

# Notes on Scattering Theory

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# Chapter 1

## Theoretical background

Scattering Theory aims at describing experiments in which a beam of incoming particle is scattered by the interaction with something else (other particles, a surface, a crystal, etc.).

The physical picture of Scattering Theory is that we can split the hamiltonian in two terms

$$H = H_0 + V$$

a free hamiltonian and an interaction hamiltonian. For  $t \rightarrow \pm\infty$  the system is described by an asymptotic state, that evolves according to  $H_0$ . Inbetween the system feels the interaction and evolves according to the total hamiltonian  $H$ .

For example, two colliding particles<sup>1</sup> interacting with a potential  $V$  will be described by the hamiltonian

$$H = T_1 + T_2 + V_{12}$$

where  $T_i$  is the kinetic energy operator of the  $i$ th particle. In this case the obvious choice is to set  $H_0 = T_1 + T_2$ , i.e. the evolution of the particle in absence of interaction.

As further example, the full hamiltonian of a biatomic molecule in an external potential is

$$H = T_{trasl}(\mathbf{R}) + T_{rot+vib}(\mathbf{r}) + V_{internal}(\mathbf{r}) + V_{ext}(\mathbf{R}, \mathbf{r})$$

where  $\mathbf{R}$  and  $\mathbf{r}$  are respectively the coordinates of the center of mass and the difference between the position of the two atoms (in spherical coordinates the bond lenght  $r$  and the orientation angles  $\varphi, \vartheta$ ). If we assume that in the scattering process the molecule does not dissociate, we can set  $H_0 = T_{trasl}(\mathbf{R}) + T_{rot+vib}(\mathbf{r}) + V_{internal}(\mathbf{r})$ . In this way the free evolution will describe the translation and the rotation of the molecule and the vibrational degrees of freedom of the surface, without the external potential.

In a scattering experiment, the information that are accessible are the state in which the system is prepared (which we will call the “incoming asymptote”) and the properties measured after the scattering (the “outcoming asymptote”). On the other hand, theoretical methods describe how the system evolves according to the full potential, and the link between the actual state and the asymptotic states may not be trivial. The goal of Scattering Theory is to relate these informations: the asymptotic states and the interaction potential.

In the following we will very often make use the free hamiltonian eigenstates. Before going on, some comments about them are needed. In general free hamiltonian eigenstates are a combination of two parts: a plane wave for the scattering coordinate (e.g. the relative distance of two colliding particle, or the center of mass of the molecule experiencing the external potential) and another part for the other degrees of freedom.

In the following we will generally write the free hamiltonian eigenstates as

$$|\mathbf{p}\alpha\rangle, |\mathbf{p}'\beta\rangle, |\mathbf{p}''\gamma\rangle, \dots$$

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<sup>1</sup>in this example we assume no internal degrees of freedom, e.g. two atoms from a “chemical” point of view

where the letter  $\mathbf{p}$  is the momentum associated to the plane wave and the greek letter is a collective index labelling the state for the other coordinates. For simplicity of notation, we will assume  $\alpha$  to be discrete. This is not always true, e.g. the vibrations of the molecule may become continuous in the dissociation limit. Anyway, the generalization of the equations in this sense is usually straightforward and implies the substitution of the sum over  $\alpha$  with an integral.

## 1.1 Time dependent formalism

### 1.1.1 Time evolution operator

According to a quantum mechanics postulate, time evolution of a state is described by *time dependent Schrödinger equation*:

$$H |\psi\rangle = i\hbar \frac{d|\psi\rangle}{dt} \quad (1.1)$$

The first step in the development of a quantum description of an evolving system is expressing this differential equation with a continuous group of operators describing the time dependence of the system, the **time evolution operators**. We briefly recall some useful properties of such operator group.

Schrödinger equation is a first-order linear differential equation: given an initial condition, the solution is uniquely determined for every time. Hence we can define the time evolution of a system with an operator  $U(t)$ , such that

$$|\psi_{\tau+t}\rangle = U(t) |\psi_{\tau}\rangle \quad (1.2)$$

where  $|\psi_{\tau+t}\rangle$  is the wave-function at time  $\tau + t$  and  $|\psi_{\tau}\rangle$  is the wave-function at time  $\tau$ .

Time evolutions operator are linear unitary operators satisfying the composition relation

$$U_{t_1+t_2} = U_{t_1} U_{t_2}$$

From the unitarity and the composition relation we can relate the evolution for positive times and negative times

$$U_t^\dagger = U_{-t}$$

Substituting Eq. (1.2) in Schrödinger equation we get

$$HU(t) |\psi\rangle = i\hbar \frac{d(U(t) |\psi\rangle)}{dt}$$

which can be rewritten as an operator equivalence<sup>2</sup>:

$$\frac{\partial U(t)}{\partial t} = -\frac{i}{\hbar} HU(t)$$

In our case,  $H$  does not have an explicit time dependence and the equation can be formally integrated, giving a very simple and useful expression for the time evolution operator

$$U(t) = \exp\left(-\frac{i}{\hbar} Ht\right) \quad (1.3)$$

As for the full hamiltonian, we can build a time evolution operator corresponding to the free hamiltonian  $H_0$ , which is solution of Schrödinger equation for the non-interacting system

$$\frac{\partial U_0(t)}{\partial t} = -\frac{i}{\hbar} H_0 U_0(t)$$

and can be simply written as

$$U_0(t) = \exp\left(-\frac{i}{\hbar} H_0 t\right) \quad (1.4)$$

when the free hamiltonian does not depend explicitly on time, as in our case.

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<sup>2</sup>The total derivative symbol has been replaced by the partial derivative one, to distinguish the operator derivative (which can be defined similarly as in calculus) from the dynamical derivative of an operator (see appendix A.2).

### 1.1.2 Møller operators and S matrix

We have already spent some words on the physical picture underneath Scattering Theory. Now we want to make this picture more precise.

A scattering experiment can be idealized in the following way. The system is initially prepared in a state which is a combination of free eigenstates  $|\mathbf{p}\alpha\rangle$ . For the results to be as detailed as possible, we want this incoming asymptote to be prepared in a very specific quantum state  $\alpha$ , or at least with a very narrow distribution. Long time before the interaction takes place, the system evolves according to  $U_0(t)$ , since in this asymptotic regime  $V(\mathbf{p}_{asym}) = 0$ . When the interaction is “switched on” (e.g. the particles collide, or the molecule reach the surface) the evolution of the system is given by the full hamiltonian  $U(t)$ , whose effect is usually to couple some degrees of freedom which are uncoupled in the free evolution. Long time after the interaction, the state will be a superposition of free eigenstates  $|\mathbf{p}\alpha\rangle$  possibly different from the initial one and evolving according to  $U_0(t)$  again.

The relevant information that can be extracted from this experiment, is the probability for the system to go from the initial state  $|\mathbf{p}\alpha\rangle$  to one other free state  $|\mathbf{p}'\beta\rangle$

$$w(\mathbf{p}\alpha \leftarrow \mathbf{p}'\beta)$$

For this purpose, we need some tool to relate the in and out asymptotes to the interacting system. These tools are Møller operators, defined as

$$\Omega_{\pm} = \lim_{t \rightarrow \mp\infty} U(t)^{\dagger} U_0(t) \quad (1.5)$$

For a detailed discussion of the conditions under which the definition makes sense and a review of the mathematical properties of Møller operators, the reader should refer to Taylor, Newton.

