

CHM 673

Lecture 2: Born-Oppenheimer (BO) approximation

Suggested reading:

Review of basic QM:

<http://vergil.chemistry.gatech.edu/notes/quantrev/quantrev.pdf>

BO approximation:

<http://vergil.chemistry.gatech.edu/notes/bo/bo.pdf>

chapter 3.1 from Jensen; chapter 2.1 from S&O.

Homework (due next class):

- Search online resources and scientific literature for examples (model systems or real applications in chemistry, biology, materials) of BO failure
- Be prepared to briefly explain your favorite example in the class

Numerical solution of SE: art of approximations

Approximations:

- *Born-Oppenheimer approximation*
- Representation of wave function in a basis set
- Approximate treatment of electron correlation (interactions between electrons)

Molecular Hamiltonian in atomic units

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

$$\hat{H}(\mathbf{r}, \mathbf{R}) = \hat{T}_N(\mathbf{R}) + \hat{T}_e(\mathbf{r}) + \hat{V}_{NN}(\mathbf{R}) + \hat{V}_{eN}(\mathbf{r}, \mathbf{R}) + \hat{V}_{ee}(\mathbf{r})$$

$$\hat{T}_N = -\sum_i \frac{1}{2M_A} \nabla_A^2$$

kinetic energy of nuclei

$$\hat{T}_e = -\frac{1}{2} \sum_i \nabla_i^2$$

kinetic energy of electrons

$$\hat{V}_{NN} = \sum_{A>B} \frac{Z_A Z_B}{R_{AB}}$$

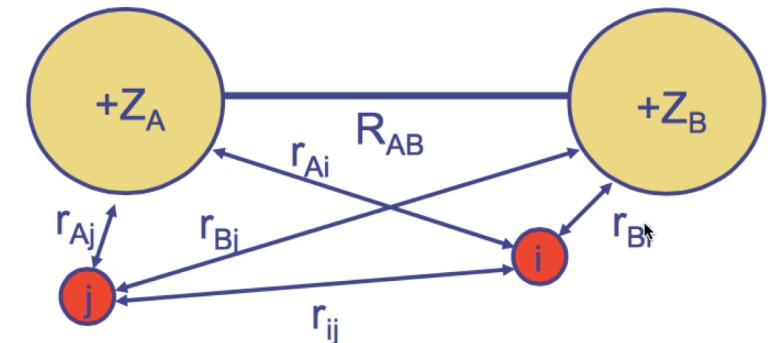
potential energy of nuclei

$$\hat{V}_{eN} = -\sum_{A,i} \frac{Z_A}{r_{Ai}}$$

potential energy of interactions of nuclei and electrons

$$\hat{V}_{ee} = \sum_{i>j} \frac{1}{r_{ij}}$$

potential energy of electrons



\mathbf{r} – electronic coordinates

\mathbf{R} - nuclear coordinates

This is exact non-relativistic Hamiltonian in a field-free space.

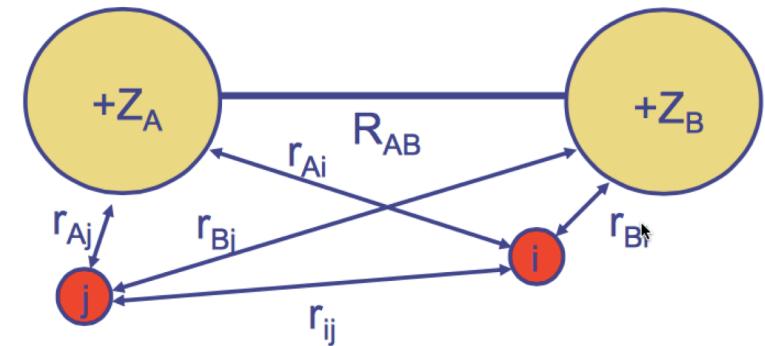
This Hamiltonian does not describe relativistic effects & spin-orbit interactions.

Indeed, it is not aware of electronic spins at all!

Molecular Hamiltonian in atomic units

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

$$\hat{H}(\mathbf{r}, \mathbf{R}) = \hat{T}_N(\mathbf{R}) + \hat{T}_e(\mathbf{r}) + \hat{V}_{NN}(\mathbf{R}) + \hat{V}_{eN}(\mathbf{r}, \mathbf{R}) + \hat{V}_{ee}(\mathbf{r})$$



We want to simplify the SE by separating it into two parts: one containing nuclear coordinates and one containing electronic coordinates, i.e.

$$\Psi(\mathbf{r}, \mathbf{R}) = \Psi_e(\mathbf{r}) \Psi_N(\mathbf{R})$$

\mathbf{r} – electronic coordinates

\mathbf{R} - nuclear coordinates

Separation of variables

We know that if a Hamiltonian is separable into two or more terms, then the total eigenfunctions are products of the individual eigenfunctions of the separated Hamiltonian terms, and the total eigenvalues are sums of individual eigenvalues of the separated Hamiltonian terms:

If $\hat{H}(q_1, q_2) = \hat{H}_1(q_1) + \hat{H}_2(q_2)$ with

$$\hat{H}(q_1, q_2)\Psi(q_1, q_2) = E\Psi(q_1, q_2)$$

$$\hat{H}_1(q_1)\Psi_1(q_1) = E_1\Psi_1(q_1), \quad \hat{H}_2(q_2)\Psi_2(q_2) = E_2\Psi_2(q_2)$$

Then the total wavefunction can be represented as a product $\Psi(q_1, q_2) = \Psi_1(q_1)\Psi_2(q_2)$

