TAF2

Summer 2017

Born - Oppenheimer approximation

by Roman Čunčk

Role of the approximation is to separate electronic and nuclear motions. The idea is based on the electronic and nuclear mass difference.

- Non-relativistic molecular Hamiltonian (N electrons, M nuclei) (atomic units)

$$H = -\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2 - \sum_{i=1}^{N}\sum_{A=1}^{M}\frac{Z_A}{|\vec{r}_i-\vec{R}_A|} + \sum_{i>j}^{N}\frac{1}{|\vec{r}_i-\vec{r}_j|} + \sum_{A>B}^{M}\frac{Z_A Z_B}{|\vec{R}_A-\vec{R}_B|} - \sum_{A=1}^{M}\frac{1}{2M_A}\nabla_A^2$$

$H_{el}(\vec{r};\vec{R})$ $\qquad$ $T_N(\vec{R})$

$\vec{r} \equiv \{\vec{r}_1 \dots \vec{r}_N\}$; $\vec{R} \equiv \{\vec{R}_1 \dots \vec{R}_M\}$

$T_N = \sum_{A,\alpha}\frac{1}{2M_A}P_{A\alpha}P_{A\alpha}$; $P_{A\alpha} = -i\frac{\partial}{\partial R_{A\alpha}}$ $\quad \alpha \in \{x,y,z\}$

- $H_{el}(\vec{r};\vec{R})$ is fixed (clamped) - nuclei ~~Hami~~ electronic Hamiltonian

1.) $H_{el}\,\phi_k(\vec{r};\vec{R}) = E_k(\vec{R})\,\phi_k(\vec{r};\vec{R})$

2.) Normalization $\langle\phi_k(\vec{r};\vec{R})\,|\,\phi_{k'}(\vec{r};\vec{R})\rangle_r = \delta_{kk'}$ ... independent of $\vec{R}$

$\Rightarrow P_{A\alpha}\langle\phi_k(\vec{r};\vec{R})\,|\,\phi_{k'}(\vec{r};\vec{R})\rangle_r = 0 = \underbrace{\langle P_{A\alpha}^{+}\phi_k\,|\,\phi_{k'}\rangle_r}_{\langle\phi_k|P_{A\alpha}^{+}\phi_{k'}\rangle_r^{*}\ \overset{\text{real }\phi_k}{=}\ \langle\phi_k|P_{A\alpha}\phi_{k'}\rangle_r} + \langle\phi_k|P_{A\alpha}|\phi_{k'}\rangle_r$ $\quad \langle\phi_k|P_{A\alpha}\phi_{k'}\rangle = 0$

3.) $H\Psi = E\Psi$

$$\Psi(\vec{r},\vec{R}) = \sum_{k'}\phi_{k'}(\vec{r};\vec{R})\,\chi_{k'}(\vec{R})$$

Expansion is exact

$\int d\vec{r}\,\phi_k^{*}$ $\quad (H_{el}+T_N)\sum_{k'}\phi_{k'}\chi_{k'} = E\sum_{k'}\phi_{k'}\chi_{k'}$

$(E_k(\vec{R}) - E)\chi_k + \sum_{k'}\langle\phi_k|T_N|\phi_{k'}\chi_{k'}\rangle_r = 0$

$$\left[E_k(\vec{R}) - E\right]\chi_k + \sum_{k'}\sum_{A\alpha}\frac{1}{2M_A}\Big[P_{A\alpha}P_{A\alpha}\chi_{k'}\delta_{kk'} + 2\langle\phi_k|P_{A\alpha}\phi_{k'}\rangle_r P_{A\alpha}\chi_{k'} + \underbrace{\langle\phi_k|P_{A\alpha}P_{A\alpha}\phi_{k'}\rangle_r}_{\sim U_{kk'}}\chi_{k'}\Big] = 0$$

$$\left(T_N + E_k(\vec{R}) + U_{kk} - E\right)\chi_k(\vec{R}) = \sum_{k'\neq k}\left[\sum_{A,\alpha}\frac{1}{M_A}\langle\phi_k|P_{A\alpha}|\phi_{k'}\rangle_r P_{A\alpha} + \sum_{A,\alpha}\frac{1}{2M_A}\langle\phi_k|P_{A\alpha}P_{A\alpha}\phi_{k'}\rangle_r\right]\chi_{k'}(\vec{R})$$