In the present discussion, we will just give a heuristic justification of this definition. The operator  $\Omega_+$  can be viewed as the product  $U(-\infty)^{\dagger} U_0(-\infty)$ , which acting on a state vector bring it from  $t = 0$  to  $t = -\infty$  as a free evolving state and then from  $t = -\infty$  to  $t = 0$  as an interacting state. The idea is that  $\Omega_+$  map a free state evolving from the incoming asymptote in absence of the interaction to the state that would evolve from the same asymptote in the presence of the interaction potential. The same holds for  $\Omega_-$  and the outgoing asymptote. Schematically

$$\begin{array}{ccccc} \text{in asymptote} & & \text{actual state} & & \text{out asymptote} \\ |\Psi\rangle & \xrightarrow{\Omega_+} & |\Psi+\rangle & & \\ & & |\Psi-\rangle & \xleftarrow{\Omega_-} & |\Psi\rangle \end{array}$$

Now let's turn back to our problem. We want to express the probability  $w(\mathbf{p}\alpha \leftarrow \mathbf{p}'\beta)$  that the free state  $|\mathbf{p}\alpha\rangle$  evolves to  $|\mathbf{p}'\beta\rangle$  due to the interaction. The transition probability will be the overlap between  $|\mathbf{p}\alpha-\rangle$  (the actual state evolving to asymptote of  $|\mathbf{p}\alpha\rangle$ ) and  $|\mathbf{p}'\beta+\rangle$  (the actual state evolving from the asymptote of  $|\mathbf{p}'\beta\rangle$ )

$$w(\mathbf{p}\alpha \leftarrow \mathbf{p}'\beta) = |\langle \mathbf{p}\alpha- | \mathbf{p}'\beta+ \rangle|^2$$

With Møller operators we have a way to express the unknown actual states in terms of the free states

$$|\mathbf{p}'\beta+\rangle = \Omega_+ |\mathbf{p}'\beta\rangle \quad |\mathbf{p}\alpha-\rangle = \Omega_- |\mathbf{p}\alpha\rangle$$

and the transition probability is conveniently expressed as

$$w(\mathbf{p}\alpha \leftarrow \mathbf{p}'\beta) = \left| \langle \mathbf{p}\alpha | \Omega_+^{\dagger} \Omega_- | \mathbf{p}'\beta+ \rangle \right|^2$$

This is the central result on which scattering theory is based. The transition probability is the squared modulus of the matrix element of the Scattering operator, defined as

$$S = \Omega_+^{\dagger} \Omega_-$$

## 1.2 Time independent formalism

In the previous section, we have introduced the main tools of scattering theory from a dependent point of view, namely by showing their definition in terms of evolution operator. The same can be done in a time independent fashion. The first step will be transforming the dynamical operator from the time to the energy domain. We will then introduce the  $T$  operator in function of this energy domain propagator. Finally we will show how  $T$  operator can be related to Scattering operator.

### 1.2.1 Green operator

We define the green operator as

$$G(z) = \begin{cases} -i \int_{-\infty}^0 dt \exp(-i(z-H)t) = G^+(z) & \text{Im } z > 0 \\ +i \int_0^{+\infty} dt \exp(-i(z-H)t) = G^-(z) & \text{Im } z < 0 \end{cases} \quad (1.6)$$

where the superscript  $\pm$  indicates the restriction of  $G(z)$  to the upper or lower complex half-plane.

When  $\text{Re } z$  does not belong to the spectrum of  $H$

$$\lim_{\varepsilon \rightarrow 0^+} G^+(x + i\varepsilon) = \lim_{\varepsilon \rightarrow 0^+} G^-(x - i\varepsilon) = G(x)$$

Otherwise  $G(x)$  is not defined, and

$$\lim_{\varepsilon \rightarrow 0^+} G^+(x + i\varepsilon) \neq \lim_{\varepsilon \rightarrow 0^+} G^-(x - i\varepsilon)$$

Basically,  $G^+(z)$  and  $G^-(z)$  are a complex extension of the fourier transform of the  $t > 0$  and  $t < 0$  restriction of the time evolution operator. In this sense it should be reasonably accepted that they are an alternative time-independent way of describing the dynamics of the system.

The necessity to let  $z \in \mathbb{C}$  (and not just a physical meaningful real energy) comes from the fact that the operator is not defined for  $z$  in the spectrum of  $H$ . Hence in the manipulation of the equations involving the green operator is often convenient to take  $\text{Im } z \neq 0$  and then let  $\text{Im } z \rightarrow 0$  after integration. This is equivalent to introduce a dumping factor  $e^{-\varepsilon t}$  in the integrals (e.g. in eq. 1.6, putting  $z = x + i\varepsilon$ ) and then to let  $\varepsilon \rightarrow 0$  (and  $e^{-\varepsilon t} \rightarrow 1$ ).

Formally, if  $z$  is not in the spectrum of  $H$ , we can integrate eq.1.6

$$G(z) = \frac{1}{z - H} \quad (1.7)$$

This is the most common way in which  $G(z)$  is represented, and is of course the more convenient form to compute its matrix element (as long as  $z$  is not in the spectrum of  $H$ ).

In the following we will make use of both the green operator corresponding to the full Hamiltonian  $H$  and the free Hamiltonian  $H_0$ . As usual we will distinguish them with a 0 subscript

$$G(z) = \frac{1}{z - H} \quad G_0(z) = \frac{1}{z - H_0}$$

Useful formulas relating  $G(z)$  and  $G_0(z)$  are

$$G(z) = G_0(z) + G_0(z)VG(z) \quad (1.8)$$

$$G(z) = G_0(z) + G(z)VG_0(z) \quad (1.9)$$

which can be directly proven by substituting  $V = (H + z) - (H_0 - z)$ .

### 1.2.2 The operator $T$

We define the operator  $T(z)$  ( $z \in \mathbb{C}$ ) as

$$T(z) = V + V G(z) V \quad (1.10)$$

It is evident that as a function of  $z$ ,  $T$  and  $G$  have the very same properties.

As we already mentioned, and as we will show later, the interest in  $T$  lies in the fact that it can be directly related to the scattering probability.

From equations 1.8 and 1.9 and the definition of  $T(z)$ , we can find other useful relations concerning  $T(z)$

$$T(z) G_0(z) = V G(z) \quad (1.11)$$

$$G_0(z) T(z) = G(z) V \quad (1.12)$$

With the first relation, we can remove the operator  $G(z)$  from the definition of  $T(z)$  and get

$$T(z) = V + V G_0(z) T(z) \quad (1.13)$$

which is known as Lippman-Schwinger equation for  $T(z)$ . This equation is the cornerstone of the perturbative approach to scattering problems, but we will not develop further this topic (the interested reader should refer to Chapter ... of Taylor).

### 1.2.3 S matrix and T matrix

As we mentioned before, the  $T(z)$  operator can be directly related to the S-matrix element. First we need to write  $S$  as an integral in a time variable:

$$S = \Omega_-^\dagger \Omega_+ = \lim_{t \rightarrow +\infty} \lim_{t' \rightarrow -\infty} U_0^\dagger(t) U(t) U^\dagger(t') U_0(t')$$

If the limit exists, the two limits can be taken simultaneously

$$S = \lim_{t \rightarrow -\infty} U_0^\dagger(-t) U(-t) U^\dagger(t) U_0(t) = \lim_{t \rightarrow -\infty} U_0(t) U^\dagger(2t) U_0(t)$$

Differentiating the expression,

$$\frac{d}{dt} U_0(t) U^\dagger(2t) U_0(t) = +i U_0(t) [V U^\dagger(2t) + U^\dagger(2t) V] U_0(t)$$

Introducing a dumping factor that will be necessary for further manipulations

$$S = \mathbb{I} + i \lim_{\varepsilon \rightarrow 0^+} \int_{-\infty}^0 dt e^{+\varepsilon t} e^{-iH_0 t} [V e^{2iHt} + e^{2iHt} V] e^{-iH_0 t} \quad (1.14)$$