Proof: $\hat{H}(q_1, q_2)\Psi(q_1, q_2) = (\hat{H}_1(q_1) + \hat{H}_2(q_2))\Psi(q_1, q_2) = (\hat{H}_1(q_1) + \hat{H}_2(q_2))\Psi_1(q_1)\Psi_2(q_2)$

$$= \boxed{\hat{H}_1(q_1)\Psi_1(q_1)}\Psi_2(q_2) + \boxed{\hat{H}_2(q_2)\Psi_1(q_1)}\Psi_2(q_2)$$
$$= \boxed{E_1\Psi_1(q_1)}\Psi_2(q_2) + \boxed{E_2\Psi_1(q_1)}\Psi_2(q_2)$$
$$= (E_1 + E_2)\Psi_1(q_1)\Psi_2(q_2) = E\Psi(q_1, q_2)$$

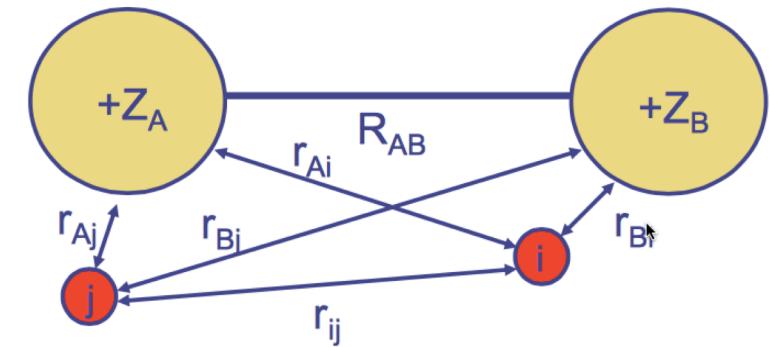
Molecular Hamiltonian in atomic units

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

$$\hat{H}(\mathbf{r}, \mathbf{R}) = \hat{T}_N(\mathbf{R}) + \hat{T}_e(\mathbf{r}) + \hat{V}_{NN}(\mathbf{R}) + \hat{V}_{eN}(\mathbf{r}, \mathbf{R}) + \hat{V}_{ee}(\mathbf{r})$$

However, motions of electrons
and nuclei is coupled!

$$\hat{V}_{eN} = -\sum_{A,i} \frac{Z_A}{r_{Ai}}$$



\mathbf{r} – electronic coordinates

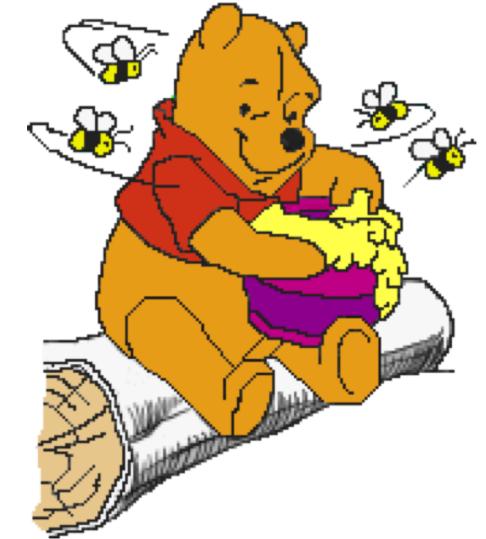
\mathbf{R} - nuclear coordinates

The Born-Oppenheimer approximation assumes
that this separation is approximately correct

Born-Oppenheimer approximation

The Born-Oppenheimer approximation:
The separation into nuclear and electronic
coordinates is approximately correct

The nuclei are much more massive than the electrons →
the nuclei are nearly fixed with respect to electron motion →
electrons move in the field of nearly fixed nuclei



Kinetic energy of nuclei is much smaller than kinetic energy of electrons:

$$T_N \ll T_e \quad (\text{by a factor of } M_A/m_e) \rightarrow T_N = 0$$

assume that dependence on nuclear coordinates R is **parametric**:

$$\Psi(\mathbf{r}, \mathbf{R}) = \Phi_e(\mathbf{r}, \{\mathbf{R}\}) \Phi_N(\mathbf{R})$$

↑
{ parametric dependence }

Clamped-nuclei Hamiltonian

Hamiltonian for fixed nuclear coordinates:

$$\hat{H} = \cancel{\hat{T}_N(\mathbf{R})} + \hat{T}_e(\mathbf{r}) + \hat{V}_{NN}(\mathbf{R}) + \hat{V}_{eN}(\mathbf{r}, \mathbf{R}) + \hat{V}_{ee}(\mathbf{r})$$

$$\hat{H}_{el} = \hat{T}_e(\mathbf{r}) + \boxed{\hat{V}_{NN}(\{\mathbf{R}\})} + \boxed{\hat{V}_{eN}(\mathbf{r}; \{\mathbf{R}\})} + \hat{V}_{ee}(\mathbf{r})$$

constant parametrically depends on nuclear coordinates R

$$\hat{H}_{el}\Phi_e(\mathbf{r}; \{\mathbf{R}\}) = U(\mathbf{R})\Phi_e(\mathbf{r}; \{\mathbf{R}\}) \quad \text{"clamped-nuclei" SE; this is our "first principle"}$$

$\hat{V}_{NN}(\{\mathbf{R}\})$ is a constant term; it shifts eigenvalues by some constant amount. We can leave it out of SE:

$$\hat{H}_e = \hat{T}_e(\mathbf{r}) + \hat{V}_{eN}(\mathbf{r}; \{\mathbf{R}\}) + \hat{V}_{ee}(\mathbf{r})$$

H_e - electronic Hamiltonian
 E_e – electronic energy

$$\hat{H}_e\Phi_e(\mathbf{r}; \{\mathbf{R}\}) = E_e(\mathbf{R})\Phi_e(\mathbf{r}; \{\mathbf{R}\})$$