(1)

BO diagonal correction

non-adiabatic coupling 1st order

second order

- Estimate for the second order:

$\nabla_A \phi_{k'}(\vec{r};\vec{R}) \sim \nabla_i \phi_{k'}(\vec{r};\vec{R})$ .... similar differences over the same distance ~~scale~~ scale

$\sim p_e \phi_{k'}(\vec{r};\vec{R})$ ... electronic momentum p_e

$$\Rightarrow \frac{1}{2M_A}\nabla_A^2 \phi_{k'}(\vec{r};\vec{R}) \sim \frac{p_e^2}{2M_A}\phi_{k'}(\vec{r};\vec{R}) \sim E_{el}\left(\frac{m_e}{M_A}\right)\phi_k(\vec{r};\vec{R})$$

$\sim 10^{-4}$

Born - Oppenheimer approximation (1927)

$$\left(T_N + E_k(\vec{R}) - E\right)\chi_k(\vec{R}) = 0$$

Nuclei move in the effective potential $E_k(\vec{R})$

For each $\phi_k(\vec{r};\vec{R})$ we have $\chi_k(\vec{R})$ and $\Psi(\vec{r},\vec{R}) = \phi_k(\vec{r};\vec{R})\,\chi_k(\vec{R})$

Is it always valid? When does it fail. Do we have some signature property of its failure?

~~$\langle \phi_k | P_{A\alpha}\phi_{k'}\rangle = E_{k'}\langle \phi_k | P_{A\alpha}\phi_{k'}\rangle$~~

$$\langle \phi_k | P_{A\alpha} H_{el} | \phi_{k'}\rangle = E_{k'}\langle \phi_k | P_{A\alpha} | \phi_{k'}\rangle$$
$$\langle \phi_k | H_{el} P_{A\alpha} | \phi_{k'}\rangle = E_k \langle \phi_k | P_{A\alpha} | \phi_{k'}\rangle$$

$$\Rightarrow \langle \phi_k | P_{A\alpha} | \phi_{k'}\rangle = \frac{\langle \phi_k | [P_{A\alpha}, H_{el}] | \phi_{k'}\rangle}{E_{k'}(\vec{R}) - E_k(\vec{R})}$$

Can we evaluate $\langle \phi_k [P_{A\alpha}, H_{el}] | \phi_{k'}\rangle$?

1.) $\langle \phi_k | P_{A\alpha}\frac{1}{R_{AB}} | \phi_{k'}\rangle - \langle \phi_k | \frac{1}{R_{AB}} P_{A\alpha} | \phi_{k'}\rangle = \langle \phi_k | \left(P_{A\alpha}\frac{1}{R_{AB}}\right) | \phi_{k'}\rangle = 0$ for $k \neq k'$

2.) $\langle \phi_k | \left[P_{A\alpha} - \sum_{i,A}^{N,M} \frac{Z_A}{|\vec{r}_i - \vec{R}_A|}\right] | \phi_{k'}\rangle = i Z_A \langle \phi_k | \sum_{i=1}^{N} \frac{(r_{i\alpha} - R_{A\alpha})}{|\vec{r}_i - \vec{R}_A|^3} | \phi_{k'}\rangle$

