Quantum Chemistry of Atoms and Molecules

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Lecture-67
The Last Word

Well I am back for one last time in this course we have come a long, long way through the quantum world of atoms and molecules it is time now that our journey ends for now. And this is the time to look back and reflect upon the path we have traversed and also to think what is it that lies ahead. What have we learned?

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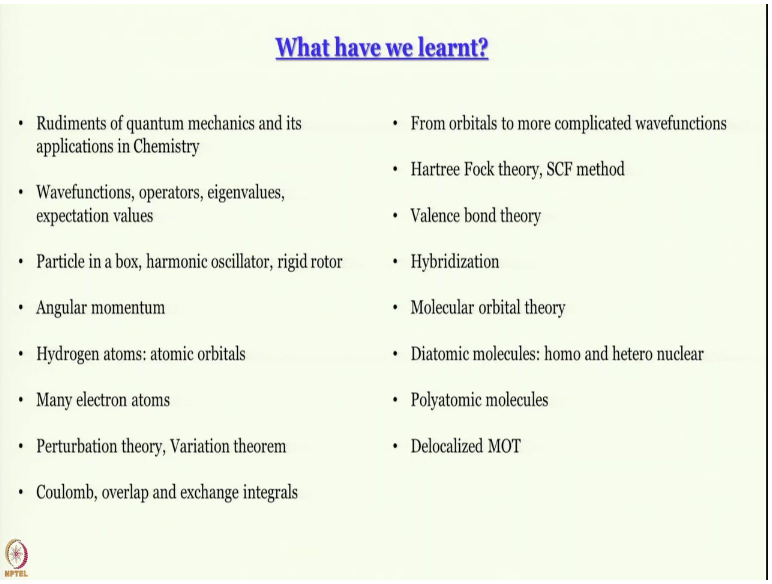

What have we learnt?

- Rudiments of quantum mechanics and its applications in Chemistry
- Wavefunctions, operators, eigenvalues, expectation values
- Particle in a box, harmonic oscillator, rigid rotor
- Angular momentum
- Hydrogen atoms: atomic orbitals
- Many electron atoms
- Perturbation theory, Variation theorem
- Coulomb, overlap and exchange integrals
- From orbitals to more complicated wavefunctions
- Hartree Fock theory, SCF method
- Valence bond theory
- Hybridization
- Molecular orbital theory
- Diatomic molecules: homo and hetero nuclear
- Polyatomic molecules
- Delocalized MOT

We have actually learned a lot we have learned the rudiments of quantum mechanics and its applications of chemists in chemistry. As promised at the beginning we did not really go very deep into this we tried not to go very deep into the mathematics but mathematics cannot be avoided as I hope you are now convinced. So what we have essentially learnt is how to handle wave functions operators. How operators operate on wave functions to give you eigen values when you can determine eigen values and when you have to be satisfied working with average or expectation values.

And how all this is done within the mathematical framework of quantum mechanics knowing this we have actually solved Schrodinger equation for a simple systems like particle in a box harmonic oscillator and rigid rotor systems in which this equation can be solved exactly. While doing this we learned quite a few things. First important thing that we learnt is where does quantization come from Schrodinger equation does not have any quantum number.

In fact if you try to solve Schrodinger equation for a free particle you do not get quantum number at all put the same particle in a box you get boundary conditions arising out of Born interpretation of the wave function. And hence arises the quantization and hence arises quantization and we have learned how quantum numbers arise in all these systems and we have understood what the boundary conditions are in different cases.

While talking about rigid rotors we realize that it is not enough to talk in I mean you can but it is very complicated to talk in terms of Cartesian coordinates. So we switch to spherical polar coordinates and we formulated our problem in terms of the angular coordinates theta and phi. So we got two quantum numbers from there one from theta part one from phi part L well j and M as we called it.

