Q&A Lecture 3

Is there any physical moning for D_alpha,beta and how its value is determined using simulation?

The D_{\alpha,\beta} represent the fact that the adiabatic states (derived for fixed nuclear position) are NOT eigenstates of the full Hamiltonian (i.e. the one in which we include also the nuclear kinetic energy). This means that when the nuclei move, the electrons can change state as a result of how they change when the nuclear position change. Remember that the electronic Hamiltonian depends on the nuclear position via the nuclear-electronic interactions, and therefore the adiabatic eigenstates depend on the nuclear position. The terms in D_{\alpha \beta} are proportional to derivatives of the electronic eigenstates with respect to the nuclear positions, i.e. they are non-zero when the electronic state changes “due to" R.

What exactly is the adiabatic basis? I don't understand the R and the \phi_\alpha. I understand the R is the position of the "fixed" nuclei, but is a 3N dimensional vector? 3 values for each nuclei? And the wavefunction phi_alpha is it the state of all electrons or only those which are in the alpha energy state, like in Fock spaces?

The adiabatic basis is the basis of eigenstates of the electronic Hamiltonian. R is the set of nuclear coordinates, so 3N dimensional, and \phi_\alpha is the electronic state with electrons in eigenstate \alpha. The electronic label is a state for the full number of electrons in the system but it orders the states in order of increasing energy. so \phi_0 is the state of the electrons that corresponds to the lowest eigenvalue of the electronic Hamiltonian. If we projected this state onto a coordinate basis for the electrons (neglecting spin for simplicity), it would be a wave function depending on 3n electronic positions for a system with n electrons.

In what case do we consider continuous coefficients in the context of this lecture ?

The last equation that was discussed (the coupled channel equation), we use discrete labels to order the electronic states (the \phi_\alpha) while the nuclei are described using the continuous coordinate basis.

Why it is called the adiabatic basis?

It is the basis of eigenstates for the situation in which there is no transfer/change of energy associated to the electronic motion and the nuclei are fixed. Adiabaticicy - in thermodynamics - refers to this type of situations, hence the name.

Since the time-dependent expansion coefficients $\chi_l(\mathbf{R}, t) \equiv \chi_l$ are functions of the nuclear coordinates $\mathbf{R}$, when we apply $\hat{T}_n$ to $\chi_l|\mathbf{R}, \Psi_l\rangle$ we have $\chi_l \hat{T}_n|\mathbf{R}, \Psi_l\rangle$ and not $\hat{T}_n(\chi_l|\mathbf{R}, \Psi_l\rangle)$ i.e. why $\hat{T}_n$ is not applied to χ_l? Here $|\Psi_l\rangle$ are electronic eigenstates

it is. The action of the nuclear kinetic energy on the coefficients is accounted for in the first term of the right hand side of the equation (as written for example in the notes that are on the Moodle). It contributes to the part that is interpreted as motion of the system on a single electronic state.

Why is the adiabatic basis, defined by the eigenstates of the electronic Hamiltonian, particularly convenient for describing the nuclei–electron system? How to deal with the continuous nature of this basis in terms of position, when running a simulation?

The solution of the equation is made "simpler" by the fact that we know how the electronic Hamiltonian acts on those states (as a simple eigenvalue multiplication) and that we can work out (although often implicitly) how the nuclear kinetic energy acts on them too.

To what extent is the approximation that electrons are "fast" relative to nuclei actually valid? Are there cases where this assumption breaks down? And if so, how can we model these transient, non-adiabatic effects?

The coupled-channel equation derived in class does not rely on the notion of a time scale separation between electrons and nuclei and can be used when this assumption (usually indicated as the Born-Oppenheimer approximation) breaks down. This break down does happen in photo physical and photochemical processes (e.g. vision by cis trans isomerization of rhodopsin or photosynthesis).

I'm still a little bit confused about the origin of coupling. Does this arise from the interaction between the Hel and KN, or is there some other origin? If it is the interaction between the Hel and KN, what is the intuition for this? Is this type of coupling related to spin-orbit coupling?

