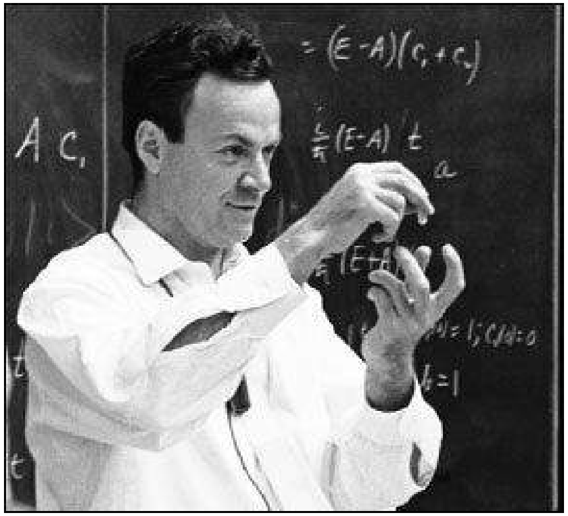
Atoms in Motion

Atoms in Motion

If, in some cataclysm, all of scientific knowledge were to be destroyed, and only one sentence passed on to the next generation of creatures, what statement would contain the most information in the fewest words? I believe it is the atomic hypothesis (or the atomic fact, or whatever you wish to call it) that all things are made of atoms — little particles that move around in perpetual motion, attracting each other when they are a little distance apart, but repelling upon being squeezed into one another. In that one sentence, you will see, there is an enormous amount of information about the world, if just a little imagination and thinking are applied.

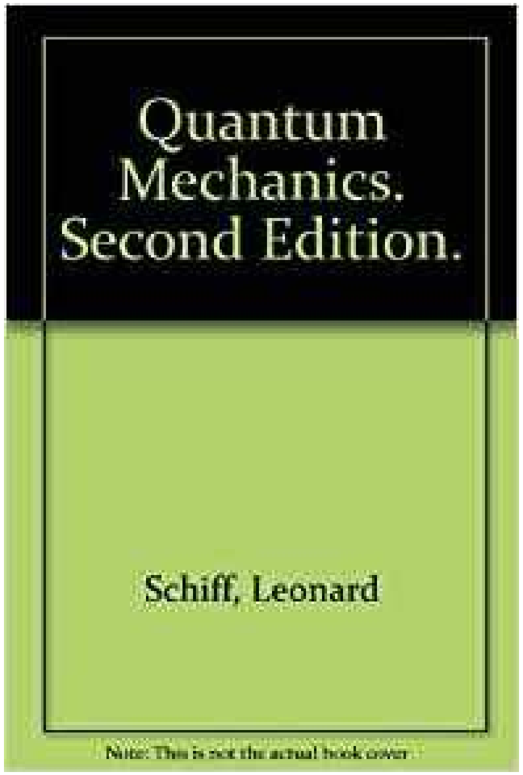


R.P. Feynman,
Lectures on Physics, vol.I, lect.I (1964)

Quantum Mechanics is the key

At the present status of human knowledge, quantum mechanics can be regarded as the fundamental theory of atomic phenomena.

L.I. Schiff, *Quantum Mechanics*, 1955



Quantum Mechanics is the key

The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble. <u>It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed</u>, which can lead to an explanation of the main features of complex atomic systems without too much computation.

P.A.M. Dirac,
Quantum Mechanics of Many-Electron Systems
Proc. Royal Soc. 129, 714 (1929).

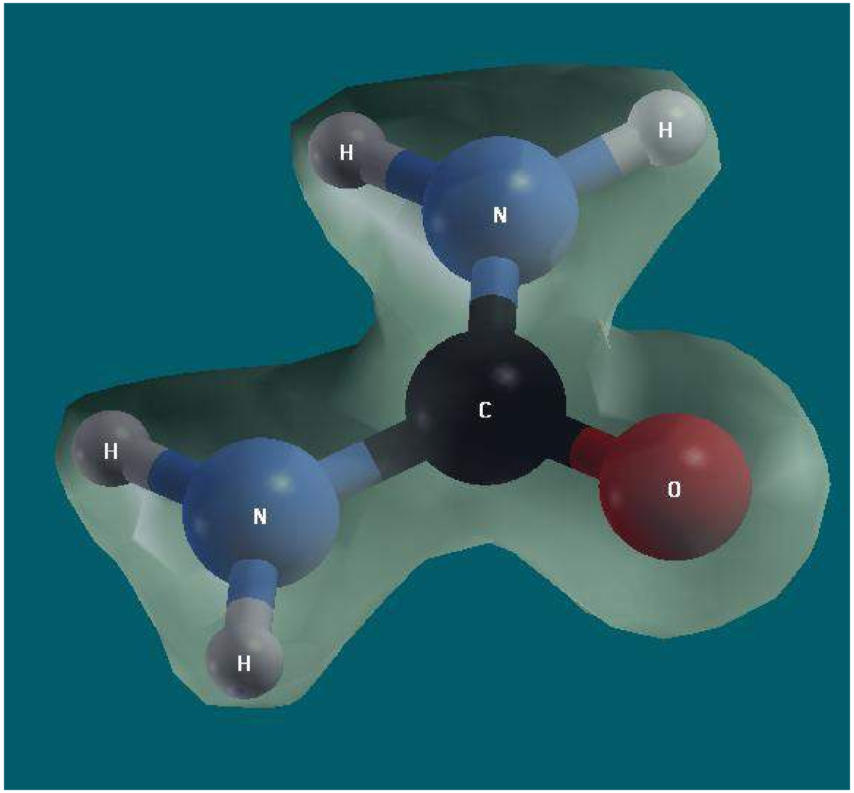
Adiabatic approximation

Independent electrons in an effective potential

Hartree–Fock

Density Functional Theory

MBPT - GW



Adiabatic Approximation

The Molecular Problem

$$\mathcal{H} = \left[\sum_{I=1}^{Nat} \frac{P_I^2}{2M_I} + \sum_{i=1}^{Nel} \frac{p_i^2}{2m_e} \quad - \sum_{I,i} \frac{Z_I e^2}{|r_i - R_I|} \right.$$

$$\left. + \frac{1}{2} \sum_{i,j}^{Nel} \frac{e^2}{|r_i - r_j|} + \frac{1}{2} \sum_{I,J}^{Nat} \frac{Z_I Z_J e^2}{|R_I - R_J|} \right]$$

$$\mathbf{r} = r_1, r_2, ..., r_{Nel}$$
$$\mathbf{p} = p_1, p_2, ..., p_{Nel}$$
$$\mathbf{R} = R_1, R_2, ..., R_{Nat}$$
$$\mathbf{P} = P_1, P_2, ..., P_{Nat}$$

$(m_e, -e)$ electrons

ions

$(M_1, Z_1 e), (M_2, Z_2 e), ..., (M_{Nat}, Z_{Nat} e)$

The Molecular Problem

$$\mathcal{H} = \left[\sum_{I=1}^{Nat} \frac{P_I^2}{2M_I} + \sum_{i=1}^{Nel} \frac{p_i^2}{2m_e} \quad - \sum_{I,i} \frac{Z_I e^2}{|r_i - R_I|} \right.$$

$$\left. + \frac{1}{2} \sum_{i,j}^{Nel} \frac{e^2}{|r_i - r_j|} + \frac{1}{2} \sum_{I,J}^{Nat} \frac{Z_I Z_J e^2}{|R_I - R_J|} \right]$$

$$\mathbf{r} = r_1, r_2, ..., r_{Nel}$$

$$\mathbf{p} = p_1, p_2, ..., p_{Nel}$$

$$\mathbf{R} = R_1, R_2, ..., R_{Nat}$$

$$\mathbf{P} = P_1, P_2, ..., P_{Nat}$$

The only term that keeps matter together is the attractive electron-ion interaction