And while doing this rigid rotor we realized that we need to know a little bit about the quantum mechanical treatment of angular momentum we have not really gone very deep but we have gone deeper than what I intended to do at the beginning of this course. We have learnt something about how angular momentum is handled in quantum mechanics. Angular momentum is a most important quantity in this context.

With this background we have studied hydrogen atoms we have learnt how to separate the variables the angular part of the equation is more or less the same as that of the rigid rotor. And then looking at the different r theta phi dependent parts we have constructed the wave functions and these one electron wave functions we learned are the atomic orbitals. So for one last time let me repeat the cliché orbitals are one electron wave functions.

Acceptable solutions of Schrodinger equation for one electron systems it is not what might be written in several textbooks. And with atomic orbitals we had a lot of fun we learnt how to plot them I hope you have plotted them by yourself and we got familiarized with us with them and we learned that many times the diagrams that we draw really psi versus some coordinate r or theta phi or two of them.

And we also realize that we need more dimensionality which you cannot do so we use different things like color shading so on and so forth to depict these wave functions. Then we use try to use this orbitals for many electron atoms using orbital approximation but then we realized that you cannot ignore the electron-electron repulsion term. So you have to modify not only the Hamiltonian but also the wave function that is what we did by incorporating a screening or shielding constant and working with effective nuclear charge.

But that was only the beginning we learnt approximation techniques, perturbation theory well we have learnt only time dependent perturbation theory here and variation theorem by which we learnt how to handle systems that cannot be solved exactly well Schrodinger equation of which cannot be solved exactly if the deviation from an exact system is small we learn we can use perturbation theory.

But we also realize that first order perturbation may not be enough in some cases you might need a higher order perturbation terms also. And for systems for which there is no similar exact solution that we can propose we learnt that we can still use variation theorem and using the upper limit theorem we could get an upper bound to the energy of the system. To do this we while doing this we came across very useful quantities coulomb integral, overlap integral, exchange integrals that is going to stay with us as long as we do any discussion in quantum mechanics.

As you have seen even in the last class that we had we did talk about these integrals. And while doing this since variation theorem allowed us to play around with the wave functions we said that we do not have to stick to orbitals. We might want to start from them but we can actually synthesize wave functions using a sufficient number of exponential terms Gaussian terms polynomial, polynomials and so on and so forth.

We showed you some examples of different wave functions that are used in quantum chemistry and to do that you need Hartree Fock theory we have discussed Hartree Fock theory not in all detail but in some detail and we said that you have to do a self use a self consistent field method by which you play around with parameters of the wave function to find the minimum value of calculated energy which would be the upper bound of the energy upper bound of the actual energy.

And then this point onwards we said the problem becomes a computational one because it is an iterative technique things like goodness of fit come in you want a good match things like convergence coming and that is where computers creep in big time. Well creeping is a bad word here that is where computers make a grand entry in quantum chemistry. Having talked about many electron atoms we moved on to molecules.

First of all we discussed valence bond theory and while talking about valence bond theory we had to invoke hybridization. We studied hybrid hybridization in some detail and I hope that all of us now have a little better idea of hybrid orbitals than what we had earlier. And the biggest advantage of hybridization is that it gave us orbitals in the disposition we needed them to be in order to have the polyatomic molecules of the shape that it is required to have from valence shell electron pair repulsion theory.

So hybridization is all about localization of electron cloud on the other hand when we talked about molecular orbital theory and the approach we have used here is we have constructed the molecular orbitals by taking linear combinations of atomic orbitals. In this theory we learned that the strength is delocalization. With this theory we build descriptions of diatomic molecules we started with H 2+ which is the well molecular analog of hydrogen atom one electron system.

But even for that we did not try to solve the Schrodinger equation using elliptical coordinates rather we used linear combination of atomic orbitals to synthesize the molecular vital. And then we moved on to a discussion of homonuclear and heteronuclear dynamic molecules. For homonuclear diatomic molecules we understood that as you go higher up the series this electron-electron repulsion effective nuclear charge shielding screening all these come into play.