There is no coupling between H_el and K_N (at least, I don't understand what you mean by that). There is, however, coupling between the nuclei and electrons due to the Coulomb interactions. These depend on the distance between nuclei and electrons (so on their positions). When we solve the H_el problem in the adiabatic basis, we fix the nuclear positions and obtain the "separate" eigenenergies for the electrons at those fixed nuclear positions. As long as the nuclei don't move, these eigenstates remain separate. When we allow for the nuclei to move, their motion (i.e. changes in the nuclear positions represented in the coordinate basis by derivatives with respect to those variables) causes the coupling. So, no spin-orbit involved…

The adiabatic approximation claims that we can write the wave function of the nuclei and electrons as two separate parts. Under what conditions does this approximation work well, and under what conditions is this approximation not valid?

I disagree: the adiabatic approximation claims that we can think about the problem with a hierarchy of effects. We don't treat the state (not the wave function, we never use coordinates to represent the electrons in what we have discussed so far) as two separate parts: the basis is a tensor product of nuclear and electronic basis but the total state is never separated when the couplings are taken into account. Indeed, the coupled channels equation describes precisely situations in which the full separation is not active and transitions between different adiabatic eigenstates are possible.

In addition, how different is the wave function of electrons here from that in an isolated atom? For example, do the energy levels correspond one-to-one?

Not sure I understand. The state (again not the wave function) depends on the Hamiltonian which in turn depends on the system. If the system is a molecule or a system of molecules (or other, e.g. a solid) or there are interacting sets of degrees of freedom the states will be very different from those of isolated atoms.

Computing the full molecular wave function seems to require computing a 3N-dimensional integral, with each point requiring a full electronic structure calculation. What kind of approximations could make this tractable in practice?

This is indeed the topic of most of the remaining lectures….starting from the next one!

What does the choice of the couplings physically signify?

The D_{\alpha,\beta} represent the fact that the adiabatic states (derived for fixed nuclear position) are NOT eigenstates of the full Hamiltonian (i.e. the one in which we include also the nuclear kinetic energy). This means that when the nuclei move, the electrons can change state as a result of how they change when the nuclear position change. Remember that the electronic Hamiltonian depends on the nuclear position via the nuclear-electronic interactions, and therefore the adiabatic eigenstates depend on the nuclear position. The terms in D_{\alpha \beta} are proportional to derivatives of the electronic eigenstates with respect to the nuclear positions, i.e. they are non-zero when the electronic state changes "due to" R.

Further, does the adiabatic basis mean that the nuclei are firmly held?

No, the adiabatic basis is constructed by without taking into account the nuclear kinetic operator (ca equal to fixing the nuclear positions) but then it is used (a basis can represent more or less conveniently ALL systems) also when the nuclei are allowed to move.

What's the difference between this approximation and the born-oppenheimer's one ? And how do we choose which one to use?

In the Born-Oppenheimer approximation, the nuclei move on only one of the electronic states. The equation that was derived relaxes this (so motion can occur on multiple states) and is exact. We'll discuss more the Born-Oppeneimer approximation in the next class.

What is the link between the Born-Oppenheimer approximation and the Condon approximation ?

Not sure that there is one…can you explain better what you are wondering about?

My question is related to the eigenfunctions of the adiabatic basis, $|R\ \psi\alpha(R)\rangle$. I understand that, since R represents the position of the nuclei, $|R\rangle$ is an eigenfunction of the nuclear position operator. Also, $|\psi\alpha(R)\rangle$ is an eigenfunction of the electronic Hamiltonian. Therefore, an adiabatic eigenfunction represents the tensor product between $|R\rangle$ and $|\psi\alpha(R)\rangle$?

Yes. Note that both |R> and $|\psi\alpha(R)\rangle$ are needed to define eigenstates of the electronic Hamiltonian since this operator depends on the operator identifying the nuclear positions in the Coulomb interactions.

