

Chapter 24

Fermi's Golden Rule

24.1 Introduction

In this chapter, we derive a very useful result for estimating transition rates between quantum states due to time-dependent perturbation. The results will be used heavily in subsequent chapters to understand the optical and electronic transport properties of semiconductors.

24.2 Fermi's Golden Rule

Consider an unperturbed quantum system in state $|\Psi_{t_0}\rangle$ at time $t = t_0$. It evolves to the state $|\Psi_t\rangle$ at a future instant t . The time evolution of the state vector is governed by the unperturbed Hamiltonian H_0 according to the time-dependent Schrodinger equation

$$i\hbar\frac{\partial}{\partial t}|\Psi_t\rangle = H_0|\Psi_t\rangle. \quad (24.1)$$

If the system was in an eigenstate $|\Psi_{t_0}\rangle = |0\rangle$ of energy E_0 at time t_0 , then the state at a future time differs from the initial state by a phase factor

$$H_0|\Psi_{t_0}\rangle = E_0|\Psi_{t_0}\rangle \implies |\Psi_t\rangle = e^{-i\frac{E_0}{\hbar}(t-t_0)}|\Psi_{t_0}\rangle. \quad (24.2)$$

This is a *stationary* state; if the quantum state started in an eigenstate, it remains in that eigenstate as long as there is no perturbation. But the eigen-state vector still 'rotates' in time with frequency $\omega_0 = E_0/\hbar$ in the Hilbert space as indicated schematically

in Figure 24.1. It is called stationary because physical observables of the eigenstate will require not the amplitude, but the inner product, which is $\langle \Psi_t | \Psi_t \rangle = \langle \Psi_{t_0} | \Psi_{t_0} \rangle$. This is manifestly stationary in time.

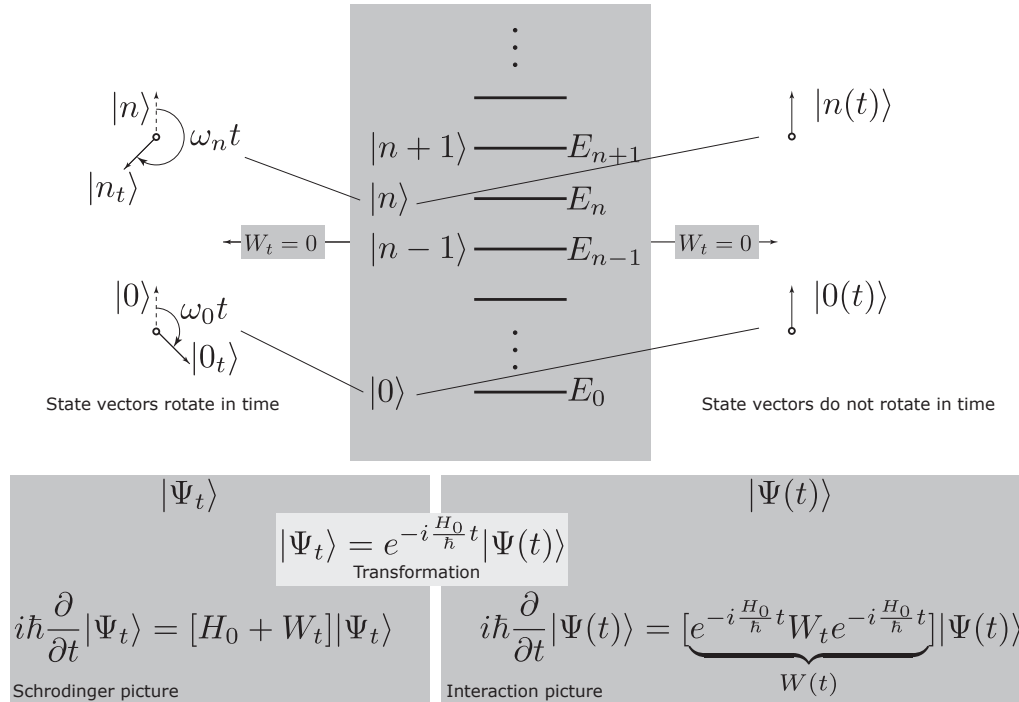


FIGURE 24.1: Schrodinger vs. Interaction pictures of time-evolution of quantum state.