And also this sp mixing is no longer there if effective if nuclear charge is too long too much. So we observe this change in relative ordering of molecular orbitals between nitrogen and oxygen and using this model we could nicely describe the magnetic properties and other properties reactivity of this homonuclear diatomics. Now discussion of heteronuclear diatomics we learnt that atomic orbitals of compatible symmetry and comparable energy will only participate in the linear combination.

And that is why in heteronuclear diatomic molecules like HF you have polarized you have lopsided electron clouds you have some molecule of molecular orbitals that are more towards one atom you have some others that are more towards the other. Using this we discussed the polarized covalent bonds in hydrogen halides and we also discussed why carbon monoxide forms good sigma bonds from the carbon center and how it can accept electron cloud in its pi star orbital in the same carbon atom.

Then we moved on to poly atomic molecules. First we talked about polyatomic molecules which are only sigma bond and the case in point was I do not think we talked about BF 3 we did talk about ammonia and in ammonia we used this delocalized molecular orbital theory to arrive at this realization that well molecular orbitals are delocalized over the molecule. But when you talk about bond that bond is all about the electron cloud concentration between two particular atoms.

And we also said that molecular orbitals each molecule orbital contributes to each bond and this is something that we have actually used in our Huckel treatment of butadiene when we found out from the coefficients of atomic orbitals the charge distribution and bond order. Huckel method is a simple semi empirical method by which we learnt to treat bimolecular systems.

So few that is a lot we have actually learned a lot and I hope it has been an enriching as well as enjoyable experience for you but is it the end of the road? No way.

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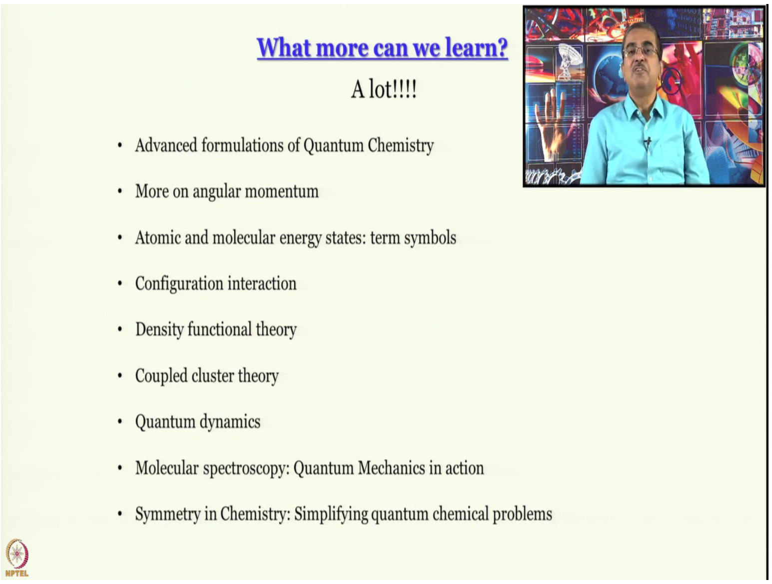

What more can we learn?

A lot!!!!

- Advanced formulations of Quantum Chemistry
- More on angular momentum
- Atomic and molecular energy states: term symbols
- Configuration interaction
- Density functional theory
- Coupled cluster theory
- Quantum dynamics
- Molecular spectroscopy: Quantum Mechanics in action
- Symmetry in Chemistry: Simplifying quantum chemical problems

If you ask the question what more can we learn the simple answer would be a lot and I will give you some examples this list that I am going to show now is by no means comprehensive it is representative. First thing that we can learn is more advanced formulations of quantum chemistry matrix formulation in more detail direct formulation. Angular momentum is something that we did not complete discussing in this course.

