6.11 in Ziman

Lectures on the theory of the charge transfer in molecular and nano-scale systems

Lecture 4. Ingredients, Born Oppenheimer.

Let's talk about inter-atomic forces and how they hold everything together. Consider a simple ionic crystal NaCl (it is table salt, as you know), for example. We are told by chemists that it consists of positive Na^+ and negative Cl^- ions arranged on a crystal lattice as Na-Cl-Na-Cl-...etc., or as a crystallographer among you would astutely notice on two interpenetrating face centered cubic (*fcc*) lattices shifted by a vector $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ with respect to each other. The attractive Coulomb potential $-e^2\frac{Z_iZ_j}{|\vec{R}_{ij}|}$ holds the system together. The vector $\vec{R}_{ij}$ goes from the i-th Na ion to the j-th Cl ion, and scales with the lattice constant ($|\vec{R}_{ij}| \sim a$). We can sum over all distinct Na/Cl pairs and calculate the energy of the crystal:

$$E = -e^2\sum_{i,j}\frac{Z_iZ_j}{|\vec{R}_{ij}|}.$$

But wait, something is wrong in this picture! If we make the lattice constant smaller the energy gets more negative, so there will be a force $\vec{F} = -\frac{dE}{d\vec{R}_{ij}}$ trying to shrink the crystal!!! Max Born has noticed this in the early 30's (*M. Born and J.E. Mayer, Z. Physik 75, 1 (1932)*), and suggested adding an *ad-hoc* short ranged repulsive force to prevent the collapse of the crystal. Born potential has the following form:

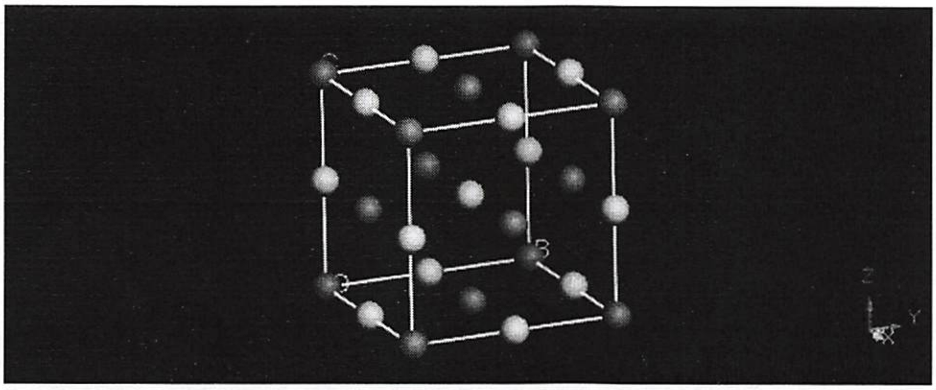
$$V_{ij} = -e^2\frac{Z_iZ_j}{|\vec{R}_{ij}|} + b_{ij}e^2\frac{Z_iZ_j}{|\vec{R}_{ij}|^n}$$

If you sum over all ions you will get the total energy of the crystal. It is hard to do, but surprisingly, if you assume the crystal is infinite, there is a solution! A decade before the Born-Mayer paper P. P. Ewald had suggested a very elegant way of calculating such infinite sums (*P.P. Ewald, Ann. Physic. 64, 253 (1921)*), and the final answer looks like this:

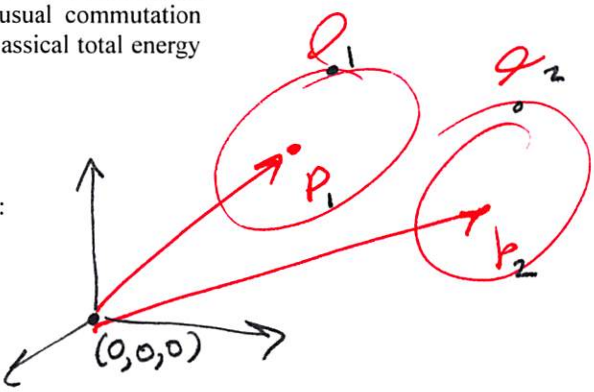
$$V = -\frac{Ae^2Z^2}{a} + \frac{Be^2}{a^n}$$

A is called the Madelung constant after a German physicist E. Madelung who introduced it in 1918 (*E. Madelung, Physic C. 19, 254 (1918)*). This was the year of Spanish Influenza pandemic and the end of the First World War (both killed more people in a year than four years of plague in the 14th century, which wiped out one third of the population of Europe!).

The question still remains however, where this intriguing repulsion is coming from? Classically, it is usually attributed to the repulsion between the nuclei as two atoms are brought really close to each other. This doesn't really fit well with our chemical picture of a positively charged Na and negatively charged Cl. The consistent picture emerges if we use Quantum Mechanics. Let's take a look at the hydrogen molecule. This is the simplest molecular system: we have two protons and two electrons.