Now let us perturb the system with a *time-dependent* term W_t . This perturbation can be due to a voltage applied on a semiconductor device, or electromagnetic waves (photons) incident on a semiconductor. The new Schrodinger equation for the time evolution of the state is

$$i\hbar \frac{\partial}{\partial t} |\Psi_t\rangle = [H_0 + W_t] |\Psi_t\rangle. \tag{24.3}$$

In principle, solving this equation will yield the complete future quantum states. In practice, this equation is unsolvable, even for the simplest of perturbations. Physically, the perturbation will ‘scatter’ a particle that was, say in state $|0\rangle$ to state $|n\rangle$. However, we had noted that even in the *absence* of perturbations, the eigen-state vectors were already evolving with time in the Hilbert space. For example, state vector $|0\rangle$ was rotating at an angular frequency ω_0 , and state vector $|n\rangle$ at ω_n . This is shown schematically in the left of Figure 24.1. It would be nice to work with *unperturbed* state vectors that do not change in time, as in the right of Figure 24.1. This calls for a transformation to a vector space that ‘freezes’ the time evolution of the unperturbed eigen state-vectors. Such a transformation is achieved by the relation

$$|\Psi_t\rangle = e^{-i\frac{H_0}{\hbar}t}|\Psi(t)\rangle, \quad (24.4)$$

where H_0 is the Hamiltonian *operator*. Note that the operator now sits in the exponential, but it should not worry us much. We will see that it is rather useful to have it up there. The reason for this non-obvious transformation is because when we put this into the Schrodinger equation in Equation 24.3, we get

$$i\hbar \left(-\frac{i}{\hbar}H_0 e^{-i\frac{H_0}{\hbar}t}|\Psi(t)\rangle + e^{-i\frac{H_0}{\hbar}t} \frac{\partial}{\partial t}|\Psi(t)\rangle \right) = [H_0 + W_t]e^{-i\frac{H_0}{\hbar}t}|\Psi(t)\rangle, \quad (24.5)$$

and there is a crucial cancellation, leaving us with

$$\boxed{i\hbar \frac{\partial}{\partial t}|\Psi(t)\rangle = [e^{+i\frac{H_0}{\hbar}t}W_t e^{-i\frac{H_0}{\hbar}t}]|\Psi(t)\rangle = W(t)|\Psi(t)\rangle} \quad (24.6)$$

where $W(t) = e^{+i\frac{H_0}{\hbar}t}W_t e^{-i\frac{H_0}{\hbar}t}$. Can we take the *operator* $e^{-i\frac{H_0}{\hbar}t}$ from the left to the right side as $e^{+i\frac{H_0}{\hbar}t}$? Yes we can, because $e^{+i\frac{H_0}{\hbar}t} \cdot e^{-i\frac{H_0}{\hbar}t} = I$, the identity operator.

The boxed form of the time-evolution is called the *interaction* picture, as opposed to the conventional form of Equation 24.3, which is called the ‘Schrodinger’ picture. Note that if there is no perturbation, $W_t = 0 \implies W(t) = 0 \implies i\hbar \frac{\partial |\Psi(t)\rangle}{\partial t} = 0$. Then, $|\Psi(t)\rangle = |\Psi(t_0)\rangle$, and we have managed to find the state vector representation in which the unperturbed eigenvectors are indeed frozen in time.

Now lets turn the perturbation W_t on. Formally, the state vector at time t in the interaction representation is obtained by integrating both sides:

$$|\Psi(t)\rangle = |\Psi(t_0)\rangle + \frac{1}{i\hbar} \int_{t_0}^t dt' W(t') |\Psi(t')\rangle, \quad (24.7)$$

and it looks as if we have solved the problem. However, there is a catch - the unknown state vector $|\Psi(t)\rangle$ appears also on the right side - inside the integral. This is also a recursive relation! It reminds of the Brilloiun-Wigner form of non-degenerate perturbation theory. Let's try to iterate the formal solution once:

$$|\Psi(t)\rangle = |\Psi(t_0)\rangle + \frac{1}{i\hbar} \int_{t_0}^t dt' W(t') \left[|\Psi(t_0)\rangle + \frac{1}{i\hbar} \int_{t_0}^{t'} dt'' W(t'') |\Psi(t'')\rangle \right], \quad (24.8)$$