Well it is beyond the scope of this course as we have announced in the first place but we can learn significantly more about angular momentum and that will give us a better idea about workings of quantum mechanics, quantum chemistry also. One thing that we did not get time to do is term symbols for atomic and molecular energy states. Well usually this is discussed in inorganic chemistry courses but I would have loved to discuss it in this course as well.

But I hope that many of you would have got exposed to it from your inorganic chemistry courses. Next configuration interaction we have so far behaved as if I mean so far pretended as if a configuration is a state actually configurations also interact. So it is more complex than what we might have seem to have told you. So configuration interaction and further interactions is something that is to be learnt.

And that takes us to the realm of density functional theory which is the by far the largest computational chemist; the most popular computational chemistry theory that is used the theory that is used in computational chemistry DFT anti-DFT. And couple cluster theory is another approach to the same problem. So, these are advanced topics in quantum chemistry. Quantum dynamics is a different ball game altogether until now we were talking about electronic structure theory.

But then what about interactions what about reactions what about electron scattering all these come within the reams of quantum dynamics. And finally if you repeat things that I must have said 3, 4 times already as Max Planck had said experimental results are the only truth how do we know that all this theory that we are developing is true we know it from molecular spectroscopy and in this course also we have had two three small examples of how spectroscopy and quantum mechanics go hand in hand.

As one of my ex colleagues a very eminent quantum chemist used to say molecular spectroscopy is really quantum mechanics in action. So, if you want to learn quantum mechanics quantum chemistry you cannot not learn molecular spectroscopy and vice versa. So these are things that you can of course in physical chemistry a lot more things your thermodynamics chemical thermodynamics, molecular thermodynamics, rate processes, physical chemistry materials a lot.

But immediate in the well first salvation shell if I may call it that of quantum chemistry these are the things that I could think of that you might want to learn in future as a follow up of the present course, how do you do it? Well one more thing is symmetry in chemistry in the last few lectures we have referred to symmetry again and again and the biggest role that symmetry plays in this context is that it simplifies quantum chemical problems.

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Old NPTEL course on Symmetry in Chemistry, available on YouTube

https://www.youtube.com/watch?v=9DkkduG68SE&list=PLOzRYVmoa65eOFUUrwIEA4ZCSu9M9iyzQ

Actually I did teach an NPTEL course on symmetry in chemistry I forgotten which year it was run but I recorded it in 2014. So, now all the videos are available in YouTube you can just search my name and symmetry and chemistry will get them linked to the first lecture I hope this is correct is provided here.

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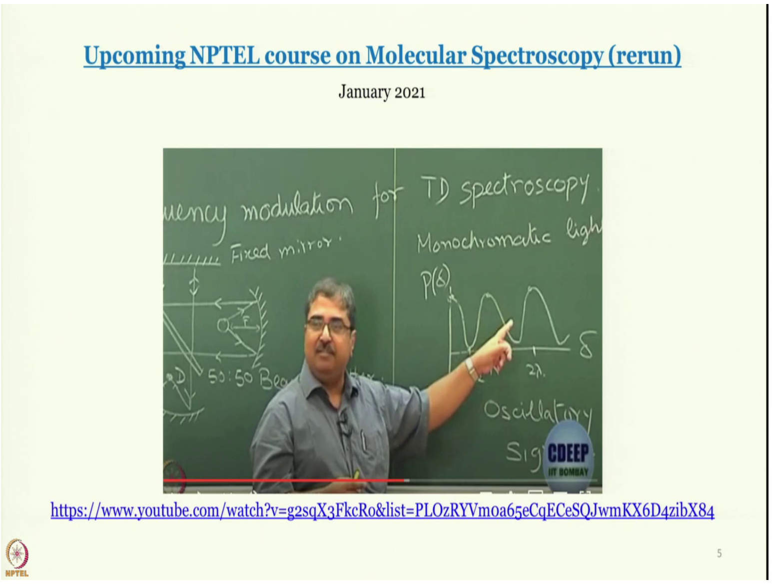

Upcoming NPTEL course on Molecular Spectroscopy (rerun)

January 2021

https://www.youtube.com/watch?v=g2sqX3FkcRo&list=PLOzRYVmoa65eCqECeSQJwmKX6D4zibX84

And we talked about spectroscopy, we said spectroscopy is quantum mechanics in action I am happy to announce that in the next semester and a course that I had already taught in NPTEL last year is going to be rerun. This course is in molecular spectroscopy what you see is a video grab from that course and as you can understand this course in this course all the lectures were actually on blackboard most of the lectures I did use Power Point presentation.