The Molecular Problem

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$$\left. + \frac{1}{2} \sum_{i,j}^{Nel} \frac{e^2}{|r_i - r_j|} + \frac{1}{2} \sum_{I,J}^{Nat} \frac{Z_I Z_J e^2}{|R_I - R_J|} \right]$$

$\mathbf{r} = r_1, r_2, ..., r_{Nel}$

$\mathbf{p} = p_1, p_2, ..., p_{Nel}$

$\mathbf{R} = R_1, R_2, ..., R_{Nat}$

$\mathbf{P} = P_1, P_2, ..., P_{Nat}$

two very different phases

$$M_I >> m_e$$

$$M_H = 1836\, m_e, \quad M_{Au} = 196.97\, amu \approx 4 \times 10^5\, m_e$$

The Molecular Problem

$$\mathcal{H} = \left[\sum_{I=1}^{Nat} \frac{P_I^2}{2M_I} + \sum_{i=1}^{Nel} \frac{p_i^2}{2m_e} \quad - \sum_{I,i} \frac{Z_I e^2}{|r_i - R_I|} \right.$$

$$\left. + \frac{1}{2}\sum_{i,j}^{Nel} \frac{e^2}{|r_i - r_j|} + \frac{1}{2}\sum_{I,J}^{Nat} \frac{Z_I Z_J e^2}{|R_I - R_J|} \right]$$

$$\mathbf{r} \; = r_1, r_2, ..., r_{Nel}$$

$$\mathbf{p} = p_1, p_2, ..., p_{Nel}$$

$$\mathbf{R} = R_1, R_2, ..., R_{Nat}$$

$$\mathbf{P} \; = P_1, P_2, ..., P_{Nat}$$

two very different phases

$$M_I >> m_e$$

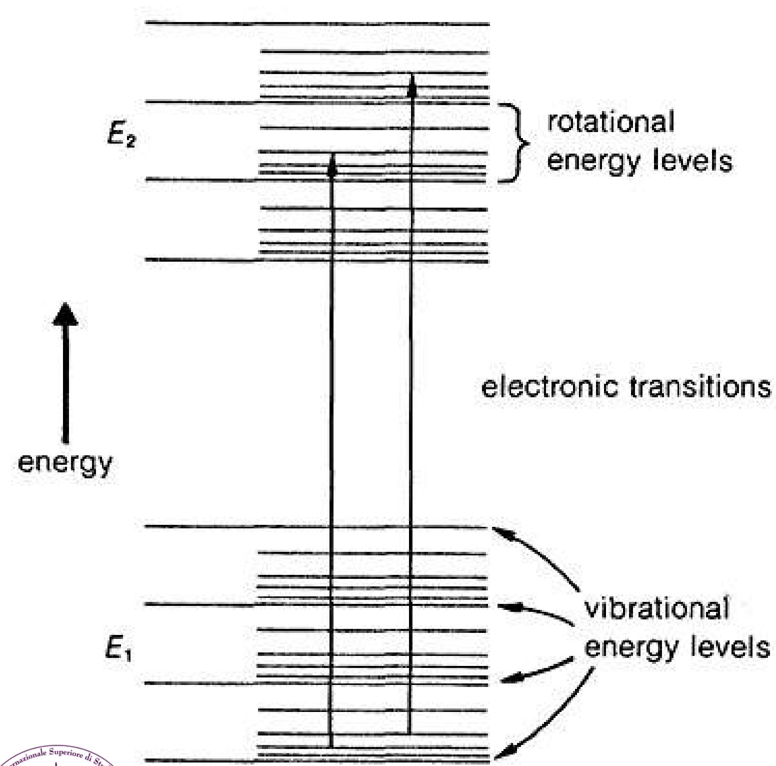
$$\mathcal{H} = [T_I(\mathbf{P}) + T_e(\mathbf{p}) + W_{eI}(\mathbf{r}, \mathbf{R}) + W_{ee}(\mathbf{r}) + W_{II}(\mathbf{R})]$$

Adiabatic Approximation

$$[T_I + T_e + W_{eI} + W_{ee} + W_{II}]\,\Psi_\alpha(\mathbf{r},\mathbf{R}) = E_\alpha \Psi_\alpha(\mathbf{r},\mathbf{R})$$

$$M_I >> m_e$$

The slow nuclei move in the potential energy surface (PES) generated by the fast electrons



$$\hbar\omega_{nuc} << \hbar\omega_{el}$$

$$\Downarrow$$

$$\tau_{nuc} >> \tau_{el}$$

ps fs

electrons see the nuclei as fixed

Adiabatic Approximation

$$\left[T_I + T_e + W_{eI} + W_{ee} + W_{II}\right] \Psi_\alpha(\mathbf{r}, \mathbf{R}) = E_\alpha \Psi_\alpha(\mathbf{r}, \mathbf{R})$$

$$\Psi(\mathbf{r}, \mathbf{R}) = \Phi(\mathbf{r}|\mathbf{R})\chi(\mathbf{R}), \qquad M_I >> m_e$$

no approximation here yet

$$P_I \Phi(\mathbf{r}|\mathbf{R}) = -i\hbar\nabla_{R_I}\Phi(\mathbf{r}|\mathbf{R}) \approx 0$$

assuming it to be negligible is the
Adiabatic (a.k.a. Born-Oppenheimer) Approximation

Adiabatic Approximation

$$\left[T_I + T_e + W_{eI} + W_{ee} + W_{II}\right]\Psi_\alpha(\mathbf{r},\mathbf{R}) = E_\alpha \Psi_\alpha(\mathbf{r},\mathbf{R})$$

$$\Psi(\mathbf{r},\mathbf{R}) = \Phi(\mathbf{r}|\mathbf{R})\chi(\mathbf{R}), \qquad\qquad M_I >> m_e$$

$$\mathcal{H}\Psi(\mathbf{r},\mathbf{R}) =$$

$$\left[T_I + T_e + W_{eI} + W_{ee} + W_{II}\right]\Phi(\mathbf{r}|\mathbf{R})\chi(\mathbf{R}) \;=$$

$$T_I\Phi(\mathbf{r}|\mathbf{R})\chi(\mathbf{R}) + \chi(\mathbf{R})\left[T_e + W_{eI} + W_{ee} + W_{II}\right]\Phi(\mathbf{r}|\mathbf{R})$$