Now if we compute the S matrix element of the free hamiltonian eigenstates

$$\begin{aligned} \langle \beta \mathbf{p}' | S | \alpha \mathbf{p} \rangle &= \langle \beta \mathbf{p}' | \alpha \mathbf{p} \rangle + \\ &- \frac{1}{2} \lim_{\varepsilon \rightarrow 0^+} \left\langle \beta \mathbf{p}' \left| V G \left( \frac{E_{\alpha \mathbf{p}} + E_{\beta \mathbf{p}'}}{2} + i \frac{\varepsilon}{2} \right) + G \left( \frac{E_{\alpha \mathbf{p}} + E_{\beta \mathbf{p}'}}{2} + i \frac{\varepsilon}{2} \right) V \right| \alpha \mathbf{p} \right\rangle \end{aligned}$$

Recognizing that

$$i \int_{-\infty}^0 dt \exp(-i(E_{\alpha \mathbf{p}} + E_{\beta \mathbf{p}'} + i\varepsilon - 2H)t) = -\frac{1}{2} G \left( \frac{E_{\alpha \mathbf{p}} + E_{\beta \mathbf{p}'}}{2} + i \frac{\varepsilon}{2} \right)$$

Employing eq. 1.11 and 1.12, the second term of the equation becomes

$$\lim_{\varepsilon \rightarrow 0^+} \left\langle \beta \mathbf{p}' \left| T(\tilde{E} + i \frac{\varepsilon}{2}) G_0(\tilde{E} + i \frac{\varepsilon}{2}) + G_0(\tilde{E} + i \frac{\varepsilon}{2}) T(\tilde{E} + i \frac{\varepsilon}{2}) \right| \alpha \mathbf{p} \right\rangle$$

with  $\tilde{E} = \frac{E_{\alpha\mathbf{p}} + E_{\beta\mathbf{p}'}}{2}$ . Now we can let  $G_0$  act on the ket obtaining

$$\lim_{\varepsilon \rightarrow 0^+} \left( \frac{1}{\tilde{E} + i\frac{\varepsilon}{2} - E_{\beta\mathbf{p}'}} + \frac{1}{\tilde{E} + i\frac{\varepsilon}{2} - E_{\alpha\mathbf{p}}} \right) \langle \beta\mathbf{p}' | T(\tilde{E}) | \alpha\mathbf{p} \rangle$$

With some simple manipulations, we can recognize in this expression one of the standard representation of Dirac delta as limit of Lorentzian distributions

$$\begin{aligned} \lim_{\varepsilon \rightarrow 0^+} \left( \frac{2}{E_{\alpha\mathbf{p}} - E_{\beta\mathbf{p}'} + i\varepsilon} - \frac{2}{E_{\alpha\mathbf{p}} - E_{\beta\mathbf{p}'} - i\varepsilon} \right) &= -4i\pi \lim_{\varepsilon \rightarrow 0^+} \frac{1}{\pi} \frac{\varepsilon}{(E_{\alpha\mathbf{p}} - E_{\beta\mathbf{p}'} + i\varepsilon)^2 + \varepsilon^2} = \\ &= -4i\pi \delta(E_{\alpha\mathbf{p}} - E_{\beta\mathbf{p}'}) \end{aligned}$$

In conclusion, the S matrix element is related to T matrix element by

$$\langle \alpha\mathbf{p} | S | \beta\mathbf{p}' \rangle = \delta_{\alpha\beta} \delta(\mathbf{p} - \mathbf{p}') + 2i\pi \delta(E_{\alpha\mathbf{p}} - E_{\beta\mathbf{p}'}) \langle \beta\mathbf{p}' | T(E_{\alpha\mathbf{p}} + i0^+) | \alpha\mathbf{p} \rangle \quad (1.15)$$

Comparing this expression, with eq. ————— we conclude

$$\langle \beta\mathbf{p}' | T(E_{\alpha\mathbf{p}} + i0^+) | \alpha\mathbf{p} \rangle = t(\beta\mathbf{p}' \leftarrow \alpha\mathbf{p}) \quad (1.16)$$

## 1.3 Scattering states

### 1.3.1 Definition

see notes on the notebook

Lippman-Schwinger equation for scattering states

$$|\mathbf{p}\alpha+\rangle = \Omega_+ |\mathbf{p}\alpha\rangle$$

in an analogous way as before, we write  $\Omega_+$  in integral form

$$\Omega_+ = \mathbb{I} - i \lim_{\varepsilon \rightarrow 0^+} \int_{-\infty}^0 d\tau \exp(\varepsilon\tau) U(\tau)^\dagger V U_0(\tau)$$

hence

$$|\mathbf{p}\alpha+\rangle = |\mathbf{p}\alpha\rangle - i \lim_{\varepsilon \rightarrow 0^+} \int_{-\infty}^0 d\tau \exp(-i(\varepsilon - H + E_{\mathbf{p}\alpha})\tau) V |\mathbf{p}\alpha\rangle$$

$$|\mathbf{p}\alpha+\rangle = |\mathbf{p}\alpha\rangle + G(E_{\mathbf{p}\alpha} + i0^+) V |\mathbf{p}\alpha\rangle$$

$$|\mathbf{p}\alpha+\rangle = |\mathbf{p}\alpha\rangle + G_0(E_{\mathbf{p}\alpha} + i0^+) T(E_{\mathbf{p}\alpha} + i0^+) |\mathbf{p}\alpha\rangle$$

substituting A and B (B to be included in remarks on scattering states definition), we get the Lippman-Schwinger relation for the scattering states

$$|\mathbf{p}\alpha+\rangle = |\mathbf{p}\alpha\rangle + G_0(E_{\mathbf{p}\alpha} + i0^+) V |\mathbf{p}\alpha+\rangle \quad (1.17)$$

## 1.4 Time dependent and time independent approach

In the previous section we have developed all the necessary tools to deal with a dynamical problem. We can now briefly consider the philosophy behind actual methods to study the evolution of a system.

The main idea of the **time independent** approach is to look for the scattering states  $|p\alpha+\rangle$ . As seen in previous section, scattering states are eigenfunctions of the complete hamiltonian  $H$  and so they are solution of the time independent Schrödinger equation, with appropriate boundary conditions. These conditions are usually introduced by fixing the asymptotic behaviour of the scattering states, that can be calculated from LS equation for the scattering states

$$\lim_{R \rightarrow \infty} \langle \mathbf{R} | p\alpha+\rangle = \langle \mathbf{R} | p\alpha\rangle + \lim_{R \rightarrow \infty} \langle \mathbf{R} | G_0(E_{p\alpha} + i0^+) V | p\alpha+\rangle$$

In the **time dependent** approach, on the other hand, the actual time evolution of the system is considered by solving the time dependent Schrödinger equation with given initial conditions. In detail we take an initial wavepacket

$$|\Psi\rangle = \int d\mathbf{p} \psi(\mathbf{p}) |\mathbf{p}\alpha\rangle$$

By representing both the wavepacket and the evolution operator on a suitable basis, we evolve the wavepacket in time and then we analyse the results.

One would expect these approach to be equivalent, and this is indeed the case. Later we will prove this fact in a particular case, showing that with a the time-energy fourier trasform we can go from one description to the other.



## Chapter 2

# Scattering of molecules on surfaces

In this part, we will specify our consideration to the system of our interest. We suppose a biatomic molecule to be scattered by the interaction with a surface, which has two dimensional periodicity. The system can conveniently described by the 3D position of the center of mass of the particle  $\mathbf{R} = (X, Y, Z)$  and by another nD coordinate  $\mathbf{r} = (r, \theta, \phi, Q_1 \dots)$ , such that the Hamiltonian in  $\mathbf{r}$  has only discrete eigenfunctions. In particular, in our case  $\mathbf{r}$  represent both the internal coordinate of the biatomic molecule and the phonon coordinates of the surface. Since we are assuming that the molecule cannot dissociate, the molecule hamiltonian has just discrete states.