But this was recorded from a live class with students sitting with our third year BS and first year MS students sitting in the class. I think we recorded it in 2018 and so what will do is by and large the lectures will be the same. So, if you just want to see those lectures here is a link but if you want activation or if you want to learn the additional topics that we there is going to be some 7, 8, 10 lectures that will be recorded afresh.

If you are interested in those as well then the course is going to be available for registration sometime soon and hopefully it will run from January 2021. So this is what is going to happen in near future.

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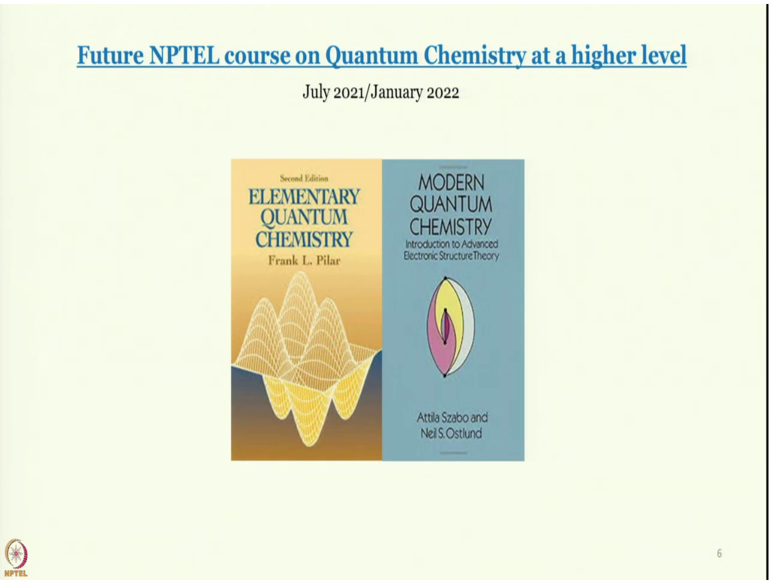

Future NPTEL course on Quantum Chemistry at a higher level

July 2021/January 2022

Later hopefully in July 2021 or in January 2022 I would like to do the second part of the present course quantum chemistry at a higher level. And there we did discuss things from Frank Piller's book in this course but not too much. So for that course the main textbooks are going to be elementary quantum chemistry by Pillar and modern quantum chemistry by Szabo and Ostlund. So, let us hope that it will run in July 2021 or January 2022.

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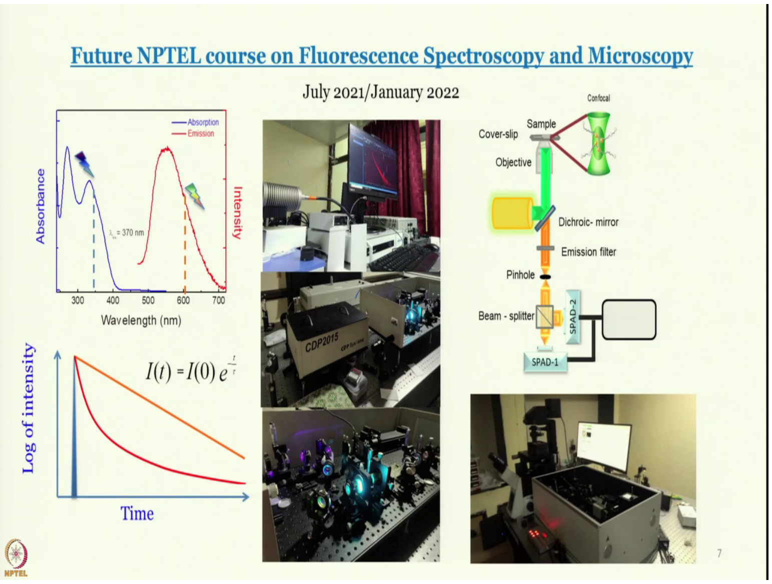

