

# Quantum reactive scattering: basic principles

Rocco Martinazzo

May 27, 2019

## A simple model for a gas-phase chemical reaction

We consider here a simple model of chemical reaction, a one-dimensional model system with Hamiltonian

$$H = \frac{p^2}{2m} + V(x)$$

describing the motion of a point mass on a reaction coordinate. The values of the potential for  $x \rightarrow \pm\infty$  sets the system energetics, in particular the reaction energy  $\Delta E = V_{+\infty} - V_{-\infty}$ , and define the reagent and product Hamiltonians

$$H_R^0 = \frac{p^2}{2m} + V_{-\infty} \quad H_P^0 = \frac{p^2}{2m} + V_{+\infty}$$

(where  $V_{\pm\infty} = \lim_{x \rightarrow \pm\infty} V(x)$ ) which are appropriate to describe the motion of the free reagents and products, respectively. The configuration space is then partitioned into two asymptotic regions, the reagent ( $\mathcal{R}$ ) and product ( $\mathcal{P}$ ) regions, and an **interaction region** between them. In Fig. 1 this is accomplished by defining two “**dividing surfaces**”,  $x = x_R$  and  $x = x_P$ , such that  $V(x_R) \approx V_{-\infty}$  and  $V(x_P) \approx V_{+\infty}$ .

Fig. 1 also shows a typical energy profile, featuring two potential wells and an energy barrier. The system energetics (*i.e.*,  $V_- = \min\{V_{-\infty}, V_{+\infty}\}$  and  $V_+ = \max\{V_{-\infty}, V_{+\infty}\}$ ) determines the nature of the possible motions at a given total energy  $E$ . Specifically, for  $E < V_-$  (in Fig. 1,  $V_- = V_{+\infty}$ ) only confined motions are possible and the spectrum is purely discrete. This follows of course from the Schrödinger equation in the asymptotic regions

$$\left( -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \right) \psi(x) = (E - V_{\mp\infty}) \psi(x) \quad \text{for } x \in \mathcal{R}, \mathcal{P}$$

from which it is evident that the condition  $E - V_{\mp\infty} \leq 0$  allows evanescent waves only. With the same token, when  $E \in [V_-, V_+]$  it is clear that the motion is unbound in one direction only, and it is an (elastic) collision in the only arrangement that is “open” in this energy range (the product side, in Fig. 1). Any potential bound-state lying in this energy range is actually unbound, and it is at most a *quasi-bound* state, *i.e.* a state that, if carefully prepared, behaves like a true bound state for a while but in the long run it decays into

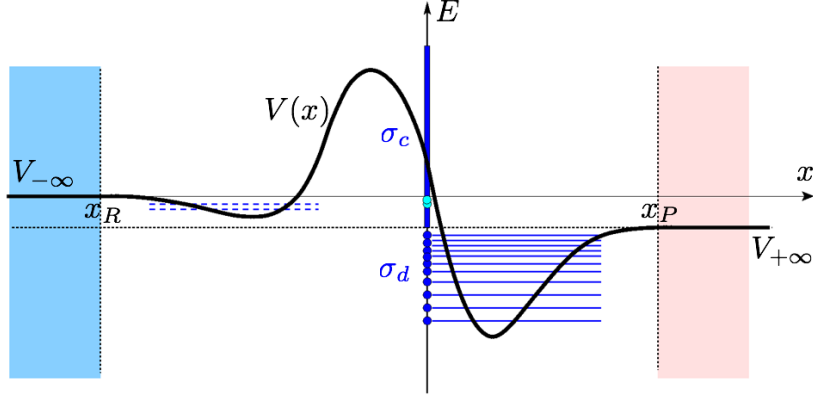


Figure 1: Energy profile of the model chemical reaction considered in the main text, showing the reagent and product regions (light blue and light red boxes) and the interaction region. Also shown are the bound states of the system (horizontal blue lines) and resonances (dotted horizontal lines), and the discrete and continuous part of the energy spectrum.

the open channel. Reaction is only possible when  $E \geq V_+$ , a condition that guarantees a non-negative kinetic energy in *both* the reagent and the product side ( $T_{R,P}^0 = E - V_{\mp\infty} \geq 0$ ).

