer Slide Time: 11:39)



```
Parameters for potential well: V_0, b > 1 2
V_0, b = 1.0000 2.0000
Parameters for plane waves: a, n > 5 5
a, n = 5.0000 5
Lowest eigenvalues: -0.521007 1.191738 1.240160
norm: 1.000011
Parameters for plane waves: a, n > 5 10
a, n = 5.0000 10
Lowest eigenvalues: -0.521155 1.191735 1.239995
norm: 1.000014
Parameters for plane waves: a, n > 5 15
a, n = 5.0000 15
Lowest eigenvalues: -0.521171 1.191734 1.239974
norm: 1.000013
Parameters for plane waves: a, n > 5 20
a, n = 5.0000 20
Lowest eigenvalues: -0.521175 1.191734 1.239968
norm: 1.000013
Parameters for plane waves: a, n > 5 40
a, n = 5.0000 40
Lowest eigenvalues: -0.521177 1.191734 1.239964
norm: 1.000013
Parameters for plane waves: a, n > 10 40
a, n = 10.0000 40
Lowest eigenvalues: -0.456413 0.197450 0.330125
norm: 1.000039
Parameters for plane waves: a, n > |
```

So, this is what I get for the eigen values. Now, what I will do is I will increase my  $a$  say let me go from 5 to 10 the value of  $a$ , I keep the number of plane waves to be same and then I run it again. So, what you see is if you look at the energies now the lowest the ground state energy, so, when my  $a$  is equal to 5 that means and if you compare that with the value when my  $a$  equals to 10, so, what has happened here is when I go from this



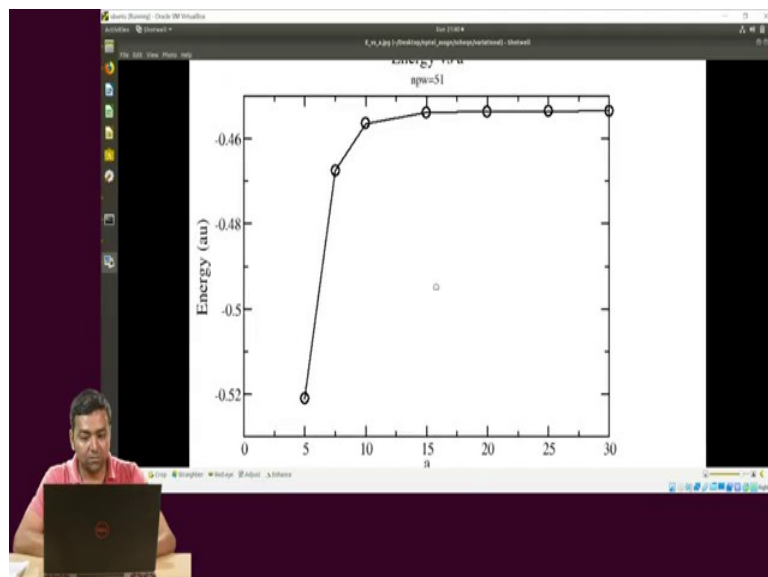
particular case to this particular case the distance between the periodic images have increased.

What it means is that now the interaction between the two square well potential have reduced. Now, if you remember the potentials which we are using these potentials are attractive potentials. So, when you bring two attractive potentials together the their interaction will also be attractive. So, when you move them apart, so, what we will expect is that the energy eigenvalue the energy will go higher up in energy.

So, and that is what we is find here. So, for 5 the my energy is for a equals to 5 my energy is 0.52177, but the moment I change a or increase a to 10 my energy goes to 0.456413. Now, if I change a further to 15 we will see that the energy goes much higher. So, now, from 0.456 point minus 0.456413, it goes to minus 0.453836; if I go to larger value it will go even higher.

So, actually what one needs to do is one needs to systematically increase the value of a and see that at what value of a the energy does not change beyond a certain threshold. So, that value of a will be the correct value of a to describe my system within the periodic boundary conditions. So, let me show you a plot of that what happens.