In particular, the hamiltonian for the system will be

$$H = T(\mathbf{R}) + T(\mathbf{r}) + V_{asymp}(\mathbf{r}) + V_{interaction}(\mathbf{r}, \mathbf{R})$$

where we have conveniently divided the potential in two terms.  $V_{asymp}(\mathbf{r})$ , which is the limit of the full potential as the molecule-surface distance becomes infinite, depends just on  $\mathbf{r}$  and describe the vibrations of the free molecule and the phonon degrees of freedom.  $V_{interaction}(\mathbf{r}, \mathbf{R})$ , the difference between the full potential and the asymptotic potential, describe the interaction of the molecule with the surface and the correlations between surface and molecule degrees of freedom. In the following, our free hamiltonian will be  $H^0 = T(\mathbf{R}) + T(\mathbf{r}) + V_{asymp}(\mathbf{r})$  and consequently  $V = V_{interaction}(\mathbf{r}, \mathbf{R})$ .

### 2.1 Asymptotic limit of the scattering states

From LS equation (eq. 2.3), we can write the asymptotic state as

$$\langle \mathbf{Rr} | \mathbf{p}\alpha+ \rangle = \langle \mathbf{Rr} | \mathbf{p}\alpha \rangle + \langle \mathbf{Rr} | G_0(E_{\mathbf{p}\alpha} + i0^+) V | \mathbf{p}\alpha+ \rangle \quad (2.1)$$

where  $\mathbf{p} = (p_X, p_Y, -p_Z)$  is the momentum along  $\mathbf{R}$  while  $\alpha = (n, j, m_j, \nu_1 \dots)$  is a collective discrete index labelling the bound state for the  $\mathbf{r}$  wavefunction (i.e. the rovibrational state of the molecule and the phonon state of the surface). For future convinience, we choose the  $Z$  component of the momentum to be  $-p_Z$ , so that  $p_Z$  is by definition a positive quantity when the incoming molecule approaches the surface. The free state energy  $E_{\mathbf{p}\alpha}$  is

$$E_{\mathbf{p}\alpha} = \frac{p^2}{2M} + \epsilon_\alpha$$

with  $\epsilon_\alpha$  collecting all the energy term depending on the quantum numbers  $\alpha$ .

We insert in LS equation the resolution of the identity on the free states

$$\langle \mathbf{Rr} | \mathbf{p}\alpha+ \rangle = \langle \mathbf{Rr} | \mathbf{p}\alpha \rangle + \sum_{\beta} \int d\mathbf{p}' \langle \mathbf{Rr} | G_0(E_{\mathbf{p}\alpha} + i0^+) | \mathbf{p}'\beta \rangle \langle \mathbf{p}'\beta | V | \mathbf{p}\alpha+ \rangle$$

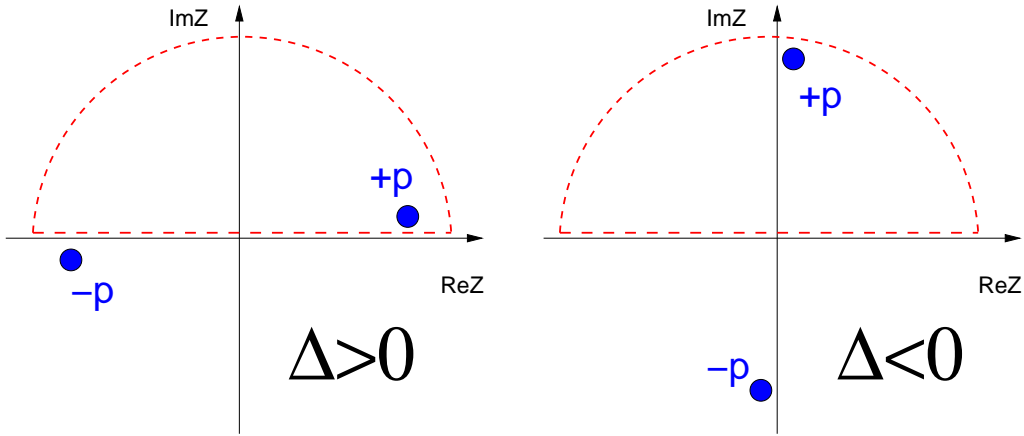


Figure 2.1: Poles of the integrating function and path of integration

The periodicity of the the surface implies the invariance of the interaction potential  $V$  with respect to translations of  $\rho = (X, Y)$ . Both the free state  $\langle \mathbf{p}\alpha |$  the scattering states  $\langle \mathbf{p}\alpha + |$  span the representation

$$\exp(i\mathbf{p}^{\parallel} \cdot \tau_{mn})$$

of the lattice translations group  $\{\tau_{mn}\}$  ( $\mathbf{p}^{\parallel} = (p_X, p_Y)$  is the momentum component parallel to the surface). This implies that

$$\langle \mathbf{p}'\beta | V | \mathbf{p}\alpha + \rangle = 0$$

unless  $p'_x - p_x = mk_1$  and  $p'_y - p_y = nk_2$  (see section ——— “reciprocal lattice”). This allows us to convert the integration on  $\rho$  in a sum on  $m, n$

$$\int d\mathbf{p}' \dots \langle \mathbf{p}'\beta | V | \mathbf{p}\alpha + \rangle = \sum_{mn} \int dp'_z \dots \langle p'_z \mathbf{p}_{mn}^{\parallel} \beta | V | \mathbf{p}\alpha + \rangle \quad (2.2)$$

where the vector  $\mathbf{p}_{mn}^{\parallel}$  is the momentum  $(p_X + nk_1, p_X + mk_2)$  parallel to the surface.

After having introduced the symmetry of the surface, we can evaluate the action of the free Green operator  $G_0(E_{\mathbf{p}\alpha} + i0^+)$  on the following free state using eq. 1.7

$$\langle \mathbf{R}\mathbf{r} | \mathbf{p}\alpha + \rangle = \langle \mathbf{R}\mathbf{r} | \mathbf{p}\alpha \rangle + \sum_{mn\beta} \lim_{\varepsilon \rightarrow 0^+} \int dp'_z \frac{\langle \mathbf{R}\mathbf{r} | p'_z \mathbf{p}_{mn}^{\parallel} \beta \rangle \langle p'_z \mathbf{p}_{mn}^{\parallel} \beta | V | \mathbf{p}\alpha + \rangle}{E_{\mathbf{p}\alpha} - E_{\mathbf{p}'\beta} + i\varepsilon} \quad (2.3)$$

We want to evaluate the integral in  $p'_z$  with the methods of complex analysis. Expliciting the energy  $E_{\mathbf{p}'\beta}$

$$E_{\mathbf{p}\alpha} - E_{\mathbf{p}'\beta} = E_{\mathbf{p}\alpha} - \frac{p_Z'^2 + p_{mn}^{\parallel 2}}{2M} - \epsilon^\beta = \frac{1}{2M} \left[ \underbrace{2M \left( E_{\mathbf{p}\alpha} - \epsilon^\beta - \frac{p_{mn}^{\parallel 2}}{2M} \right)}_{\Delta} - p_Z'^2 \right]$$

So we can factorize the denominator as

$$E_{\mathbf{p}\alpha} - E_{\mathbf{p}'\beta} + i0^+ = \frac{1}{2M} (\tilde{p} - p'_z)(\tilde{p} + p'_z)$$

where  $\tilde{p}$  is any complex root of  $\Delta + i\varepsilon$  (for later convenience, we choose  $\tilde{p}$  to be the root with  $Im \tilde{p} > 0$ ).

To evaluate the integral, we extend the function in the complex plane, by taking  $p'_z \in \mathbb{C}$  and we consider the integration along the path schematically represented in Fig.