Thus, the energy spectrum is continuous for  $E > V_-$  but only for  $E > V_+$  it is relevant for the reaction. The corresponding energy eigenstates are degenerate and can be conveniently chosen to describe waves traveling to the right in the  $\mathcal{P}$  region ( $|E, \rightarrow\rangle$ ) and waves traveling to the left in the  $\mathcal{R}$  region ( $|E, \leftarrow\rangle$ ). The first represents a scattering event in which the system starts from the reagent side and moves towards the product, producing both a product component (moving to the right) and a reflected reagent component (moving to the left). As a result, in the  $\mathcal{R}$  side one finds both an **incoming** and an **outgoing** component, while in the  $\mathcal{P}$  side there is a purely outgoing wave. In other words, it holds<sup>1</sup>

$$\langle x|E, \rightarrow\rangle \propto \exp\left(\frac{i}{\hbar}p_-x\right) + R \exp\left(-\frac{i}{\hbar}p_-x\right) \quad \text{for } x \in \mathcal{R}$$

$$\langle x|E, \rightarrow\rangle \propto T \exp\left(\frac{i}{\hbar}p_+x\right) \quad \text{for } x \in \mathcal{P}$$

where  $R, T$  and amplitude coefficients and  $p_{\pm} = \sqrt{2m(E - V_{\pm\infty})}$  is the appropriate momentum for the product/reagent region. Similarly for  $|E, \leftarrow\rangle$ , which presents purely outgoing waves in the  $\mathcal{R}$  region.

<sup>1</sup>The proportionality constant is here left unspecified. It may be set by enforcing normalization of the vectors on the energy scale,  $\langle E|E'\rangle = \delta(E - E')$ , as implicitly assumed below.

In view of the above, we write the energy-based resolution of the identity in the form

$$1 = \sum_n \epsilon_n |\epsilon_n\rangle \langle \epsilon_n| + \int_{V_-}^{V_+} |E\rangle \langle E| dE + \sum_{i=\rightarrow, \leftarrow} \int_{V_+}^{+\infty} |E, i\rangle \langle E, i| dE$$

keeping in mind that only the last term on the r.h.s. is relevant for a reactive event. We expand on this issue in the following, where a time-dependent picture of such event is established and the reaction probabilities are related to the time evolution of the wavepacket.

## Reaction probability

Let  $|\Psi_0\rangle$  be a state at  $t = 0$  describing a collision process forming the reaction product, *i.e.*, **a state localized in  $\mathcal{R}$  with solely “rightward” momentum components**. Let  $\hat{h}_P = \Theta(\hat{x} - x_P)$  be the product projection operator and  $P_t[\Psi_0] = \langle \Psi_t | \hat{h}_P | \Psi_t \rangle$  the population of products at time  $t$  (the argument  $\Psi_0$  reminds us that it depends on the state chosen at time  $t = 0$ ). Then

$$P_{t_f}[\Psi_0] = P_{t_i}[\Psi_0] + \int_{t_i}^{t_f} \langle \Psi_t | F | \Psi_t \rangle dt$$

where

$$F_P = \frac{i}{\hbar} [H, \hat{h}_P] = \frac{i}{2m\hbar} \left( \hat{p}[\hat{p}, \hat{h}_P] + [\hat{p}, \hat{h}_P]\hat{p} \right) \equiv \Re(\hat{v}\delta(\hat{x} - x_P))$$

$\hat{v} = \hat{p}/m$  being the velocity operator. With the above initial state we can easily take the limit for  $t_i \rightarrow -\infty$  since the wavepacket moves “leftward” (*i.e.*, it remains in the asymptotic region of the reagents) and thus

$$P_\infty[\Psi_0] = \int_{-\infty}^{+\infty} \langle \Psi_t | F_P | \Psi_t \rangle dt$$

is the appropriate expression for the reaction probability.