The quantization recipe is simple. Let's write the classical energy function for these four interacting particles, and then assuming that for each particle its position and momentum are operators forming a pair of conjugated variables obeying the usual commutation relations. The Schrödinger equation then can easily be written. The classical total energy is given by:



$$E = T_{electrons} + T_{protons} + U_{electron-electron} + U_{electron-proton} + U_{proton-proton}$$

Here *T* is the kinetic energy and *U* is the potential energy, for example:

$$T_{electrons} = T_e = \frac{\vec{p}_1^{\,2}}{2m_e} + \frac{\vec{p}_2^{\,2}}{2m_e}$$

$$T_{protons} = T_p = \frac{\vec{P}_1^{\,2}}{2m_p} + \frac{\vec{P}_2^{\,2}}{2m_p}$$

$$U_{electron-proton} = U_{ep} = \frac{-e^2}{|\vec{r}_1 - \vec{R}_1|} + \frac{-e^2}{|\vec{r}_1 - \vec{R}_2|} + \frac{-e^2}{|\vec{r}_2 - \vec{R}_1|} + \frac{-e^2}{|\vec{r}_2 - \vec{R}_2|}$$

Comment [TCM1]: Corrected spelling of electron. Also, did you want to include Uee & Upp?

yes there is the p-p repulsion $\frac{e^2}{R_1 - R_2} = U_{pp}$.

and e-e repulsion $\frac{e^2}{|r_1 - r_2|} = U_{ee}$

$Me = 0.9 \times 10^{-30}$ kg

$mp = 1.7 \times 10^{-27}$ kg

$\hbar = 1.05 \times 10^{-34}$ J.s

We use lower case variables for electrons and upper case variables for protons. The commutation relations are $\left[\hat{r}_i, \hat{p}_j\right] = i\hbar\delta_{ij}$ and $\left[\hat{R}_i, \hat{P}_j\right] = i\hbar\delta_{ij}$ (here $i, j = x, y, z$). Here the hats symbolize that these are operators, we shall drop this notation for simplicity. The variables describing different particles commute, and the Schrödinger equation is:

$$\left(\hat{T}_e + \hat{T}_p + \hat{U}_{ee} + \hat{U}_{pp} + \hat{U}_{ep}\right)\Psi_s(\vec{r}_1, \vec{r}_2, \vec{R}_1, \vec{R}_2) = E_s\Psi_s(\vec{r}_1, \vec{r}_2, \vec{R}_1, \vec{R}_2)$$

We have neglected the spin, but even so the equation for the wave function of a combined system of electrons and protons looks very complicated!!! It turns out that we can greatly simplify the task if we note that electrons are much lighter than protons, 1836 times lighter as a matter of fact (this is the year of the Alamo!!!). The original idea belongs to Max Born and Robert Oppenheimer (Max Born was born in Breslau, Germany in1882, Robert Oppenheimer was born in New York in 1904) and was published in 1927 (*M. Born and R. Oppenheimer, Ann. Phys.* ***84****, 458 (1927)*). Note that Oppenheimer was only 23 years old when the paper came out. ← Reference!

more like 5 ?

There are *four simple steps* in the Born-Oppenheimer solution. Because the masses are so different, the electrons move very fast against the background of almost stationary protons. On the other hand from the slow protons point of view, they can't follow electrons zipping around and so are immersed in the "electronic fog" feeling only the potential averaged over many electronic orbits. (1) This suggests that we can try first to solve the electronic problem for some fixed configuration of protons $\overline{R}$:

$$\hat{H}_{el}\varphi_i(\vec{r}_1, \vec{r}_2; \overline{R}) = E_i^{el}(\overline{R})\varphi_i(\vec{r}_1, \vec{r}_2; \overline{R})$$ ← complicated, 2 electron problem!

It is customary to include the proton-proton repulsion (it is simply $\dfrac{e^2}{\left|\vec{R}_1 - \vec{R}_2\right|}$) into the electronic Hamiltonian, so $\hat{H}_{el}$ is given by:

$$\hat{H}_{el} = \hat{T}_e + \hat{U}_{ee} + \hat{U}_{ep} + \hat{U}_{pp}$$

Note that this is actually a two-electron problem, which ~~in a more complicated case would be~~ a many-body electronic problem! We will discuss possible solutions of this later. For now, let's assume we have solved it! *In other words we have a complete set of two-electron wave functions* $\left\{\varphi_i(\vec{r}_1, \vec{r}_2; \overline{R})\right\}$ *which can be used as a basis*! The basis does depend on the proton configuration through the set $\overline{R} = (\vec{R}_1; \vec{R}_2)$ parametrically.

Comment [TCM2]: Inserted a)

(2) Since we have a complete set, let's use it to expand the total wave function of the system:

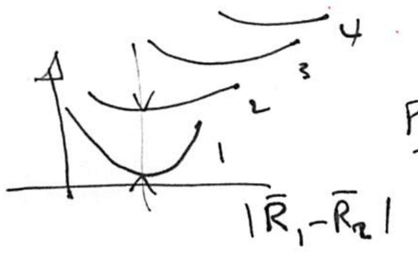
$$\Psi_s(\vec{r}_1, \vec{r}_2, \vec{R}_1, \vec{R}_2) = \sum_i \chi_i(\overline{R})\varphi_i(\vec{r}_1, \vec{r}_2; \overline{R})$$

all electronic states!

coefficients.

electronic state! i=0 ground state.

i = electronic state. E.g., CI 6x6 matrix ⇒ $E_1 \ldots E_6(\overline{R})$



PES

CI

$$\sum_1^6 \chi_i \varphi_i \approx \underbrace{\chi_0 \varphi_0}_{\text{Naive BO}}$$

Of course, the complete set we are using is changing all the time as the protons move. So you may say we have not gained much, but wait! Remember in your electrostatics class you did the separation of variables F(x,y,z)=f(x)g(y)k(z)? This is also a separation of variables, but a subtle one. We separate fast variables describing the electrons from the slow ones describing the ions.

