Let us consider a system of nuclei and electrons, interacting via Coulomb potential.

The Hamiltonian of the system is

$$\hat{H} = \sum_{i=1}^{N} \frac{\hat{P}_i^2}{2M_i} + \sum_{\alpha=1}^{n} \frac{\hat{p}_\alpha^2}{2m} + \frac{1}{2}\sum_{i,j} \frac{Z_i Z_j e^2}{4\pi\varepsilon_0} \frac{1}{|\hat{R}_i - \hat{R}_j|}$$

$$\frac{1}{2}\sum_{\alpha,\beta} \frac{e^2}{4\pi\varepsilon_0} \frac{1}{|\hat{r}_\alpha - \hat{r}_\beta|} - \sum_{i,\alpha} \frac{Z_i e^2}{4\pi\varepsilon_0} \frac{1}{|\hat{R}_i - \hat{r}_\alpha|}$$

$$= \sum_{i=1}^{N} \frac{\hat{P}_i^2}{2M_i} + \hat{h}_{el}(\hat{p}, \hat{r}, \hat{R})$$

where the electronic Hamiltonian

$$\hat{h}_{el}(\hat{p}, \hat{r}, \hat{R}) = \sum_{\alpha=1}^{n} \frac{\hat{p}_\alpha^2}{2m} + \underbrace{\frac{1}{2}\sum_{i,j} \frac{Z_i Z_j e^2}{4\pi\varepsilon_0} \frac{1}{|\hat{R}_i - \hat{R}_j|}}_{V_{NN}(\hat{R})}$$

$$+ \frac{1}{2}\sum_{\alpha,\beta} \frac{e^2}{4\pi\varepsilon_0} \frac{1}{|\hat{r}_\alpha - \hat{r}_\beta|} \underbrace{- \sum_{i,\alpha} \frac{Z_i e^2}{4\pi\varepsilon_0} \frac{1}{|\hat{R}_i - \hat{r}_\alpha|}}_{V_{Ne}(\hat{R}, \hat{r})}$$

was defined. Let us consider for the time being the situation in which the nuclei do not move, i.e. we set the nuclear kinetic operator to zero.

Define the basis set

$$|R, \phi_\alpha(R)\rangle$$

R: nuclear coordinates; $\phi_\alpha(R)$: electronic eigenstates

such that

$$\boxed{\hat{h}(\hat{p}, \hat{r}, \hat{R})\, |R\, \phi_\alpha(R)\rangle = E_\alpha(R)\, |R\, \phi_\alpha(R)\rangle}$$

n_{es} number of el. states $\qquad \alpha = 0, 1, \dots n_{es} - 1$

$|R\,\phi_\alpha(R)\rangle$ is known as the adiebetic basis. The (parametric) dependence of $E_\alpha(R)$ and $|\phi_\alpha(R)\rangle$ on R is due to the fact that V_{NN} and V_{Ne} depend on $\hat{R}$; the nuclei create an external field in which the electrons move.

Let us now go back to the full problem described by the Hamiltonian $\hat{H}$. Consider a general state of the system of nuclei and electrons $|\Psi\rangle$ and express it in the adiabetic basis

$$\boxed{|\Psi\rangle = \sum_\alpha \int dR \; c_\alpha(R)\,|R\,\phi_\alpha(R)\rangle}$$

with $\boxed{c_\alpha(R) = \langle R\,\phi_\alpha(R)|\Psi\rangle}$. Note that the modulus squared of this coefficient is, by definition, the probability to find the nuclei at position(s) R and in electronic state α, i.e.

$$\boxed{P_\alpha(R) = |\langle R\,\phi_\alpha(R)|\Psi\rangle|^2}$$

The evolution of state $|\Psi\rangle$ is determined by the time dependent Schrödinger equation

$$i\hbar\frac{d}{dt}|\Psi\rangle = \hat{H}|\Psi\rangle$$

This is the abstract form of the equation, our goal now is to use the adiabetic representation of the state and transform it into a system of ordinary differential equations for the coefficients $c_\alpha(R)$

To pave the way for this, let us rewrite the equation as

$$i\hbar \frac{d}{dt}|\Psi\rangle = (\hat{K}_N + \hat{h}_{el})|\Psi\rangle$$

↑ nuclear kinetic energy operator

$$= \hat{K}_N |\Psi\rangle + \hat{h}_{el}|\Psi\rangle$$

Three steps:

1/ Express $|\Psi\rangle$ in the adiabatic basis

2/ Take the scalar product with a generic basis element and work out the terms that appear

3/ Combine the results of step 2 to obtain the system of evolution equations for the coefficients.