Potential energy function

Solve "clamped-nuclei" SE for a given value of $\mathbf{R}=\mathbf{R}_a$:

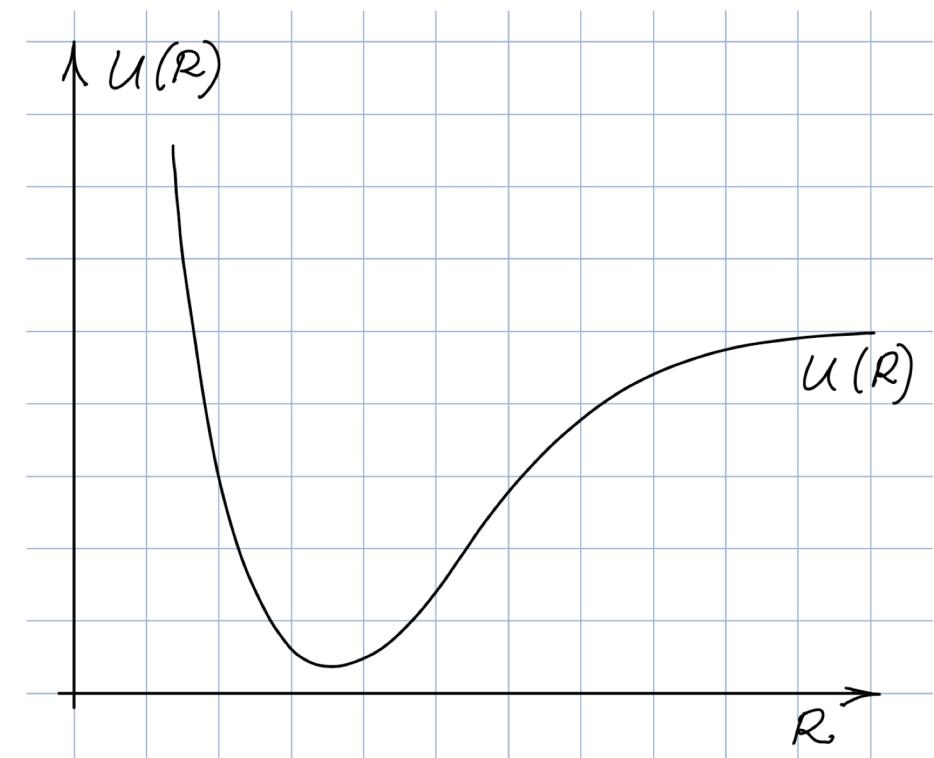
$$\hat{H}_{el}\Phi_e(\mathbf{r}; \{\mathbf{R}_a\}) = U(\mathbf{R}_a)\Phi_e(\mathbf{r}; \{\mathbf{R}_a\})$$

Repeat such calculations for different values of $\mathbf{R}_a \rightarrow$
obtain molecular potential energy function:

$$U(\mathbf{R}) = E_e(\mathbf{R}) + \hat{V}_{NN}(\mathbf{R}) =$$

$$E_e(\mathbf{R}) + \sum_{A>B}^{nuc} \frac{Z_A Z_B}{R_{AB}}$$

$U(\mathbf{R})$ – potential energy function
that governs nuclear motion
(vibrational levels, dissociation,
etc)



Nuclear repulsion energy

$$\hat{V}_{NN}(\mathbf{R}) = \sum_{A>B}^{nuc} \frac{Z_A Z_B}{R_{AB}}$$

nuclear repulsion energy

- Nuclear repulsion energy is sensitive to (and depends only on) molecular geometry
- It is a great diagnostic to ensure that two molecular geometries are identical (should be able to compare to 10^{-4} Hartree or better)

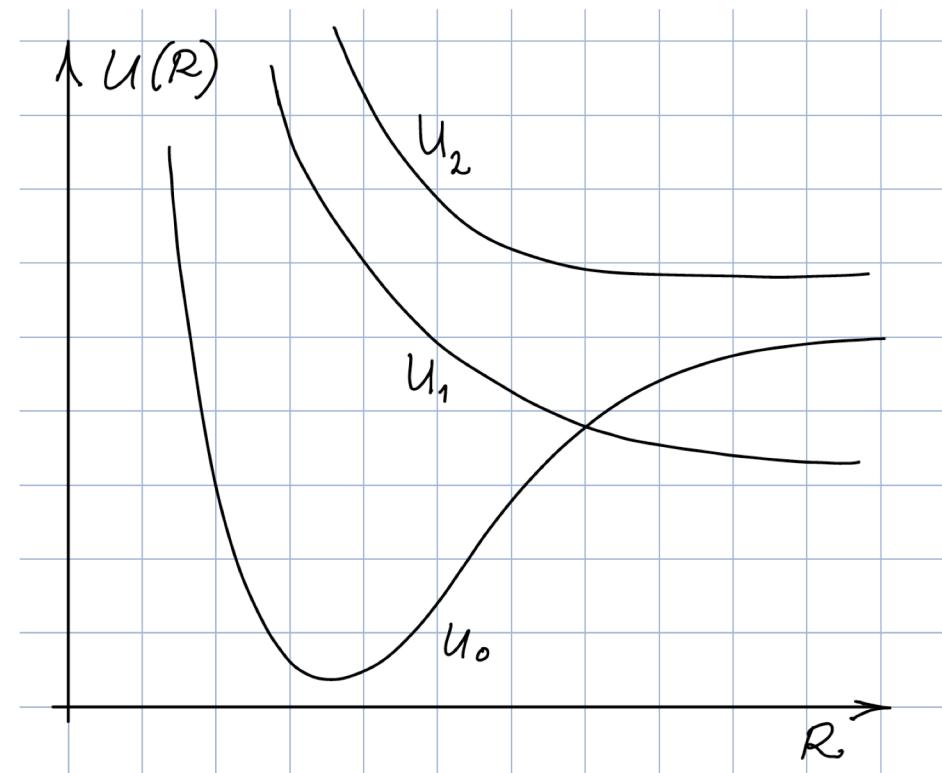
Potential energy surfaces

$$\hat{H}_e \Phi_e (\mathbf{r}; \{\mathbf{R}\}) = E_e (\mathbf{R}) \Phi_e (\mathbf{r}; \{\mathbf{R}\}) \quad \text{electronic SE}$$

