Chemistry I
Introduction to Quantum Chemistry and Molecular Spectroscopy

Lecture 19B
Assignment 1
Solution/Hints

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Chemistry I.

Introduction to quantum chemistry and molecular spectroscopy.

Assignment 1. Solutions / hints. PART A ✓

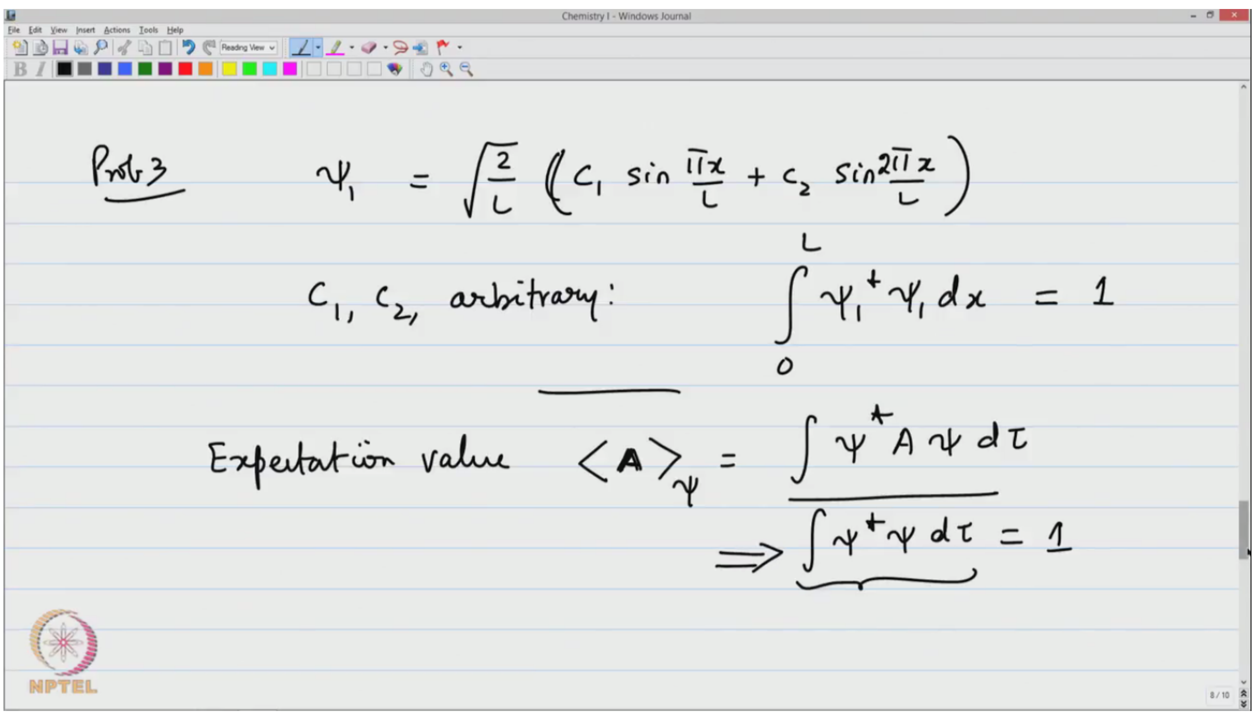
PART B

Problem 3 →

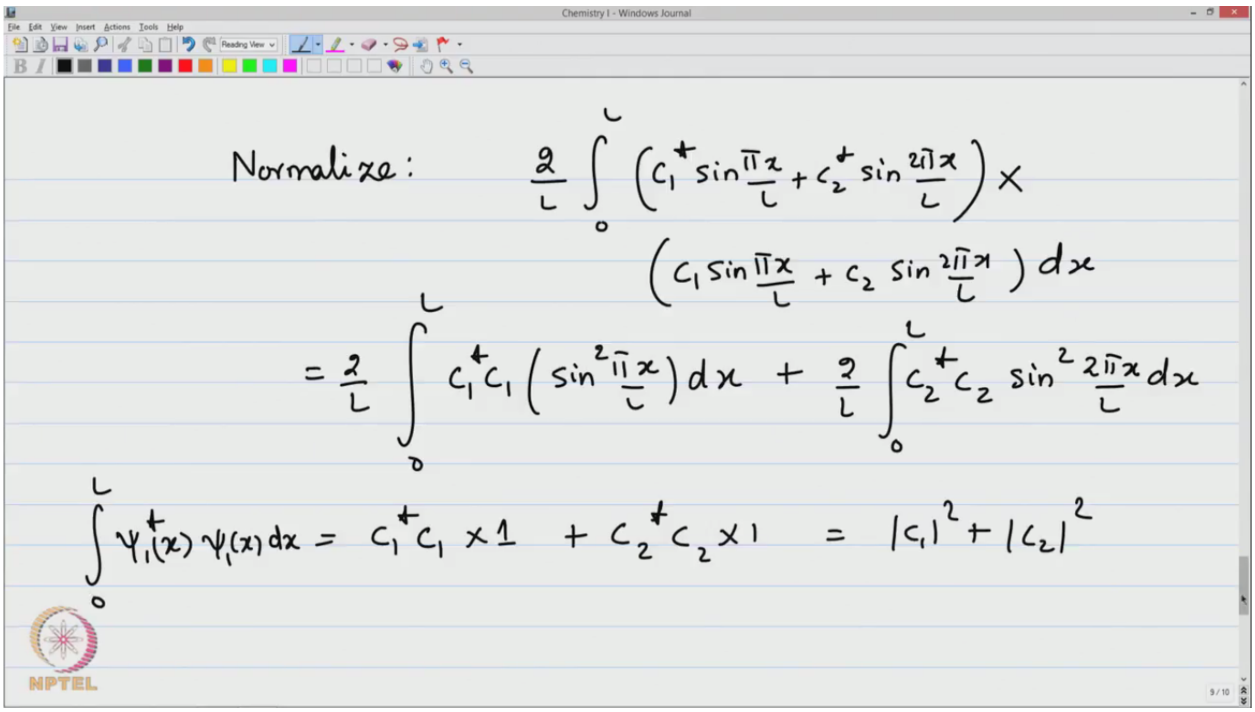
Welcome back to the lectures on quantum chemistry and molecular spectroscopy. This is the continuation of the assignment 1 solutions discussion and we will now look at part B a few more problems and let me recall the problem set from the assignment that was there in the website.

Now problem 3 the question is to obtain the expectation value a wave function for a particle in one dimensional box is given. It's slightly different from what you are used to that it is a combination of two wave functions for the particle in the one dimensional box with coefficient c1 and c2 and you are asked to calculate the expectation value for the energy and momentum of this particle.

