Chapter 28

Quantum scattering

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So far the trace formulas have been derived assuming that the system under consideration is bound. As we shall now see, we are in luck - the semiclassics of bound systems is all we need to understand the semiclassics for open, scattering systems as well. We start by a brief review of the quantum theory of elastic scattering of a point particle from a (repulsive) potential, and then develop the connection to the standard Gutzwiller theory for bound systems. We do this in two steps - first, a heuristic derivation which helps us understand in what sense density of states is "density", and then we sketch a general derivation of the central result of the spectral theory of quantum scattering, the Krein-Friedel-Lloyd formula. The end result is that we establish a connection between the scattering resonances (both positions and widths) of an open quantum system and the poles of the trace of the Green function, which we learned to analyze in earlier chapters.

28.1 Density of states

For a scattering problem the density of states (23.17) appear ill defined since formulas such as (27.6) involve integration over infinite spatial extent. What we will now show is that a quantity that makes sense physically is the difference of two densities - the first with the scatterer present and the second with the scatterer absent.

In nonrelativistic dynamics the relative motion can be separated from the center-of-mass motion. Therefore the elastic scattering of two particles can be treated as the scattering of one particle from a static potential $V(q)$. We will study the scattering of a point-particle of (reduced) mass m by

a short-range potential $V(q)$, excluding *inter alia* the Coulomb potential. (The Coulomb potential decays slowly as a function of q so that various asymptotic approximations which apply to general potentials fail for it.) Although we can choose the spatial coordinate frame freely, it is advisable to place its origin somewhere near the geometrical center of the potential. The scattering problem is solved, if a scattering solution to the time-independent Schrödinger equation (23.5)

$$\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial q^2} + V(q)\right)\phi_{\vec{k}}(q) = E\phi_{\vec{k}}(q) \tag{28.1}$$

can be constructed. Here E is the energy, $\vec{p} = \hbar\vec{k}$ the initial momentum of the particle, and $\vec{k}$ the corresponding wave vector.

When the argument $r = |q|$ of the wave function is large compared to the typical size a of the scattering region, the Schrödinger equation effectively becomes a free particle equation because of the short-range nature of the potential. In the asymptotic domain $r \gg a$, the solution $\phi_{\vec{k}}(q)$ of (28.1) can be written as superposition of ingoing and outgoing solutions of the free particle Schrödinger equation for fixed angular momentum:

$$\phi(q) = A\phi^{(-)}(q) + B\phi^{(+)}(q)\,, \qquad (+ \text{ boundary conditions})\,,$$

where in 1-dimensional problems $\phi^{(-)}(q)$, $\phi^{(+)}(q)$ are the "left", "right" moving plane waves, and in higher-dimensional scattering problems the "incoming", "outgoing" radial waves, with the constant matrices A, B fixed by the boundary conditions. What are the boundary conditions? The scatterer can modify only the outgoing waves (see fig. 28.1), since the incoming ones, by definition, have yet to encounter the scattering region. This defines the quantum mechanical scattering matrix, or the S *matrix*

$$\phi_m(r) = \phi^{(-)}_m(r) + S_{mm'}\phi^{(+)}_{m'}(r)\,. \tag{28.2}$$

For concreteness, we have specialized to two dimensions, although the final formula is true for arbitrary dimensions. The indices m and m' are the angular momenta quantum numbers for the incoming and outgoing state of the scattering wave function, labeling the S-matrix elements $S_{mm'}$. More generally, given a set of quantum numbers β, γ, the S matrix is a collection $S_{\beta\gamma}$ of transition amplitudes $\beta \to \gamma$ normalized such that $|S_{\beta\gamma}|^2$ is the probability of the $\beta \to \gamma$ transition. The total probability that the ingoing state β ends up in some outgoing state must add up to unity