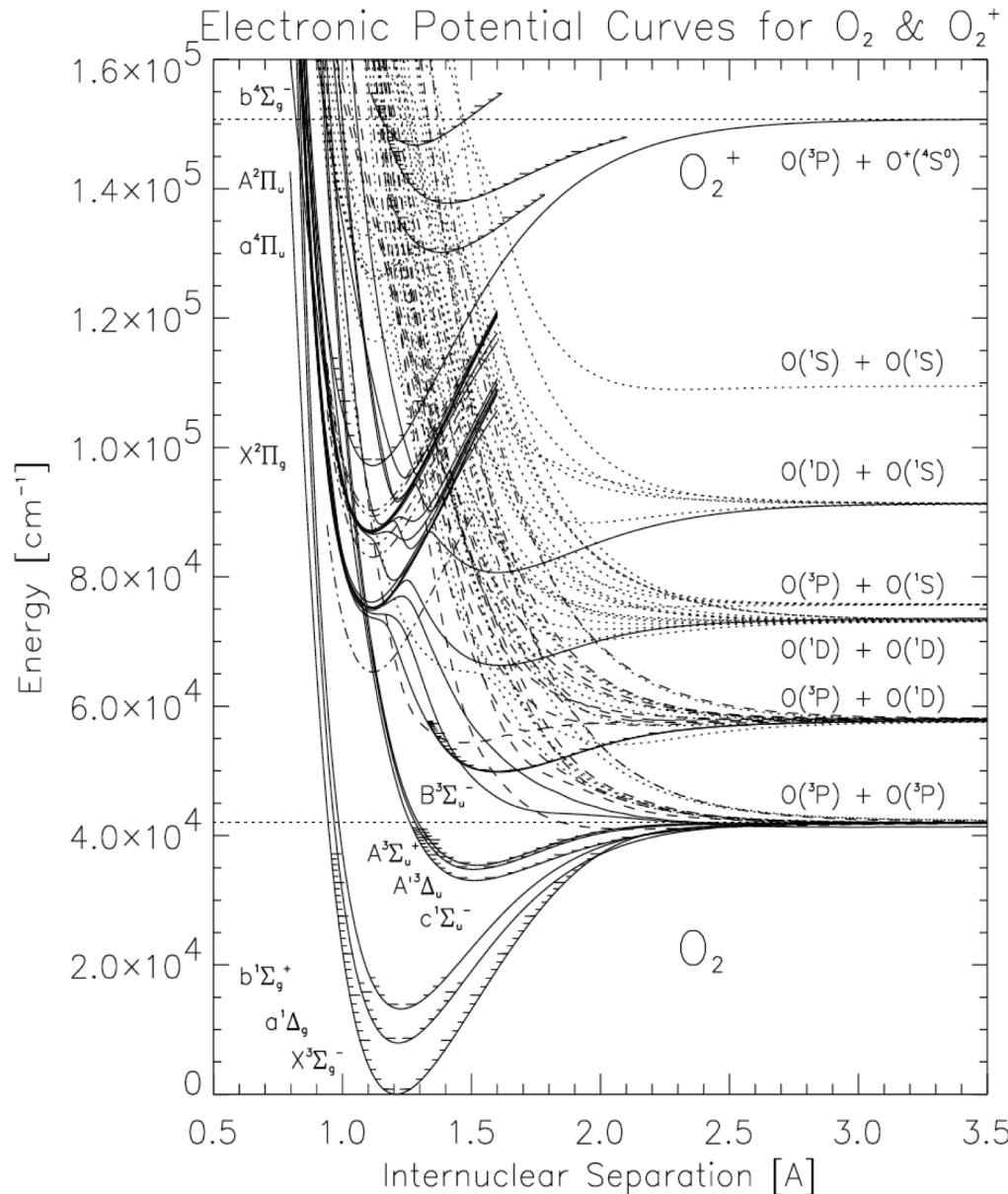
$$\hat{H}_e \Phi_{e,k} (\mathbf{r}; \{\mathbf{R}\}) = E_{e,k} (\mathbf{R}) \Phi_{e,k} (\mathbf{r}; \{\mathbf{R}\}) \quad \text{electronic SE might have infinite number of solutions}$$

$$U_k(\mathbf{R}) = E_{e,k} (\mathbf{R}) + \sum_{A>B}^{nuc} \frac{Z_A Z_B}{R_{AB}}$$

At each \mathbf{R} , the lowest $U_k(\mathbf{R})$ –
the ground state,
higher solutions – excited states



Potential energy surfaces



Calculated potential energy curves of O_2 molecule.

