# Derivation of the Born-Oppenheimer approximation

Exact (non-relativistic) Hamiltonian

$$H = T_{\mathrm{n}} + T_{\mathrm{e}} + V(\mathbf{r}, \mathbf{R})$$

with

$$T_{\mathrm{e}} = -\sum_i \frac{\hbar^2}{2m}\nabla_i^2 \qquad \text{and} \qquad T_{\mathrm{n}} = -\sum_A \frac{\hbar^2}{2M_A}\nabla_A^2$$

$$V(\mathbf{r}, \mathbf{R}) = \sum_{A>B} \frac{Z_A Z_B e^2}{|\mathbf{R}_A - \mathbf{R}_B|} - \sum_{i,A} \frac{Z_A e^2}{|\mathbf{r}_i - \mathbf{R}_A|} + \sum_{i>j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$$

Electronic Hamiltonian (clamped nuclei)

$$H_{\mathrm{e}} = T_{\mathrm{e}} + V(\mathbf{r}, \mathbf{R})$$

The total Schrödinger equation reads

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

Expand the total wave function

$$\Psi(\mathbf{r},\mathbf{R}) = \sum_k \phi_k(\mathbf{r};\mathbf{R})\chi_k(\mathbf{R})$$

in solutions $\phi_k(\mathbf{r};\mathbf{R})$ of the electronic Schrödinger equation

$$H_\mathrm{e}\,\phi_k(\mathbf{r};\mathbf{R}) = E_k(\mathbf{R})\,\phi_k(\mathbf{r};\mathbf{R})$$

and substitute it into the total Schrödinger equation.

Multiply by the function $\phi_{k'}(\mathbf{r};\mathbf{R})$ from the left and integrate over the electronic coordinates $\mathbf{r}$. The electronic Hamiltonian $H_\mathrm{e}$ is diagonal

$$\langle\phi_{k'}(\mathbf{r};\mathbf{R})|H_\mathrm{e}|\phi_k(\mathbf{r};\mathbf{R})\rangle_{(\mathbf{r})} = \delta_{k'k}E_k(\mathbf{R})$$

and the electronic wave functions are orthogonal

$$\langle\,\phi_{k'}(\mathbf{r};\mathbf{R})\,|\,\phi_k(\mathbf{r};\mathbf{R})\rangle_{(\mathbf{r})} = \delta_{k'k}$$

This yields a set of coupled eigenvalue equations for the nuclear wave functions

$$[\,T_{\mathsf{n}} + E_{k'}(\mathbf{R}) - E\,]\;\chi_{k'}(\mathbf{R}) = \sum_{k} [\,\mathbb{F}_{\mathsf{n}}]_{k'k}\;\chi_{k}(\mathbf{R})$$

Coupling between different electronic states $k', k$

$$[\,\mathbb{F}_{\mathsf{n}}]_{k'k}\,(\mathbf{R}) = \langle \phi_{k'}(\mathbf{r};\mathbf{R}) | T_{\mathsf{n}} |\, \phi_{k}(\mathbf{r};\mathbf{R}) \rangle_{(\mathbf{r})} - T_{\mathsf{n}}\,\delta_{k'k}$$

occurs through the nuclear kinetic energy operator $T_{\mathsf{n}}$.

When this coupling is neglected one obtains the Born-Oppenheimer nuclear Schrödinger equation for electronic state $k'$

$$[T_{\mathsf{n}} + E_{k'}(\mathbf{R})]\,\chi_{k'}(\mathbf{R}) = E\,\chi_{k'}(\mathbf{R})$$

The (non-adiabatic) coupling terms are

$$[\mathbb{F}\mathsf{n}]_{k'k}(\mathbf{R}) = -\sum_A \frac{\hbar^2}{2M_A}\Big[2\langle\phi_{k'}|\Big(\boldsymbol{\nabla}_A\phi_k\Big)\rangle_{(\mathbf{r})}\cdot\boldsymbol{\nabla}_A + \langle\phi_{k'}|\Big(\nabla_A^2\phi_k\Big)\rangle_{(\mathbf{r})}\Big]$$

They are small because of the large nuclear masses $M_A$ in the denominator.