Adiabatic Approximation

$$\left[T_I + T_e + W_{eI} + W_{ee} + W_{II}\right]\Psi_\alpha(\mathbf{r},\mathbf{R}) = E_\alpha \Psi_\alpha(\mathbf{r},\mathbf{R})$$

$$\Psi(\mathbf{r},\mathbf{R}) = \Phi(\mathbf{r}|\mathbf{R})\chi(\mathbf{R}), \qquad M_I >> m_e$$

$$\mathcal{H}\Psi(\mathbf{r},\mathbf{R}) =$$

$$\left[T_I + T_e + W_{eI} + W_{ee} + W_{II}\right]\Phi(\mathbf{r}|\mathbf{R})\chi(\mathbf{R}) \ =$$

$$T_I\Phi(\mathbf{r}|\mathbf{R})\chi(\mathbf{R}) + \chi(\mathbf{R})\left[T_e + W_{eI} + W_{ee} + W_{II}\right]\Phi(\mathbf{r}|\mathbf{R}) \approx$$

$$\Phi(\mathbf{r}|\mathbf{R})\ T_I\chi(\mathbf{R}) + \chi(\mathbf{R})\left[T_e + W_{eI} + W_{ee} + W_{II}\right]\Phi(\mathbf{r}|\mathbf{R})$$

because $P_I(\Phi(\mathbf{r}|\mathbf{R})\chi(\mathbf{R})) \approx \cancel{P_I(\Phi(\mathbf{r}|\mathbf{R}))\ \chi(\mathbf{R})} + \Phi(\mathbf{r}|\mathbf{R})\ P_I\chi(\mathbf{R})$

$P_I^2(\Phi(\mathbf{r}|\mathbf{R})\chi(\mathbf{R})) \approx \cancel{P_I(\Phi(\mathbf{r}|\mathbf{R}))P_I\chi(\mathbf{R})} + \Phi(\mathbf{r}|\mathbf{R})\ P_I^2\chi(\mathbf{R})$

Adiabatic Approximation

$$\left[T_I + T_e + W_{eI} + W_{ee} + W_{II}\right]\Psi_\alpha(\mathbf{r},\mathbf{R}) = E_\alpha \Psi_\alpha(\mathbf{r},\mathbf{R})$$

$$\Psi(\mathbf{r},\mathbf{R}) = \Phi(\mathbf{r}|\mathbf{R})\chi(\mathbf{R}), \qquad\qquad M_I >> m_e$$

$$\mathcal{H}\Psi(\mathbf{r},\mathbf{R}) =$$

$$\left[T_I + T_e + W_{eI} + W_{ee} + W_{II}\right]\Phi(\mathbf{r}|\mathbf{R})\chi(\mathbf{R}) \;=$$

$$T_I\Phi(\mathbf{r}|\mathbf{R})\chi(\mathbf{R}) + \chi(\mathbf{R})\left[T_e + W_{eI} + W_{ee} + W_{II}\right]\Phi(\mathbf{r}|\mathbf{R}) \approx$$

$$\Phi(\mathbf{r}|\mathbf{R})\,T_I\chi(\mathbf{R}) + \chi(\mathbf{R})\left[T_e + W_{eI} + W_{ee} + W_{II}\right]\Phi(\mathbf{r}|\mathbf{R})$$

hence $\qquad T_I(\Phi(\mathbf{r}|\mathbf{R})\chi(\mathbf{R})) \approx \Phi(\mathbf{r}|\mathbf{R})\,T_I\chi(\mathbf{R})$

Adiabatic Approximation

$$[T_I + T_e + W_{eI} + W_{ee} + W_{II}]\,\Psi_\alpha(\mathbf{r},\mathbf{R}) = E_\alpha \Psi_\alpha(\mathbf{r},\mathbf{R})$$

$$\Psi(\mathbf{r},\mathbf{R}) = \Phi(\mathbf{r}|\mathbf{R})\chi(\mathbf{R}), \qquad\qquad M_I >> m_e$$

$$\mathcal{H}\Psi(\mathbf{r},\mathbf{R}) =$$

$$[T_I + T_e + W_{eI} + W_{ee} + W_{II}]\,\Phi(\mathbf{r}|\mathbf{R})\chi(\mathbf{R}) \;=$$

$$T_I\Phi(\mathbf{r}|\mathbf{R})\chi(\mathbf{R}) + \chi(\mathbf{R})\,[T_e + W_{eI} + W_{ee} + W_{II}]\,\Phi(\mathbf{r}|\mathbf{R}) \approx$$

$$\Phi(\mathbf{r}|\mathbf{R})\;T_I\chi(\mathbf{R}) + \chi(\mathbf{R})\,[T_e + W_{eI} + W_{ee} + W_{II}]\,\Phi(\mathbf{r}|\mathbf{R}) =$$

$$E\;\Phi(\mathbf{r}|\mathbf{R})\chi(\mathbf{R})$$

dividing both sides by $\Phi(\mathbf{r}|\mathbf{R})\chi(\mathbf{R})$ ... one gets

Adiabatic Approximation

$$\underbrace{\frac{T_I\chi(\mathbf{R})}{\chi(\mathbf{R})}}_{\text{function of } \mathbf{R}} + \underbrace{\frac{\left[T_e + W_{eI} + W_{ee} + W_{II}\right]\Phi(\mathbf{r}|\mathbf{R})}{\Phi(\mathbf{r}|\mathbf{R})}}_{\text{function of } \mathbf{R}} = E$$

$\Rightarrow$ function of $\mathbf{R}$

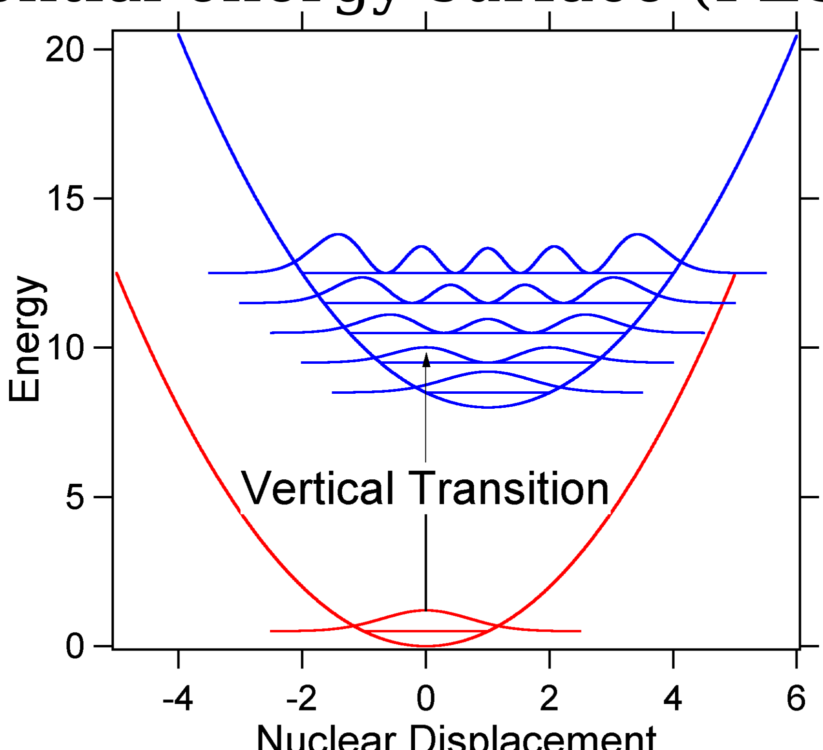
let's call it $E(\mathbf{R})$

$$\begin{cases} \left[T_e + W_{eI} + W_{ee} + W_{II}\right]\Phi(\mathbf{r}|\mathbf{R}) = E(\mathbf{R})\,\Phi(\mathbf{r}|\mathbf{R}) \\ \\ \left[T_I + E(\mathbf{R})\right]\chi(\mathbf{R}) = E\,\chi(\mathbf{R}) \end{cases}$$