and then keep going:

$$|\Psi(t)\rangle = \underbrace{|\Psi(t_0)\rangle}_{\sim W^0} + \underbrace{\frac{1}{i\hbar} \int_{t_0}^t dt' W(t') |\Psi(t_0)\rangle}_{\sim W^1} + \underbrace{\frac{1}{(i\hbar)^2} \int_{t_0}^t dt' W(t') \int_{t_0}^{t'} dt'' W(t'') |\Psi(t_0)\rangle}_{\sim W^2} + \dots \quad (24.9)$$

We thus obtain a formal perturbation series to many orders. The hope is that the series converges rapidly if the perturbation is ‘small’, because successive terms increase as a power law, which for a small number gets even smaller. Let’s accept that weak argument now at face value, and we return later to address, justify, and where possible, fix this cavalier approximation.

Let $|\Psi(t_0)\rangle = |0\rangle$ be the initial state of the quantum system. The perturbation is turned on at time t_0 . The probability *amplitude* for the system to be found in state $|n\rangle$ at time $t (> t_0)$ is $\langle n|\Psi_t\rangle$. Note the Schrodinger representation! But the transformation from Schrodinger to interaction picture helps: $\langle n|\Psi_t\rangle = \langle n|e^{-i\frac{H_0}{\hbar}t}\Psi(t)\rangle = e^{-i\frac{E_n}{\hbar}t}\langle n|\Psi(t)\rangle$. This implies $|\langle n|\Psi_t\rangle|^2 = |\langle n|\Psi(t)\rangle|^2$ - for all eigenstates $|n\rangle$. Let us make an approximation in this section and retain only the first order term in the perturbation series. We will return later and discuss the higher order terms that capture multiple-scattering events. Retaining only the terms of Eq. 24.9 to first order in the perturbation W gives

$$\langle n|\Psi(t)\rangle \approx \underbrace{\langle n|0\rangle}_{=0} + \frac{1}{i\hbar} \int_{t_0}^t dt' \langle n|W(t')|0\rangle = \frac{1}{i\hbar} \int_{t_0}^t dt' \langle n|e^{+i\frac{H_0}{\hbar}t'} W_{t'} e^{-i\frac{H_0}{\hbar}t'} |0\rangle. \quad (24.10)$$

Let us assume the perturbation to be of the form $W_t = e^{\eta t}W$ representing a ‘slow turn on’, with $\eta = 0^+$, and $W = W(r)$ a function that depends only on space. If $\eta = 0$, then the perturbation is time-independent. But if $\eta = 0^+$, then $e^{\eta t_0} \rightarrow 0$ as $t_0 \rightarrow -\infty$. This construction thus effectively kills the perturbation far in the distant past, but slowly turns it on to full strength at $t = 0$. We will discuss more of the physics buried inside η later. For now, we accept it as a mathematical construction, with the understanding to take the limit $\eta \rightarrow 0$ at the end. Then, the amplitude in state $|n\rangle$ simplifies:

$$\langle n|\Psi(t)\rangle \approx \frac{1}{i\hbar} \int_{t_0}^t dt' \underbrace{\langle n|e^{+i\frac{H_0}{\hbar}t'}}_{e^{+i\frac{E_n}{\hbar}t'}\langle n|} e^{\eta t'} W \underbrace{e^{-i\frac{H_0}{\hbar}t'}|0\rangle}_{e^{-i\frac{E_0}{\hbar}t'}|0\rangle} = \frac{\langle n|W|0\rangle}{i\hbar} \int_{t_0}^t dt' e^{i\left(\frac{E_n-E_0}{\hbar}\right)t'} e^{\eta t'}, \quad (24.11)$$

and the integral over time may be evaluated exactly to yield

$$\int_{t_0}^t dt' e^{i\left(\frac{E_n-E_0}{\hbar}\right)t'} e^{\eta t'} = \frac{e^{i\left(\frac{E_n-E_0}{\hbar}\right)t} e^{\eta t} - e^{i\left(\frac{E_n-E_0}{\hbar}\right)t_0} e^{\eta t_0}}{i\left(\frac{E_n-E_0}{\hbar}\right) + \eta} \underset{t_0 \rightarrow -\infty}{=} \frac{e^{i\left(\frac{E_n-E_0}{\hbar}\right)t} e^{\eta t}}{i\left(\frac{E_n-E_0}{\hbar}\right) + \eta}. \quad (24.12)$$