In the first term one may write

$$\langle\phi_{k'}|\Big(\boldsymbol{\nabla}_A\phi_k\Big)\rangle_{(\mathbf{r})} = \frac{\langle\phi_{k'}|\Big[\boldsymbol{\nabla}_A, H_\mathsf{e}\Big]|\phi_k\rangle_{(\mathbf{r})}}{E_k(\mathbf{R}) - E_{k'}(\mathbf{R})}\,,$$

which shows that the coupling is small only when the electronic energies $E_k(\mathbf{R})$ and $E_{k'}(\mathbf{R})$ are well separated. This is normally the case, and the Born-Oppenheimer approximation holds.

For certain geometries $\mathbf{R}$ the energies $E_k(\mathbf{R})$ and $E_{k'}(\mathbf{R})$ may be equal: two (or more) electronic states are degenerate. The Born-Oppenheimer approximation breaks down.

# Breakdown of the Born-Oppenheimer approximation

Examples:

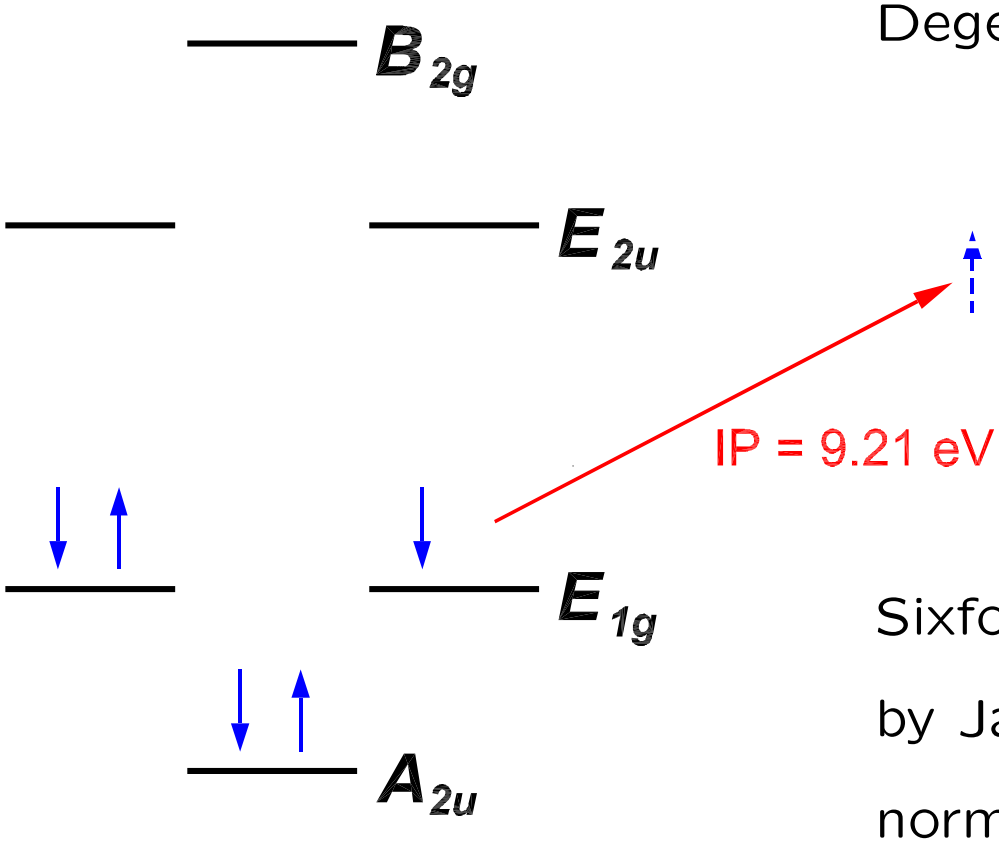
- Open-shell systems: radicals, molecules in excited states

  Degeneracies at symmetric structures
  $\Rightarrow$ Jahn-Teller, Renner-Teller distortions

  (Conical) intersections of different potential surfaces
  important in photochemistry

- Metals

# Jahn-Teller effect in Benzene$^+$




$\pi$ molecular orbitals

Degenerate ground state $E_{1g}$

Sixfold symmetry distorted by Jahn-Teller coupling with normal modes of $e_{2g}$ symmetry