2.1. In detail, the integration path is a line between  $-R$  and  $+R$  on the real axis, and half circumference of radius  $R$  in the upper complex halfplane. As  $R \rightarrow +\infty$ , the integral on the real axis becomes the integral we want to compute while the integral along the half circumference tends to 0. To prove that

$$\left| \frac{\langle \mathbf{Rr} | p'_Z \mathbf{p}_{mn}^\parallel \beta \rangle \langle p'_Z \mathbf{p}_{mn}^\parallel \beta | V | \mathbf{p}\alpha + \rangle}{\tilde{p}^2 - p'^2_Z} \right| \rightarrow 0 \quad \text{for } R \rightarrow +\infty$$

we have to show that for  $p'_Z \in \mathbb{C}$  the modulus of the numerator of the integrand  $\left| \langle \mathbf{Rr} | p'_Z \mathbf{p}_{mn}^\parallel \beta \rangle \right| \left| \langle p'_Z \mathbf{p}_{mn}^\parallel \beta | V | \mathbf{p}\alpha + \rangle \right|$  is bounded. The absolute value of the first factor can be explicitly computed

$$\left| \langle \mathbf{Rr} | p'_Z \mathbf{p}_{mn}^\parallel \beta \rangle \right| = \left| \frac{1}{\sqrt{2\pi A}} \phi_\beta(r) \right| e^{-\frac{1}{\hbar} (\text{Im } p'_Z) Z}$$

and is bounded for  $p'_Z \in \mathbb{C}$  if  $\text{Im } p'_Z \geq 0$ . The second factor can more easily be analyzed when in coordinate representation. If we again assume  $\text{Im } p'_Z \geq 0$

$$\begin{aligned} \left| \langle p'_Z \mathbf{p}_{mn}^\parallel \beta | V | \mathbf{p}\alpha + \rangle \right| &= \left| \int d\mathbf{r}' \int d\mathbf{R}' \langle p'_Z \mathbf{p}_{mn}^\parallel \beta | \mathbf{R}' \mathbf{r}' \rangle V(\mathbf{R}' \mathbf{r}') \langle \mathbf{R}' \mathbf{r}' | \mathbf{p}\alpha + \rangle \right| \leq \\ &\leq \left( \sup_{\mathbf{R}' \mathbf{r}'} V(\mathbf{R}' \mathbf{r}') \right) \langle (Re p'_Z) \mathbf{p}_{mn}^\parallel \beta | \mathbf{p}\alpha + \rangle \end{aligned}$$

Any reasonable potential can be assumed to be bounded except for some repulsive regions. Anyway the scattering eigenstates are eigenstates of the full hamiltonian, and we can reasonably assume that in the repulsive regions they go to 0 faster than the potential itself.

From this analysis it becomes clear why we choose an integration path in the upper complex halfplane. If we chose the symmetric path in the lower halfplane, we couldn't assume  $\text{Im } p'_Z \geq 0$  and the numerator of the integrand would no longer be bounded.

From the well known Cauchy's theorem of complex analysis, the integral along the closed path is  $2\pi i$  times the sum of the residues of the integrand in the area contained in the integration path. In our case the integrand has just one simple pole in the upper half plane, namely  $+\tilde{p}$ . So

$$\int dp'_Z \frac{f(p'_Z)}{(\tilde{p} - p'_Z)(\tilde{p} + p'_Z)} = 2\pi i \lim_{p'_Z \rightarrow \tilde{p}} \frac{f(p'_Z)}{(\tilde{p} + p'_Z)} = -\frac{\pi i f(\tilde{p})}{\tilde{p}}$$

In conclusion, eq. 2.3 becomes

$$\langle \mathbf{Rr} | \mathbf{p}\alpha + \rangle = \langle \mathbf{Rr} | \mathbf{p}\alpha \rangle - 2i\pi \sum_{mn\beta} \lim_{\varepsilon \rightarrow 0^+} \frac{M}{\tilde{p}} \langle \mathbf{Rr} | \tilde{p} \mathbf{p}_{mn}^\parallel \beta \rangle \langle \tilde{p} \mathbf{p}_{mn}^\parallel \beta | V | \mathbf{p}\alpha + \rangle \quad (2.4)$$

Next step is to take the limit  $\varepsilon \rightarrow 0^+$ . Now two possibilities arise, corresponding to the possible sign of  $\Delta$ . For  $\Delta < 0$  we have scattering channels for which the energy  $\epsilon^\beta + \frac{p_{mn}^{\parallel 2}}{2M}$  is greater than the initial energy (for reason that will become evident later, we call these **closed channels**). In this case the limit of  $\tilde{p}$  for  $\varepsilon \rightarrow 0^+$  is a purely imaginary momentum  $i\tilde{p}$  and the free eigenstates  $\langle \mathbf{Rr} | \tilde{p} \mathbf{p}_{mn}^\parallel \beta \rangle$  becomes

$$\langle \mathbf{Rr} | \tilde{p} \mathbf{p}_{mn}^\parallel \beta \rangle = \frac{1}{\sqrt{2\pi A}} e^{-\frac{1}{\hbar} \tilde{p} Z} e^{\frac{i}{\hbar} \mathbf{p}_{mn}^\parallel \cdot \rho}$$

This term contains an exponentially decaying function of  $Z$ . So, if we let  $Z \rightarrow +\infty$ , the closed channels do not contribute to the sum on eq. 2.4.

For the other channels  $\Delta > 0$  and for  $\varepsilon \rightarrow 0^+$   $\tilde{p}$  becomes a real positive momentum  $p'_Z$  and the free states survive in the limit  $Z \rightarrow +\infty$ . From a physical point of view, since

$\bar{p}$  is the square root of  $2M \left( E_{\mathbf{p}\alpha} - \epsilon^\beta - \frac{p_{mn}^2}{2M} \right)$ ,  $p'_Z$  is the momentum along  $Z$  determined by energy conservation when the system goes from the state  $|\mathbf{p}\alpha\rangle$  to a state with parallel momentum  $p_{mn}^{\parallel}$  and quantum numbers  $\beta$ . The positive sign of  $p'_Z$  (meaning that the scattered molecules move far from the surface) is set by the choice of the integration path which in turn is connected to the presence of a repulsive wall for negative values of  $Z$ .

From eq. .... we can recognize the element of the onshell T matrix

$$\langle \tilde{p}\mathbf{p}_{mn}^{\parallel}\beta | V | \mathbf{p}\alpha + \rangle = \langle \tilde{p}\mathbf{p}_{mn}^{\parallel}\beta | T | \mathbf{p}\alpha \rangle = t(\tilde{p}\mathbf{p}_{mn}^{\parallel}\beta \leftarrow \mathbf{p}\alpha)$$

In conclusion, the limit of the scattering states as  $Z \rightarrow +\infty$

$$\langle \mathbf{Rr} | \mathbf{p}\alpha + \rangle \rightarrow \frac{1}{\sqrt{2\pi A}} \left[ e^{\frac{i}{\hbar}\mathbf{p}\cdot\mathbf{R}} \phi_\alpha(\mathbf{r}) - 2\pi i \sum_{mn\beta} \frac{M}{p'_Z} e^{\frac{i}{\hbar}\mathbf{p}'\cdot\mathbf{R}} \phi_\beta(\mathbf{r}) t(\mathbf{p}'\beta \leftarrow \mathbf{p}\alpha) \right]$$

where the component of the momentum  $\mathbf{p}'$  parallel to the surface are constrained by symmetry

$$\begin{aligned} p'_X &= p_X + mk_1 \\ p'_Y &= p_Y + nk_2 \end{aligned} \quad (2.5)$$

and the component along  $Z$  is given from conservation of energy

$$p'_Z = [2M (E_{\mathbf{p}\alpha} - \epsilon^\beta) - p_X'^2 - p_Y'^2]^{1/2} \quad (2.6)$$

## 2.2 Asymptotic flux and Cross Section

The first result that we will get from the asymptotic expression of the scattering states is the cross section for the relevant events: elastic and inelastic scattering.