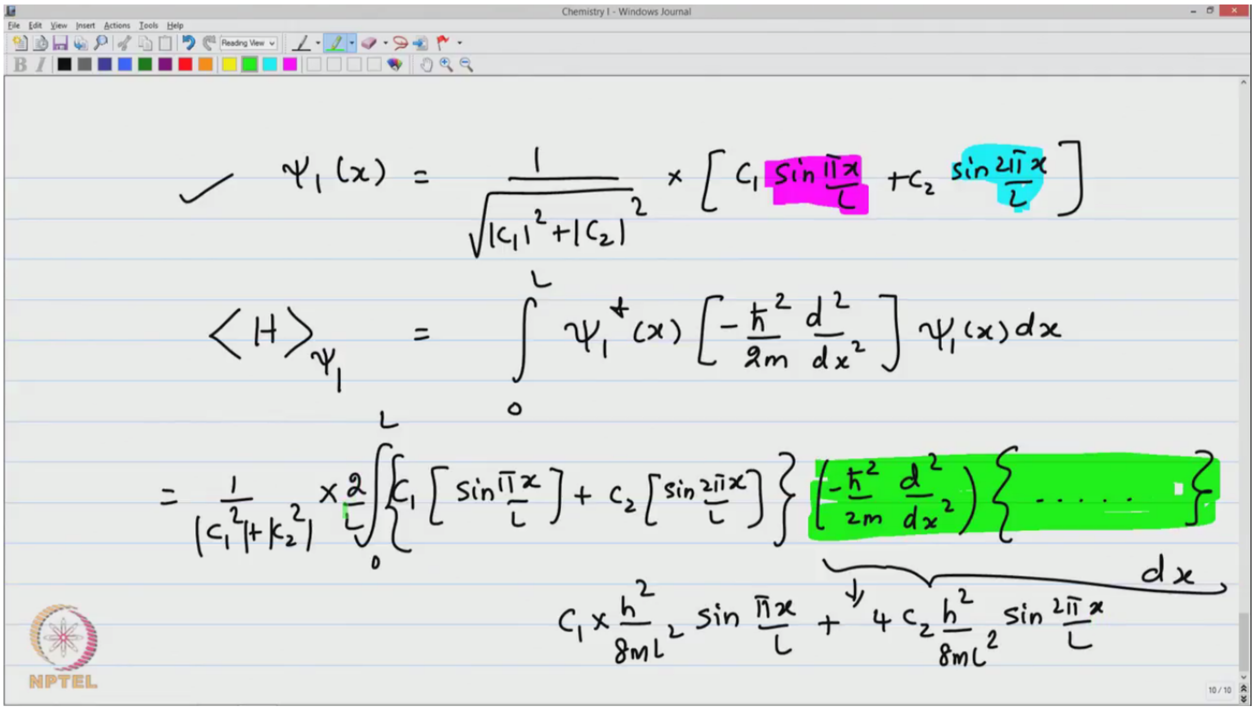
Now this is typically what is known as a linear superposition of the wave functions. So let me go to the new page. So you have a wave function Ψ 1 this is problem 3 which is root 2 by l c1 sine π x by l plus c2 sine π 2 π x by l. c1 and c2 are arbitrary coefficients but they have to be determined the relation between them should be determined by making the wave function Ψ 1 star Ψ 1 dx between 0 to l from the particle in the box to unity. Then recall the expectation value of any operator A which is written as A within the expectation value within the angular brackets is given by the integral Ψ star A Ψ d tau divided by the integral Ψ star Ψ d tau which is usually 1 because we have normalized to the wave function to unity. This is in the state Ψ. we are asked to calculate the expectation value for the energy and momentum for the state. So the first thing we have to do is to ensure that the wave function has this property namely it is normalized. Normalized is the wave function.