Step 1: Substitute $|\Psi\rangle = \sum_\alpha \int dR\, c_\alpha(R)\, |R\, \phi_\alpha(R)\rangle$ in the time-dependent Schrödinger equation

$$i\hbar \frac{d}{dt} \sum_\alpha \int dR\, c_\alpha(R)\, |R\, \phi_\alpha(R)\rangle$$

$$= \hat{K}_N \sum_\alpha \int dR\, c_\alpha(R)\, |R\, \phi_\alpha(R)\rangle$$

$$+ \hat{h}_{el} \sum_\alpha \int dR\, c_\alpha(R)\, |R\, \phi_\alpha(R)\rangle$$

Nb. the time dependence is only in the $c_\alpha(R)$, the basis is time independent

Due to linearity, the equation above can also be written as

$$i\hbar \sum_\alpha \int dR \left[\frac{d\, c_\alpha(R,t)}{dt}\right] |R\, \phi_\alpha\rangle = \sum_\alpha \int dR\, c_\alpha(R,t)\, \hat{K}_N |R\, \phi_\alpha(R)\rangle$$

$$+ \sum_\alpha \int dR\, c_\alpha(R,t)\, \hat{h}_{el} |R\, \phi_\alpha(R)\rangle$$

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where the time dependence of the coefficients was indicated explicitely.

Step 2: Multiply on the left by the generic basis element $\langle R' \phi_\beta(R')|$

We have to consider three terms

(a) $$i\hbar \sum_\alpha \int dR \left[\frac{d}{dt} c_\alpha(R,t)\right] \langle R' \phi_\beta(R') | R \phi_\alpha(R)\rangle$$

(b) $$\sum_\alpha \int dR \; c_\alpha(R,t) \langle R' \phi_\beta(R') | \hat{K}_N | R \phi_\alpha(R)\rangle$$

(c) $$\sum_\alpha \int dR \; c_\alpha(R,t) \langle R' \phi_\beta(R') | \hat{h}_{el} | R \phi_\alpha(R)\rangle$$

Let's start with (a). The scalar product in the integral is

$$\boxed{\langle R' \phi_\beta(R') | R \phi_\alpha(R)\rangle = \delta(R'-R)\,\delta_{\alpha\beta}}$$

due to the orthonormality of the basis. Then

$$(a) = i\hbar \sum_\alpha \int dR \left[\frac{d}{dt} c_\alpha(R,t)\right] \delta(R'-R)\,\delta_{\alpha\beta}$$

$$= i\hbar \sum_\alpha \left[\frac{d}{dt} c_\alpha(R',t)\right] \delta_{\alpha\beta}$$

$$= i\hbar \frac{d}{dt} c_\beta(R',t)$$

Let us then consider (c). Since $\hat{h}_{el} |R \phi_\alpha(R)\rangle = E_\alpha(R) |R \phi_\alpha(R)\rangle$

we have
$$\boxed{\begin{aligned} &\langle R' \phi_\beta(R') | \hat{h}_{el} | R \phi_\alpha(R)\rangle \\ &= \langle R' \phi_\beta(R') | R \phi_\alpha(R)\rangle E_\alpha(R) \\ &= \delta(R'-R)\,\delta_{\alpha\beta} E_\alpha(R) \end{aligned}}$$

Then

$$(c) = \sum_\alpha \int dR \; c_\alpha(R,t)\, \delta(R'-R)\, \delta_{\alpha\beta}\, E_\alpha(R)$$

$$= E_\beta(R')\, c_\beta(R',t)$$

The third term, (b), is more complicated. Let us consider

$$\langle R' \phi_\beta(R') | \hat{K}_N | R \phi_\alpha(R) \rangle$$

$$= \langle R' \phi_\beta(R') | \frac{\hat{P}^2}{2M} | R \phi_\alpha(R) \rangle$$

We know that $\boxed{\langle R' | \frac{\hat{P}^2}{2M} | R \rangle = -\frac{\hbar^2}{2M} \frac{\partial^2 \delta(R'-R)}{\partial R^2}}$

and that

$$\boxed{\int dx\; f(x) \frac{d^2}{dx^2} \delta(x-x') = \int dx\, \frac{d^2 f(x)}{dx^2}\, \delta(x-x')}$$