Adiabatic Approximation

$$\begin{cases} \left[T_e + W_{eI} + W_{ee} + W_{II}\right]\Phi_\nu(\mathbf{r}|\mathbf{R}) = E_\nu(\mathbf{R})\,\Phi_\nu(\mathbf{r}|\mathbf{R}) \\[2ex] \left[T_I + E_\nu(\mathbf{R})\right]\chi_{\nu\mu}(\mathbf{R}) = E_{\nu\mu}\,\chi_{\nu\mu}(\mathbf{R}) \end{cases}$$

The slow nuclei move in the potential energy surface (PES) generated by the fast electrons



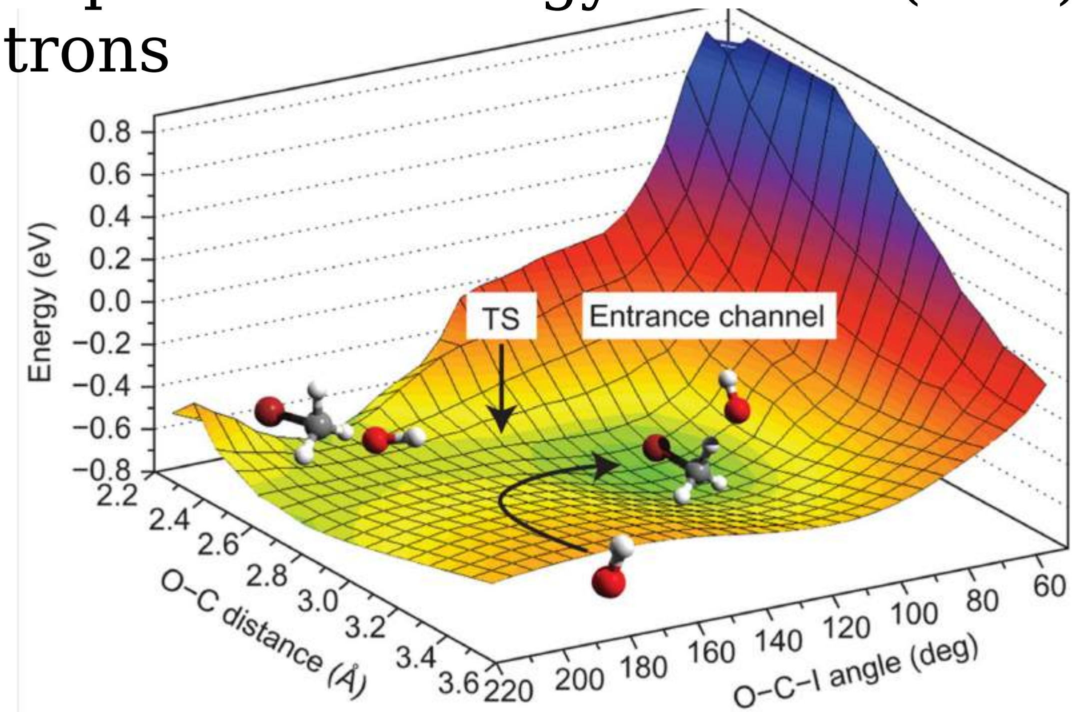
Adiabatic Approximation

$$\begin{cases} [T_e + W_{eI} + W_{ee} + W_{II}]\, \Phi_0(\mathbf{r}|\mathbf{R}) = E_{GS}(\mathbf{R})\; \Phi_0(\mathbf{r}|\mathbf{R}) \\ [T_I + E_{GS}(\mathbf{R})]\, \chi_{0\mu}(\mathbf{R}) = E_\mu\; \chi_{0\mu}(\mathbf{R}) \end{cases}$$

The slow nuclei move in the potential energy surface (PES) generated by the fast electrons

The GS PES is the most important one.

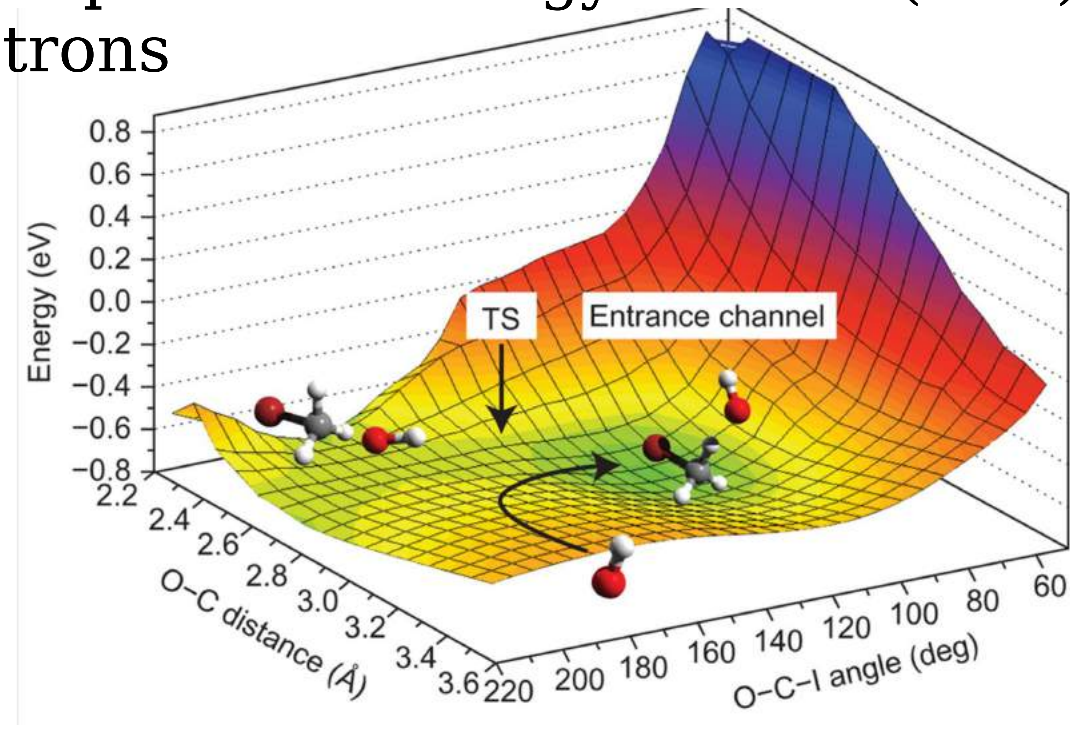
Quantum Mechanics is mandatory to solve the electronic problem



Adiabatic Approximation

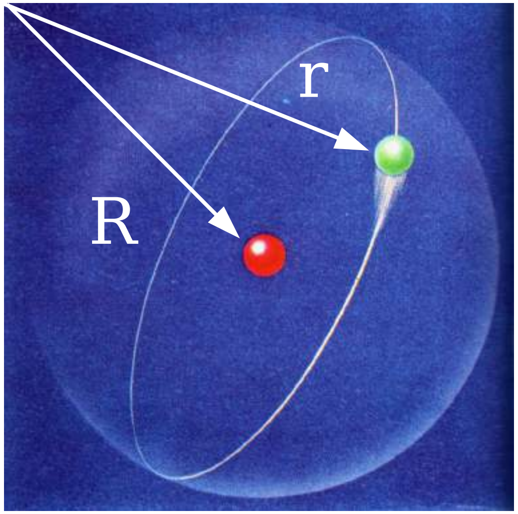
$$\begin{cases} [T_e + W_{eI} + W_{ee} + W_{II}]\,\Phi_0(\mathbf{r}|\mathbf{R}) = E_{GS}(\mathbf{R})\;\Phi_0(\mathbf{r}|\mathbf{R}) \\ M_I \ddot{R}_I = F_I(\mathbf{R}) = -\nabla_{R_I} E_{GS}(\mathbf{R}) \end{cases}$$

The slow nuclei move in the potential energy surface (PES) generated by the fast electrons



The GS PES is the most important one.