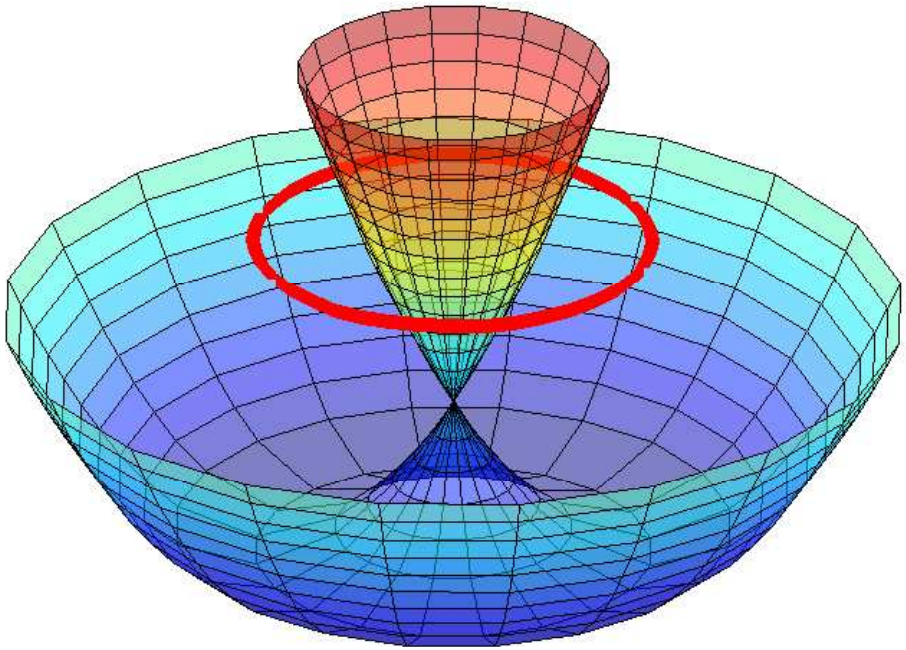
# Potential surfaces

Two adiabatic potentials

corresponding to the $E_{1g}$ state

as functions of the two $\nu_6$

$e_{2g}$ normal mode coordinates



Red circle shows the vibrational zero-point level