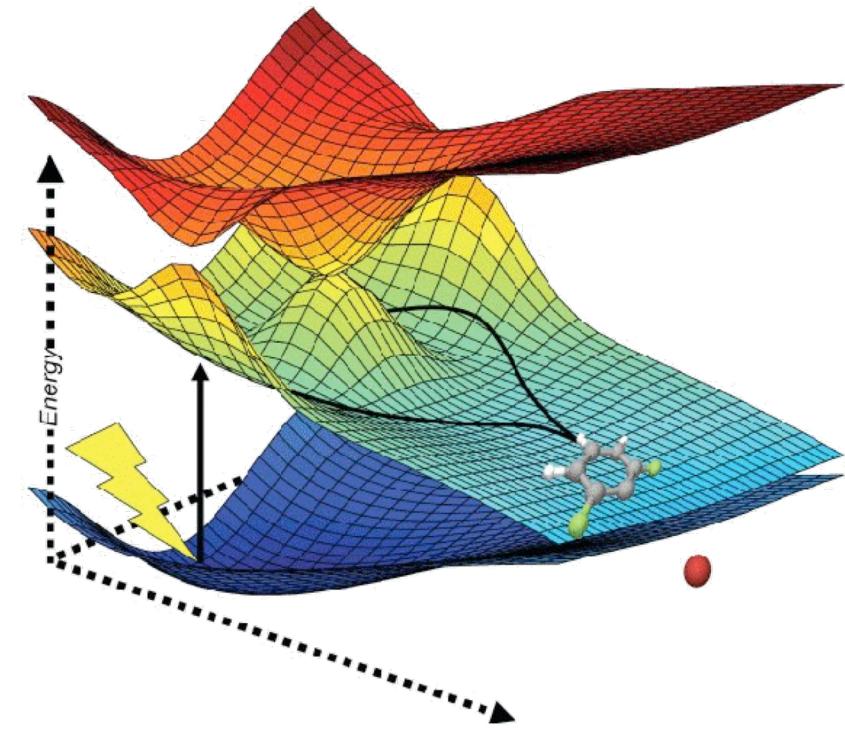
Reproduced from Morill et al., *Review of electronic structure of molecular oxygen*.

Potential energy surfaces: polyatomic molecules

$$U_k(\mathbf{R}) = E_{e,k}(\mathbf{R}) + \sum_{A>B}^{nuc} \frac{Z_A Z_B}{R_{AB}}$$

$U_k(\mathbf{R})$ are potential energy surfaces for nuclei, imposed by electrons

- Potential energy surface for polyatomic molecule is generally very complicated
- Different solutions of electronic SE give different (excited state) surfaces
- A molecule might undergo electronic transitions (electronic excitations) upon interactions with light, electromagnetic field, mechanical stress, high temperature, etc.



\mathbf{R} is $(3N-6)$ -dimensional for non-linear N-atomic molecules

Is Born-Oppenheimer always valid?

Let's express solutions of the full problem in terms of the solutions of the electronic problem:

$$\Psi_k(\mathbf{r}, \mathbf{R}) = \sum_j \Phi_j(\mathbf{r}, \{\mathbf{R}\}) \xi_j^k(\mathbf{R})$$

exact w.f.
electronic w.f., ~basis
nuclear functions
Expansion coefficients that we want to determine

We want to derive equation to define $\xi_j^k(\mathbf{R})$. Total SE:

$$(\hat{H}_{el} + \hat{T}_N) \sum_j \Phi_j(\mathbf{r}, \{\mathbf{R}\}) \xi_j^k(\mathbf{R}) = E_k \sum_j \Phi_j(\mathbf{r}, \{\mathbf{R}\}) \xi_j^k(\mathbf{R})$$

Multiply by Φ_m on the left and integrate over electronic coordinates:

$$\sum_j \langle \Phi_m | \hat{H}_{el} | \Phi_j \rangle \xi_j^k + \sum_j \langle \Phi_m | \hat{T}_N | \Phi_j \xi_j^k \rangle = E_k \sum_j \langle \Phi_m | \Phi_j \rangle \xi_j^k$$

electronic w.f. $\{\Phi_j\}$ are orthonormal!

Is Born-Oppenheimer always valid?

$$\sum_j \langle \Phi_m | \hat{H}_{el} | \Phi_j \rangle \xi_j^k + \sum_j \langle \Phi_m | \hat{T}_N | \Phi_j \xi_j^k \rangle = E_k \sum_j \langle \Phi_m | \Phi_j \rangle \xi_j^k$$

electronic w.f. $\{\Phi_j\}$
are orthonormal!

$$\sum_j \langle \Phi_m | \hat{H}_{el} | \Phi_j \rangle \xi_j^k = \sum_j \langle \Phi_m | U_j \Phi_j \rangle \xi_j^k = U_m \xi_m^k$$

$$\begin{aligned} \sum_j \langle \Phi_m | \hat{T}_N | \Phi_j \xi_j^k \rangle &= - \sum_A \frac{1}{2M_A} \sum_j \langle \Phi_m | \nabla_A \nabla_A | \Phi_j \xi_j^k \rangle \\ &= - \sum_A \frac{1}{2M_A} \left(\sum_j \langle \Phi_m | \nabla_A^2 | \Phi_j \rangle \xi_j^k + 2 \sum_j \langle \Phi_m | \nabla_A | \Phi_j \rangle \nabla_A \xi_j^k + \nabla_A^2 \xi_m^k \right) \end{aligned}$$

$$(U_m(\mathbf{R}) + \hat{T}_N) \xi_m^k - \sum_A \frac{1}{2M_A} \left(\sum_j \langle \Phi_m | \nabla_A^2 | \Phi_j \rangle \xi_j^k + 2 \sum_j \langle \Phi_m | \nabla_A | \Phi_j \rangle \nabla_A \xi_j^k \right) = E_k \xi_m^k$$

coupling

Is Born-Oppenheimer always valid?