(Refer Slide Time: 13:49)

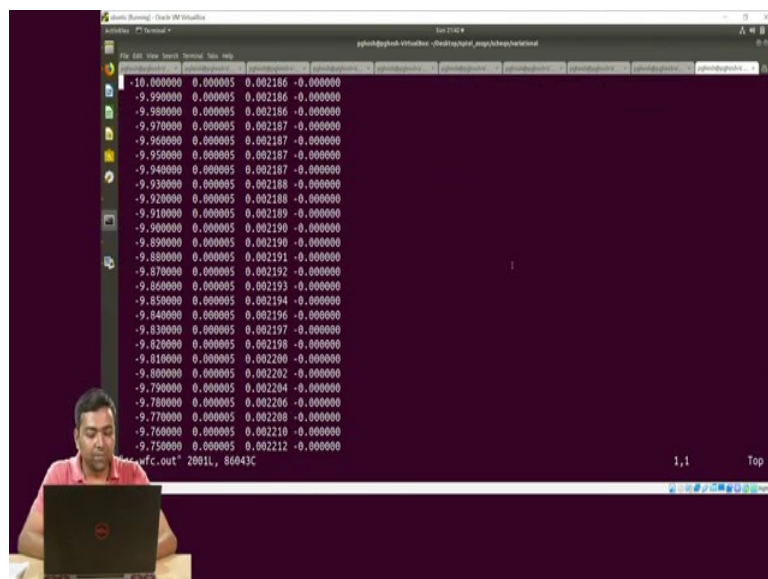


So, this plot shows the variation of the total line of the ground state energy as a function of the periodicity of my plane wave which is a here and the number of plane waves I

have used here is 51 in this for each of these calculations. So, as I was showing when running the code. So, when I start with a small value of  $a$ ; small value of  $a$  that means, the potential actual potential is interacting with this periodic image and the ground state energy is lower and then as I gradually increase the value of  $a$ , so, from example if I go from this point to this point to this point, so what is happening as I move towards the right? The separation between the potential and its periodic image is increasing, therefore, their interaction is decreasing they do not see each other much. And as a result the energy goes high and then beyond a certain value you see there is not a significant change in the energy as I increase  $a$ .

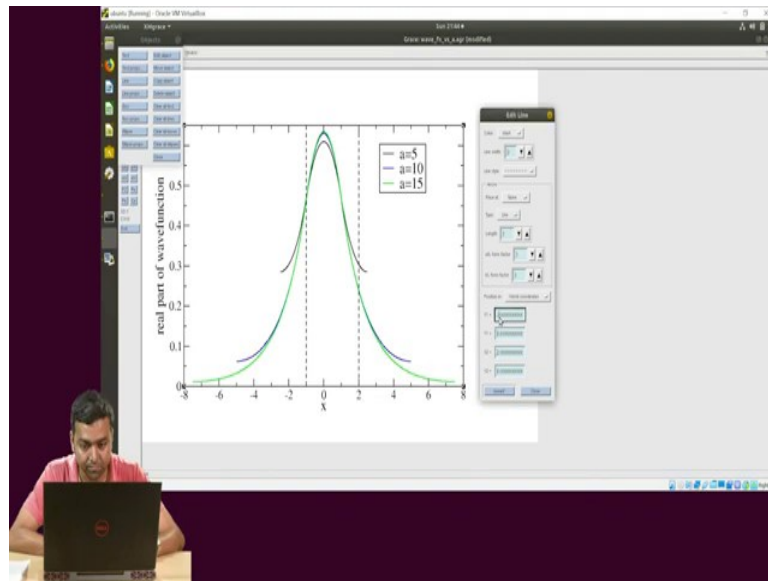
So, a good choice of the value of  $a$  will be something around say 25 units here in this picture. So, now, let us look into how my wave function look like. So, if I open the now if I open the input the output file which I have here where I am stored my wave function.

(Refer Slide Time: 15:22)



So, you see there are 4 columns here. So, the first column this is this column contains the value of  $x$ ; the position, this column contains the value of the probability density and this column contains the real part of the wave function and this column contains the imaginary part of the wave function. So, if I plot the same thing, so let me just show you the plots.

(Refer Slide Time: 15:51)



So, here what I have plotted in this figure is the real part of the wave function for three values of  $a$ . So, let us see with along the  $a$  as a function of  $x$  here.