Also, since $|\psi\alpha(R)\rangle$ is an eigenfunction of the electronic Hamiltonian, the TISE:

$$\widehat{H_{el}}|\psi_\alpha(R)\rangle = E_\alpha(R)|\psi_\alpha(R)\rangle$$

holds. However, by taking the tensor product of $|\psi\alpha(R)\rangle$ with $|R\rangle$, the electronic eigenfunction is modified into $|R\ \psi\alpha(R)\rangle$ if I understand correctly. Therefore, why do the eigenfunctions $|R\ \psi\alpha(R)\rangle$ still verify the electronic TISE

$$\widehat{H_{el}}|R\psi_\alpha(R)\rangle = E_\alpha(R)|R\psi_\alpha(R)\rangle$$

as stated in the lecture, if these eigenfunctions are different from $|\psi\alpha(R)\rangle$?

The first equation you write is not fully correct due to the fact that the nuclear position operator appears in the electronic Hamiltonian. The second is the correct writing.

Is the adiabatic basis discussed in the lecture the same as we get from Born-Huang expansion?

It is stated like this: since H_e is Hermitian, it has, for any given value of R, a complete basis of eigenfunctions ϕ_m(r,R) which can be used to write any other function of r. In particular, they can be used to write the eigenfunctions of the full Hamiltonian H exactly as

Ψ(r,R) =\sum_m χ_m(R) ϕ_m(r,R).

and then, if I remember correctly, these χ_m(R) are not just 'coefficients of expansion' but directly related to the nuclear wavefunction.

The basis introduced is more general (and the electrons are not represented in the coordinate basis as in the Born-Huang that you have used). The interpretation of the coefficients that was given in class is the more rigorous. They can only be interpreted as related to nuclear wave functions when there are no transitions among the eigenstates of the electronic Hamiltonian.

I wanted to know if the Hamiltonian, that we initially choose, is a general H that works for all systems or does it have any restrictions (only for atoms / specific atoms such as He) ?

The Hamiltonian is general: it describes a system of interacting charges that we have (a bit for convenience) identified as nuclei and electrons because we have in mind mostly molecular or solid systems (condensed phase or gas phase). We are neglecting relativistic effects and spin (the latter for the time being) since they are not critical for the discussion that we are setting up.

Also, I didn't understand why, in the beginning of the class, we did a comparison between discrete and continuous systems ?

In the coupled channel equation we have a "mixed" situation in which we use a continuous (coordinate) basis for the nuclei and a discrete (eigenstates of the electronic Hamiltonian) basis. This is a slightly unusual situation in that (as demonstrated by the initial examples) one typically chooses one of the two types. However, the mechanism to identify equations for the coefficients is analogous. We wanted to highlight these facts at the beginning of class.

What is the relation of the evolution equation of the expansion coefficients to the coupled channel equation?

The coupled channels equation IS the evolution for the expansion coefficients of a system of nuclei and electrons interacting via Coulomb potential when the adiabatic basis is chosen.

Why are we performing this expansion? What is our motive?

Coefficients are functions of the nuclear coordinates and of the discrete electronic state labels. These can be manipulated by a computer, while the abstract form of the equation cannot. Also, the modulus square of the coefficients is physically interpretable as the probability to find the system with nuclei in coordinates R AND electrons in state \alpha.

Why are the basis called 'adiabatic'? Is there any property associated with them?

The basis is determined by solving a problem in which the nuclei don't move. in this situation, there is no transfer between electronic energy eigenvalues (this transfer can only occur if we allow the nuclei to move as in the general equation). Systems that do not exchange energy in thermodynamics are called adiabatic so the name comes from this analogy.

What would be the intuition behind splitting the Hamiltonian to nuclei kinetic energy then the rest, instead of just dividing kinetic from the potential ?

We are setting the stage to exploit the fact that nuclei are slower than electrons (hence their kinetic energy is an effect that can be added on top of the electronic features).

Also what is the meaning of adiabatic basis in this context, other than the convention dq= 0 ?

The basis is determined by solving a problem in which the nuclei don't move. in this situation, there is no transfer between electronic energy eigenvalues (this transfer can only occur if we allow the nuclei to move as in the general equation). Systems that do not exchange energy (e.g. in the form of heat) in thermodynamics are called adiabatic so the name comes from this analogy.