Let’s now express such probability in terms of separate energy contributions. To this end, we notice that when  $|\Psi_0\rangle$  is localized well inside the reagent region it does not overlap with either the bound states  $|\epsilon_n\rangle$  or the unbound states  $|E\rangle$  with energy  $E < V_+$ . Furthermore, since it contains purely right-moving components in the reagent region, it holds to a good approximation

$$|\Psi_0\rangle = \sum_i \int_{V_+}^{+\infty} dE |E, i\rangle \langle E, i | \Psi_0 \rangle \approx \int_{V_+}^{+\infty} dE |E, \rightarrow\rangle \langle E, \rightarrow | \Psi_0 \rangle$$

It follows<sup>2</sup>, at any time,

$$|\Psi_t\rangle = \int dE e^{-\frac{i}{\hbar}Et} |E, \rightarrow\rangle \langle E, \rightarrow | \Psi_0 \rangle$$

---

<sup>2</sup>Here and below, we omit the energy range, assuming that it is always that part of the continuous spectrum that is relevant for the reaction.

and thus

$$P_\infty[\Psi_0] = \int dE \int dE' \int_{-\infty}^{+\infty} dt e^{+\frac{i}{\hbar}(E'-E)t} \langle \Psi_0 | E', \rightarrow \rangle \langle E', \rightarrow | F_P | E, \rightarrow \rangle \langle E, \rightarrow | \Psi_0 \rangle$$

Integrating over time, upon noticing that it holds

$$\int_{-\infty}^{+\infty} dt e^{+\frac{i}{\hbar}(E'-E)t} = 2\pi\hbar\delta(E' - E)$$

we get

$$P_\infty[\Psi_0] = \int dE P(E) |\langle E, \rightarrow | \Psi_0 \rangle|^2$$

where

$$P(E) = 2\pi\hbar \langle E, \rightarrow | F_P | E, \rightarrow \rangle$$

is the **energy-resolved reaction probability**.

**Exercise.** Compute the reaction probability in the trivial case where  $V = 0$ , *i.e.*,  $H \equiv H^0 = H_R^0 = H_P^0$ .

## Time-to-energy mapping

The energy eigenstates can be obtained either by solving the time *independent* Schrödinger equation at energy  $E$  (for a range of energies) or by the appropriate **time-to-energy mapping** of the dynamics (for all times). We follow the second route, that closely resembles the physical “collisional” process described above. Let  $\Phi_E^\pm(x) = \langle x | E, \rightarrow \rangle$  be the coordinate representation of the required energy eigenstate. According to the flux expression above,

$$P(E) = \frac{2\pi\hbar^2}{m} \Im \left[ (\Phi_E^+(x_P))^* \frac{\partial \Phi_E^+}{\partial x}(x_P) \right]$$

one only needs the value of  $\Phi_E^\pm$  and its spatial derivative at the position  $x_P$  of the **flux-dividing surface** (line in our 1D example). For our evolving wavepacket we have (see above)

$$\Psi_t(x) = \int dE e^{-\frac{i}{\hbar}Et} \Phi_E^+(x) \langle E, \rightarrow | \Psi_0 \rangle$$

and

$$\frac{\partial \Psi_t(x)}{\partial x} = \int dE e^{-\frac{i}{\hbar}Et} \frac{\partial \Phi_E^+(x)}{\partial x} \langle E, \rightarrow | \Psi_0 \rangle$$

and thus, upon Fourier transforming,

$$\Phi_E^+(x) = \frac{1}{2\pi\hbar \langle E, \rightarrow | \Psi_0 \rangle} \int_{-\infty}^{+\infty} e^{+\frac{i}{\hbar}Et} \Psi_t(x) dt$$

and similarly for its (spatial) derivative. Notice that here, in the product region (e.g., for  $x = x_P$ ), it holds  $\Psi_t(x) \equiv 0$  for  $t \leq 0$  by construction, hence the integral above effectively runs over positive times only, *i.e.* it only requires propagating the wavepacket forward in time, a rather reasonable result. Hence<sup>3</sup>,

$$P(E) = \frac{1}{mg(E)} \Im \left[ (\xi_E^+(x_P))^* \frac{\partial \xi_E^+}{\partial x}(x_P) \right]$$

where

$$\xi_E^+(x) = \int_0^{+\infty} e^{+\frac{i}{\hbar}Et} \Psi_t(x) dt \quad \frac{\partial \xi_E^+(x)}{\partial x} = \int_0^{+\infty} e^{+\frac{i}{\hbar}Et} \frac{\partial \Psi_t(x)}{\partial x} dt$$

and

$$g(E) = 2\pi |\langle E, \rightarrow | \Psi_0 \rangle|^2$$

are energy weights.

Assuming that we are able to follow the wavepacket  $\Psi_t(x)$  for sufficiently long times  $t$  that the contributions of  $\Psi_t(x_P)$  (and its spatial derivative) to the integrals above become negligible, there remains only to determine  $g(E)$ , a measure of the overlap of the initial wavepacket with the desired energy eigenstate.