The approach that we will follow is to compute the  $Z$  component of the flux along an analysis surface far from the surface, in which we will assume that the scattering state is equal to its asymptotic limit. We will find that the flux is a sum of different terms, each corresponding to a specific event.

As we briefly recalled in appendix (Section B) the flux along a surface  $S$  can be computed as

$$\Phi = \frac{\hbar}{\mu} \int_S \text{Im} [\Psi^* \vec{\nabla} \Psi] \cdot \vec{\delta n}$$

where  $\vec{\delta n}$  is the direction perpendicular to the surface.

In our case we will compute the flux on a hyperplane  $Z = Z_\infty$ , that is located in the asymptotic region. We will take the normal to the plane in the  $+Z$  direction. We will allow  $X$  and  $Y$  to vary in one unit cell of the surface. On the other hand, the coordinate  $\mathbf{r}$  will assume all the acceptable values. The expression of the flux hence become

$$\Phi = \frac{\hbar}{\mu} \int d\mathbf{r} \int_0^{L_X} dX \int_0^{L_Y} dY \text{Im} (\Psi^* \partial_Z \Psi) |_{Z=Z_\infty}$$

Deriving and taking the complex conjugate of the expression of the asymptotic limit of the scattering wavefunction (remember that  $\mathbf{p} = (p_X, p_Y, -p_Z)$ )

$$\langle \mathbf{Rr} | \partial_Z | \mathbf{p}\alpha + \rangle \rightarrow \frac{1}{\sqrt{2\pi A}} \left[ \underbrace{-\frac{i}{\hbar} p_Z e^{\frac{i}{\hbar}\mathbf{p}\cdot\mathbf{R}} \phi_\alpha(\mathbf{r})}_{A1} + \underbrace{\frac{2\pi M}{\hbar} \sum_{mn\beta} e^{\frac{i}{\hbar}\mathbf{p}'\cdot\mathbf{R}} \phi_\beta(\mathbf{r}) t(\mathbf{p}'\beta \leftarrow \mathbf{p}\alpha)}_{A2} \right]$$

$$\langle \mathbf{Rr} | \mathbf{p}\alpha \rangle^* \rightarrow \frac{1}{\sqrt{2\pi A}} \left[ \underbrace{e^{-\frac{i}{\hbar} \mathbf{p} \cdot \mathbf{R}} \phi_\alpha^*(\mathbf{r})}_{B1} + 2\pi i M \underbrace{\sum_{mn\beta} \frac{1}{p'_Z} e^{-\frac{i}{\hbar} \mathbf{p}' \cdot \mathbf{R}} \phi_\beta^*(\mathbf{r}) t^*(\mathbf{p}'\beta \leftarrow \mathbf{p}\alpha)}_{B2} \right]$$

From the multiplication of these two expression, four terms arise. One term comes from the incident part of the scattering state ( $A1 \times B1$ ), another term from the scattering part ( $A2 \times B2$ ) while the other two ( $A1 \times B2$  and  $A2 \times B1$ ) represent the interference between the two waves. We take into account these three parts separately.

**Incident Flux** The first term  $A1 \times B1$  is

$$-\frac{1}{2\pi A} \frac{i}{\hbar} p_Z e^{i\mathbf{p} \cdot \mathbf{R}} \phi_\alpha(\mathbf{r}) e^{-i\mathbf{p} \cdot \mathbf{R}} \phi_\alpha^*(\mathbf{r}) = -\frac{ip_Z}{2\pi \hbar A} |\phi_\alpha(\mathbf{r})|^2$$

The flux coming from this term is

$$\Phi_{inc} = -\frac{1}{2\pi} \frac{p_Z}{M}$$

which can evidently be associated with an incident beam of particle with velocity  $\frac{p_Z}{M}$  approaching the surface ( $p_Z$  is positive by definition so the flux is negative)

**Scattering flux** The term  $A2 \times B2$

$$\begin{aligned} \frac{1}{2\pi A} \left( \frac{2\pi M}{\hbar} \sum_{ij\gamma} e^{\frac{i}{\hbar} \mathbf{p}'' \cdot \mathbf{R}} \phi_\gamma(\mathbf{r}) t(\mathbf{p}''\gamma \leftarrow \mathbf{p}\alpha) \right) \left( 2\pi i M \sum_{mn\beta} \frac{1}{p'_Z} e^{-\frac{i}{\hbar} \mathbf{p}' \cdot \mathbf{R}} \phi_\beta^*(\mathbf{r}) t^*(\mathbf{p}'\beta \leftarrow \mathbf{p}\alpha) \right) = \\ \frac{2\pi i}{\hbar} \sum_{kl\gamma} \sum_{mn\beta} \frac{M^2}{Ap'_Z} e^{\frac{i}{\hbar} (\mathbf{p}'' - \mathbf{p}') \cdot \mathbf{R}} \phi_\gamma(\mathbf{r}) \phi_\beta^*(\mathbf{r}) t(\mathbf{p}''\gamma \leftarrow \mathbf{p}\alpha) t^*(\mathbf{p}'\beta \leftarrow \mathbf{p}\alpha) = \end{aligned}$$

Not that the symmetry condition on  $\mathbf{p}'$  (eq. 2.5) imply that

$$\frac{1}{A} \int_0^{L_X} dX \int_0^{L_Y} dY e^{\frac{i}{\hbar} (\mathbf{p}'' - \mathbf{p}') \cdot \mathbf{R}} = e^{\frac{i}{\hbar} (p''_Z - p'_Z)Z} \frac{1}{A} \int_0^{L_X} dX \int_0^{L_Y} dY e^{\frac{i}{\hbar} (m-k)k_1 X} e^{\frac{i}{\hbar} (n-l)k_2 Y} = e^{\frac{i}{\hbar} (p''_Z - p'_Z)Z} \delta_{mk} \delta_{nl}$$

while the orthonormality of the discrete states

$$\int d\mathbf{r} \phi_\gamma(\mathbf{r}) \phi_\beta^*(\mathbf{r}) = \delta_{\gamma\beta}$$

so the integration gives

$$\begin{aligned} \frac{2\pi i}{\hbar} \sum_{kl\gamma} \sum_{mn\beta} \delta_{mk} \delta_{nl} \delta_{\gamma\beta} \frac{M^2}{p'_Z} e^{\frac{i}{\hbar} (p''_Z - p'_Z)Z} t(\mathbf{p}''\gamma \leftarrow \mathbf{p}\alpha) t^*(\mathbf{p}'\beta \leftarrow \mathbf{p}\alpha) = \\ = \frac{2\pi i}{\hbar} \sum_{mn\beta} \frac{M^2}{p'_Z} |t(\mathbf{p}'\beta \leftarrow \mathbf{p}\alpha)|^2 \end{aligned}$$

recognizing that if  $m = k$ ,  $n = l$  and  $\gamma = \beta$  then  $p''_Z = p'_Z$  (since both values are constrained by conservation of energy).

The flux is

$$\Phi_{scattering} = 2\pi \sum_{mn\beta} \frac{M}{p'_Z} |t(\mathbf{p}'\beta \leftarrow \mathbf{p}\alpha)|^2$$

Which represents the scattering of particles in all the channels that are consistent with energy conservation. Each scattering event has a probability which is given by the square of the on shell T matrix, as expected from the theory.

