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On the rate of the chemical reactions and the teleportation of the wavepackets

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Abstract

Quantal wavepackets suggestive of classical particles which move along clasical trajectories are shown to be instantaneously teleported at the same time through potential barriers. The rate constant of the chemical reactions is derived as an application of such quantal motion of classical objects.

We focus on a particle of coordinate q in quasi-bound states in a potential well around the origin, capable of passing through a potential barrier to the right and perfectly reflected at the origin in its motion to the left; such a motion is supposed to illustrate a chemical reaction; we are interested in the probability $P(q,t)$ of locating the particle at q at the moment of time t; $P(t)=\int_{q_1}dq\cdot P(q,t)$ is the probability of chemical reaction, where q_1 denotes conventionally the outer boundary of the potential barrier.

Let $\varphi(E,q)$ be the eigenfunctions of the motion corresponding to energies E. The original wavefunction of the particle unperturbed by the potential barrier is a superposition

$$\psi(q,t)=\sum_E c(E)\varphi(E,q)e^{-iEt/\hbar}\ ; \tag{1}$$

the corresponding probability is given by

$$P(q,t)=\sum_{EE'}c*(E)c(E')\varphi^*(E,q)\varphi(E',q)e^{-i(E'-E)t/\hbar}\ . \tag{2}$$

For relatively high energies E, as those close to the top of a high barrier, the states are dense and the eigenfunctions are quasi-plane waves; they may be labelled by wavevectors k; this is a quasi-classical description, and the above probability reads

$$P(q,t)=\frac{1}{2\pi}\int dkdk'\cdot c_k*c_{k'}e^{i(k'-k)q}e^{-i(E_{k'}-E_k)t/\hbar}\ ; \tag{3}$$

the coefficients c_k depend slightly on k around a certain k-value corresponding to the energy E_k, so that one may expand them in powers of $k'-k$ and write also $E_{k'}=E_k+\hbar v(k'-k)$, where $v=\partial E/\hbar\partial k$ is the group velocity; indeed, doing so we get a wavepacket

$$P(q,t)=\frac{1}{2\pi}\int dk\cdot e^{i(q-vt)k}=\delta(q-vt)\ \ , \tag{4}$$

propagating to the right with velocity v; since E_k is quadratic in k, there exists another wavepacket $\delta(q+vt)$ propagating to the left, which, however, at $q,t=0$ vanishes; we may discard it. If the quadratic, or higher-order terms would be retained in the energy expansion the integral would give another representtion of the δ-function; actually, such terms are irrelevant, though they spread out the packet in time, because the limits of integration in (4) are in fact limited to a certain Δk range around k; this is done conveniently by introducing a gaussian α-cutoff in (4), leading to

$$P(q,t)=\frac{1}{2\pi}\int dk\cdot e^{-\alpha k^2}e^{i(q-vt)k}=\frac{1}{2\sqrt{\pi\alpha}}e^{-(q-vt)^2/4\alpha}\ , \tag{5}$$

i.e. a gaussian instead of a δ-peak, and we assume that the localization time in the potential well is much shorter than the diffusion time of the packet as due to its own time evolution; this assumption is consistent with the quasiclassical description. Indeed, quadratic or higher-order terms in energy expansion introduce a wavevector uncertainty of the order of k (and the position uncertainty is of the order of q_0), which means that they spread out the wavepacket over a distance of the order of the wavelength $\lambda=1/k$ (rigorously speaking the width of the δ-function in (4) is of the order of λ); the perturbing potential barrier produces however a tighter k-uncertainty, as expressed by the α-cutoff in (5), so the wavepacket is spread over a distance Λ larger than λ, but of course much shorter than q_0; we can see, therefore, that the effect of the time-diffusion terms on the wavepacket is substantial only after a very long time; as it is well-known this time is measured by $v\lambda t\sim\Lambda^2$ and $v\lambda t\sim q_0$. This is a worth noting point, because it tells that the width of the quantal wavepackets is governed by the wavelength λ, in contrast with statistical wavepackets which are governed by a mean-free path similar to the length Λ above. In addition, it is also worth noting that the normalization of the wavepacket above is extended to the whole space; this is convenient because we are interested in transmission and reflection coefficients through the potential barrier which are fractions of the square amplitude of the original wavepacket, so that the normalization constant is immaterial.