The amplitude then is

$$\langle n|\Psi(t)\rangle \approx \frac{\langle n|W|0\rangle}{i\hbar} \cdot \frac{e^{i\left(\frac{E_n-E_0}{\hbar}\right)t} e^{\eta t}}{i\left(\frac{E_n-E_0}{\hbar}\right) + \eta} = \langle n|W|0\rangle \cdot \frac{e^{i\left(\frac{E_n-E_0}{\hbar}\right)t} e^{\eta t}}{(E_0 - E_n) + i\hbar\eta}. \quad (24.13)$$

The *probability* of the state making a transition from $|0\rangle$ to $|n\rangle$ at time t is

$$|\langle n|\Psi_t\rangle|^2 = |\langle n|\Psi(t)\rangle|^2 \approx |\langle n|W|0\rangle|^2 \frac{e^{2\eta t}}{(E_0 - E_n)^2 + (\hbar\eta)^2}. \quad (24.14)$$

The *rate* of transitions from state $|0\rangle \rightarrow |n\rangle$ is

$$\frac{1}{\tau_{|0\rangle \rightarrow |n\rangle}} = \frac{d}{dt} |\langle n|\Psi(t)\rangle|^2 \approx |\langle n|W|0\rangle|^2 \left(\frac{2\eta}{(E_0 - E_n)^2 + (\hbar\eta)^2} \right) e^{2\eta t}. \quad (24.15)$$

Now we take $\eta \rightarrow 0^+$. The third term $e^{2\eta t} \rightarrow 1$, but we must be careful with the quantity in the bracket. When $\eta \rightarrow 0$, this quantity is 0, *except* when the term $E_0 - E_n = 0$; then the term seems indeterminate. By making a plot of this function, we can convince ourselves that it approaches a Dirac delta function in the variable $E_0 - E_n$. The mathematical identity $\lim_{\eta \rightarrow 0^+} \frac{2\eta}{x^2 + \eta^2} = \lim_{\eta \rightarrow 0^+} \frac{1}{i} \left[\frac{1}{x - i\eta} - \frac{1}{x + i\eta} \right] = 2\pi\delta(x)$, where $\delta(\dots)$ confirms this: in the limit, the term indeed becomes the Dirac-delta function.

Then, using $\delta(ax) = \delta(x)/|a|$, the rate of transitions is given by

$$\boxed{\frac{1}{\tau_{|0\rangle \rightarrow |n\rangle}} \approx \frac{2\pi}{\hbar} |\langle n|W|0\rangle|^2 \delta(E_0 - E_n)}, \quad (24.16)$$

which is the Fermi's golden rule. The general form is $2\pi/\hbar$ times the transition matrix element squared, times a Dirac-delta function as a statement of energy conservation.

24.3 Perturbations oscillating in time

Now suppose the perturbation potential was oscillating in time. We will encounter such perturbations frequently, in the form of electron-photon, or electron-phonon interactions. The mathematical nature of such perturbations with a slow turn-on is

$$W_t = 2W e^{\eta t} \cos(\omega t) = e^{\eta t} W (e^{i\omega t} + e^{-i\omega t}) \quad (24.17)$$

which leads to a $|0\rangle \rightarrow |n\rangle$ transition amplitude

$$\langle n|\Psi(t)\rangle \approx \frac{\langle n|W|0\rangle}{i\hbar} \left(\int_{t_0}^t dt' e^{i\left(\frac{E_n - E_0 + \hbar\omega}{\hbar}\right)t'} e^{\eta t'} + \int_{t_0}^t dt' e^{i\left(\frac{E_n - E_0 - \hbar\omega}{\hbar}\right)t'} e^{\eta t'} \right), \quad (24.18)$$