Then

$$(b) = \sum_\alpha \int dR\; c_\alpha(R,t) \langle R' \phi_\beta(R') | \frac{\hat{P}^2}{2M} | R \phi_\alpha(R) \rangle$$

$$= -\frac{\hbar^2}{2M} \sum_\alpha \int dR\; c_\alpha(R,t) \langle \phi_\beta(R') | \phi_\alpha(R) \rangle \frac{d^2}{dR^2} \delta(R-R')$$

$$= -\frac{\hbar^2}{2M} \sum_\alpha \int dR\, \frac{d^2}{dR^2} \left\{ c_\alpha(R,t) \langle \phi_\beta(R') | \phi_\alpha(R) \rangle \right\} \delta(R-R')$$

$$= -\frac{\hbar^2}{2M} \sum_\alpha \int dR \left\{ \frac{d^2 c_\alpha(R,t)}{dR^2} \right\} \langle \phi_\beta(R') | \phi_\alpha(R) \rangle\, \delta(R-R') \quad (1)$$

$$-\frac{\hbar^2}{2M}\, 2 \sum_\alpha \int dR \left\{ \frac{d}{dR} c_\alpha(R,t) \right\} \left\{ \frac{\partial}{\partial R} \langle \phi_\beta(R') | \phi_\alpha(R) \rangle \right\} \times \delta(R-R') \quad (2)$$

$$-\frac{\hbar^2}{2M} \sum_\alpha \int dR\; c_\alpha(R,t) \left\{ \frac{\partial^2}{\partial R^2} \langle \phi_\beta(R') | \phi_\alpha(R) \rangle \right\} \delta(R-R') \quad (3)$$

Let us consider separately the Three terms.
To begin with, let us focus on 1. We have

$$-\frac{\hbar^2}{2M}\sum_\alpha \int dR \left\{\frac{d^2}{dR^2} c_\alpha(R,t)\right\} \langle \phi_\beta(R') | \phi_\alpha(R)\rangle \, \delta(R-R')$$

$$= -\frac{\hbar^2}{2M}\sum_\alpha \left\{\frac{d^2}{dR'^2} c_\alpha(R',t)\right\} \underbrace{\langle \phi_\beta(R') | \phi_\alpha(R')\rangle}_{\delta_{\beta\alpha}}$$

$$= -\frac{\hbar^2}{2M} \frac{d^2}{dR'^2} c_\beta(R',t)$$

As for 2, we have that

$$\frac{\partial}{\partial R} \langle \phi_\beta(R') | \phi_\alpha(R)\rangle = \langle \phi_\beta(R') | \frac{d}{dR} \phi_\alpha(R)\rangle$$

Then

$$② = -\frac{\hbar^2}{M}\sum_\alpha \int dR \left\{\frac{d}{dR} c_\alpha(R,t)\right\} \langle \phi_\beta(R') | \frac{d}{dR}\phi_\alpha(R)\rangle \times \delta(R-R')$$

$$= -\frac{\hbar^2}{M}\sum_\alpha \frac{d}{dR'} c_\alpha(R',t) \cdot \langle \phi_\beta(R') | \frac{d}{dR'}\phi_\alpha(R')\rangle$$

And similarly, using

$$\frac{\partial^2}{\partial R^2} \langle \phi_\beta(R') | \phi_\alpha(R)\rangle = \langle \phi_\beta(R') | \frac{d^2}{dR^2} \phi_\alpha(R)\rangle$$

$$③ = -\frac{\hbar^2}{2M}\sum_\alpha c_\alpha(R',t) \langle \phi_\beta(R') | \frac{d^2}{dR^2}\phi_\alpha(R)\rangle$$

We now have explicit expressions for all the terms in the system of equations for the coefficients.

Step 3

Substituting the explicit expressions for (a), (b) and (c) in the projected Schrödinger equation, we obtain

$$\overset{(a)}{i\hbar \frac{d}{dt} c_\beta(R',t)} = \overset{(b)}{-\frac{\hbar^2}{2M}\frac{d^2}{dR'^2} c_\beta(R',t)}$$

$$\overset{(b)}{-\frac{\hbar^2}{M}\sum_\alpha \langle \phi_\beta(R') | \frac{d}{dR'} \phi_\alpha(R')\rangle c_\alpha(R',t)}$$

$$\overset{(b)}{-\frac{\hbar^2}{2M}\sum_\alpha \langle \phi_\beta(R') | \frac{d^2}{dR'^2} \phi_\alpha(R')\rangle c_\alpha(R',t)}$$

$$\underset{(c)}{+ E_\beta(R')\, c_\beta(R',t)}$$

where the origin of each term is indicated as a reminder.

The structure and meaning of this system of equations (one for each value of β) will be discussed in the next lecture

The system above is known as the set of the coupled channels equations

Note that, if we can solve this system, we can

1/ describe the time evolution of the state

$$|\Psi(t)\rangle = \sum_\alpha \int dR\, \underbrace{c_\alpha(R,t)}_{\text{solutions}}\, |R\, \phi_\alpha(t)\rangle$$

2/ (equivalently) determine the probability to find the system with nuclei at R and electrons in state α via $|c_\alpha(R,t)|^2$