In its motion to the right the wavepacket reaches the inner boundary q_0 of the potential barrier after $t_0=q_0/v$ time; actually, the velocity v may depend slightly on position, according to its quasiclassical expression $v=\sqrt{2m(E-V)}$, where m is the mass of the particle and V denotes the potential well over its regions of slight variations; however, this only brings small corrections to the time t_0, which may be discarded. At this very moment t_0 a similar wavepacket appears at the outer boundary of the potential barrier, of the form $|T|^2\,\delta(q-q_1-v(t-t_0))$, where T is the transmission coefficient through the potential barrier. This is a teleportation of the wavepackets through potential barriers, as required by Schrodinger's equation and the superpositions (2) and (3). Indeed, such superpositions of waves interfere vanishingly outside the packet $q\sim vt$-region, but their components are continuous (together with their derivatives) at the boundaries of the potential barrier; just when the packet reaches the inner boundary of the barrier this superposition becomes "constructive" at the other boundary of the barrier too, and the wavepacket is therefore teleported over there instantaneously. This is not a propagation of the signal with an infinite velocity, because the signal vanishes and does not propagate inside the barrier; it is instead an instantaneous teleportation of the signal, as required by the non-local nature of the waves obeying Schrodinger's (or wave) equation. This can be seen more directly perhaps if we have in mind Schrodinger's equation $(-\hbar^2/2m)\psi''=(E-V)\psi$; then, we can see that for a free motion $V=0$ the second derivative of the wavefunction is positive for a negative wavefunction and negative for a positive wavefunction (for $E>0$ of course); this implies an oscillatory motion which propagates; on the contrary, inside the potential barier $(E<V)$ both ψ'' and ψ have the same sign, which implies the teleportation through the barier.

Turning back now to the wavepacket motion one can see that at the same moment t_0 when it reaches the inner q_0-boundary of the barrier the wavepacket is not only transmitted through the barrier but it is also reflected by this boundary into $|R|^2\,\delta(q_0-q-v(t-t_0))$ that propagates to the left, where R is the reflection coefficient of the barrier; there, it is perfectly reflected rightwards and transmited as $|R|^2\,|T|^2$ after a time $2t_0$; and so on, so that after time

$$t = t_0 + 2t_0 + 2t_0 + ... = t_0 + 2nt_0 \tag{6}$$

the probability of finding the particle outside the barrier is

$$\begin{aligned} P(t) &= |T|^2 + |R|^2\,|T|^2 + |R|^4\,|T|^2 + ... = \\ &= |T|^2\,\tfrac{1-|R|^{2(n+1)}}{1-|R|^2} = 1 - |R|^{2(n+1)}\ ; \end{aligned} \tag{7}$$

it is easy to see that $P(t)$ can also be written as

$$P(t) = 1 - |R|^{t/t_0} = 1 - e^{(\ln|R|/t_0)t}\ , \tag{8}$$

for long times, which is the well-known law of chemical reactivity and of e^{-Ct}-decay for the survival probability $1-P(t)$, where

$$C = -\ln|R|\,/t_0 = -v\ln|R|\,/q_0 \tag{9}$$

is the rate constant of the chemical reaction. It is worth noting that it is derived here by working with localized wavepackets suggestive of a classical motion (and classical trajectories), which move classically (are reflected for instance by a potential barier), but obeying at the same time quantal laws of motion as concerns the teleportation, for instance, through the potential barrier, as well as the reflection and transmission coefficients; the wave transmitted through the potential barrier appears as a succession of packets, which may be termed quanta of chemical reactivity, smaller and smaller, as indicated by the geometric series (7), and more and more flat on increasing the time.

This succession of peaks is reminiscent of the interference of the transmitted trains of waves; indeed, for wave packets sufficiently large we may write down for the transmitted wave

$$Te^{i(q-vt)k} + TRe^{i(q-(vt-2t_0))k} + TR^2e^{i(q-v(t-4t_0))k} + ... \tag{10}$$

which leads to a square amplitude

$$|T|^2\,\frac{1+e^{-Ct}-2e^{-Ct/2}\cos(vk+\Phi_0/2t_0)t}{1+|R|^2-2\,|R|\cos(2vkt_0+\Phi_0)} \tag{11}$$

for long times, where Φ_0 is the phase of the reflection coefficient; or, because $2vkt_0+\Phi_0=2\pi$, this square amplitude given by (10) becomes

$$1+e^{-Ct}-2e^{-Ct/2}\cos 2\pi t/t_0\ , \tag{12}$$

which exhibits small oscillations around unity. Equation (12) is to be compared with the probability $P(t)$ given by (8) for wavepackets; one can see the presence of the interference oscillatory contributions in the transmitted wave (12).