$$(U_m(\mathbf{R}) + \hat{T}_N)\xi_m^k - \underbrace{\sum_A \frac{1}{2M_A} \left(\sum_j \langle \Phi_m | \nabla_A^2 | \Phi_j \rangle \xi_j^k + 2 \sum_j \langle \Phi_m | \nabla_A | \Phi_j \rangle \nabla_A \xi_j^k \right)}_{\text{coupling}} = E_k \xi_m^k$$

If coupling is 0, $(U_m(\mathbf{R}) + \hat{T}_N)\xi_m^k = E_k \xi_m^k$ $\Psi_k(\mathbf{r}, \mathbf{R}) = \Phi_m(\mathbf{r}, \{\mathbf{R}\}) \xi_m^k(\mathbf{R})$

- Nuclei move in potential $U_m(\mathbf{R})$ (mean field potential of electrons or electron cloud)
- For each $U_m(\mathbf{R})$ exist nuclear eigenstates; eigenstates for different $U_m(\mathbf{R})$ are independent
- Nuclei will stay on $U_m(\mathbf{R})$ forever, then cannot jump to other $U_k(\mathbf{R})$ upon nuclear motion.
- This is adiabatic (BO) approximation.

Coupling terms

$$(U_m(\mathbf{R}) + \hat{T}_N)\xi_m^k - \underbrace{\sum_A \frac{1}{2M_A} \left(\sum_j \langle \Phi_m | \nabla_A^2 | \Phi_j \rangle \xi_j^k + 2 \sum_j \langle \Phi_m | \nabla_A | \Phi_j \rangle \nabla_A \xi_j^k \right)}_{\text{coupling}} = E_k \xi_m^k$$

Introduce

$$\hat{T}'_{mm'} = - \sum_A \frac{1}{M_A} \langle \Phi_m | \nabla_A | \Phi_{m'} \rangle \nabla_A$$

$$\hat{T}''_{mm'} = - \sum_A \frac{1}{2M_A} \langle \Phi_m | \nabla_A^2 | \Phi_{m'} \rangle$$

and rewrite:

$$(U_{mm}(\mathbf{R}) + \hat{T}_N + \underbrace{\hat{T}'_{mm} + \hat{T}''_{mm}}_{\text{Diagonal coupling terms: small correction to energy}} - E_k) \xi_m^k = - \sum_{m \neq m'} (\hat{T}'_{mm'} + \hat{T}''_{mm'}) \xi_{m'}^k$$

Diagonal coupling terms:
small correction to energy

Off-diagonal coupling terms:
mixing (coupling) nuclear dynamics on
different electronic states

Diagonal coupling terms

$$(U_{mm}(\mathbf{R}) + \underbrace{\hat{T}_N + \hat{T}'_{mm} + \hat{T}''_{mm}}_{\text{Diagonal coupling terms}} - E_k) \xi_m^k = - \sum_{m \neq m'} (\hat{T}'_{mm'} + \hat{T}''_{mm'}) \xi_{m'}^k$$

Diagonal coupling terms

Off-diagonal coupling terms

diagonal terms provide small correction to energy

$$\hat{T}'_{mm} = - \sum_A \frac{1}{M_A} \langle \Phi_m | \nabla_A | \Phi_m \rangle \nabla_A = 0 \quad \text{if } \Phi_m \text{ can be made real}$$

$$\hat{T}''_{mm} = - \sum_A \frac{1}{2M_A} \langle \Phi_m | \nabla_A^2 | \Phi_m \rangle - \text{diagonal BO correction ("adiabatic correction")}$$

$$-\frac{1}{2M_A} \langle \Phi_m | \nabla_A^2 | \Phi_m \rangle = \frac{1}{2M_A} \langle \nabla_A \Phi_m | \nabla_A \Phi_m \rangle \sim \frac{1}{2M_A} \langle \nabla_i \Phi_m | \nabla_i \Phi_m \rangle = \frac{p_e^2}{2M_A} = \frac{m_e}{M_A} E_e$$

derivatives over nuclear and electronic
coordinates are of the same order

Off-diagonal coupling terms

$$(U_{mm}(\mathbf{R}) + \underbrace{\hat{T}_N + \hat{T}'_{mm} + \hat{T}''_{mm}}_{\text{Diagonal coupling terms}} - E_k) \xi_m^k = - \sum_{m \neq m'} (\hat{T}'_{mm'} + \hat{T}''_{mm'}) \xi_{m'}^k$$

Off-diagonal coupling terms

Off-diagonal terms couple nuclear dynamics on different electronic states

$\hat{T}''_{mm'} \xi_{m'}^k = - \sum_A \frac{1}{2M_A} \langle \Phi_m | \nabla_A^2 | \Phi_{m'} \rangle \xi_{m'}^k$, provides some additional potential for nuclei. Importance of this term depends on the ratio of integral $\langle \Phi_m | \nabla_A^2 | \Phi_{m'} \rangle$ and potential U_m . Typically this term is neglected.