$\Rightarrow$ dynamic Jahn-Teller effect

# Conical intersection

between

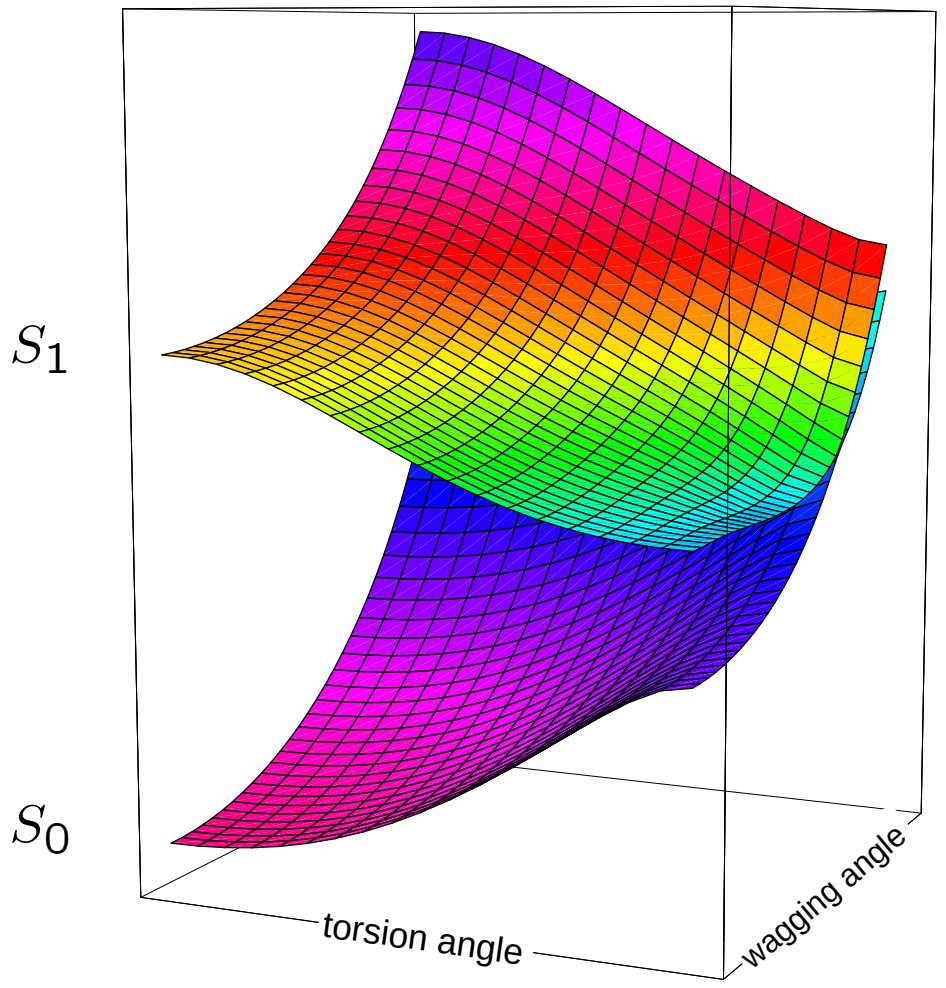
excited $S_1$ and

ground state $S_0$

potentials

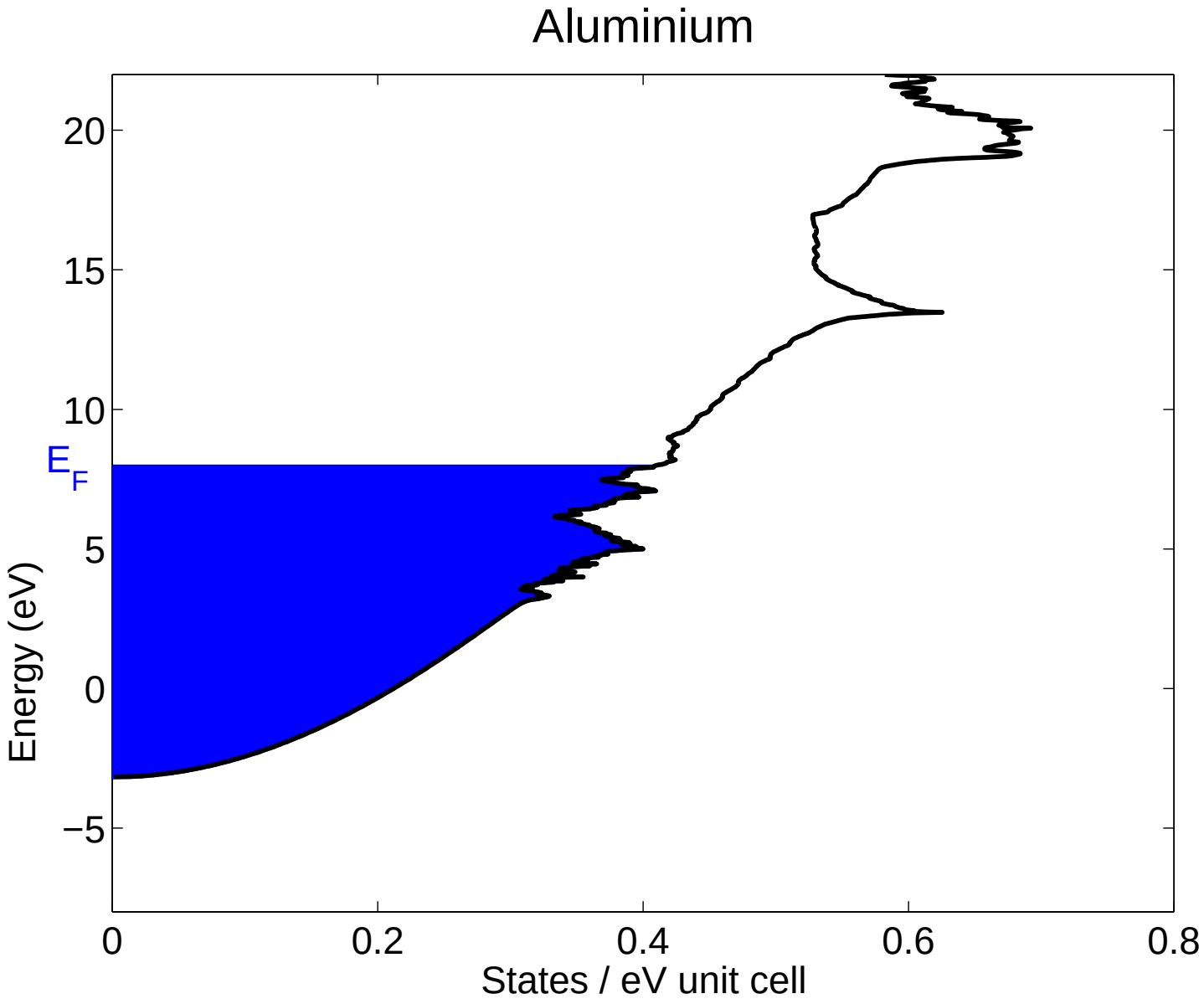
of ethene

$C_2H_4$