There is a large variety of computations for the transmission coefficient T; for a square potential barrier it is given by the well-known formula

$$|T|^2 = \frac{4k^2\kappa^2}{b^4 \sinh^2 a\kappa + 4k^2\kappa^2} \ , \tag{13}$$

where $b^2 = k^2 + \kappa^2 = 2mV/\hbar^2$, $k^2 = 2mE/\hbar^2$ and a is the extension of the potential barrier, *i.e.* $a = q_1 - q_0$ approximately, with our notations. It is naturally to assume $a \sim q_0$, and $E \sim V$ both very high, *i.e.* $k \gg 1/a$ (for low E the reflection coefficient tends to unity, on one side; and, on the other it is not in accordance with our quasiclassical description assumed here); under these circumstances one gets easily from (13) the reflection coefficient as given by $|R|^2 = 1 - 4/b^2a^2$ and the rate constant $C = \hbar^2/a^3m\sqrt{mE}$. Among several interesting things (as, for instance, a very low rate constant for a large mass) this later formula shows that the decay rate diminishes on increasing the energy (at the top of the barrier, of course, *i.e.* increasing at the same time the barrier too); this happens because the reflection coefficient increases, and the particle spends more time in the potential well; in fact, slightly above the top of the potential barrier, the wavepacket propagates, but with a very slow velocity; such quasi-bound, or, of course, quasi-free, states are termed more properly resonant states. The transmission coefficient in this region ($E > V$) is given by

$$|T|^2 = \frac{4k^2\kappa^2}{(k^2-\kappa^2)^2 \sin^2 a\kappa + 4k^2\kappa^2} \ , \tag{14}$$

where $\kappa^2 = 2m(E-V)/\hbar^2$ this time. One can see that the reflection coefficient is the same as in the previous case, and, since the propagation time a/v is very long now, it follows that the relevant time is $\tau = 1/C$, as before; this is also a teleportation, as the wavelength of the packet in the region of the potential barrier is very long, in any case much longer than the width of the barrier. Therefore, a characteristic time

$$\tau = 1/C = -q_0/v \ln|R| \tag{15}$$

can be introduced, according to (9), as being the time needed for transmitting the wavepacket through teleportation through a potential barrier, with an energy close the the top of the barier, either below or above; it may be termed transmission time. The rate constant obtained above can also be put in another form, namely $C = (v/a)(\varepsilon_0/E)$, where $\varepsilon_0 = \hbar^2/ma^2$ is the localization energy in the potential well, and the transmission time is therefore given by

$$\tau = (a/v)(E/\varepsilon_0) \ , \tag{16}$$

where E is close to V, either larger or smaller.

All of the above applies also to waveguides and the wave equation. Indeed, the wave equation reads$-\psi'' = (\omega^2/c^2)\psi$, where ω denotes the frequency and c is the wave velocity; in a waveguide the tranverse oscillations are steady waves and we are left with $-\psi'' + (\omega_c^2/c^2)\psi = (\omega^2/c^2)\psi$, where the cutoff (or critical) frequency ω_c is given by $\omega_c \sim \pi c/d$, d being the transverse dimension of the waveguide; a similar equation holds also for waveguides with dielectric and magnetic media. The similarity with Schrodinger's equation is obvious, with notations $\omega^2/c^2 = 2mE/\hbar^2$ and $\omega_c^2/c^2 = 2mV/\hbar^2$. The wavepackets propagates through the waveguide for $\omega > \omega_c$, as quantal particles above the potential barriers, with a group velocity $v = \partial\omega/\partial k$, in a transit time $\tau_t = l/v$, where l is the length of the waveguide; the phase propagates with velocity ω/k in a different time, and the difference is a delay time; for ω slightly above the critical frequency ω_c the wavepacket "resonates" within the waveguide, and "dwells" for long there; this lingering time of the wavepacket inside the guide is the transit time of course, with the only difference that it is very long because the group velocity is very low. Below the critical frequency the propagation is "evanescent", *i.e.* there is no propagation at all, but the wavepackets are teleported instantaneously through the guide. A similar regime applies also for a frequency slightly above the critical frequency, so that in both cases a rate constant C and a characteristic time $\tau = 1/C$ can also be derived for the teleportation of the wavepackets through waveguides, similar with the rate constant of the chemical reactions given by (9); however, they depend on the length q_0 of the start-up region of the guide; for instance, the characteristic time of transmission of the wavepackets near the critical frequency is given by

$$\tau = q_0 l^2 \omega_c^2 / 2c^3 \ , \tag{17}$$

according to (13) or (14), for a waveguide. Above the critical frequency it is relevant as long as it is shorter than the transit time $\tau_t = l/v$ (plus q_0/c). A more detalied analysis requires the dependence of the reflection coefficient on frequency (with $\omega = \sqrt{\omega_c^2 + c^2\kappa^2}$ in the propagating region), as given by (13) and (14).