non-divergent, non-zero

TAF 2

Summer 2017

Born - Oppenheimer approximation

by Roman Čurík

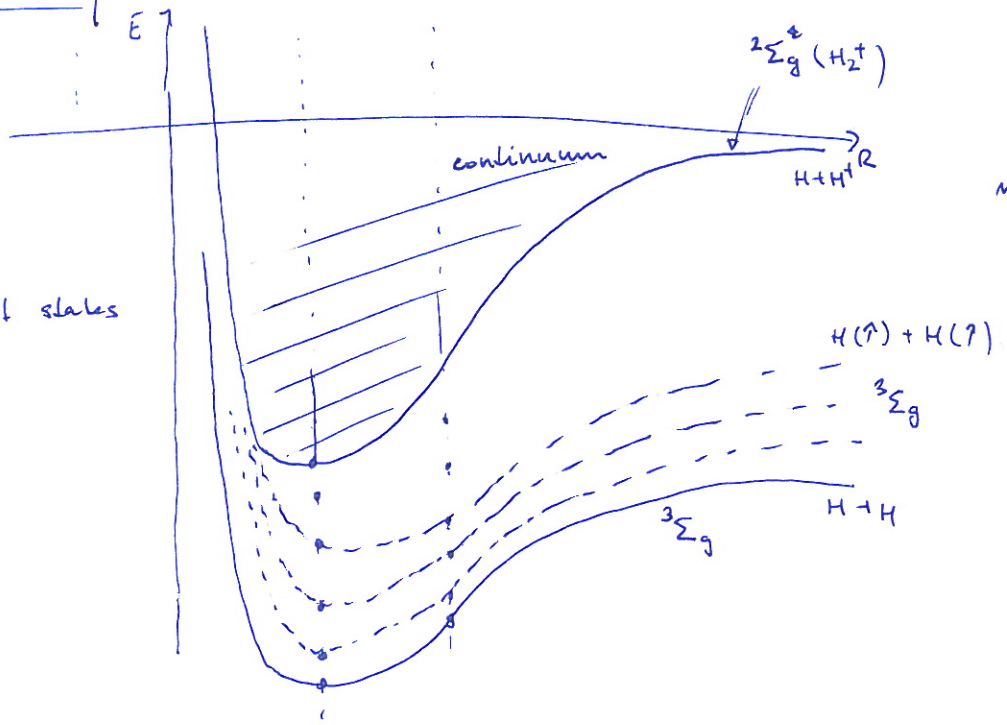
doublet
$S = \frac{1}{2}$

$^2\Sigma_g$

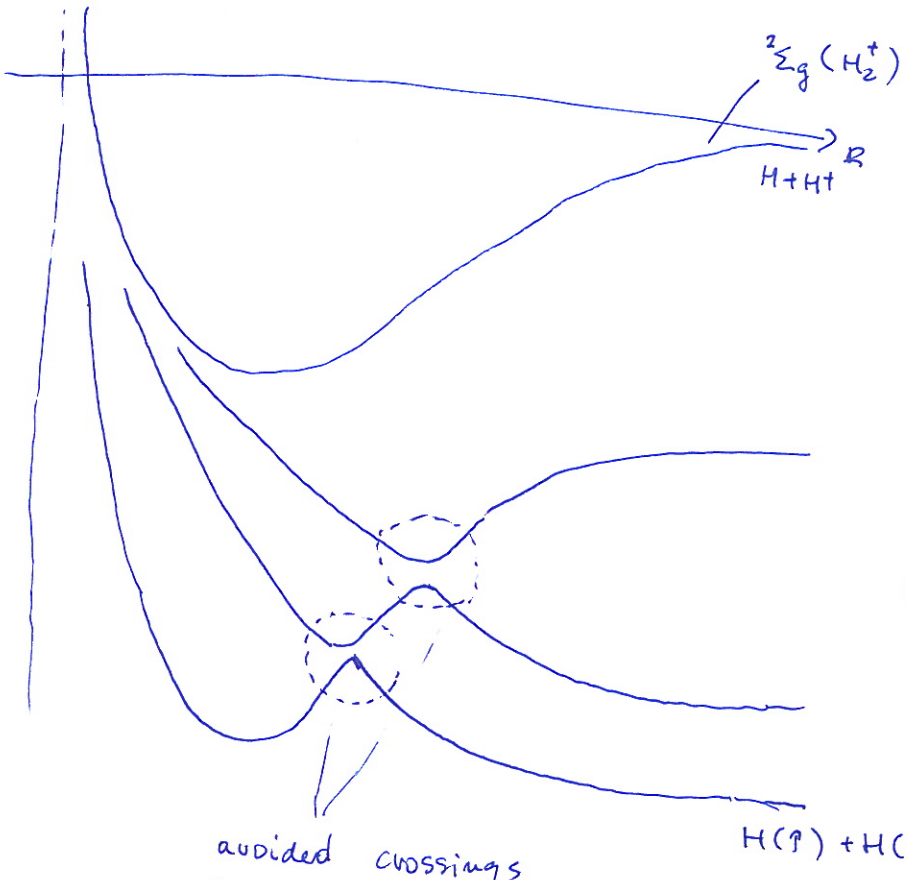
$m = 0$

gerade (inversion from center)

H_2 triplet states



H_2 singlet gerade states



$^1\Sigma_g$

avoided crossings

BOA breaks down and full vibronic coupled system (1) must be solved