# Born–Oppenheimer (single-surface) and its TD breakdown

## Part I: Single-surface BO from $H = H_{\text{electron}} + H_{\text{ion}}$

**Hamiltonian split.** Write the full Hamiltonian as a sum of an *electronic* part (acts on $\mathbf{r}$; depends on $\mathbf{R}$ only as parameters) and an *ionic* part (acts on $\mathbf{R}$):

$$\begin{aligned} H &= H_{\text{electron}}(\mathbf{r};\mathbf{R}) + H_{\text{ion}}(\mathbf{R},\{\nabla_A\}),\\ H_{\text{electron}}(\mathbf{r};\mathbf{R}) &= T_e + V_{ee} + V_{\textit{e-ion}}(\mathbf{R}),\\ H_{\text{ion}}(\mathbf{R},\{\nabla_A\}) &= T_{\text{ion}} + V_{\textit{ion-ion}}(\mathbf{R}), \qquad T_{\text{ion}} = -\sum_A \frac{\hbar^2}{2M_A}\nabla_A^2. \end{aligned}$$

**Product ansatz and electronic ground state.** For each fixed $\mathbf{R}$, define the electronic ground state

$$H_{\text{electron}}(\mathbf{r};\mathbf{R})\,\phi_0(\mathbf{r};\mathbf{R}) \;=\; E_0(\mathbf{R})\,\phi_0(\mathbf{r};\mathbf{R}), \qquad \langle\phi_0(\mathbf{R})|\phi_0(\mathbf{R})\rangle_{\mathbf{r}} = 1.$$

Assume the total wavefunction is a single-surface product

$$\Psi(\mathbf{r},\mathbf{R}) \;=\; \chi(\mathbf{R})\,\phi_0(\mathbf{r};\mathbf{R}).$$

**Action of $H_{\text{electron}}$ and $H_{\text{ion}}$.** Since $H_{\text{electron}}$ acts only on $\mathbf{r}$,

$$\langle\phi_0|H_{\text{electron}}|\Psi\rangle_{\mathbf{r}} \;=\; E_0(\mathbf{R})\,\chi(\mathbf{R}).$$

The ion–ion potential multiplies the product:

$$\langle\phi_0|V_{\textit{ion-ion}}|\Psi\rangle_{\mathbf{r}} \;=\; V_{\textit{ion-ion}}(\mathbf{R})\,\chi(\mathbf{R}).$$

The nuclear kinetic energy acts on both $\chi$ and the $\mathbf{R}$-dependence of $\phi_0$; using $\nabla_A^2(\chi\phi_0) = (\nabla_A^2\chi)\phi_0 + 2(\nabla_A\chi)\cdot(\nabla_A\phi_0) + \chi(\nabla_A^2\phi_0)$ and defining the derivative couplings

$$\mathbf{D}_A(\mathbf{R}) \equiv \langle\phi_0|\nabla_A\phi_0\rangle_{\mathbf{r}}, \qquad \tau_A(\mathbf{R}) \equiv \langle\phi_0|\nabla_A^2\phi_0\rangle_{\mathbf{r}},$$

one finds the *exact* single-surface nuclear equation

$$-\sum_A \frac{\hbar^2}{2M_A}\Big[\nabla_A^2\chi + 2\,\mathbf{D}_A\cdot\nabla_A\chi + \tau_A\,\chi\Big] \;+\; \underbrace{\big[E_0(\mathbf{R}) + V_{\textit{ion-ion}}(\mathbf{R})\big]}_{U_{\text{BO}}(\mathbf{R})}\,\chi(\mathbf{R}) \;=\; E\,\chi(\mathbf{R}).$$