Classical Dynamics is often sufficient for the ionic degrees of freedom.



An Example: Hydrogen Atom

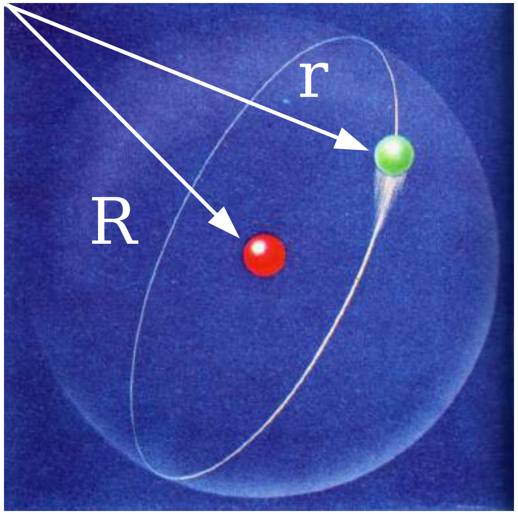
$$\mathcal{H} = \frac{P^2}{2M_H} + \frac{p^2}{2m_e} - \frac{e^2}{|r-R|}$$

A.A.: $\Psi(r,R) = \Phi(r|R)\chi(R)$

$$\begin{cases} \left[\frac{p^2}{2m_e} - \frac{e^2}{|r-R|}\right]\Phi(r|R) = E_{GS}(R)\,\Phi(r|R) \\ \left[\frac{P^2}{2M_H} + E_{GS}(R)\right]\chi(R) = E\,\chi(R) \end{cases}$$

$$\Phi(r|R) = \phi_{1s}(|r-R|) = \frac{1}{\sqrt{\pi}\,a_o^{3/2}} e^{-\frac{|r-R|}{a_o}}, \quad a_o = \frac{\hbar^2}{m_e e^2} \approx 0.529\mathring{A}$$

$$E_{GS}(R) = -\frac{m_e e^4}{2\hbar^2} = -\frac{e^2}{2a_o} = -1\ Ry \approx -13.6058\ eV$$



An Example: Hydrogen Atom

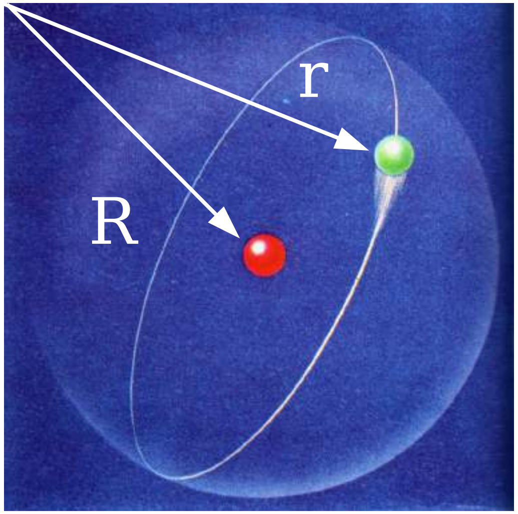
$$\mathcal{H} = \frac{P^2}{2M_H} + \frac{p^2}{2m_e} - \frac{e^2}{|r - R|}$$

A.A.: $$E^{AA}_{GS} = -e^2/2a_o, \quad a_o = \frac{\hbar^2}{m_e e^2}$$

Exact solution:

$$\begin{cases} r, p \\ R, P \end{cases} \longrightarrow \begin{cases} r_{rel} = r - R & , p_{rel} \\ R_{CM} = \frac{m_e r + M_H R}{m_e + M_H} & , P_{CM} \end{cases}$$

$$\begin{cases} p_{rel} = ap + bP \\ P_{CM} = Ap + BP \end{cases} \xrightarrow[\substack{[r_{rel}, p_{rel}] = i\hbar, \ [r_{rel}, P_{CM}] = 0 \\ [R_{CM}, p_{rel}] = 0, \ [R_{CM}, P_{CM}] = i\hbar}]{} \begin{cases} p_{rel} = \frac{M_H \, p + m_e \, P}{m_e + M_H} \\ P_{CM} = p + P \end{cases}$$



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Exact solution:

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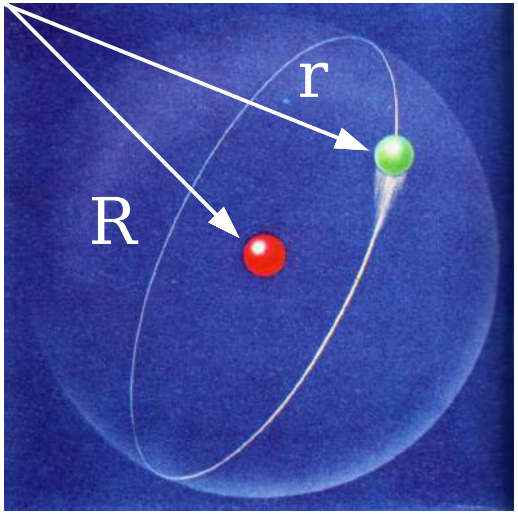
$$\mathcal{H} = \underbrace{\frac{P_{CM}^2}{M_{tot}}}_{(R_{CM},\, P_{CM})} + \underbrace{\frac{p_{rel}^2}{2\mu} - \frac{e^2}{|r_{rel}|}}_{(r_{rel},\, p_{rel})}$$

$$M_{tot} = m_e + M_H, \quad \frac{1}{\mu} = \frac{1}{m_e} + \frac{1}{M_H}$$



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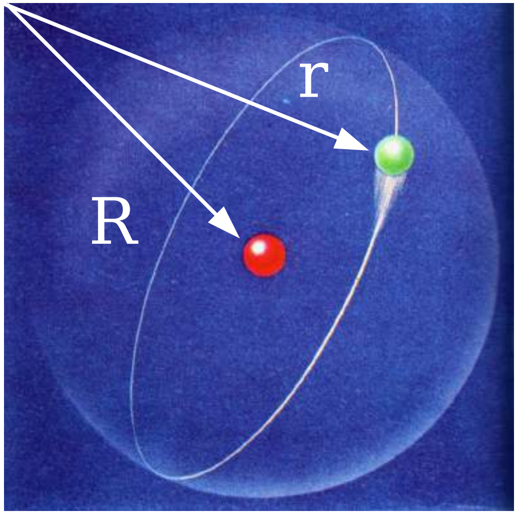
Exact solution:

$$\begin{cases} r, p \\ R, P \end{cases} \longrightarrow \begin{cases} r_{rel} = r - R & , p_{rel} \\ R_{CM} = \frac{m_e r + M_H R}{m_e + M_H} & , P_{CM} \end{cases}$$