To this end, we recall once again that our initial wavepacket  $\Psi_0(x)$  is localized in the asymptotic region of the reagents, where the appropriate energy eigenstates takes the form

$$\Phi_E^+(x) \approx N \left( \exp\left(\frac{i}{\hbar}px\right) + R \exp\left(-\frac{i}{\hbar}px\right) \right) = \Phi_{\text{in}}(x) + \Phi_{\text{refl}}(x)$$

where  $N$  is a normalization constant,  $p = \sqrt{2m(E - V_{-\infty})}$  and  $R$  is an amplitude coefficient (the **reflection amplitude**). In short, it contains both an **incoming** and an **outgoing** component but, by construction, only the first overlaps with our initial wavepacket, and this is precisely the same state that describes a **free incoming** particle. That is, for our purposes, it holds to a very good approximation

$$\langle E, \rightarrow | \Psi_0 \rangle \approx \langle E^0, \rightarrow | \Psi_0 \rangle$$

where  $|E^0, \rightarrow\rangle$  is a **free-particle** right-moving state with kinetic energy  $E^0 = E - V_{-\infty}$  (normalized on the energy scale). One can further write this overlap in terms of the amplitude of the momentum wavefunction, since

$$|E^0, i\rangle = N(E) |p_E\rangle$$

where  $N(E)$  is the appropriate normalization constant and  $p_E = \pm \sqrt{2m(E - V_{-\infty})}$  for  $i = \rightarrow, \leftarrow$  respectively. Since it holds

$$\sum_i \int_0^{+\infty} dE^0 |E^0, i\rangle \langle E^0, i| = \int_{-\infty}^{+\infty} dp |p\rangle \langle p|$$

---

<sup>3</sup>We factor out the mass because, though not evident from the model considered here, this is the mass appropriate for the relative motion of the reaction *products*.

and  $dE^0 = \frac{v_E}{m} dp_E$  we have

$$\sum_i \int_0^{+\infty} dE |E^0, i\rangle \langle E^0, i| \equiv \int_{-\infty}^{+\infty} dp \frac{p}{m} N^2(E) |p\rangle \langle p|$$

from which it follows  $N^2 \equiv m/p = \frac{1}{v_E}$  where  $v_E$  is the particle velocity at energy  $E$ . Hence,

$$\langle E^0, \rightarrow | \Psi_0 \rangle = \frac{1}{\sqrt{v_E}} \Psi_0(p_E)$$

and

$$g(E) = \frac{2\pi}{|v_E|} |\Psi_0(p_E)|^2$$

where  $p_E = +\sqrt{2m(E - V_{-\infty})}$ .

**Exercise.** Let be  $\Psi_0(x) = N \exp\left(-\frac{(x-x_0)^2}{4\Delta x^2}\right) \exp\left(\frac{i}{\hbar} p_0 x\right)$  where  $N$  is a normalization constant and  $x_0, p_0$  and  $\Delta x$  are parameters. Find the normalization constant and show that  $x_0 = \langle \Psi_0 | \hat{x} | \Psi_0 \rangle$  and  $\Delta x^2 = \langle \Psi_0 | (\hat{x} - x_0)^2 | \Psi_0 \rangle$ .

**Exercise.** For the wavefunction above shows that  $p_0 = \langle \Psi_0 | \hat{p} | \Psi_0 \rangle$  and that  $\Delta p_0 = \sqrt{\langle \Psi_0 | (\hat{p} - p_0)^2 | \Psi_0 \rangle}$  satisfies  $\Delta p = \hbar/2\Delta x$ .

**Exercise.** For  $|\Psi_0\rangle$  above find the momentum space wavefunction,  $\Psi_0(p)$ .

## Absorbing potentials

Numerical implementation (“simulation”) of the scattering dynamics described above requires, among other things, that the particle is “confined” in a region of finite dimension, as set, for instance, by the extension of the grid used to represent the wavefunction in real space. This implies that such confinement region needs to be augmented with two further regions where an **absorbing potential** (a negative imaginary potential) absorbs the wavepacket and prevents its unphysical behavior at the grid edges. Without such a trick the evaluation of the flux would be spoiled by, *e.g.*, that part of the wavepacket that gets reflected at the grid edge. Absorbing potentials can be “optimized” to minimize both reflection (typical of the low-energy components) and transmission (typical of high-energy components), and thus effectively implement the **open boundary conditions** that are required to describe a scattering process.