Similar to Equations 24.12 and 24.13, evaluating the integral with $t_0 \rightarrow -\infty$, we get the amplitude for transitions

$$\langle n|\Psi(t)\rangle \approx \langle n|W|0\rangle \cdot \left(\frac{e^{i\left(\frac{E_n - E_0 + \hbar\omega}{\hbar}\right)t} e^{\eta t}}{(E_0 - E_n + \hbar\omega) + i\hbar\eta} + \frac{e^{i\left(\frac{E_n - E_0 - \hbar\omega}{\hbar}\right)t} e^{\eta t}}{(E_0 - E_n - \hbar\omega) + i\hbar\eta} \right). \quad (24.19)$$

The probability is then

$$|\langle n|\Psi(t)\rangle|^2 \approx |\langle n|W|0\rangle|^2 \cdot \left[\frac{e^{2\eta t}}{(E_0 - E_n + \hbar\omega)^2 + (\hbar\eta)^2} + \frac{e^{2\eta t}}{(E_0 - E_n - \hbar\omega)^2 + (\hbar\eta)^2} + \frac{e^{2i\omega t} e^{2\eta t}}{(E_0 - E_n + \hbar\omega + i\hbar\eta)(E_0 - E_n - \hbar\omega - i\hbar\eta)} + \frac{e^{-2i\omega t} e^{2\eta t}}{(E_0 - E_n + \hbar\omega - i\hbar\eta)(E_0 - E_n - \hbar\omega + i\hbar\eta)} \right] \quad (24.20)$$

The rate of transition is then

$$\frac{d}{dt} |\langle n|\Psi(t)\rangle|^2 \approx |\langle n|W|0\rangle|^2 \cdot \left[\frac{2\eta e^{2\eta t}}{(E_0 - E_n + \hbar\omega)^2 + (\hbar\eta)^2} + \frac{2\eta e^{2\eta t}}{(E_0 - E_n - \hbar\omega)^2 + (\hbar\eta)^2} + \frac{2(\eta + i\omega) e^{2i\omega t} e^{2\eta t}}{(E_0 - E_n + \hbar\omega + i\hbar\eta)(E_0 - E_n - \hbar\omega - i\hbar\eta)} + \frac{2(\eta - i\omega) e^{-2i\omega t} e^{2\eta t}}{(E_0 - E_n + \hbar\omega - i\hbar\eta)(E_0 - E_n - \hbar\omega + i\hbar\eta)} \right]. \quad (24.21)$$

Notice that the last two (interference) terms are a complex conjugate pair, which they must be, because the rate of transition is real. The sum is then $2\times$ the real part of either term. After some manipulations, one obtains

$$\frac{d}{dt}|\langle n|\Psi(t)\rangle|^2 \approx \langle n|W|0\rangle|^2 e^{2\eta t} \cdot \left(\frac{2\eta}{(E_0 - E_n + \hbar\omega)^2 + (\hbar\eta)^2} + \frac{2\eta}{(E_0 - E_n - \hbar\omega)^2 + (\hbar\eta)^2} \right) [1 - \cos(2\omega t)] + 2\sin(2\omega t) \left(\frac{E_0 - E_n + \hbar\omega}{(E_0 - E_n + \hbar\omega)^2 + (\hbar\eta)^2} - \frac{E_0 - E_n - \hbar\omega}{(E_0 - E_n - \hbar\omega)^2 + (\hbar\eta)^2} \right). \quad (24.22)$$

Note that the rate has a part that does not oscillate, and another which does, with *twice* the frequency of the perturbing potential. If we average over a few periods of the oscillation, $\langle \cos(2\omega t) \rangle_t = \langle \sin(2\omega t) \rangle_t = 0$. Then, by taking the limit $\eta \rightarrow 0^+$ in the same fashion as in Equation 24.16, we obtain the Fermi's golden rule for oscillating perturbations:

$$\frac{1}{\tau_{|0\rangle \rightarrow |n\rangle}} \approx \frac{2\pi}{\hbar} \times |\langle n|W|0\rangle|^2 \times \underbrace{[\delta(E_0 - E_n + \hbar\omega)]}_{\text{absorption}} + \underbrace{[\delta(E_0 - E_n - \hbar\omega)]}_{\text{emission}}. \quad (24.23)$$

The Dirac-delta functions now indicate that the exchange of energy between the quantum system and the perturbing field is through *quanta* of energy: either by absorption, leading to $E_n = E_0 + \hbar\omega$, or emission, leading to $E_n = E_0 - \hbar\omega$. The rates of each individual processes are the same. Which process (emission or absorption) dominates depends on the occupation functions of the quantum states.