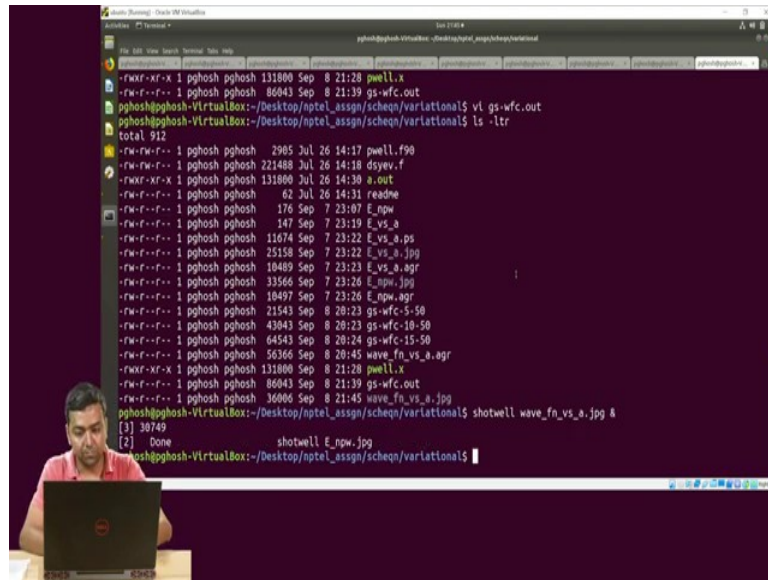
Now, this vertical lines here I am sorry with this should be the vertical lines should be here at  $x$  equals to this vertical lines should be at  $x$  equals to 1 because my total  $b$  is 2 and I am my wave file the potential is symmetric from minus  $b$  by 2 to plus  $b$  by 2. So, this vertical lines here actually should be at 1; let me just see if I can correct it ok. So, this is the same potential the actual raw data.

(Refer Slide Time: 16:48)

```
Lowest eigenvalues: -0.521171 1.191734 1.239974
norm: 1.000813
Parameters for plane waves: a, n > 5 20
a, n= 5.0000 20
Lowest eigenvalues: -0.521175 1.191734 1.239968
norm: 1.000813
Parameters for plane waves: a, n > 5 40
a, n= 5.0000 40
Lowest eigenvalues: -0.521177 1.191734 1.239964
norm: 1.000813
Parameters for plane waves: a, n > 10 40
a, n= 10.0000 40
Lowest eigenvalues: -0.456413 0.197450 0.330125
norm: 1.000039
Parameters for plane waves: a, n > 15 40
a, n= 15.0000 40
Lowest eigenvalues: -0.453836 0.070172 0.153765
norm: 1.000001
Parameters for plane waves: a, n > 20 40
a, n= 20.0000 40
Lowest eigenvalues: -0.453734 0.035008 0.089013
norm: 1.000000
Parameters for plane waves: a, n > ^C
ghosh@ghosh-VirtualBox:~/Desktop/nptel_assign/scheepq/variational$ ls
.out E_npw E_npw.jpg E_vs_a Agr E_vs_a.ps gs-wfc-15-50 gs-wfc.out pwell.x wave_fn_vs_a Agr
jyev.f E_npw Agr E_vs_a E_vs_a.jpg gs-wfc-10-50 gs-wfc-5-50 pwell.f90 readme wave_fn_vs_a.jpg
ghosh@ghosh-VirtualBox:~/Desktop/nptel_assign/scheepq/variational$ vi pw
```

So, but before that let me just double check the code what we have done. It should be minus 1 to plus 1. So, what one should do is basically let me just quickly modify this; this will be minus 1 minus 1 except this will be plus 1 ok. So, let me just print it again. So, let us see if the file has been created.

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So what we can do is let me just go back and now let me close it and open it again, this is fine. So, as I was saying. So, this vertical lines here denotes the width of my potential. So, the total width of my potential is 2 that is the value of  $b$ . So, this is the value of  $b$  which is 2 units and it goes from minus 1 to plus 1.

Now, I have plotted here the wave function; this is the real part of the wave function, the imaginary part is 0 in this case as a function of the periodicity of the plane waves which we are using. So, for three values of that, so  $a$  equals to 5, 10 and 15.

So, what you see for  $a$  equals to 5? Your wave function is significantly different from that of  $a$  equals to 10 and 15 which is which are this blue and the green lines here. So, what you see is that the wave function has not decayed by the time it reaches from the end of the periodic box. So, here my box the total value of  $a$  is 5; so, it goes from minus 2.5 to plus 2.5.