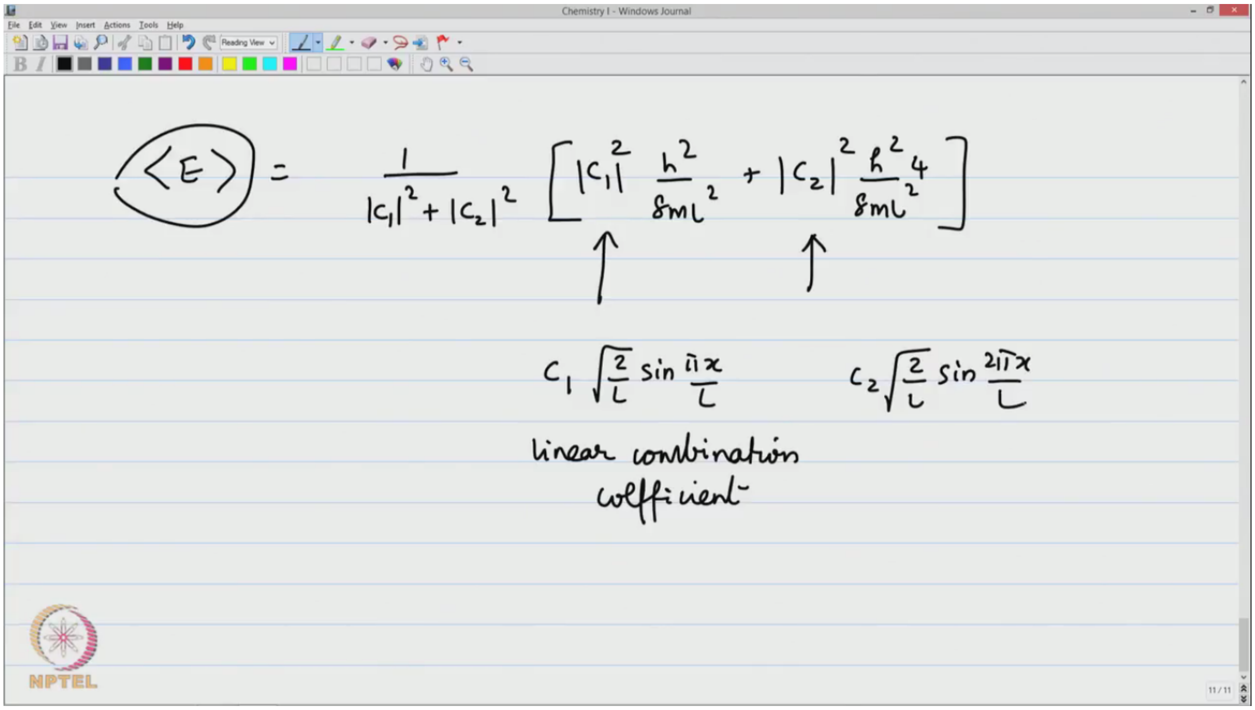
Now you have to recall the properties of the particle in the one dimensional box. The wave function square is 2 by L integral 0 to l c1 star sine π x by l plus c2 star sine 2 π x by l. This is Ψ star multiplying Ψ c1 sine π x by l plus c2 sine 2 π x by l dx and which if you write in an expanded form it is 2 by l and you have integral 0 to l. You have c1 star c1 with the integral sine square π x by l dx that's the first term and the only other term which is important for normalization is the term 0 to l c2 star c2 sine square 2 π x by l dx we do not worry about the terms c1 star c2 integral sine π x by l sine 2 π x by l dx between 0 to l because these are orthogonal wave functions and therefore this integral is 0 and so is its complex conjugate therefore of the four terms that you have when you take the product only two of them are there. Therefore this term is not needed and so I will simply get rid of this from here and what is left over is the integral with c1 star c1 and the rest of it is 2 by l 0 to L sine square π x by l you know that the wave function is normalized. This function is normalized. Therefore, this is 1 and the other is c2 star c2 times 1 so what you have is absolutely c1 square plus absolute c2 square that's equal to Ψ star Ψ 1 star x Ψ 1 x dx between 0 to l that's what we did.



Therefore, the normalized wave function Ψ 1 of x is the normalization constant which is the square the n square is this therefore you have to divide by 1 by square you have to multiply by 1 by square root of n which means that the wave function is 1 by square root of c1 square plus c2 square times you have c1 sine π x by l plus c2 sine 2 π x by l. This is the normalization property that you need to have first and then with this normalization constant you can calculate the expectation value for the energy as nothing but the expectation value with the Hamiltonian operator between the wave functions in the state Ψ 1. In the state Ψ 1 it is given by Ψ 1 star x the operator Hamiltonian is minus h bar square by 2 m d square by dx square for the particle with the mass m acting on Ψ 1 of x dx from 0 to l. Therefore this is a calculation that you have to do and you know since it contains Ψ 1 star Ψ 1 the function this is square so what you have is 1 by c1 square plus c2 squared absolute values multiplied by the integrals the integral 0 to l c1 sine φ x by l plus c2 sine 2 π x by l. This is the wave function. All of this multiplied by the operator minus h bar square 2m by 2 m d square by dx square acting on the same wave function. The same wave function times dx. You know that the individual wave functions, the wave function sine π x by l has an eigenvalue h square m square by 8 m l square m is 1. The wave function to this one has an eigenvalue h square into n square n is 2 here therefore it's 4 h square by 8 m l square. So the operator h acting on these wave functions give you -- gives you the following namely c1 times h square by 8 m l square times sine that is also 2 by l which you have to include here that's a normalization constant for the individual wave functions. So the operator gives you c1 times h square by 8 m l square π x by l plus 4 c2 h square by 8 m l square sine 2 π x by l and that is from this operator, the operator acting on the function; the linear combination that we have.