$$\sum_\gamma |S_{\beta\gamma}|^2 = 1\,, \tag{28.3}$$

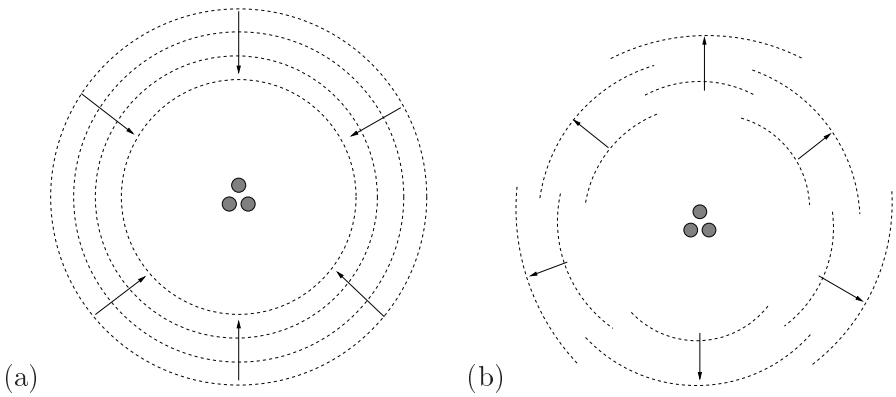

Figure 28.1: (a) *Incoming* spherical waves running into an obstacle. (b) Superposition of *outgoing* spherical waves scattered from an obstacle.

so the S matrix is unitary: $\mathbf{S}^\dagger\mathbf{S} = \mathbf{S}\mathbf{S}^\dagger = \mathbf{1}$.

We have already encountered a solution to the 2-dimensional problem; free particle propagation Green's function (26.47) is a radial solution, given in terms of the Hankel function

$$G_0(r,0,E) = -\frac{im}{2\hbar^2} H_0^{(+)}(kr)\,,$$

where we have used $S_0(r,0,E)/\hbar = kr$ for the action. The mth angular momentum eigenfunction is proportional to $\phi_m^{(\pm)}(q) \propto H_m^{(\pm)}(kr)$, and given a potential $V(q)$ we can in principle compute the infinity of matrix elements $S_{mm'}$. We will not need much information about $H_m^{(t)}(kr)$, other than that for large r its asymptotic form is

$$H^\pm \propto e^{\pm ikr}$$

In general, the potential $V(q)$ is not radially symmetric and (28.1) has to be solved numerically, by explicit integration, or by diagonalizing a large matrix in a specific basis. To simplify things a bit, we assume for the time being that a radially symmetric scatterer is centered at the origin; the final formula will be true for arbitrary asymmetric potentials. Then the solutions of the Schrödinger equation (23.5) are separable, $\phi_m(q) = \phi(r)e^{im\theta}$, $r = |q|$, the scattering matrix cannot mix different angular momentum eigenstates, and S is diagonal in the radial basis (28.2) with matrix elements given by

$$S_m(k) = e^{2i\delta_m(k)}. \tag{28.4}$$

The matrix is unitary so in a diagonal basis all entries are pure phases. This means that an incoming state of the form $H_m^{(-)}(kr)e^{im\theta}$ gets scattered

into an outgoing state of the form $S_m(k)H_m^{(+)}(kr)e^{im\theta}$, where $H_m^{(\mp)}(z)$ are incoming and outgoing Hankel functions respectively. We now embed the scatterer in a infinite cylindrical well of radius R, and will later take $R \to \infty$. Angular momentum is still conserved so that each eigenstate of this (now bound) problem corresponds to some value of m. For large $r \gg a$ each eigenstate is of the asymptotically free form

$$\begin{aligned} \phi_m(r) &\approx e^{im\theta}\left(S_m(k)H_m^{(+)}(kr) + H_m^{(-)}(kr)\right) \\ &\approx \cdots \cos(kr + \delta_m(k) - \chi_m)\,, \end{aligned} \tag{28.5}$$

where $\cdots$ is a common prefactor, and $\chi_m = m\pi/2 + \pi/4$ is an annoying phase factor from the asymptotic expansion of the Hankel functions that will play no role in what follows.

The state (28.5) must satisfy the external boundary condition that it vanish at $r = R$. This implies the quantization condition

$$k_n R + \delta_m(k_n) - \chi_m = \pi\,(n + 12)\ .$$

We now ask for the difference in the eigenvalues of two consecutive states of fixed m. Since R is large, the density of states is high, and the phase $\delta_m(k)$ does not change much over such a small interval. Therefore, to leading order we can include the effect of the change of the phase on state $n+1$ by Taylor expanding. is

$$k_{n+1}R + \delta_m(k_n) + (k_{n+1} - k_n)\delta'_m(k_n) - \chi_m \approx \pi + \pi(n + 12)\,.$$