(3) We plug this expansion of the total wave function back into our Schrödinger equation for the total system, multiply by some $\underbrace{\varphi_j(\vec{r}_1,\vec{r}_2;\bar{R})}_{\text{other}}$ and integrate over the electronic coordinates:

$$\int\int d\vec{r}_1 d\vec{r}_2 \times \left[\varphi^*_j(\vec{r}_1,\vec{r}_2;\bar{R}) \left[\hat{T}_p + \hat{T}_e + \hat{U}_{ee} + \hat{U}_{ep} + \hat{U}_{pp}\right] \sum_i \chi_i(\bar{R}) \varphi_i(\vec{r}_1,\vec{r}_2;\bar{R}) \right] =$$

$$= \int\int d\vec{r}_1 d\vec{r}_2 \times \left[E_s \varphi^*_j(\vec{r}_1,\vec{r}_2;\bar{R}) \sum_i \chi_i(\bar{R}) \varphi_i(\vec{r}_1,\vec{r}_2;\bar{R}) \right]$$

It is said that we are integrating out the fast variables. The right hand side of this expression is trivially evaluated:

$$\int\int d\vec{r}_1 d\vec{r}_2 \times \left[E_s \varphi^*_j(\vec{r}_1,\vec{r}_2;\bar{R}) \sum_i \chi_i(\bar{R}) \varphi_i(\vec{r}_1,\vec{r}_2;\bar{R}) \right] =$$

$$= E_s \sum_i \chi_i(\bar{R}) \underbrace{\int\int d\vec{r}_1 d\vec{r}_2 \varphi^*_j(\vec{r}_1,\vec{r}_2;\bar{R}) \varphi_i(\vec{r}_1,\vec{r}_2;\bar{R})}_{\text{orthogonal!!}} = E_s \sum_i \chi_i(\bar{R}) \delta_{ij} = E_s \chi_i(\bar{R}) \quad !$$

The left hand side gives us a bit of a headache, but it is only algebra! First let's take care of everything but the kinetic energy of the protons. Note that the differential operators in the electron kinetic energy gladly ignore the proton coordinates:

$$\int\int d\vec{r}_1 d\vec{r}_2 \times \left[\varphi^*_j(\vec{r}_1,\vec{r}_2;\bar{R}) \sum_i \chi_i(\bar{R}) \underbrace{\left[\hat{T}_e + \hat{U}_{ee} + \hat{U}_{ep} + \hat{U}_{pp}\right]}_{\text{we assume we know that one!}} \varphi_i(\vec{r}_1,\vec{r}_2;\bar{R}) \right] =$$

$$= \int\int d\vec{r}_1 d\vec{r}_2 \times \left[\varphi^*_j(\vec{r}_1,\vec{r}_2;\bar{R}) \sum_i \chi_i(\bar{R}) \underline{E_i(\bar{R}) \varphi_i(\vec{r}_1,\vec{r}_2;\bar{R})} \right] =$$

$$= \sum_i \chi_i(\bar{R}) E_i(\bar{R}) \times \int\int d\vec{r}_1 d\vec{r}_2 \varphi^*_j(\vec{r}_1,\vec{r}_2;\bar{R}) \varphi_i(\vec{r}_1,\vec{r}_2;\bar{R}) = \sum_i \chi_i(\bar{R}) E_i \delta_{ij} = \chi_j(\bar{R}) E_j(\bar{R})$$

Now let's take a look at the difficult terms:

$$\iint d\vec{r}_1 d\vec{r}_2 \times \left[\varphi^*_j(\vec{r}_1,\vec{r}_2;\overline{R})\hat{T}_p \sum_i \chi_{s,j}(\overline{R})\varphi_i(\vec{r}_1,\vec{r}_2;\overline{R}) \right] =$$

$$\iint d\vec{r}_1 d\vec{r}_2 \times \left[\varphi^*_j(\vec{r}_1,\vec{r}_2;\overline{R}) \frac{-\hbar^2}{2m_p}\left(\frac{\partial^2}{\partial \vec{R}_1^{\,2}} + \frac{\partial^2}{\partial \vec{R}_2^{\,2}}\right) \sum_i \chi_{s,j}(\overline{R})\varphi_i(\vec{r}_1,\vec{r}_2;\overline{R}) \right]$$

Remember, that $\overline{R} = (\vec{R}_1, \vec{R}_2)$ and $\frac{\partial^2}{\partial \vec{R}_1^{\,2}}$ only acts on the proton coordinates. Let me confuse you some more, and introduce a special operator people use to compute vector derivatives. It is called a gradient and is denoted as either *grad* or ∇, it means the following: $\nabla = \hat{i}\frac{\partial}{\partial x} + \hat{j}\frac{\partial}{\partial y} + \hat{k}\frac{\partial}{\partial z}$. We need to take a second derivative or a gradient of a gradient of the product of two wave functions:

Introduce nabla!

$$\nabla_1(\nabla_1 \chi_{s,i}(\vec{R}_1,\vec{R}_2)\varphi_i(\vec{r}_1,\vec{r}_2;\vec{R}_1\vec{R}_2)) =$$
$$= \nabla_1((\nabla_1 \chi_{s,i}(\vec{R}_1,\vec{R}_2))\varphi_i(\vec{r}_1,\vec{r}_2;\vec{R}_1\vec{R}_2) + \chi_{s,i}(\vec{R}_1,\vec{R}_2)(\nabla_1 \varphi_i(\vec{r}_1,\vec{r}_2;\vec{R}_1\vec{R}_2))) =$$
$$= (\nabla_1\nabla_1 \chi_{s,i}(\vec{R}_1,\vec{R}_2))\varphi_i(\vec{r}_1,\vec{r}_2;\vec{R}_1\vec{R}_2) + 2(\nabla_1 \chi_{s,i}(\vec{R}_1,\vec{R}_2))(\nabla_1 \varphi_i(\vec{r}_1,\vec{r}_2;\vec{R}_1\vec{R}_2)) +$$
$$+ \chi_{s,i}(\vec{R}_1,\vec{R}_2)(\nabla_1\nabla_1 \varphi_i(\vec{r}_1,\vec{r}_2;\vec{R}_1\vec{R}_2))$$

Show this ?