$\hat{T}'_{mm'} \xi_{m'}^k = - \sum_A \frac{1}{M_A} \langle \Phi_m | \nabla_A \Phi_{m'} \rangle \nabla_A \xi_{m'}^k$ - “derivative coupling”; can become large when nuclear velocity $\nabla_A \xi_{m'}^k$ is high

Two limits:

Slow nuclei – adiabatic limit, BO approximation

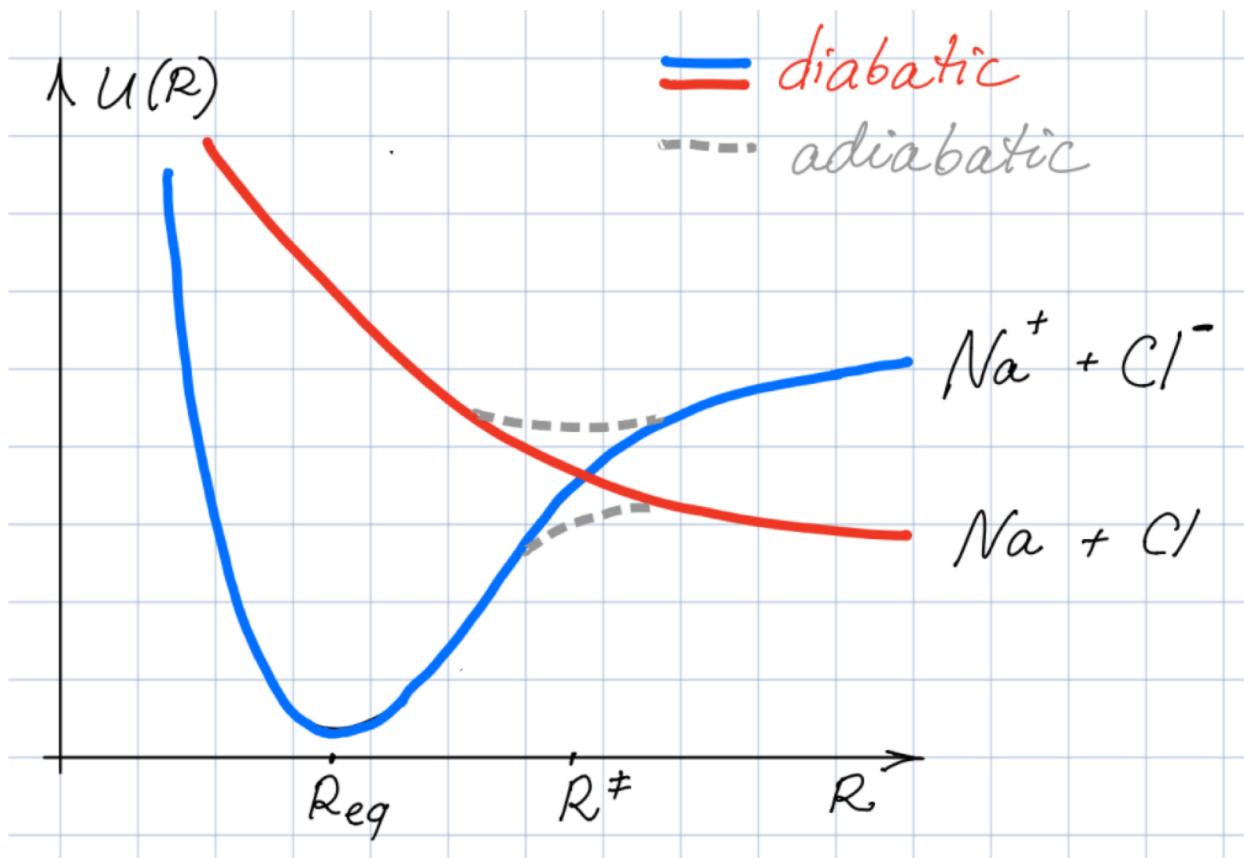
Fast nuclei – electrons cannot adjust to nuclei – non-adiabatic “hops” are possible

Non-adiabatic coupling

Off-diagonal terms couple nuclear dynamics on different electronic states

Slow nuclei – adiabatic limit, BO approximation

Fast nuclei – electrons cannot adjust to nuclei – non-adiabatic “hops” are possible



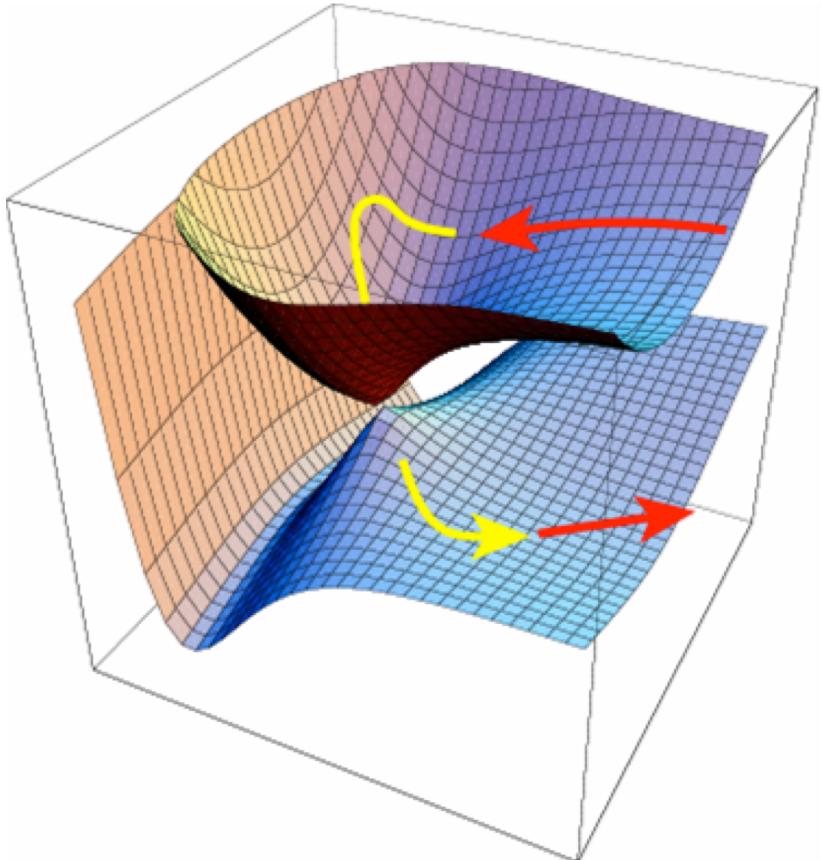
NaCl

- Ionic at equilibrium (R_{eq}), but dissociates into neutral atoms
- Non-adiabatic (derivative) coupling is large near crossing of two electronic states ($R^\#$), because interaction between electronic states changes quickly with nuclear motion ->
- BO approximation fails near $R^\#$
- Electronic structure calculations will produce adiabatic (grey) curves; but those curves do not truly reproduce nuclear dynamics near $R^\#$