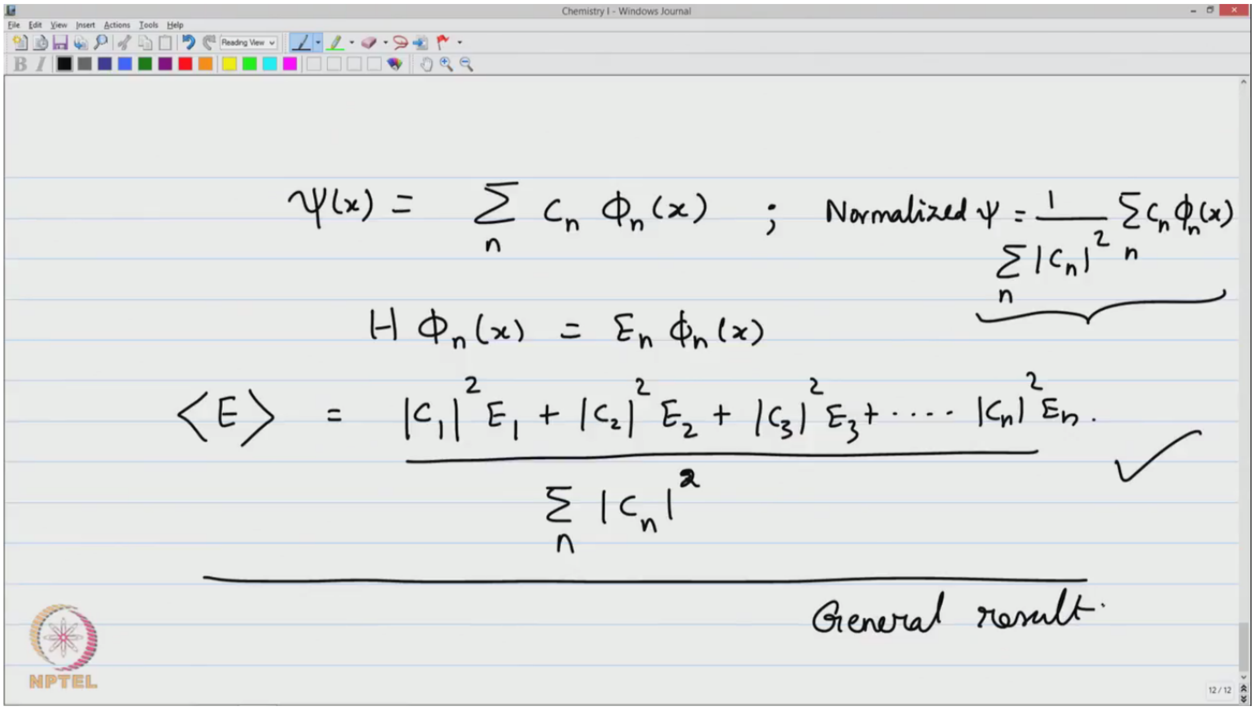


So it gives you an energy, the corresponding energy for the first wave function and the corresponding energy for the second wave function for h square and it gives you sine π x by l and sine 2 π x by l and the square root of 2 by l is already here in the integral. Therefore the expectation value E is now only given by this term multiplying the term and you know that the wave functions are orthogonal so only the term sine square π x by l and sine square 2 π x by l would contribute to the overall integral, the cross terms will not contribute. The other things are constant. Therefore you can write the answer immediately as 1 by c1 square plus c2 square times c1 square I hope I wrote the c1 square yeah so c1 star c2 star so you have 1 by the absolute value of c1 square into h square by 8 m l square plus the absolute value c2 square by h square by 8 m l square times 4. So this is the energy that you need to calculate. This is the energy. This is the average value. So what you see is that the wave function which has the component c1 multiplying root 2 by l sine π x by l contributes to the overall average energy by the factor of its eigenvalue the root 2 by L sine π x has for the energy operator this eigenvalue h square by 8 m l square multiplied by the absolute square of the coefficient the c1 is a linear combination coefficient. So the absolute square of c1 contributes with this energy and the absolute square of c2 contributes with the corresponding energy for the wave function root 2 by l sine 2 π x by l.



In fact there is a general result that if Ψ is given as sum over n cn φ n of x Ψ of x and if the Hamiltonian has φ n as the eigenfunctions with energy En φ n of x then the average value E can be calculated by first calculating the normalized wave function the normalized Ψ n will be 1 by the sum of the absolute combination, absolute squares of the combination coefficient times sum over n cn φ n of x. So this is the normalized wave function and for this normalized wave functions the average energy is contributed by the corresponding weight factors c1 square times E1 plus c2 square times E2 plus c3 square times E3 plus etc. all the way up to cn square times En divided by sum over n the absolute square, sum over I would use the label I yeah I guess I am using n here. So let's use that cn square absolute.