**Born–Oppenheimer (leading order in $1/M$).** The terms proportional to $\mathbf{D}_A$ and $\tau_A$ originate from $T_{\text{ion}}$ acting on the $\mathbf{R}$-dependence of $\phi_0$ and are $\mathcal{O}(1/M_A)$ (nonadiabatic couplings). Neglecting them gives the standard BO nuclear equation on the BO surface $U_{\text{BO}}(\mathbf{R})$:

$$\boxed{\Big[-\sum_A \frac{\hbar^2}{2M_A}\nabla_A^2 \;+\; U_{\text{BO}}(\mathbf{R})\Big]\chi(\mathbf{R}) \;=\; E\,\chi(\mathbf{R}), \qquad U_{\text{BO}}(\mathbf{R}) \equiv E_0(\mathbf{R}) + V_{\textit{ion-ion}}(\mathbf{R}).}$$

## Part II: Why one electronic state is not exact (TD nonadiabatic couplings)

**Born–Huang (multi-surface) expansion.** Expand the total wavefunction in the full adiabatic electronic basis:

$$\Psi(\mathbf{r},\mathbf{R},t)=\sum_n \chi_n(\mathbf{R},t)\,\phi_n(\mathbf{r};\mathbf{R}),\qquad H_{\text{electron}}(\mathbf{r};\mathbf{R})\,\phi_n=E_n(\mathbf{R})\,\phi_n.$$

Insert into $i\hbar\,\partial_t\Psi=H\Psi$ and project onto $\phi_m$. Defining the *nonadiabatic derivative couplings*

$$\mathbf{D}^A_{mn}(\mathbf{R})\equiv\langle\phi_m(\mathbf{R})|\nabla_A\phi_n(\mathbf{R})\rangle_{\mathbf{r}},\qquad \tau^A_{mn}(\mathbf{R})\equiv\langle\phi_m(\mathbf{R})|\nabla^2_A\phi_n(\mathbf{R})\rangle_{\mathbf{r}},$$

one obtains the coupled nuclear equations

$$\begin{aligned}i\hbar\,\partial_t\chi_m(\mathbf{R},t)=\Big[-\sum_A\frac{\hbar^2}{2M_A}\nabla^2_A+E_m(\mathbf{R})\Big]\chi_m(\mathbf{R},t)\\ -\sum_n\sum_A\frac{\hbar^2}{M_A}\,\mathbf{D}^A_{mn}(\mathbf{R})\cdot\nabla_A\chi_n(\mathbf{R},t)\;-\;\sum_n\sum_A\frac{\hbar^2}{2M_A}\,\tau^A_{mn}(\mathbf{R})\,\chi_n(\mathbf{R},t).\end{aligned}$$

The **off-diagonal** terms ($m\neq n$) *mix* electronic channels: even if initially $\chi_{n>0}=0$, they generate population in excited states during time evolution.

**Adiabatic criterion (when single-surface BO is OK).** Using Hellmann–Feynman for $m\neq n$, $\mathbf{D}^A_{mn}=\frac{\langle\phi_m|\nabla_A H_{\text{electron}}|\phi_n\rangle}{E_n-E_m}$, so couplings grow when the electronic gap $|E_n-E_m|$ is small (avoided crossings, conical intersections). A rough adiabaticity condition is that the mixing rate be small compared to the gap:

$$\big|\dot{\mathbf{R}}\cdot\mathbf{d}_{mn}\big|\ll|E_n(\mathbf{R})-E_m(\mathbf{R})|/\hbar,\qquad \mathbf{d}_{mn}\equiv\sum_A\mathbf{D}^A_{mn}\,\dot{\mathbf{R}}_A,$$

so slow nuclear motion and large gaps suppress transitions. Otherwise, multi-surface dynamics is necessary (Landau–Zener transitions provide a useful two-level estimate).

**Bottom line.** The single-surface product $\Psi=\chi(\mathbf{R},t)\phi_0(\mathbf{r};\mathbf{R})$ is an approximation. In real time evolution, the off-diagonal nonadiabatic couplings inevitably transfer amplitude to excited electronic states unless the motion is perfectly adiabatic (heavy nuclei, slow motion, large gaps). Near degeneracies (e.g., conical intersections) a multi-state treatment or a diabatic representation is essential.