**Interference flux** The term  $A1 \times B2$  is

$$+ \frac{M}{\hbar} \sum_{mn\beta} \frac{p_Z}{p'_Z} \frac{1}{A} e^{\frac{i}{\hbar}(\mathbf{p}-\mathbf{p}') \cdot \mathbf{R}} (\phi_\beta^*(\mathbf{r}) \phi_\alpha(\mathbf{r})) t^*(\mathbf{p}'\beta \leftarrow \mathbf{p}\alpha)$$

while the term  $A2 \times B1$

$$+ \frac{M}{\hbar} \sum_{mn\beta} \frac{1}{A} e^{\frac{i}{\hbar}(\mathbf{p}'-\mathbf{p}) \cdot \mathbf{R}} (\phi_\alpha^*(\mathbf{r}) \phi_\beta(\mathbf{r})) t(\mathbf{p}'\beta \leftarrow \mathbf{p}\alpha)$$

By integration we find that

$$\Phi_{interf} = \frac{M}{\hbar} \text{Im} \left( t^*(-p_Z \mathbf{p}^\parallel \alpha \leftarrow \mathbf{p}\alpha) + t(-p_Z \mathbf{p}^\parallel \alpha \leftarrow \mathbf{p}\alpha) \right) = 0$$

the interference term is equal to zero<sup>1</sup>.

**Scattering cross sections** So complessly the total flux is

$$\Phi_{total} = \Phi_{incident} + \sum_{mn\beta} \Phi_{scattering}^{mn\beta}$$

We can calculate the cross section for the scattering in each open channel as

$$\frac{\partial \sigma}{\partial \rho}(\mathbf{p}'\beta \leftarrow \mathbf{p}\alpha) = \frac{\Phi_{scattering}^{mn\beta}}{\Phi_{incident}}$$

which gives

$$\frac{\partial \sigma}{\partial \rho}(\mathbf{p}'\beta \leftarrow \mathbf{p}\alpha) = 4\pi^2 \frac{M^2}{p_Z p'_Z} |t(\mathbf{p}'\beta \leftarrow \mathbf{p}\alpha)|^2$$

In light of this result, we can define proportionality between the scattering matrix element and the on-shell T matrix as

$$S(\mathbf{p}'\beta \leftarrow \mathbf{p}\alpha) = 2\pi i \frac{M}{\sqrt{p_Z p'_Z}} t(\mathbf{p}'\beta \leftarrow \mathbf{p}\alpha)$$

so that the square of the S matrix is the cross section for the scattering event.

With these definition the asymptotic formula for the scattering states becomes

$$\langle \mathbf{Rr} | \mathbf{p}\alpha \rangle \rightarrow \frac{1}{\sqrt{2\pi A}} \left[ e^{\frac{i}{\hbar} \mathbf{p} \cdot \mathbf{R}} \phi_\alpha(\mathbf{r}) - \sum_{mn\beta} \sqrt{\frac{p_Z}{p'_Z}} e^{\frac{i}{\hbar} \mathbf{p}' \cdot \mathbf{R}} \phi_\beta(\mathbf{r}) S(\mathbf{p}'\beta \leftarrow \mathbf{p}\alpha) \right]$$

---

<sup>1</sup>For the reader who is familiar with Scattering Theory, some comments are necessary. The method that we have applied here is often used in many books to derive results which may seem to be in disagreement with our discussion. In particular, the interference is different from zero and applying flux conservation this term depending on the forward scattering T matrix element can be shown to be related to total scattering cross section (the well known “optical theorem”).

In our case, even if the flux based method is the same, some crucial assumption of the derivation mentioned above do not hold. In detail:

- our asymptotic expansion of the scattering states does not contain a forward scattering term interfering with the incoming wave. The boundary conditions of the problem forced us to choose the specular channel  $(-p_Z \mathbf{p}^\parallel \alpha \leftarrow \mathbf{p}\alpha)$  rather than the forward channel  $(p_Z \mathbf{p}^\parallel \alpha \leftarrow \mathbf{p}\alpha)$
- as a consequence of Gauss theorem, flux conservation holds for closed surface in the coordinate space. The choice of the hypersurface  $S$  that is convenient for the symmetry of our system does not allow to apply flux conservation

### 2.3 Time-Energy Fourier Transform of a wavepacket

In section 1.4 we have briefly mentioned that time dependent and time independent pictures can be related by a time-energy fourier transform. We will show now for the scattering of molecules on surfaces how this can be done, by extracting information about the scattering states from the actual evolution of the system.

Let's consider a wavepacket, with definite  $\alpha$ ,  $\mathbf{p}_{\parallel}$  and a distribution  $\psi(p_Z)$  on  $p_Z$ . Its free evolution, in absence of the molecule-surface interaction, will be given by

$$|\Psi\rangle = e^{-iH_0 t} \int dp_Z \psi(p_Z) |\mathbf{p}\alpha\rangle = \int dp_Z \psi(p_Z) e^{-iH_0 t} |\mathbf{p}\alpha\rangle \quad (2.7)$$

where  $H_0$  is the hamiltonian including the internal degrees of freedom of both the molecule and the surface.

On the other hand, the actual evolution of the wavepacket will be given by

$$|\Psi+\rangle = \Omega_+ \int dp_Z \psi(p_Z) e^{-iH_0 t} |\mathbf{p}\alpha\rangle = \int dp_Z \psi(p_Z) e^{-iH t} |\mathbf{p}\alpha+\rangle \quad (2.8)$$

where we have used the intertwining relation eq. ....

Fourier transforming the wavepacket for fixed  $E$ , we get

$$\int_{-\infty}^{+\infty} dt e^{iEt} |\Psi+\rangle = \int dp_Z \psi(p_Z) \int_{-\infty}^{+\infty} dt e^{i(E-H)t} |\mathbf{p}\alpha+\rangle \quad (2.9)$$

Since the scattering states are stationary, we can integrate on time

$$\int_{-\infty}^{+\infty} dt e^{i(E-H)t} = 2\pi\delta(E-H)$$

where  $\delta(E-H)$  is the projector on the energy shell. If we let the projector act on the scattering state  $|\mathbf{p}\alpha+\rangle$  we have the Dirac delta

$$\delta\left(E - \frac{p_{\parallel}^2}{2M} - \epsilon_{\alpha} - \frac{p_Z^2}{2M}\right) = 2M\delta(\Delta - p_Z^2)$$

where  $\mathbf{p}_{\parallel}$  and  $\epsilon_{\alpha}$  are respectively the parallel momentum and the internal energy of the initial wavepacket, and  $\Delta$  is equal to  $2M\left(E - \epsilon_{\alpha} - \frac{p_{\parallel}^2}{2M}\right)$ . Now we have two possibilities.

If the energy  $E$  we are considering is lower than  $\epsilon_{\alpha} + \frac{p_{\parallel}^2}{2M}$ ,  $\Delta$  is a negative number, and the integral on  $p_Z$  is zero. On the other hand, for  $\Delta > 0$  we set  $\bar{p} = \sqrt{\Delta}$  and we can transform the Dirac delta as

$$2M\delta(\bar{p}^2 - p_Z^2) = \frac{M}{\bar{p}} [\delta(p_Z - \bar{p}) + \delta(p_Z + \bar{p})]$$

Eq. 2.9 becomes

$$\begin{aligned} \int_{-\infty}^{+\infty} dt e^{iEt} |\Psi+\rangle &= \frac{2\pi M}{\bar{p}} [\psi(\bar{p}) |\bar{p}\mathbf{p}_{\parallel}\alpha+\rangle + \psi(-\bar{p}) |(-\bar{p})\mathbf{p}_{\parallel}\alpha+\rangle] \\ \text{with } \bar{p} &= \sqrt{2M(E - \epsilon_{\alpha}) - p_{\parallel}^2} \end{aligned}$$

If we choose an initial momentum distribution  $\psi(p_Z)$  which is centered in negative values (the particle is moving towards the surface) and narrow enough, we can assume  $\psi(\bar{p}) \approx 0$  and

$$\int_{-\infty}^{+\infty} dt e^{iEt} |\Psi+\rangle = \frac{2\pi M}{\bar{p}} \psi(-\bar{p}) |(-\bar{p})\mathbf{p}_{\parallel}\alpha+\rangle$$

In conclusion, by computing the fourier transform for different values of  $E$ , we can selectively extract from the evolving wavepacket informations on  $|\mathbf{p}\alpha+\rangle$

$$|\mathbf{p}\alpha+\rangle = \frac{|p_Z|}{2\pi M\psi(p_Z)} \int_{-\infty}^{+\infty} dt \exp(\frac{i}{\hbar}Et) |\Psi+\rangle \quad E = \epsilon_\alpha + \frac{p_{\parallel}^2}{2M} + \frac{p_Z^2}{2M} \quad (2.10)$$

Is evident from this formula, that we can get some information on the scattering event just for the internal state  $\alpha$ , the parallel momentum  $\mathbf{p}_{\parallel}$  and the values of incident momentum  $p_Z$  significantly included in the initial wavepacket.