But as I gradually increase the value of  $a$ , so, you see that its going slowly going down to 0. And not only that so, if you remember my wave function should go exponentially to 0

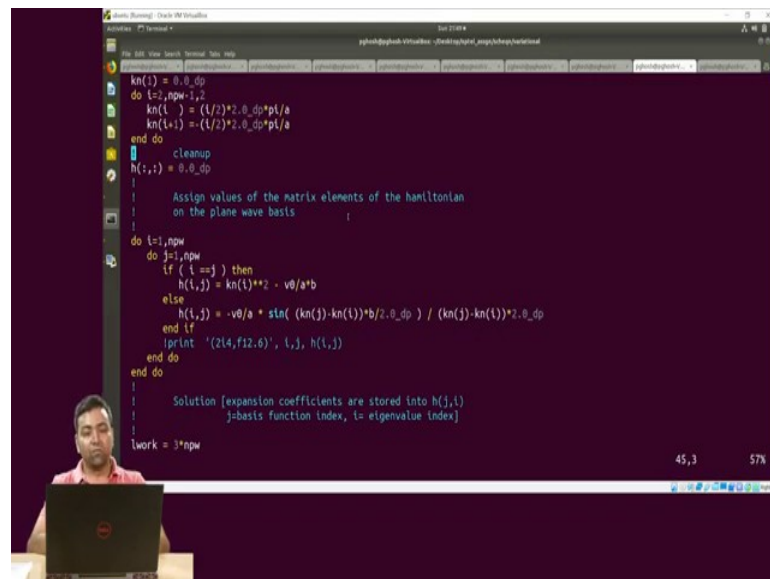
if in the actual case. So, if you look at that now the slopes of the wave function corresponding to  $a$  equals to 5 and  $a$  equals to 10 and  $a$  equals to 15.

So, you see that  $a$  equals to 10 and 15 the slope in this region outside the this outside my potential that is on the left hand side of  $x$  equals to minus 1 or on the right hand side of  $x$  equals to plus 1 the wave function decays much faster.

So, if I use a larger box, so I will expect it to go in a much quicker way to the 0. So, this is something one should be careful of and another question is so, if we look into the results as a function of  $a$ , so, why does the energy goes up? So, the reason the energy goes up here is because I am reducing the interaction between the periodic images and my wave function is attractive potential.

If my wave function is a repulsive potential then what I would see is that the energy will come down as I move the as I increase the separation between the wave functions of between the actual potential and its periodic images.

(Refer Slide Time: 21:25)



```
kn(1) = 0.0_dp
do l=1,npw-1,2
  kn(l) = (l/2)*2.0_dp*pi/a
  kn(l+1) = (l/2)*2.0_dp*pi/a
end do
cleanup
h(:,1) = 0.0_dp
! Assign values of the matrix elements of the hamiltonian
! on the plane wave basis
do l=1,npw
  do j=1,npw
    if ( l=j ) then
      h(l,j) = kn(l)**2 - v0/a*b
    else
      h(l,j) = -v0/a * sin( (kn(j)-kn(l))*b/2.0_dp ) / (kn(j)-kn(l))*2.0_dp
    end if
    !print '(2i4,f12.6)', l,j, h(l,j)
  end do
end do
! Solution [expansion coefficients are stored into h(j,l)
! j=basis function index, i= eigenvalue index]
lwork = 3*npw
```

So, this is an example of how you can solve numerically the problem the Schrodinger equation corresponding to a given attractive potential here in this particular case and that attractive potential happens to be a square well potential with a finite depth. How you can use the matrix formulation of quantum mechanics and then convert your Schrodinger convert your problem of solving the Schrodinger equation which is a problem of solving

a second order differential equation to a linear algebra problem and then diagonalize that and then get the eigen values and the eigen functions corresponding to the ground state.

So, though in this example I mean and in this lecture we have discussed only about plane waves, but there is no necessity that it has to be a plane wave. This method also applies for the case when you use for example, a localized basis set. For example, if you use atomic orbital's to solve your, I mean Schrodinger equation. So, then also this method applies equally well. In that sense this method is a much more general method.