Kinetic energy of the ions.

Now this looks like a total mess, however the first term is easily recognizable! After the integration over electron coordinates it is simply the kinetic energy of the first proton:

$$\iint d\vec{r}_1 d\vec{r}_2 \times \left[\varphi^*_j(\vec{r}_1,\vec{r}_2;\overline{R}) \frac{-\hbar^2}{2m_p} \sum_i \nabla_1\nabla_1 \chi_{s,i}(\vec{R}_1,\vec{R}_2))\varphi_i(\vec{r}_1,\vec{r}_2;\vec{R}_1\vec{R}_2) \right] =$$
$$= \frac{-\hbar^2}{2m_p} \sum_i \nabla_1\nabla_1(\chi_{s,i}(\vec{R}_1,\vec{R}_2)) \times \iint d\vec{r}_1 d\vec{r}_2 \varphi^*_j(\vec{r}_1,\vec{r}_2;\overline{R})\varphi_i(\vec{r}_1,\vec{r}_2;\vec{R}_1\vec{R}_2) =$$
$$= \frac{-\hbar^2}{2m_p} \sum_i \nabla_1\nabla_1(\chi_{s,i}(\vec{R}_1,\vec{R}_2)) \times \delta_{ij} = \frac{-\hbar^2}{2m_p} \frac{\partial^2 \chi_{j,s}(\vec{R}_1,\vec{R}_2)}{\partial \vec{R}_1^2} = -\frac{\hbar^2}{2m_p}\nabla^2 \chi_{j\,s}$$

energy of the total system

electron state!

The other two terms are not so easily understood, and we will just write them neatly and then appreciate their complexity and beauty:

$$\iint d\vec{r}_1 d\vec{r}_2 \times (\varphi^*_j(\vec{r}_1,\vec{r}_2;\overline{R}) \times \frac{-\hbar^2}{2m_p} \sum_i [2(\nabla_1 \chi_{s,i}(\vec{R}_1,\vec{R}_2))(\nabla_1 \varphi_i(\vec{r}_1,\vec{r}_2;\vec{R}_1\vec{R}_2)) +$$
$$+ \chi_{s,i}(\vec{R}_1,\vec{R}_2)(\nabla_1\nabla_1 \varphi_i(\vec{r}_1,\vec{r}_2;\vec{R}_1\vec{R}_2))] = -\sum_i C_{i1}\chi_{s,i}(\vec{R}_1,\vec{R}_2)$$

Comment [TCM3]: Inserted a 2 next to mp

yep.

Keeping in mind that there is a similar term involving the second proton, we are now in position to reassemble the Schrödinger equation, after the fast variables were integrated out:

perturbation!

$$\left[\hat{T}_p + E_j(\overline{R}) - E_s\right]\chi_{j,s}(\overline{R}) = -\overbrace{\sum_{\underset{\text{proton}}{\alpha},\underset{\text{electron state}}{i}} \hat{C}_{\alpha,i}\chi_{i,s}(\overline{R})}$$

The left hand side looks like a regular Schrödinger equation for what effectively looks like the proton wave function $\chi_{j,s}(\vec{R}_1,\vec{R}_2)$, but the right hand side says that it is not! The sum on the right hand side goes over both protons $\alpha = 1,2$ and all the electronic states ***i***! This requires some analysis.

Naive BO ⇒ only one electronic state: $\chi\,\varphi$

(4) Just to give you heads up we shall neglect the right hand side! But what are the reasons for this you might ask? Let's take a look:

vibronic interactions –

This is a diagonal term!

$$C_{\alpha j} = -\left(\sum_i \frac{\hbar^2}{2m_p} 2\langle\varphi_i|\underset{\text{proton!}}{\nabla_\alpha}|\varphi_i\rangle\nabla_\alpha + \underbrace{\sum_i \frac{\hbar^2}{2m_p}\langle\varphi_i|\nabla_\alpha^2|\varphi_i\rangle}_{\text{diagonal!!!}}\right)$$

$$(1 + \nabla_\alpha)\varphi \to \varphi(\underline{r}+\delta)$$

Tightly bound electrons!!!

Note that the matrix elements are taken between the electronic wave functions, but the operators themselves act on the proton coordinates. The first term can be thought of as an overlap between the electron wave function and the same function acted upon by a displacement operator, and if the electron wave function is localized this overlap with the shifted function will be small. As for the second term, assuming that $\frac{\partial}{\partial R}$ has the same order of magnitude as $\frac{\partial}{\partial r}$ it looks like $p^2 = E_i 2m$, thus the term scales as $\frac{m}{m_p}$ which is 1836, remember the Alamo! In other words, the mass difference and the localization of the electronic states suggest we can neglect the $C_{\alpha,j}$ in the right hand side. This is called the adiabatic approximation and $C_{\alpha,j}$ is known as non-adiabaticity operator.(also vibronic coupling operator.)