$$\mathcal{H} = \underbrace{\frac{P_{CM}^2}{M_{tot}}}_{(R_{CM},\, P_{CM})} + \underbrace{\frac{p_{rel}^2}{2\mu} - \frac{e^2}{|r_{rel}|}}_{(r_{rel},\, p_{rel})}$$

$$\Psi(r, R) = \chi(R_{CM})\Phi(r_{rel})$$

$$E_{GS}^{Ex} = -e^2/2a_o^*, \quad a_o^* = \frac{\hbar^2}{\mu e^2}$$



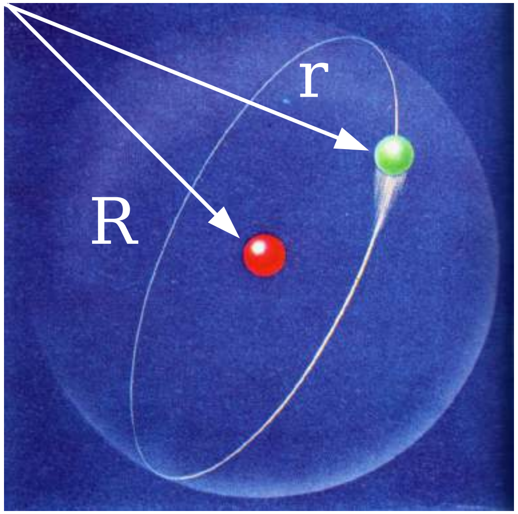
An Example: Hydrogen Atom

$$\mathcal{H} = \frac{P^2}{2M_H} + \frac{p^2}{2m_e} - \frac{e^2}{|r - R|}$$

$$E_{GS}^{AA} = -e^2/2a_o, \quad a_o = \frac{\hbar^2}{m_e e^2} \qquad E_{GS}^{Ex} = -e^2/2a_o^*, \quad a_o^* = \frac{\hbar^2}{\mu e^2}$$

$$\frac{E_{GS}^{AA}}{E_{GS}^{Ex}} = \frac{m_e}{\mu} = \left(1 + \frac{m_e}{M_H}\right) \approx 1 + 5 \times 10^{-4}$$

the exact solution is slightly less bound



An Example: Hydrogen Atom

$$\mathcal{H} = \frac{P^2}{2M_H} + \frac{p^2}{2m_e} - \frac{e^2}{|r-R|}$$

$$E_{GS}^{AA} = -e^2/2a_o, \quad a_o = \frac{\hbar^2}{m_e e^2} \qquad E_{GS}^{Ex} = -e^2/2a_o^*, \quad a_o^* = \frac{\hbar^2}{\mu e^2}$$

$$\frac{E_{GS}^{AA}}{E_{GS}^{Ex}} = \frac{m_e}{\mu} = \left(1 + \frac{m_e}{M_H}\right) \approx 1 + 5 \times 10^{-4}$$

$$\Phi^{AA}(r,R) = \frac{1}{\sqrt{\pi}\ a_o^{3/2}} e^{-\frac{|r-R|}{a_o}}, \quad \Phi^{Ex}(r,R) = \frac{1}{\sqrt{\pi}\ a_o^{*\,3/2}} e^{-\frac{|r-R|}{a_o^*}}$$

the exact solution is slightly more extended

Beyond the Adiabatic Approximation

$$\left[T_I + T_e + W_{eI} + W_{ee} + W_{II}\right]\Psi_\alpha(\mathbf{r},\mathbf{R}) = E_\alpha \Psi_\alpha(\mathbf{r},\mathbf{R})$$

Any solution of the full problem can be expanded in the complete set of orthonormal solutions of the R-dependent electronic problem.

$$\Psi_\alpha(\mathbf{r},\mathbf{R}) = \sum_\mu \chi_{\alpha\mu}(\mathbf{R})\Phi_\mu(\mathbf{r}|\mathbf{R})$$

where $$\mathcal{H}_{el}(\mathbf{R})\Phi_\mu(\mathbf{r}|\mathbf{R}) = E_\mu(\mathbf{R})\Phi_\mu(\mathbf{r}|\mathbf{R})$$

with

$$\mathcal{H}_{el}(\mathbf{r},\mathbf{p}|\mathbf{R}) = T_e(\mathbf{p}) + W_{eI}(\mathbf{r},\mathbf{R}) + W_{ee}(\mathbf{r}) + W_{II}(\mathbf{R})$$

Beyond the Adiabatic Approximation

$$\left[T_I + T_e + W_{eI} + W_{ee} + W_{II}\right]\Psi_\alpha(\mathbf{r},\mathbf{R}) = E_\alpha \Psi_\alpha(\mathbf{r},\mathbf{R})$$

$$\left[T_I(\mathbf{P}) + \mathcal{H}_{el}(\mathbf{r},\mathbf{p}|\mathbf{R})\right]\Psi_\alpha(\mathbf{r},\mathbf{R}) = E_\alpha \Psi_\alpha(\mathbf{r},\mathbf{R})$$

let $\quad \Psi_\alpha(\mathbf{r},\mathbf{R}) = \sum_\mu \chi_{\alpha\mu}(\mathbf{R})\Phi_\mu(\mathbf{r}|\mathbf{R})$

$$\mathcal{H}\Psi_\alpha(\mathbf{r},\mathbf{R}) = \left[T_I(\mathbf{P}) + \mathcal{H}_{el}(\mathbf{R})\right]\sum_\mu \chi_{\alpha\mu}(\mathbf{R})\Phi_\mu(\mathbf{r}|\mathbf{R})$$

$$= \sum_\mu \left[T_I(\mathbf{P}) + E_\mu(\mathbf{R})\right]\chi_{\alpha\mu}(\mathbf{R})\Phi_\mu(\mathbf{r}|\mathbf{R})$$

$$= \sum_\mu \Phi_\mu(\mathbf{r}|\mathbf{R})\left[T_I + E_\mu(\mathbf{R})\right]\chi_{\alpha\mu}(\mathbf{R}) + \sum_I \frac{-\hbar^2}{2M_I}\chi_{\alpha\mu}(\mathbf{R})\nabla^2_{R_I}\Phi_\mu(\mathbf{r}|\mathbf{R})$$

$$+ \sum_I \frac{-\hbar^2}{M_I}\nabla_{R_I}\chi_{\alpha\mu}(\mathbf{R})\nabla_{R_I}\Phi_\mu(\mathbf{r}|\mathbf{R})$$

Beyond the Adiabatic Approximation

$$\sum_\mu \Phi_\mu(\mathbf{r}|\mathbf{R})\left[T_I + E_\mu(\mathbf{R})\right]\chi_{\alpha\mu}(\mathbf{R}) + \sum_I \frac{-\hbar^2}{2M_I}\chi_{\alpha\mu}(\mathbf{R})\nabla^2_{R_I}\Phi_\mu(\mathbf{r}|\mathbf{R})$$

$$+\sum_I \frac{-\hbar^2}{M_I}\nabla_{R_I}\chi_{\alpha\mu}(\mathbf{R})\nabla_{R_I}\Phi_\mu(\mathbf{r}|\mathbf{R})$$

$$= E_\alpha \sum_\mu \Phi_\mu(\mathbf{r}|\mathbf{R})\chi_{\alpha\mu}(\mathbf{R})$$