So this is a general result. The average value for a state which is a linear combination of the eigenstates of the Hamiltonian with the eigenvalues En and with the linear combination coefficient cn is given by the contribution the absolute square of cn times En but from lower every such state. This is a general result.



In a similar way if you have to calculate to the p, now you can see that p in the state of Ψ is given by Ψ star the operator for p is -ih bar d by dx Ψ all our functions of x dx and in this case of course the particle in the box is 0 to L divided by the normalization property of the wave functions namely Ψ star x Ψ of x dx. For a normalized wave function of course this is equal to 1.

So all that you have to do is to calculate the p by differentiating the wave function once with the derivative and then calculating the integrals with the cross products. So if you are doing this here you would get again 1 by c1 square plus c2 square I am just writing the final form and leave it to you to calculate the integral will be 0 to L and also there is 2 by l here, the integral will be c1 star sine π x by l plus c2 star sine 2 π x by l. This is Ψ star and then the operator minus ih bar d by dx on the wave function c1 sine π x by l plus c2 sine 2 π x by l dx. So this is the action of the momentum operator on the wave function is all of this and once you have done this multiplied with the wave function and evaluate the integral. So you know that this will give you π by l times cos c1 cos π x by l and the other will give you plus 2 π by l c2 cos 2 π x by l that would be the derivative again multiplied by minus ih bar. So this is the effect of the momentum operator on the wave function. These are not eigenfunctions of the momentum operator. They give you something else and therefore then you have to calculate the momentum by evaluating the integrals sine π x cos π x dx sine π x cos 2 π x dx and likewise the sine 2 π x cos 2 π x dx and I think the answer should be 0. we verify the answer.

$$\langle p \rangle_{\psi} = \frac{\int_0^L \psi^*(x)\left(-i\hbar \frac{d}{dx}\right)\psi(x)\,dx}{\int \psi^*(x)\,\psi(x)\,dx = 1}$$

$$\frac{2}{L}\,\frac{1}{|c_1|^2+|c_2|^2}\left[\int_0^L \left(c_1^* \sin\frac{\pi x}{L} + c_2^* \sin\frac{2\pi x}{L}\right)\left(-i\hbar\frac{d}{dx}\right)\left(c_1 \sin\frac{\pi x}{L} + c_2 \sin\frac{2\pi x}{L}\right) dx \,.\right.$$

$$(-i\hbar)\left(\frac{\pi}{L}c_1 \cos\frac{\pi x}{L} + \frac{2\pi}{L}c_2\cos\frac{2\pi x}{L}\right)$$

$$\Rightarrow 0$$

So in the next part I will continue with the next problem.