$\varphi_i(r - R)$

(5) We now have an effective Schrödinger like equation for the coefficients which play the role of the proton wave functions:

$$\left[\hat{T}_p + E_j(\overline{R})\right]\chi_{js}(\overline{R}) = E_s\chi_{js}(\overline{R})$$

adiabatic potential energy surface (APES)

Note that this is a two-particle equation since $\overline{R} = (\vec{R}_1;\vec{R}_2)$ and the role of the potential energy is played by the total energy of electrons. Obviously you will have a different potential energy surface for different total energies of the electronic system!

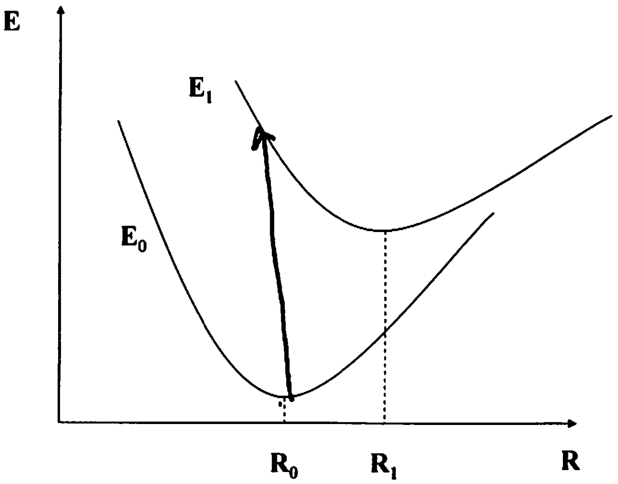
χ

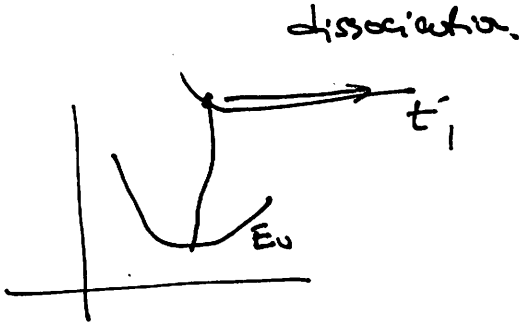
diagonal dies out

$$\int \psi^* \frac{d\psi}{dR_\alpha}\,dr = \frac{1}{i}\frac{\partial}{\partial R_\alpha}\int\psi\psi\,dr = 0$$

$$\varphi(R,r) = \varphi(r-R)$$

$$-\int\varphi\frac{\partial^2\psi}{\partial R^2} = -\int\varphi\frac{\partial^2\psi}{\partial r^2} = \boxed{\frac{m}{M}}\,E_{\text{kinetic}}$$





This is not a good strategy for Hydrogen, but let's for a second pretend that the protons can be described classically. Then we have a potential for each energy state of the electronic system. For example for the ground state:

$$V_{12}^{0} = E_0(\vec{R}_1, \vec{R}_2)$$

Now we can compute forces acting on both protons:

$$\vec{F}_1 = -\frac{\partial E_0(\vec{R}_1, \vec{R}_2)}{\partial \vec{R}_1},$$
$$\vec{F}_2 = -\frac{\partial E_0(\vec{R}_1, \vec{R}_2)}{\partial \vec{R}_2}$$

Note that in principle these do not have to be pair wise forces, they are true quantum many-body forces acting on each proton. This is a quantum derivation of the inter-atomic potential! If we have the appropriate initial conditions we now can do molecular dynamics using Newton's law:

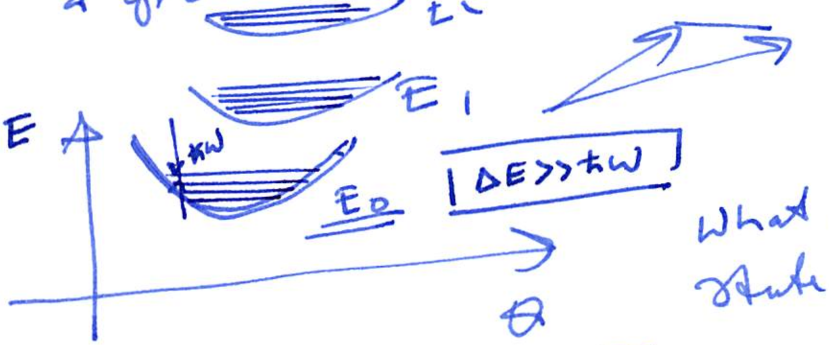
$$m_p \frac{\partial^2 \vec{R}_1}{\partial t^2} = \vec{F}_1$$
$$m_p \frac{\partial^2 \vec{R}_2}{\partial t^2} = \vec{F}_2$$

$$\left[\hat{T}_p + E_j(\vec{R}_1\vec{R}_2) - E_s\right]\chi_{js}(\vec{R}_1\vec{R}_2) = 0.$$

This looks like a Schrödinger equation for χ_{js}:

$$\boxed{\left(\hat{T}_p + E_j(\vec{R}_1\vec{R}_2)\right)\chi_{js} = E_s\,\chi_{js}}$$

What does it mean? Well $E_0(\vec{R}_1\vec{R}_2)$ is a ground state.



can go ~~to~~ the CM. and get $E_0(|\vec{R}_1 - \vec{R}_2|)$

What is a ground electronic state of a 2-electron system?

$\boxed{\text{comunque va bene così}}$

No, non e'vero! Cosa abbiamo lasciato fuori?