Taking the difference of the two equations we obtain $\Delta k \approx \pi(R+\delta'_m(k))^{-1}$. This is the eigenvalue spacing which we now interpret as the inverse of the density of states within m angular momentum sbuspace

$$d_m(k) \approx \frac{1}{\pi}\left(R + \delta'_m(k)\right).$$

The R term is essentially the $1-d$ Weyl term (27.8), appropriate to $1-d$ radial quantization. For large R, the dominant behavior is given by the size of the circular enclosure with a correction in terms of the derivative of the scattering phase shift, approximation accurate to order $1/R$. However, not all is well: the area under consideration tends to infinity. We regularize this by subtracting from the result from the free particle density of states $d_0(k)$, for the same size container, but this time without any scatterer, fig. 28.2. We also sum over all m values so that

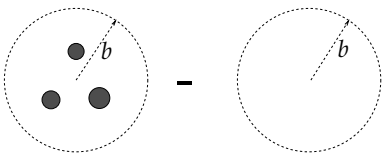

Figure 28.2: The "difference" of two bounded reference systems, one with and one without the scattering system.

$$d(k) - d_0(k) = \frac{1}{\pi}\sum_m \delta'_m(k) = \frac{1}{2\pi i}\sum_m \frac{d}{dk}\log S_m$$
$$= \frac{1}{2\pi i}\mathrm{Tr}\left(S^\dagger \frac{dS}{dk}\right). \qquad (28.6)$$

The first line follows from the definition of the phase shifts (28.4) while the second line follows from the unitarity of S so that $S^{-1} = S^\dagger$. We can now take the limit $R \to \infty$ since the R dependence has been cancelled away.

This is essentially what we want to prove since for the left hand side we already have the semiclassical theory for the trace of the difference of Green's functions,

$$d(k) - d_0(k) = -\frac{1}{2\pi k}\mathrm{Im}\left(\mathrm{tr}\left(G(k) - G_0(k)\right)\right). \qquad (28.7)$$

There are a number of generalizations. This can be done in any number of dimensions. It is also more common to do this as a function of energy and not wave number k. However, as the asymptotic dynamics is free wave dynamics labeled by the wave number k, we have adapted k as the natural variable in the above discussion.

Finally, we state without proof that the relation (28.6) applies even when there is no circular symmetry. The proof is more difficult since one cannot appeal to the phase shifts δ_m but must work directly with a non-diagonal S matrix.

28.2 Quantum mechanical scattering matrix

The results of the previous section indicate that there is a connection between the scattering matrix and the trace of the quantum Green's function (more formally between the difference of the Green's function with and without the scattering center.) We now show how this connection can be derived in a more rigorous manner. We will also work in terms of the energy E rather than the wavenumber k, since this is the more usual exposition. Suppose particles interact via forces of sufficiently short range, so that in the remote past they were in a free particle state labelled β, and

in the distant future they will likewise be free, in a state labelled γ. In the Heisenberg picture the S-matrix is defined as $\mathbf{S} = \Omega_- \Omega_+^\dagger$ in terms of the Møller operators

$$\Omega_\pm = \lim_{t\to\pm\infty} e^{iHt/\hbar} e^{-iH_0 t/\hbar} \ , \tag{28.8}$$

where H is the full Hamiltonian, whereas H_0 is the free Hamiltonian. In the interaction picture the S-matrix is given by

$$\begin{aligned} \mathbf{S} &= \Omega_+^\dagger \Omega_- = \lim_{t\to\infty} e^{iH_0 t/\hbar} e^{-2iHt/\hbar} e^{iH_0 t/\hbar} \\ &= T \exp\left(-i \int_{-\infty}^{+\infty} dt H'(t) \right) \ , \end{aligned} \tag{28.9}$$

where $H' = V = H - H_0$ is the interaction Hamiltonian and T is the time-ordering operator. In stationary scattering theory the S matrix has the following spectral representation

$$\begin{aligned} S &= \int_0^\infty dE\, S(E) \delta(H_0 - E) \\ S(E) &= Q_+(E) Q_-^{-1}(E), \qquad Q_\pm(E) = \mathbf{1} + (H_0 - E \pm i\epsilon)^{-1} V \end{aligned} \tag{28.10}$$

such that

$$\mathrm{Tr}\left[S^\dagger(E) \frac{d}{dE} S(E) \right] = \mathrm{Tr}\left[\frac{1}{H_0 - E - i\epsilon} - \frac{1}{H - E - i\epsilon} - (\epsilon \leftrightarrow -\epsilon) \right] \ . \tag{28.11}$$

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The manipulations leading to (28.11) are justified if the operators $Q_\pm(E)$ can be linked to trace-class operators.

We can now use this result to derive the Krein-Lloyd formula which is the central result of this chapter. The Krein-Lloyd formula provides the connection between the trace of the Green's function and the poles of the scattering matrix, implicit in all of the trace formulas for open quantum systems which will be presented in the subsequent chapters.