Multiplying on the left by $\Phi^*_\nu(\mathbf{r}|\mathbf{R})$ and integrating out the electronic degrees of freedom one gets

$$\sum_\mu \mathcal{H}_{\nu\mu}(\mathbf{R},\mathbf{P})\,\chi_{\alpha\mu}(\mathbf{R}) = E_\alpha\,\chi_{\alpha\nu}(\mathbf{R})$$

Beyond the Adiabatic Approximation

$$\mathcal{H}_{\nu\mu}(\mathbf{R},\mathbf{P}) = \left[T_I(\mathbf{P})+E_\mu(\mathbf{R})\right]\delta_{\nu\mu} + \overbrace{\sum_I \frac{-\hbar^2}{2M_I}\langle\Phi_\nu(\mathbf{R})|\nabla^2_{R_I}\Phi_\mu(\mathbf{R})\rangle}^{\mathcal{A}_{\nu\mu}}$$

$$+ \underbrace{\sum_I \frac{-\hbar^2}{M_I}\langle\Phi_\nu(\mathbf{R})|\nabla_{R_I}\Phi_\mu(\mathbf{R})\rangle\nabla_{R_I}}_{\mathcal{B}_{\nu\mu}}$$

$\mathcal{C}_{\nu\mu} = \mathcal{A}_{\nu\mu} + \mathcal{B}_{\nu\mu}$ are the terms that couple different PES

diagonal terms are small or vanish

$$\mathcal{A}_{\mu\mu} \approx \frac{m_e}{M_I}\langle\Phi_\mu|T_e|\Phi_\mu\rangle, \quad \mathcal{B}_{\mu\mu} = 0$$

and can be included in the PES $E_\mu \longrightarrow E_\mu + \mathcal{A}_{\mu\mu}$

Beyond the Adiabatic Approximation

$$\mathcal{A}_{\nu\mu}$$

$$\mathcal{H}_{\nu\mu}(\mathbf{R},\mathbf{P}) = [T_I(\mathbf{P}) + E_\mu(\mathbf{R})]\,\delta_{\nu\mu} + \sum_I \frac{-\hbar^2}{2M_I} \langle \Phi_\nu(\mathbf{R}) | \nabla^2_{R_I} \Phi_\mu(\mathbf{R}) \rangle$$

$$+ \sum_I \frac{-\hbar^2}{M_I} \langle \Phi_\nu(\mathbf{R}) | \nabla_{R_I} \Phi_\mu(\mathbf{R}) \rangle \nabla_{R_I}$$

$$\mathcal{B}_{\nu\mu}$$

$\mathcal{C}_{\nu\mu} = \mathcal{A}_{\nu\mu} + \mathcal{B}_{\nu\mu}$ are the terms that couple different PES

If $\mathcal{C}_{\nu\mu} \to 0$ different PES are decoupled and the motion is adiabatic with solutions

$$\Psi_{\alpha\mu}(\mathbf{r},\mathbf{R}) = \chi^{(0)}_{\alpha\mu}(\mathbf{R})\Phi_\mu(\mathbf{r}|\mathbf{R})$$

with $[T_I + E_\mu(\mathbf{R})]\ \chi^{(0)}_{\alpha\mu}(\mathbf{R}) = E_{\alpha\mu}\ \chi^{(0)}_{\alpha\mu}(\mathbf{R})$

Beyond the Adiabatic Approximation

$$\mathcal{H}_{\nu\mu}(\mathbf{R},\mathbf{P}) = [T_I(\mathbf{P})+E_\mu(\mathbf{R})]\,\delta_{\nu\mu} + \overbrace{\sum_I \frac{-\hbar^2}{2M_I}\langle\Phi_\nu(\mathbf{R})|\nabla^2_{R_I}\Phi_\mu(\mathbf{R})\rangle}^{\mathcal{A}_{\nu\mu}}$$

$$+ \underbrace{\sum_I \frac{-\hbar^2}{M_I}\langle\Phi_\nu(\mathbf{R})|\nabla_{R_I}\Phi_\mu(\mathbf{R})\rangle\nabla_{R_I}}_{\mathcal{B}_{\nu\mu}}$$

$\mathcal{C}_{\nu\mu} = \mathcal{A}_{\nu\mu} + \mathcal{B}_{\nu\mu}$ are the terms that couple different PES

If $\mathcal{C}_{\nu\mu} \neq 0$ different PES are coupled and these terms (electron-phonon interaction) drive non-adiabatic effects

- electrical resistivity
- polarons
- Cooper pairs
- ...

Beyond the Adiabatic Approximation

If $\mathcal{C}_{\nu\mu} \neq 0$, $\chi^{(0)}_{\alpha\mu}(\mathbf{R})$ have corrections that to first order are

$$\delta\chi_{\alpha\mu} = \sum_{\beta\nu} \frac{|\chi^{(0)}_{\beta\nu}\rangle\langle\chi^{(0)}_{\beta\nu}|}{E_{\alpha\mu} - E_{\beta\nu}} \mathrm{C}_{\nu\mu}|\chi^{(0)}_{\alpha\mu}\rangle$$

let's estimate the impact of $\mathcal{B}_{\mu\nu}$

(for $\mathcal{A}_{\mu\nu}$ similar arguments apply)

Beyond the Adiabatic Approximation

$$\langle \chi_\mu^{(0)} | \mathcal{B}_{\mu\nu} | \chi_\nu^{(0)} \rangle = \sum_I \langle \Phi_\mu | -i\hbar \nabla_{R_I} | \Phi_\nu \rangle \, \langle \chi_\mu^{(0)} | \underbrace{\frac{-i\hbar}{M_I} \nabla_{R_I}}_{v_I} | \chi_\nu^{(0)} \rangle$$

$$|\mathcal{B}_{\mu\nu}| \approx \hbar \overline{v} \, |\langle \Phi_\mu | \nabla_R | \Phi_\nu \rangle|$$