<u>This is what we are neglecting:</u>

Ecco:

$$\int \varphi_j^* \left[-\frac{\hbar^2}{2m_p}\sum_{i\alpha}\left\{2\left(\nabla_\alpha \chi_{si}(\vec{R}_1\vec{R}_2)\right)(\nabla_\alpha \varphi_i) + \chi_{si}(\vec{R}_1\vec{R}_2)\,\nabla_\alpha^2 \varphi_i\right\}\right. = -\sum_i C^s_{ij}\,\chi_{si}(\vec{R}_1,\vec{R}_2)$$

bad #

No, it's ok

for the i-th component of the expansion of the s-th total eigen vector $\Psi_s(R_1R_2, r_1, r_2)$.

The non-adiabatic interaction! Also known as vibronic coupling: couples different electronic states!

Let's make our theory simpler:

A naive BO approximation.

$$\Psi_s = \chi_s(R_1 R_2)\cdot\varphi_0(r_1 r_2\, R_1 R_2) \leftarrow \text{just one term.}$$

Then the sum is gone (over the electronic states).

$$\left\{ \underbrace{-\frac{\hbar^2}{2m_p}\sum_{\underset{\text{protons}}{\alpha=1,2}} 2\langle\varphi_0|\nabla_\alpha|\varphi_0\rangle}_{} \overset{\text{operator}}{\hat{\nabla}_\alpha} + \underset{\#}{\langle\varphi_0|\nabla_\alpha^2|\varphi_0\rangle} \right\} \chi_s(R_1,R_2)$$

This is a diagonal term!

$$\nabla_\alpha\langle\varphi_0|\varphi_0\rangle = 0 = (\nabla\langle\varphi_0|)|\varphi_0\rangle + \langle\varphi_0|(\nabla|\varphi_0\rangle)$$

(The off diagonal dies because $\nabla_\alpha\varphi_0 = \varphi_0(r+R) - \varphi_0(r)$

$$\underset{\text{small}}{\langle\varphi_j|\varphi_0(r+R)\rangle} - \underset{0}{\underline{\langle\varphi_j|\varphi_0\rangle}}\ \Big]$$

The second term $\nabla_\alpha \sim \nabla_i$ $\langle\varphi_0|\nabla_\alpha^2|\varphi_0\rangle \sim 2\underline{m}(KE)$

$\boxed{\frac{m_e}{m_p}}$ $\frac{1}{1836}$! so it is very small!

This is because the electron is tightly bound

$\varphi(\vec{r}-\vec{R})$ then $\frac{\partial\varphi}{\partial r} \sim \frac{\partial\varphi}{\partial R}$.

Where is the physics of this? It is the energy scale difference $\hbar\omega \ll |E_i - E_j|$

↳ for loosely bound electrons this is not true!!

What to do next

$$\left(\hat{T}_p + E_0(R_1R_2)\right)\chi_0^s(R_1R_2) = E^s\chi_0(R_1R_2)$$

$$\hat{T}_p = -\frac{\hbar^2}{2M_{Total}}\nabla^2_{COM} - \frac{\hbar^2}{2\mu}\nabla^2_{int}$$

$$\left(-\frac{\hbar^2}{2M_{tot}}\nabla^2_{com} - \frac{\hbar^2}{2\mu}\left(\frac{1}{R^2}\frac{\partial}{\partial R}\left(R^2\frac{\partial}{\partial R}\right) - \frac{L^2(\theta\phi)}{R^2}\right) + E_0(R)\right)\chi_0^s = E^s\chi_0^s$$

$$\chi = \chi_T(\vec{R}_{com})\chi_{int}(R,\theta\phi)$$

↳ a plane wave $\frac{e^{i\vec{k}\cdot R_{com}t}}{\sqrt{V}}$, $\frac{\hbar k^2}{2M_{tot}}$

If you expand

$E_{el}(R) = E(R_e) + \frac{1}{2}k x^2$ ← harmonic approximation (crude).

$x = R - R_e$ ← small diviation.

$$\left.\begin{aligned} &E(R_e) \leftarrow \text{electronic total energy} \\ &\frac{J(J+1)}{2\mu R_e^2} = E_{rot} \\ &E_{vib} = \left(n+\tfrac{1}{2}\right)\hbar\sqrt{\frac{k}{\mu}} \end{aligned}\right\} E_{int}$$

$$\boxed{\Psi = \varphi_{el}(r,R)\,\psi_{vib}(R)\,\psi_{rot}(\theta\phi)\,\chi_T(R_{com})}$$

$$E^s = E_{int} + E_{com}$$

Back to Quantum Mechanics

$$i\hbar \frac{\partial \psi}{\partial t} = \hat{H}\,\psi \quad (1)$$

$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(x,t)$, and V changes slowly on the time scales of state transitions.

Solve "instantaneous" time independent SE:

$$\hat{H}(t')\,\phi_n(x,t') = E_n(t')\,\phi_n(x,t')$$

then $\psi_n(x,t) = \phi_n(x,t)\, e^{-\frac{i}{\hbar}\int_0^t E_n(t')dt'}$ can work in (1):

$$\underbrace{i\hbar \frac{\partial \phi_n}{\partial t} e^{-\frac{i}{\hbar}\cdots}}_{\text{kill this}} + i\hbar\left(-\frac{i}{\hbar}\right)E_n(t)\, e^{-\cdots}\,\phi_n(x,t) = \hat{H}\,\phi_n(x,t)\,e^{-\cdots}$$

$E_n(t)\,\phi_n = \hat{H}\,\phi_n$!!! so it works!