28.3 Krein-Friedel-Lloyd formula

The link between quantum mechanics and semiclassics for scattering problems is provided by the semiclassical limit of the Krein-Friedel-Lloyd sum

for the spectral density which we now derive. This derivation builds on the results of the last section and extends the discussion of the opening section.

In chapter 26 we linked the spectral density (see (23.17)) of a bounded system

$$d(E) \equiv \sum_n \delta(E_n - E) \tag{28.12}$$

via the identity

$$\begin{aligned} \delta(E_n - E) &= -\lim_{\epsilon\to 0} \frac{1}{\pi} \mathrm{Im} \frac{1}{E - E_n + i\epsilon} \\ &= -\lim_{\epsilon\to 0} \frac{1}{\pi} \mathrm{Im} \langle E_n | \frac{1}{E - H + i\epsilon} | E_n \rangle \\ &= \frac{1}{2\pi\, i} \lim_{\epsilon\to 0} \left\langle E_n \left| \frac{1}{E - H - i\epsilon} - \frac{1}{E - H + i\epsilon} \right| E_n \right\rangle \end{aligned} \tag{28.13}$$

to the trace of the Green's function (27.1.1). Furthermore, in the semiclassical approximation, the trace of the Green's function is given by the Gutzwiller trace formula (27.11) in terms of a smooth Weyl term and an oscillating contribution of periodic orbits.

Therefore, the task of constructing the semiclassics of a scattering system is completed, if we can find a connection between the spectral density $d(E)$ and the scattering matrix S. We will see that (28.11) provides the clue. Note that the right hand side of (28.11) has nearly the structure of (28.13) when the latter is inserted into (28.12). The principal difference between these two types of equations is that the S matrix refers to *outgoing* scattering wave functions which are not normalizable and which have a *continuous* spectrum, whereas the spectral density $d(E)$ refers to a bound system with normalizable wave functions with a discrete spectrum. Furthermore, the bound system is characterized by a *hermitian* operator, the Hamiltonian H, whereas the scattering system is characterized by a *unitary* operator, the S-matrix. How can we reconcile these completely different classes of wave functions, operators and spectra? The trick is to put our scattering system into a finite box as in the opening section. We choose a spherical conatiner with radius R and with its center at the center of our finite scattering system. Our scattering potential $V(\vec{r})$ will be unaltered within the box, whereas at the box walls we will choose an infinitely high potential, with the Dirichlet boundary conditions at the outside of the box:

$$\phi(\vec{r})|_{r=R} = 0\,. \tag{28.14}$$

In this way, for any finite value of the radius R of the box, we have mapped our scattering system into a bound system with a spectral density $d(E;R)$ over discrete eigenenergies $E_n(R)$. It is therefore important that our scattering potential was chosen to be short-ranged to start with. (Which explains why the Coulomb potential requires special care.) The hope is that in the limit $R \to \infty$ we will recover the scattering system. But some care is required in implementing this. The smooth Weyl term $\bar{d}(E;R)$ belonging to our box with the enclosed potential V diverges for a spherical two-dimensional box of radius R quadratically, as $\pi R^2/(4\pi)$ or as R^3 in the three-dimensional case. This problem can easily be cured if the spectral density of an empty reference box of the *same* size (radius R) is subtracted (see fig. 28.2). Then all the divergences linked to the increasing radius R in the limit $R \to \infty$ drop out of the difference. Furthermore, in the limit $R \to \infty$ the energy-eigenfunctions of the box are only normalizable as a delta distribution, similarly to a plane wave. So we seem to recover a continous spectrum. Still the problem remains that the wave functions do not discriminate between incoming and outgoing waves, whereas this symmetry, namely the hermiticity, is broken in the scattering problem. The last problem can be tackled if we replace the spectral density over discrete delta distributions by a smoothed spectral density with a small finite imaginary part η in the energy E:

$$d(E+i\eta;R) \equiv \frac{1}{i\,2\pi} \sum_n \left\{ \frac{1}{E-E_n(R)-i\eta} - \frac{1}{E-E_n(R)+i\eta} \right\} . \quad (28.15)$$

Note that $d(E+i\eta;R) \neq d(E-i\eta;R) = -d(E+i\eta;R)$. By the introduction of the positive *finite* imaginary part η the time-dependent behavior of the wave function has effectively been altered from an oscillating one to a decaying one and the hermiticity of the Hamiltonian is removed. Finally the limit $\eta \to 0$ can be carried out, respecting the order of the limiting procedures. First the limit $R \to \infty$ has to be performed for a *finite* value of η, only then the limit $\eta \to 0$ is allowed. In practice, one can try to work with a finite value of R, but then it will turn out (see below) that the scattering system is only recovered if $R\sqrt{\eta} \gg 1$.