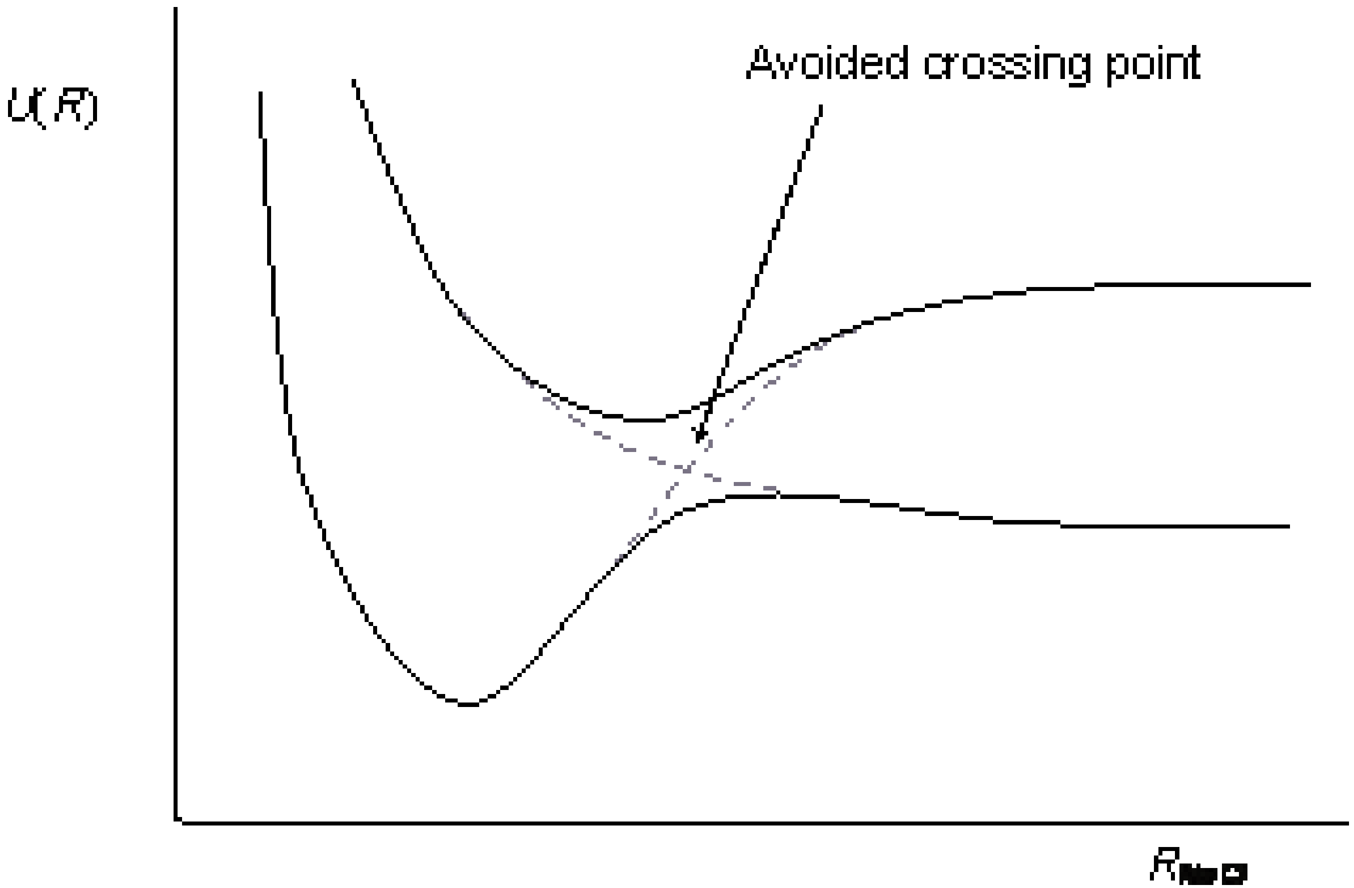
with $\overline{v} \approx \omega u_0$ where u_0 is the vibrational displacement

$\nabla_R \Phi_\nu = \delta \Phi_\nu$ is the wfc change due to ion displacement

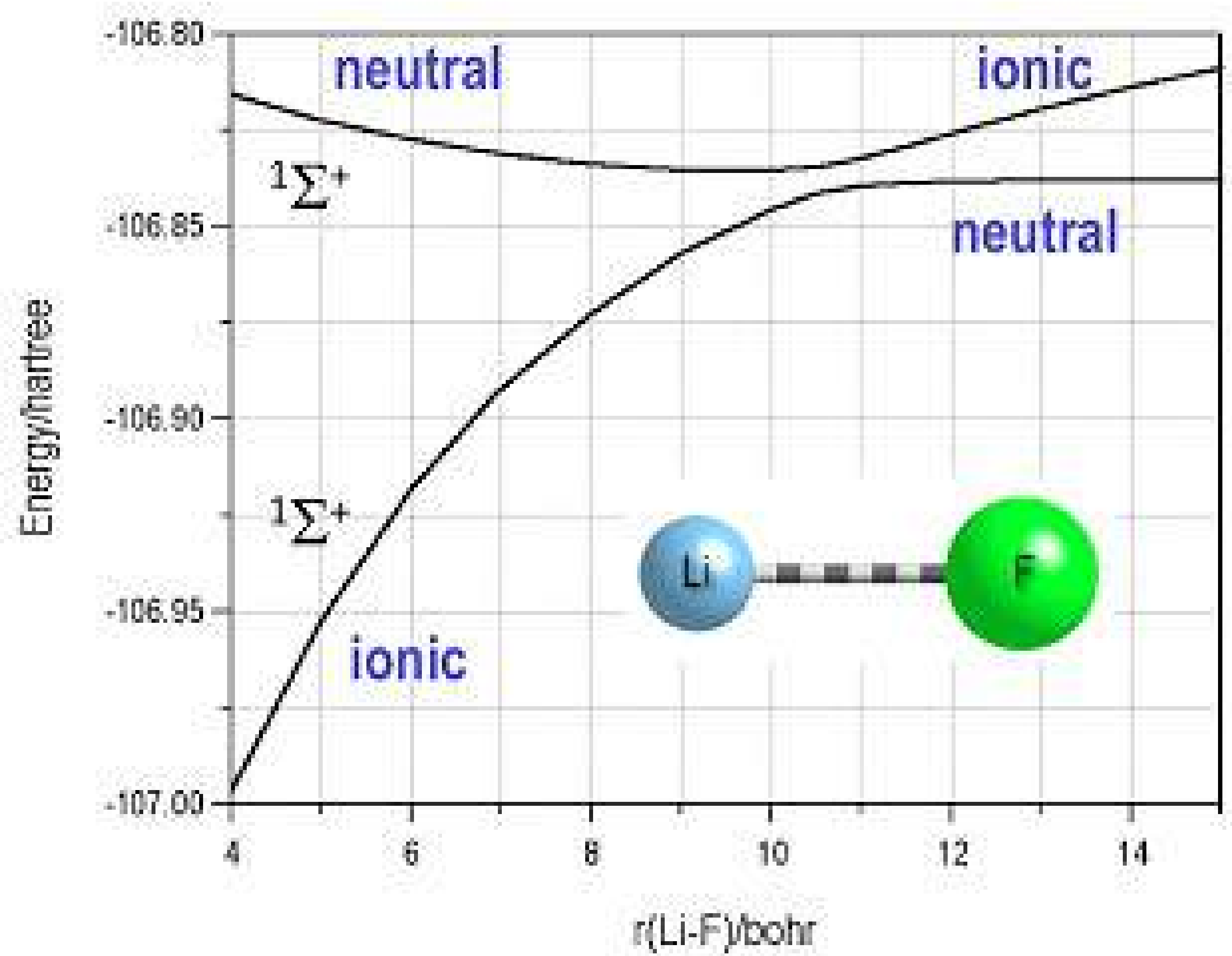
let call u_1 a displacement such that the change is of order 1

$u_1 \; |\langle \Phi_\mu | \nabla_R | \Phi_\nu \rangle| \; \approx \; 1$ and typically $u_0 \; << \; u_1$

$$\left| \frac{\mathcal{C}_{\mu\nu}}{\Delta E} \right| << 1 \quad \Longleftrightarrow \quad \left| \frac{\hbar \omega}{\Delta E_{\mu\nu}} \frac{u_0}{u_1} \right| << 1$$



$$\left| \frac{\hbar\omega}{\Delta E_{\mu\nu}} \frac{u_0}{u_1} \right| << 1$$



-106.80
-106.85
-106.90
-106.95
-107.00
Energy/hartree
neutral
ionic
$^1\Sigma^+$
$^1\Sigma^+$
neutral
ionic
Li
F
4
6
8
10
12
14
r(Li-F)/bohr

THE END