Now, $$\boxed{\psi(x,t) = \sum_n c_n(t)\,\phi_n(x,t)\, e^{-\frac{i}{\hbar}\int_0^t E_n(t')dt'}}$$

plug this into (1)

$$i\hbar \sum_n\left(\dot{c}_n\phi_n + c_n\dot{\phi}_n - \frac{i}{\hbar}E_n c_n \phi_n\right) e^{-\frac{i}{\hbar}\int_0^t E_n(t')dt'} = \sum_n c_n E_n \phi_n\, e^{-\frac{i}{\hbar}\int_0^t E_n(t')dt'}$$

As we shall see, this will give us a formula for $\dot{c}_n$!

Note: $\frac{\partial H}{\partial t}\phi_n + H\dot{\phi}_n = \frac{\partial E_n}{\partial t}\phi_n + E_n\dot{\phi}_n$ (from SE), then

$$\langle\phi_k|\frac{\partial H}{\partial t}|\phi_n\rangle + \langle\phi_k|\hat{H}\dot{\phi}_n\rangle = \frac{\partial E_n}{\partial t}\delta_{kn} + E_n\langle\phi_k|\dot{\phi}_n\rangle$$

$$\langle \phi_k | \hat{H} | \dot{\phi}_n \rangle = E_k \langle \phi_k | \dot{\phi}_n \rangle$$

$$\langle \phi_k | \frac{\partial H}{\partial t} | \phi_n \rangle = \frac{\partial E_n}{\partial t} \delta_{kn} + \langle \phi_k | \dot{\phi}_n \rangle (E_n - E_k)$$

so, for ~~E~~ $n \neq k$

$$\frac{\langle \phi_k | \frac{\partial H}{\partial t} | \phi_n \rangle}{E_k - E_n} = \langle \phi_k | \dot{\phi}_n \rangle \quad (3)$$

That's easy!

Now, why do I need this? Because I have the expression for $\dot{c}_k$! Let me see the logic of this fellow.

clearly, from the Schrödinger equation:

$$i\hbar \sum_n \left(\dot{c}\phi_n + c_n \dot{\phi}_n - \frac{i}{\hbar} E_n c_n \phi_n \right) e^{-\frac{i}{\hbar}\int^t E_n(t')dt'} = \sum_n c_n E_n \phi_n e^{-\frac{i}{\hbar}\int \cdots}$$

I can multiply by ϕ_k^* and integrate:

$\uparrow$ I still do not know what this is.

$$i\hbar \sum_n \Big(\dot{c}_n \underbrace{\langle \phi_k \phi_n \rangle}_{\delta_{nm}} + c_n \langle \phi_k | \dot{\phi}_n \rangle - \frac{i}{\hbar} E_n c_n \langle k | n \rangle \Big) e^{-\cdots} = \sum_n c_n E_n \langle k | n \rangle e$$

$$\cancel{i\hbar}\, \dot{c}_k e^{-\frac{i}{\hbar}\int E_k} + \sum_n \cancel{i\hbar}\, c_n \langle \phi_k | \dot{\phi}_n \rangle e^{-\frac{i}{\hbar}\int E_n} \cancel{+ E_k c_k e^{\int E_k} = c_k e}$$

$$\boxed{\dot{c}_k = -\sum_n c_n \langle \phi_k | \dot{\phi}_n \rangle e^{-\frac{i}{\hbar}\int_0^t dt' \, E_n(t') - E_k(t')}}$$

Now I know what (2) is, so I can use (3).

$$\boxed{\dot{c}_k = -\sum_{n\neq k}{}' c_n \frac{\langle k|\frac{\partial H}{\partial t}|n\rangle}{E_k - E_n} e^{-\frac{i}{\hbar}\int_0^t dt' E_n(t') - E_k(t')}} - c_k\langle\phi_k|\dot{\phi}_k\rangle$$

↑ be careful!

This is a differential equation to find c_k!

But I need $c_n(0) = \delta_{nj}$ This says all c_n's are zero but one! The system initially in state j.

so the 1st order correction:

$$\dot{c}_k = \frac{\langle k|\frac{\partial H}{\partial t}|j\rangle}{E_k - E_j} e^{-\frac{i}{\hbar}\int_0^t dt'(E_j - E_k)} = \frac{dc_k}{dt}$$

Assuming everything is slow

$$c_k \approx \frac{\langle k|\frac{\partial H}{\partial t}|j\rangle}{\frac{i}{\hbar}(E_j - E_k)^2}\underbrace{\left[e^{-\frac{i}{\hbar}(E_j - E_k)t} - e^{-\frac{i}{\hbar}(E_j - E_k)t_0}\right]}_{\leq 2}$$

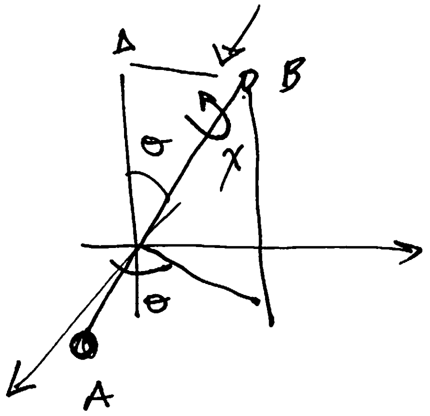
$$|c_k|^2 \sim \frac{4\hbar^2\langle\frac{\partial H}{\partial t}\rangle^2}{(E_j - E_k)^4}$$ ← probability to go from j to k!