## Appendix A

# Operator derivative and dynamical derivative

In section —————, we have introduced the time derivative of an operator which parametrically depends on time. Naively<sup>1</sup>, this derivative can be defined in analogy with calculus

$$\frac{\partial A(\bar{t})}{\partial t} = \lim_{t \rightarrow 0} \frac{A(\bar{t} + t) - A(\bar{t})}{t}$$

Operator derivative has many proprieties of ordinary derivative:

$$\frac{\partial(\alpha A + \beta B)}{\partial t} = \alpha \frac{\partial A}{\partial t} + \beta \frac{\partial B}{\partial t}$$

$$\frac{\partial(AB)}{\partial t} = \frac{\partial A}{\partial t} B + A \frac{\partial B}{\partial t}$$

Now we want to introduce a new notion of derivative, the *dynamical derivative*. We define a new operator  $\dot{A}$  such that

$$\langle \dot{A} \rangle = \frac{d}{dt} \langle A \rangle \quad (\text{A.1})$$

Since  $\langle A \rangle = \langle \psi | A | \psi \rangle$

$$\frac{d}{dt} \langle A \rangle = \left\langle \frac{d\psi}{dt} \left| A | \psi \right. \right\rangle + \left\langle \psi \left| A \left| \frac{d\psi}{dt} \right. \right\rangle + \left\langle \psi \left| \frac{\partial A}{\partial t} | \psi \right. \right\rangle$$

Substituting Schrödinger equation

$$\begin{aligned} \frac{d}{dt} \langle A \rangle &= \frac{i}{\hbar} \{ \langle \psi | HA | \psi \rangle - \langle \psi | AH | \psi \rangle \} + \left\langle \psi \left| \frac{\partial A}{\partial t} | \psi \right. \right\rangle = \\ &= \left\langle \psi \left| \frac{i}{\hbar} [H, A] + \frac{\partial A}{\partial t} | \psi \right. \right\rangle \end{aligned}$$

So we finally have

$$\dot{A} = \frac{dA}{dt} = \frac{\partial A}{\partial t} + \frac{i}{\hbar} [H, A] \quad (\text{A.2})$$

It can be proved that the dynamical derivative of a product can be evaluated with the same rule as the operator derivative:

$$\begin{aligned} \frac{dAB}{dt} &= \frac{\partial AB}{\partial t} + \frac{i}{\hbar} [H, AB] = \\ &= \frac{\partial A}{\partial t} B + A \frac{\partial B}{\partial t} + \frac{i}{\hbar} \{ [H, A] B + A [H, B] \} = \end{aligned}$$

---

<sup>1</sup>Notice that a precise definition would require to specify the notion of limit

$$= \frac{dA}{dt}B + A\frac{dB}{dt}$$

The main difference between ordinary derivative and (total and partial) operator derivatives follows from non commutativity of operator algebra. The derivative of a function of an operator, can't be computed with the usual formula:

$$\frac{\partial(f(A))}{\partial t} \neq \frac{\partial f}{\partial t}(A) \frac{\partial A}{\partial t}$$

Consider, as example

$$\frac{d}{dt}A^2 = \dot{A}A + A\dot{A}$$

## Appendix B

# Flux operator and density current

be  $\Omega$  a bounded open set of the configuration space  
we define the projector  $P$  as

$$P = \int_{\Omega} dx |x\rangle \langle x|$$

the flux operator is the dynamical derivative of the  $P$  (if the boundary of  $\Omega$  are time independent)

$$\Phi = \frac{i}{\hbar} [H, P]$$

we prove that this definition is in agreement with the usual definition of density current

$$\vec{j} = \frac{\hbar}{2mi} (\Psi^* \vec{\nabla} \Psi - \Psi \vec{\nabla} \Psi^*)$$

We assume that the hamiltonian can be written in the coordinate representation as a sum of a laplacian and a potential which is diagonal in this representation

$$H = -\frac{\hbar^2}{2\mu} \nabla^2 + V(x)$$

hence

$$[H, P] = -\frac{\hbar^2}{2\mu} [\nabla^2, P] + [V, P]$$

but  $[V, P]$  is equal to 0 since both operator are functions of the coordinate only  
so

$$\Phi = -\frac{i\hbar}{2\mu} [\nabla^2, P]$$

the expectation value of the flux operator

$$\langle \Psi | \Phi | \Psi \rangle = -\frac{i\hbar}{2\mu} (\langle \Psi | \nabla^2 P | \Psi \rangle - \langle \Psi | P \nabla^2 | \Psi \rangle)$$

substituting the expression of  $P$ , and using the self-adjointness of  $\nabla^2$

$$\langle \Psi | \nabla^2 P | \Psi \rangle - \langle \Psi | P \nabla^2 | \Psi \rangle$$

$$\begin{aligned} & \int_{\Omega} dx \langle \nabla^2 \Psi | x \rangle \langle x | \Psi \rangle - \int_{\Omega} dx \langle \Psi | x \rangle \langle x | \nabla^2 \Psi \rangle \\ \langle \Psi | \Phi | \Psi \rangle &= -\frac{i\hbar}{2\mu} \int_{\Omega} dx [(\nabla^2 \Psi^*(x)) \Psi(x) - \Psi^*(x) \nabla^2 \Psi(x)] \end{aligned}$$

the integrand expression can be written with the rules of differential calculus

$$(\nabla^2 \Psi^*) \Psi - \Psi^* \nabla^2 \Psi = \nabla \cdot ((\vec{\nabla} \Psi^*) \Psi - \Psi^* \vec{\nabla} \Psi)$$

with gauss theorem

$$\int_{\Omega} \nabla \cdot \left[ \left( \vec{\nabla} \Psi^* \right) \Psi - \Psi^* \vec{\nabla} \Psi \right] dx = \int_{\delta\Omega} \left[ \left( \vec{\nabla} \Psi^* \right) \Psi - \Psi^* \vec{\nabla} \Psi \right] \cdot \vec{\delta n}$$

where the direction of  $\vec{\delta n}$  is normal to the boundary  $\delta\Omega$  of the set  $\Omega$   
so the flux is

$$\langle \Psi | \Phi | \Psi \rangle = -\frac{i\hbar}{2\mu} \int_{\delta\Omega} \left[ \left( \vec{\nabla} \Psi^* \right) \Psi - \Psi^* \vec{\nabla} \Psi \right] \cdot \vec{\delta n}$$

if we define the current density as

$$\vec{j} = \frac{\hbar}{2\mu i} \left( \Psi^* \vec{\nabla} \Psi - \Psi \vec{\nabla} \Psi^* \right) = \frac{\hbar}{\mu} \text{Im} \left[ \Psi^* \vec{\nabla} \Psi \right]$$

we see that the flux change in a set  $\Omega$  is just the integral of the current density on the boundary of the set

$$\Delta\Phi = \int_{\delta\Omega} \vec{j} \cdot \vec{\delta n}$$

which is an equivalent formulation of the continuity equation (in integral form)