In practice, one introduces two non-negative potential terms  $W_R$  and  $W_P$  for the reagent and the product regions and uses the (no longer self-adjoint) Hamiltonian

$$\bar{H} = H - iW_R - iW_P$$

where  $W_i \equiv 0$  in the interaction region. For instance, with reference to Fig. 1, one uses the light boxes to define two finite regions where  $W_i > 0$ , small enough to guarantee a reasonably small grid length, but large enough to guarantee good

absorption properties<sup>4</sup>. In this way, the dynamics is unaltered as long as the wavepacket moves in the interaction region and gets modified only when the wavepacket enters the asymptotic regions, where its outgoing components are removed from the grid.

The use of absorbing potentials offers an alternative way to compute the energy-resolved reaction probabilities

$$P(E) = 2\pi\hbar \langle \Phi_E^+ | F_P | \Phi_E^+ \rangle \quad | \Phi_E^+ \rangle \approx \frac{1}{2\pi\hbar \langle E, \rightarrow | \Psi_0 \rangle} \int_0^{+\infty} e^{+\frac{i}{\hbar}(E-\bar{H})t} | \Psi_0 \rangle dt$$

where we have replaced  $H$  with  $\bar{H}$  and set the lower limit of the integration to  $t = 0$  since the energy eigenstates are only needed in the product region where  $F$  localizes. It follows

$$P(E) = \frac{1}{2\pi\hbar |\langle E, \rightarrow | \Psi_0 \rangle|^2} \int_0^{+\infty} \int_0^{+\infty} \langle \tilde{\Psi}_t | F_P | \tilde{\Psi}_{t'} \rangle dt dt'$$

where  $|\tilde{\Psi}_t\rangle = e^{+\frac{i}{\hbar}(E-\bar{H})t} | \Psi_0 \rangle$ . Notice that it holds

$$\left( \frac{d}{dt'} + \frac{d}{dt} \right) \langle \tilde{\Psi}_t | \hat{h}_P | \tilde{\Psi}_{t'} \rangle = \langle \tilde{\Psi}_t | F_P | \tilde{\Psi}_{t'} \rangle - \frac{2}{\hbar} \langle \tilde{\Psi}_t | W_P | \tilde{\Psi}_{t'} \rangle$$

since  $[W_i, \hat{h}_P] = 0$  and  $W_i \hat{h}_P = \delta_{iR} W_P$ . On the other hand, it also holds

$$\begin{aligned} \int_0^\infty dt \int_0^\infty dt' \left( \frac{d}{dt'} + \frac{d}{dt} \right) \langle \tilde{\Psi}_t | \hat{h}_P | \tilde{\Psi}_{t'} \rangle &= \int_0^\infty dt \langle \tilde{\Psi}_t | \hat{h}_P | \tilde{\Psi}_{t'} \rangle \Big|_{t'=0}^{t'=\infty} + \\ &+ \int_0^\infty dt' \langle \tilde{\Psi}_t | \hat{h}_P | \tilde{\Psi}_{t'} \rangle \Big|_{t=0}^{t=\infty} \equiv 0 \end{aligned}$$

since the wavepackets vanish on the long run and have zero amplitude in the product region  $\mathcal{P}$  at  $t = 0$ . Hence,

$$P(E) = \frac{1}{2\pi\hbar |\langle E, \rightarrow | \Psi_0 \rangle|^2} \frac{2}{\hbar} \int_0^{+\infty} \int_0^{+\infty} e^{\frac{i}{\hbar}E(t'-t)} \langle \Psi_t | W_P | \Psi_{t'} \rangle dt dt'$$

which shows that the reaction probability can also be obtained from a correlation function involving only the wavefunction in the (product) absorbing potential region.

---

<sup>4</sup>One needs also to ensure that the initial wavepacket is not affected by the absorbing potential. This can be accomplished by either setting  $W_R = 0$  in a narrow region  $x < x_R$  that it is used to accommodate  $\Psi_0(x)$  or by “switching on”  $W_R$  after  $\Psi_0$  has moved from the reagent region.