If $E_j - E_k = h\nu = \frac{h}{\tau}$

$$\boxed{\frac{\tau}{2\pi}\langle k|\frac{\partial H}{\partial t}|\phi_j\rangle \ll |E_j - E_k|}$$ No transition!!!

$$E = E_{\text{transl.}} + E_{\text{rot}} + E_{\text{vib}} + E_{\text{electr.}} + E_{\text{spin}}.$$

$$\Psi = \psi_{\text{transl}}(XYZ)\,\psi_{\text{rot}}(\theta, \phi\,\chi)\,\psi_{\text{vib}}(R)\,\psi_{\text{el}}(r)\,\psi_{\text{spin}}$$



χ rotation is not important!

$$E_{\text{rot}} = \frac{\hbar^2}{2I} = \frac{\hbar^2}{2\mu R_e^2} J(J+1) = B\,J(J+1).$$

$h/8\pi^2 c\mu R_e^2$ in cm^{-1}

$\boxed{B \sim 2\ \text{cm}^{-1}}$ or 6×10^{10} Hz.

$$-J < M < J$$

$$\boxed{\begin{array}{c}\Delta J = \pm 1 \\ \Delta M = 0, \pm 1\end{array}}$$

selection rules.

vibrational energy $E_{\text{vib}} = \hbar\omega(v + 1/2)$.

$$\mu \sim \overset{\text{lin.}}{\wedge}\alpha(R-R_e) + \beta(R-R_e)^2$$

$\hbar\omega \sim 10 - 1000\ \text{cm}^{-1}$

$$\langle v|(R-R_e)|v'\rangle \sim \delta(v, v'\pm1)$$

$$\langle v|(R-R_e)^2|v'\rangle \sim \delta(v, v'\pm2)$$

Rotovibrations

homonuclear molecules

[illegible]

[illegible]

[illegible] $\langle n | [\ldots] | n \rangle$ [illegible]

[illegible] $\langle n | [\ldots] | n \rangle$ [illegible]

[illegible]

$$E^{NP} = \hbar\omega(n+\tfrac{1}{2})$$

[illegible]

[illegible]

[illegible]

[illegible]

SSP 2

~~[illegible]~~

OK, so we have got the Born-Oppenheimer:

$$\left[\hat{T}_p + W(R) - E_s\right]\chi = -\sum \hat{C}\,\chi$$

$$\hat{C} = \sum_\alpha \frac{\hbar^2}{2m_p}\sum_i 2\,\langle\varphi_i|\nabla_\alpha|\varphi_j\rangle\,\hat{\nabla}_\alpha + \sum_i\langle\varphi_i|\nabla_\alpha^2|\varphi_i\rangle\,\frac{\hbar^2}{2m_p}.$$

proton

~~$\langle\varphi_i|\varphi_j\rangle = 0$~~

~~$\nabla\langle\varphi_i|\varphi_j\rangle = \langle\nabla\varphi_i|\varphi_j\rangle + \langle\varphi_i|\nabla\varphi_j\rangle = 0$~~

Simple arguments:

$$\Psi = \chi\cdot\varphi_0(r,R)$$

$$\hat{C} = \sum_\alpha \frac{\hbar^2}{2m_p}\left(\langle\varphi_0|\nabla_\alpha|\varphi_0\rangle\,\hat{\nabla}_\alpha + \langle\varphi_0|\nabla_\alpha^2|\varphi_0\rangle\right)$$

small

$$\frac{\partial}{\partial R}\sim\frac{\partial}{\partial r} \qquad \boxed{\varphi_0(|r-R|)}$$

kinetic energy of electron

$$p^2 = E_i\,\boxed{2m_e}\,.$$

OK.

Now a few words about E_{el}!

H_2 is complicated!

consider H_2^+ first. then add the second electron.

$$H(r) = \underbrace{\frac{p^2}{2m} - \frac{e^2}{|r-R_1|}}_{\text{hydrogen atom!}} + \frac{e^2}{|R_1-R_2|} - \frac{e^2}{|r-R_2|}$$

Let's to LCAO $\psi = c_1\,\Phi_1(r) + \Phi_2(r)$

$S = \langle\Phi_1|\Phi_2\rangle = \langle\Phi_2|\Phi_1\rangle.$

$\hat{H}\psi = E\psi$

$$c_1^B = \frac{1}{\sqrt{2(1+S)}} = c_2^B$$

diff. equation is a matrix equation now!

$$E_B = \frac{E_0 + E_{12}}{1+S}$$

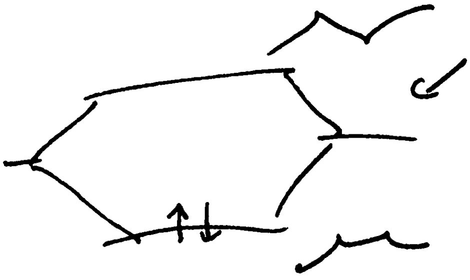
$$c_1^A = \frac{1}{\sqrt{2(1-S)}} \qquad c_2^A = -\frac{1}{\sqrt{2(1-S)}}$$

$$E_A = \frac{E_0 - E_{12}}{1-S}$$

$$E_0 = \langle\Phi_1|\hat{H}|\Phi_1\rangle$$

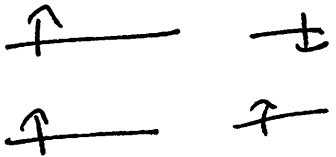
$$\boxed{E_{12} = \langle\Phi_1|H|\Phi_2\rangle = t(R)}$$

hopping matrix element!



ground state

Chemical Bond!



excited state.