Breaking of BO approximation

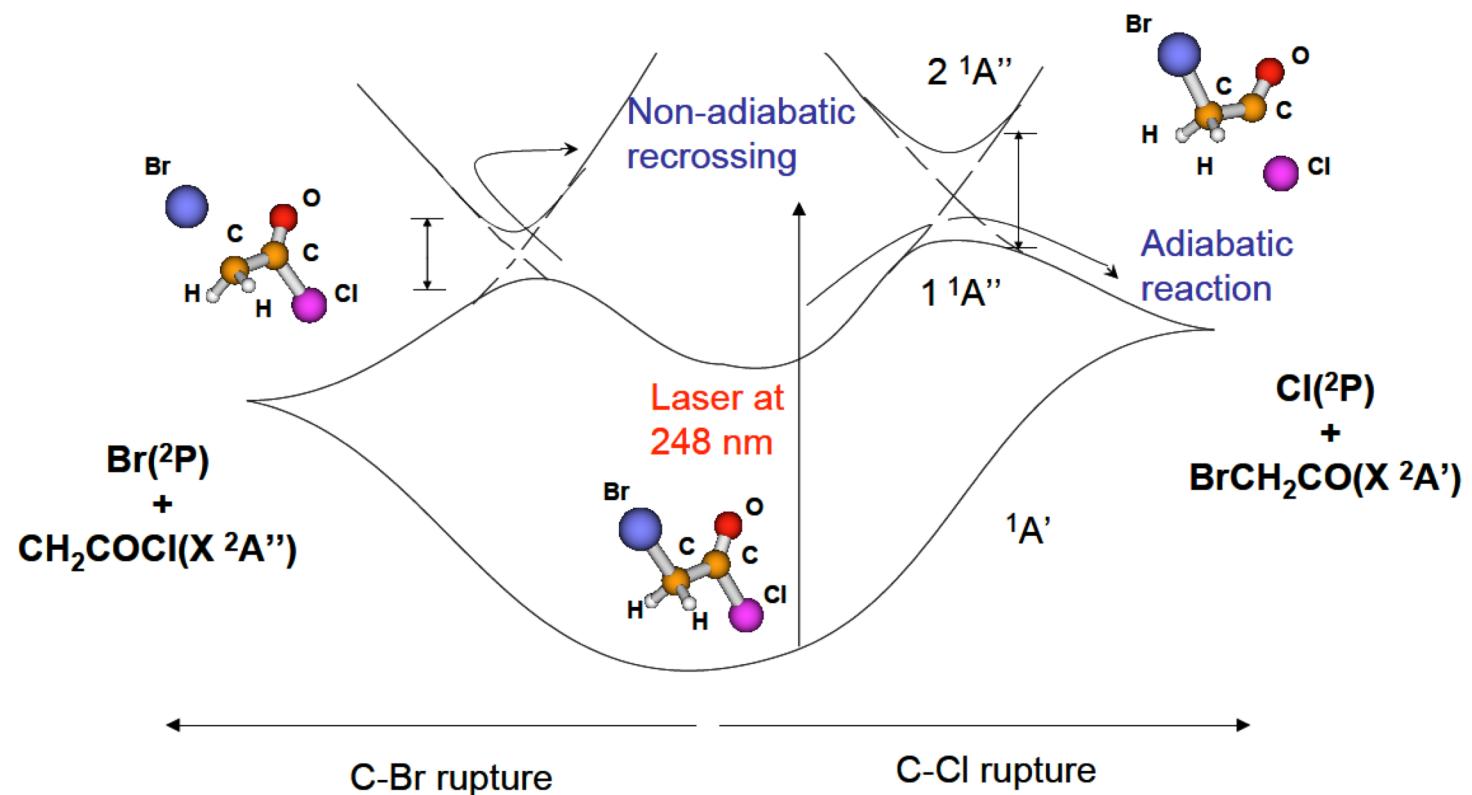
$$(U_m(R) + \hat{T}_N)\xi_m^k - \sum_A \frac{1}{2M_A} \left(\sum_j \langle \Phi_m | \nabla_A^2 | \Phi_j \rangle \xi_j^k + 2 \sum_j \langle \Phi_m | \nabla_A | \Phi_j \rangle \nabla_A \xi_j^k \right) = E_k \xi_m^k$$

coupling derivative coupling term



The derivative coupling becomes large when PESs approach each other. The probability of non-adiabatic transitions are significant around so-called *conical intersections*.

Example: photodissociation of $\text{Br}(\text{CH}_2)_n\text{COCl}$



Two competing channels found in the photodissociation of $\text{Br}(\text{CH}_2)_n\text{COCl}$. Despite the higher adiabatic barrier in the C-Cl dissociation channel (0.4 eV difference), the actual branching ratio 1:0.4 is in favor of this reaction.

C-Br dissociation is strongly non-adiabatic → the molecule fails to switch its initial bonding electronic configuration to the antibonding one of the fragmentation products. As a result, the molecule rebounces from the potential wall and recrosses back to the region of reagents.

Conversely, the C-Cl bond cleavage does successfully proceed via the adiabatic route.