Let us summarize the relation between the smoothed spectral densities $d(E+i\eta;R)$ of the boxed potential and $d^{(0)}(E+i\eta;R)$ of the empty reference system and the S matrix of the corresponding scattering system:

$$\begin{aligned} \lim_{\eta\to+0} \lim_{R\to\infty} \Big(d(E+i\eta;R) - d^{(0)}(E+i\eta;R) \Big) &= \frac{1}{2\pi i} \mathrm{Tr} \left[S^\dagger(E) \frac{d}{dE} S(E) \right] \\ = \frac{1}{2\pi i} \mathrm{Tr} \frac{d}{dE} \ln S(E) &= \frac{1}{2\pi i} \frac{d}{dE} \ln \det S(E) \end{aligned} \quad (28.16)$$

This is the *Krein-Friedel-Lloyd formula*. It replaces the scattering problem by the difference of two bounded reference billiards of the same radius

R which finally will be taken to infinity. The first billiard contains the scattering region or potentials, whereas the other does not (see fig. 28.2). Here $d(E+i\eta;R)$ and $d^{(0)}(E+i\eta;R)$ are the *smoothed* spectral densities in the presence or in the absence of the scatterers, respectively. In the semiclassical approximation, they are replaced by a Weyl term (27.10) and an oscillating sum over periodic orbits. As in (27.2), the trace formula (28.16) can be integrated to give a relation between the smoothed staircase functions and the determinant of the S-matrix:

$$\lim_{\eta\to+0}\lim_{R\to\infty}\Big(N(E+i\eta;R)-N^{(0)}(E+i\eta;R)\Big) \;=\; \frac{1}{2\pi i}\ln\det S(E) \qquad (28.17)$$

Furthermore, in both versions of the Krein-Friedel-Lloyd formulas the energy argument $E+i\eta$ can be replaced by the wavenumber argument $k+i\eta'$. These expressions only make sense for wave numbers on or above the real k-axis. In particular, if k is chosen to be real, η' must be greater than zero. Otherwise, the exact left hand sides (28.17) and (28.16) would give discontinuous staircase or even delta function sums, respectively, whereas the right hand sides are continuous to start with, since they can be expressed by continuous phase shifts. Thus the order of the two limits in (28.17) and (28.16) is essential.

The necessity of the $+i\eta$ prescription can also be understood by purely phenomenological considerations in the semiclassical approximation: Without the $i\eta$ term there is no reason why one should be able to neglect spurious periodic orbits which are there solely because of the introduction of the confining boundary. The subtraction of the second (empty) reference system removes those spurious periodic orbits which never encounter the scattering region – in addition to the removal of the divergent Weyl term contributions in the limit $R\to\infty$. The periodic orbits that encounter both the scattering region and the external wall would still survive the first limit $R\to\infty$, if they were not exponentially suppressed by the $+i\eta$ term because of their

$$e^{iL(R)\sqrt{2m(E+i\eta)}} = e^{iL(R)k}\, e^{-L(R)\eta'}$$

behavior. As the length $L(R)$ of a spurious periodic orbit grows linearly with the radius R. The bound $R\eta'\gg 1$ is an essential precondition on the suppression of the unwanted spurious contributions of the container if the Krein-Friedel-Lloyd formulas (28.16) and (28.17) are evaluated at a finite value of R.

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Finally, the semiclassical approximation can also help us in the interpretation of the Weyl term contributions for scattering problems. In scattering problems the Weyl term appears with a negative sign. The reason is the

subtraction of the empty container from the container with the potential. If the potential is a dispersing billiard system (or a finite collection of dispersing billiards), we expect an excluded volume (or the sum of excluded volumes) relative to the empty container. In other words, the Weyl term contribution of the empty container is larger than of the filled one and therefore a negative net contribution is left over. Secondly, if the scattering potential is a collection of a finite number of non-overlapping scattering regions, the Krein-Friedel-Lloyd formulas show that the corresponding Weyl contributions are completely independent of the position of the single scatterers, as long as these do not overlap.