In the MSOFT notebook, we can pick ourselves the form of the potentials and coupling terms. From the derivation of the coupled channel equations, I expect these potentials to have something to do with the original form of the electronic Hamiltonian. E_1(R) and E_2(R) are eigenvalues of the electronic Hamiltonian while coupling terms are related to the form of the adiabatic basis and its derivatives. Hence, if we are picking the form of the potentials ourselves, how do we make sure the forms we picked accurately represent the underlying electronic Hamiltonian? Aka How do we make sure the result actually describes the wave function of nuclei and electrons?

In the MSOFT notebook, both the electronic eigenvalues and the couplings are defined by us, as you say. They shapes were chosen to represent typical properties of bound (harmonic) or molecular (morse) or scattering (tully) systems. These are “exercises” to illustrate the main features of the coupled channels equations. In real calculations, these quantities are either calculated (e.g. via time-dependent DFT, quantum chemistry or, increasingly, machine learning) or fit on experimental data.

What does the "tensor product" intuitively mean? I'm not super clear on it.

It’s a bit like a chessboard (except in more than two d). Assign the x and y basis to the horizontal and vertical cases (in chess notation, I think that one would be a letter and the other a number). Each one of them is one of the elements in the basis product. The individual cases (that all together are the tensor product basis) are identified by pairs of x and y.

How was the actual ansatz arrived at? And are there further resources I could look at to understand the adiabatic basis better?

The ansatz is physically motivated by the different time-scales of the nuclear and electronic motions. I’ll say more about this in class. As for additional resources, you can have a look at the chapter by David Coker here

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Which is the physical meaning of the coupling potential term in the couple channel equation?

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By using the adiabatic basis $|R \Phi_{alpha}(R)\rangle$ we assumed our system having decoupled electronic states and nuclear states (if I understood it correctly). What are typical systems/examples for which this decoupling is not valid?

The nuclear and electronic states are coupled via the Coulomb interactions. What we do when we build the adiabatic basis is to start by considering a problem in which the nuclear kinetic energy is not taken into account. The rest of the Hamiltonian defines the electronic Hamiltonian (that depends on the operators nuclear coordinates - via Coulomb - electronic momenta - their kinetic energy - and electronic coordinates - via the Coulomb) and the adiabatic states are eigenstates of this Hamiltonian. The coupled channels equation then enables us to consider situations in which nuclear motion causes coupling between them and describe, e.g., photochemical reactions (cis trans isomerization of rodophsine in vision).

In which cases does this general derivation with non-zero kinetic energies of the nuclei deviate significantly from the often used Born-Oppenheimer approximation?

When eigenstates of the electronic Hamiltonian are “close” for some values of the nuclear positions. These situations are described as conical intersections. They occur often, for example, between eigenstates of diatomic molecules or in more complex systems like photosynthetic centers.

I am just not totally sure about what the simulation showed in class describes? Did it represent the time-evolution of the expansion coefficients? To my understanding, the expansion coefficients are just scalars, so it doesn’t make sense to me that this is what was being shown. Was it then the time-evolution of the ket Psi(t)?

The expansion coefficients are not just scalars (think about any wave function, i.e. the expansion coefficient in the x basis of a generic state) but are functions of the continuous (e.g. coordinate) or discrete (e.g. principal number of harmonic oscillator) label used to identify the basis function they are associated with. When evaluated FOR A SPECIFIC VALUE OF THE LABEL they are indeed scalars.

More precisely, what do the coupling terms physically represent?

The D_{\alpha,\beta} represent the fact that the adiabatic states (derived for fixed nuclear position) are NOT eigenstates of the full Hamiltonian (i.e. the one in which we include also the nuclear kinetic energy). This means that when the nuclei move, the electrons can change state as a result of how they change when the nuclear position change. Remember that the electronic Hamiltonian depends on the nuclear position via the nuclear-electronic interactions, and therefore the adiabatic eigenstates depend on the nuclear position. The terms in D_{\alpha \beta} are proportional to derivatives of the electronic eigenstates with

respect to the nuclear positions, i.e. they are non-zero when the electronic state changes “due to" R.

Does the existence of another energy state influence the behaviour of the system? In that sense, do the coupling terms represent some sort of the model of possible electronic transitions? In the animation shown in class, the wavepacket gets split into multiple parts. Does that represent the possibility of electronic transitions?

Yes: it enables switching on and off coefficients on the various states - more on this in the next class.