Future NPTEL course on Fluorescence Spectroscopy and Microscopy

July 2021/January 2022

$I(t) = I(0)\, e^{-\frac{t}{\tau}}$

And we are fluorescence spectroscopy's that is what we do for a living fluorescence spectroscopy and microscopy. So again either in January 22 or in July 21 I do not know which course will come up first whether it will come. But I do want to float another course on fluorescence spectroscopy and microscopy. There is an NPTEL course that I taught last semester on ultrafast processes those videos are available.

So some of those classes and these will be same may be 78 classes but this will focus more on a more complete discussion of fluorescence spectroscopy as well as microscopy and we are going to go to our lab and do experiments and show you how they are done and how data is analyzed right. So this is a summary of what we have done and what we propose to do in future.

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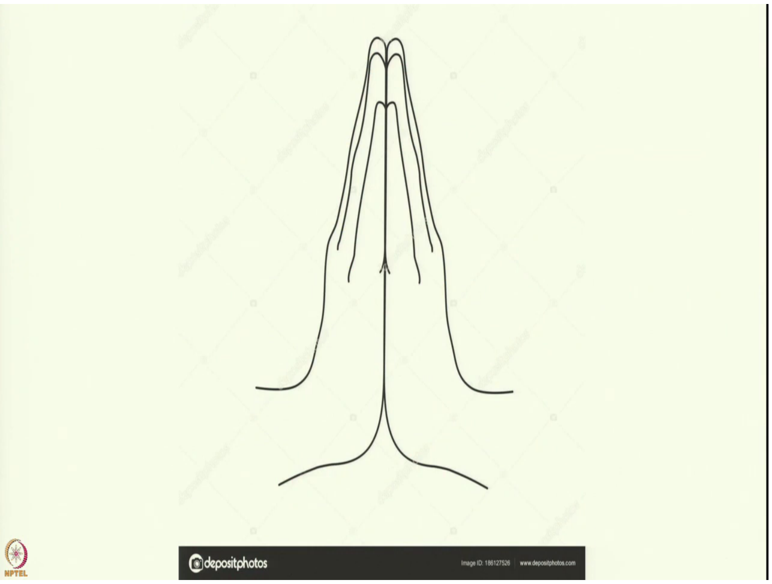

And now the time has come for me to say goodbye before I do so let me thank all the people who made this course possible Tushar and Ameen NPTEL staff who have recorded and processed this course Bharatitari, Bharati sakpal the managers I have given them a lot of trouble because I have never done things on time sorry about that NPTEL entire NPTEL team of IIT Bombay and IIT madras thank you very much.

Let me also thank the Souradip and Prajeet my students throughout this course well they are their job is actually going to start now they are going to maintain the course and let me also thank everybody in my research group and all the students I have taught because you know teaching is an exercise in learning. So when we teach we actually learn the subject. So whatever little I have been able to learn is by teaching the students including new people.

So thank you very much for your interest and participation in the course I apologize for any inadvertent errors that might have occurred but I hope that you have noticed them and you have rectified them. Once again I hope that this has been a good experience enriching experience and an enjoyable experience as well for those of you who are going to write the exams all the best I am sure that you are going to do well.

But exams are false gods learning is the true god I hope that we have been able to perform justice to this exercise in worshiping the true god that is knowledge that we have tried to do in this course, thank you very much.