28.4 Wigner time delay

The term $\frac{d}{dE}\ln\det S$ in the density formula (28.16) is dimensionally time. This suggests another, physically important interpretation of such formulas for scattering systems, the Wigner delay, defined as

$$\begin{aligned} d(k) &= \frac{d}{dk}\mathrm{Argdet}\left(\mathbf{S}(k)\right) \\ &= -i\frac{d}{dk}\log\det\left(\mathbf{S}(k)\right) \\ &= -i\,\mathrm{tr}\left(\mathbf{S}^\dagger(k)\frac{d\mathbf{S}}{dk}(k)\right) \end{aligned} \tag{28.18}$$

and can be shown to equal the total delay of a wave packet in a scattering system. We now review this fact.

A related quantity is the total scattering *phase shift* $\Theta(k)$ defined as

$$\det\mathbf{S}(k) = e^{+i\,\Theta(k)}\,,$$

so that $d(k) = \frac{d}{dk}\Theta(k)$.

The time delay may be both positive and negative, reflecting attractive respectively repulsive features of the scattering system. To elucidate the connection between the scattering determinant and the time delay we study a plane wave:

The phase of a wave packet will have the form:

$$\phi = \vec{k}\cdot\vec{x} - \omega\,t \;+\; \Theta\,.$$

Here the term in the parenthesis refers to the phase shift that will occur if scattering is present. The center of the wave packet will be determined by the principle of stationary phase:

$$0 = d\phi = d\vec{k} \cdot \vec{x} - d\omega\, t \; + \; d\Theta\,.$$

Hence the packet is located at

$$\vec{x} = \frac{\partial \omega}{\partial \vec{k}}\, t \; - \frac{\partial \Theta}{\partial \vec{k}}\,.$$

The first term is just the group velocity times the given time t. Thus the the packet is retarded by a length given by the derivative of the phase shift with respect to the wave vector $\vec{k}$. The arrival of the wave packet at the position $\vec{x}$ will therefore be delayed. This *time delay* can similarly be found as

$$\tau(\omega) = \frac{\partial \Theta(\omega)}{\partial \omega}.$$

To show this we introduce the *slowness* of the phase $\vec{s} = \vec{k}/\omega$ for which $\vec{s} \cdot \vec{v}_g = 1$, where $\vec{v}_g$ is the group velocity to get

$$d\vec{k} \cdot \vec{x} = \vec{s} \cdot \vec{x}\, d\omega = \frac{x}{v_g}\, d\omega\,,$$

since we may assume $\vec{x}$ is parallel to the group velocity (consistent with the above). Hence the arrival time becomes

$$t = \frac{x}{v_g} \; + \frac{\partial \Theta(\omega)}{\partial \omega}\,.$$

If the scattering matrix is not diagonal, one interprets

$$\Delta t_{ij} = \mathrm{Re}\left(-i\, S_{ij}^{-1} \frac{\partial S_{ij}}{\partial \omega}\right) = \mathrm{Re}\left(\frac{\partial \Theta_{ij}}{\partial \omega}\right)$$

as the delay in the jth scattering channel after an injection in the ith. The probability for appearing in channel j goes as $|S_{ij}|^2$ and therefore the average delay for the incoming states in channel i is

$$\begin{aligned} \langle \Delta t_i \rangle &= \sum_j |S_{ij}|^2 \Delta t_{ij} = \mathrm{Re}\,(-i \sum_j S_{ij}^* \frac{\partial S_{ij}}{\partial \omega}) = \mathrm{Re}\,(-i\, \mathbf{S}^\dagger \cdot \frac{\partial \mathbf{S}}{\partial \omega})_{ii} \\ &= -i \left(\mathbf{S}^\dagger \cdot \frac{\partial \mathbf{S}}{\partial \omega}\right)_{ii}\,, \end{aligned}$$

where we have used the derivative, $\partial/\partial\omega$, of the unitarity relation $\mathbf{S}\cdot\mathbf{S}^\dagger = \mathbf{1}$ valid for real frequencies. This discussion can in particular be made for wave packets related to partial waves and superpositions of these like an incoming plane wave corresponding to free motion. The total Wigner delay therefore corresponds to the sum over all channel delays (28.18).

Commentary

Remark 28.1 Krein-Friedel-Lloyd formula. The Krein-Friedel-Lloyd formula (28.16) was derived in refs. [28.3, 28.4, 28.5, 28.6], see also refs. [28.7, 28.8, 28.9, 28.10, 28.11].

Remark 28.2 Weyl term for empty container. For a discussion of why the Weyl term contribution of the empty container is larger than of the filled one and therefore a negative net contribution is left over, see ref. [28.9].

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