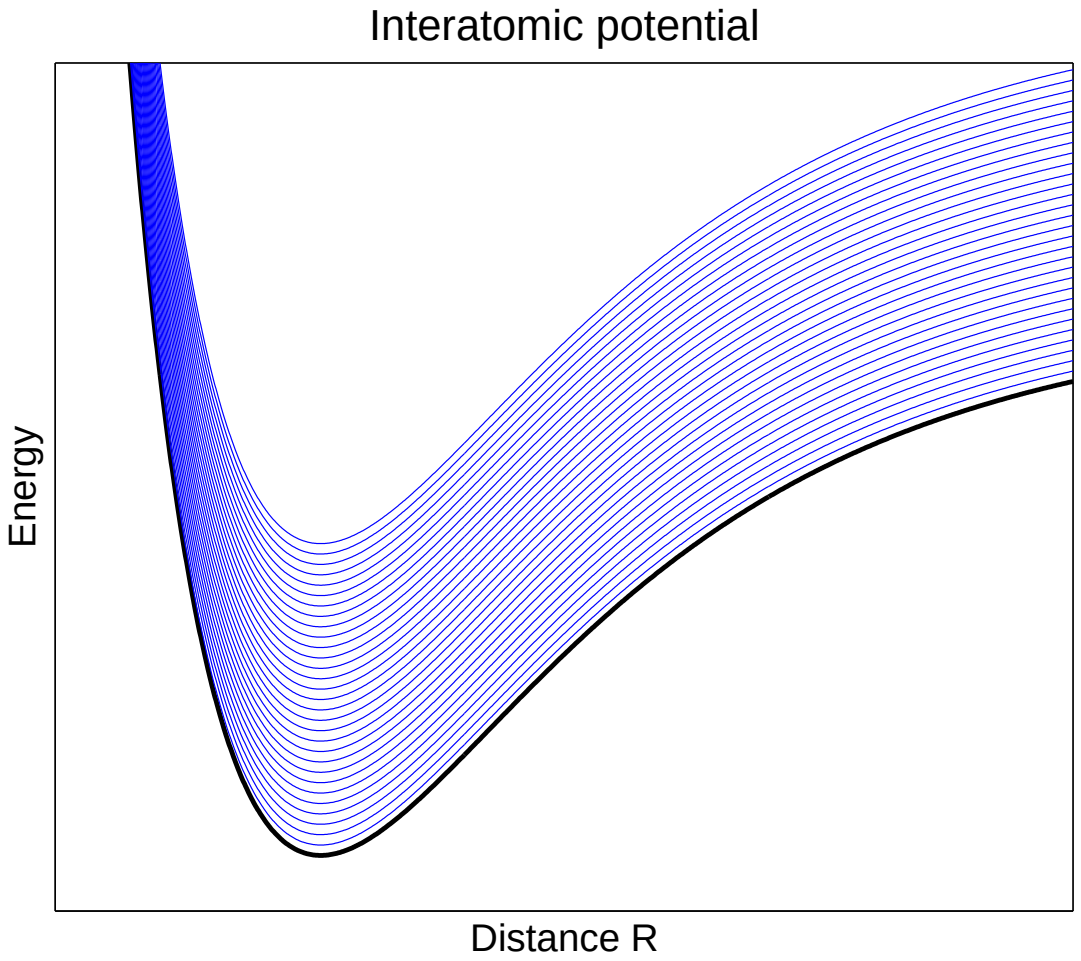

Fast non-radiative transition to ground state through
non-adiabatic coupling prevents UV radiation damage in DNA

# Metals




Thanks to Jisk Attema

# For metals




$\Rightarrow$ electron-phonon (non-adiabatic) coupling