24.4 Transitions to a continuum of states

The Fermi golden rule results in Equation 24.16 and 24.23 are in a form suitable for tracking transitions between *discrete*, or individual states $|0\rangle$ and $|n\rangle$. For many situations encountered in semiconductors, these transitions will be between states within, or between energy bands, where a *continuum* of states exist. In those cases, the *net* transition rate will be obtained by summing over all relevant states. Even the transition between manifestly discrete states - for example the electron ground state of hydrogen atom to the first excited state - by the absorption of a photon - occurs by the interaction between the discrete electron states and the states of the electromagnetic spectrum, which forms a continuum.

As an example, consider the transitions between electron states in the conduction band due to a point scatterer in a 3D semiconductor. Let us say the point scatterer potential is $W(r) = V_0\delta(\mathbf{r})$, with V_0 in units of $\text{eV}\cdot\text{m}^3$. This is not an oscillating potential, so we use the golden rule result of Equation 24.16. We first find the matrix element between electron states $|\mathbf{k}\rangle$ and $|\mathbf{k}'\rangle$:

$$\langle\mathbf{k}'|V_0\delta(\mathbf{r})|\mathbf{k}\rangle = \int d^3\mathbf{r} \left(\frac{e^{-i\mathbf{k}'\cdot\mathbf{r}}}{\sqrt{V}} \right) V_0\delta(\mathbf{r}) \left(\frac{e^{+i\mathbf{k}\cdot\mathbf{r}}}{\sqrt{V}} \right) = \frac{V_0}{V}, \quad (24.24)$$

where we have used the property that the Fourier transform of a Dirac-delta function is equal to 1. Then, the transition (or scattering) rate to any state $|\mathbf{k}'\rangle$ is

$$\frac{1}{\tau(|\mathbf{k}\rangle \rightarrow |\mathbf{k}'\rangle)} = \frac{2\pi}{\hbar} \left(\frac{V_0}{V} \right)^2 \delta(E_{\mathbf{k}} - E_{\mathbf{k}'}). \quad (24.25)$$

The net scattering 'out' of state $|\mathbf{k}\rangle$ into the continuum of states $|\mathbf{k}'\rangle$ is then given by

$$\frac{1}{\tau(|\mathbf{k}\rangle)} = \sum_{\mathbf{k}'} \frac{1}{\tau(|\mathbf{k}\rangle \rightarrow |\mathbf{k}'\rangle)} = \frac{2\pi}{\hbar} \left(\frac{V_0}{V} \right)^2 \underbrace{\sum_{\mathbf{k}'} \delta(E_{\mathbf{k}} - E_{\mathbf{k}'})}_{D(E_{\mathbf{k}})}, \quad (24.26)$$

where we note that the sum over final states of the Dirac-delta function is the density of states $D(E_{\mathbf{k}})$ in units eV^{-1} of the electron at energy $E_{\mathbf{k}}$. This procedure illustrates an important result - the scattering rate for continuum of states is in general proportional to a density of states relevant to the problem. The strength of scattering increases as the square of the scattering potential. The occurrence of the $(\text{volume})^2$ term in the denominator may be disconcerting at first. However, the macroscopic volume (or area, or length) terms will for most cases cancel out because of purely physical reasons. For example, for the problem illustrated here, if instead of just *one* point scatterer, we had N , the *density* of scatterers is $n_{sc} = N/V$. Together with the conversion process $\sum_{\mathbf{k}'} \rightarrow V \int d^3\mathbf{k}'/(2\pi)^3$, we obtain

$$\frac{1}{\tau(E_{\mathbf{k}})} = \frac{2\pi}{\hbar} \left(\frac{V_0}{V} \right)^2 n_{sc} V \int \frac{d^3\mathbf{k}'}{(2\pi)^3} \delta(E_{\mathbf{k}} - E_{\mathbf{k}'}) = \frac{2\pi}{\hbar} V_0^2 n_{sc} g(E_{\mathbf{k}}). \quad (24.27)$$

Here the density of states $g(E_{\mathbf{k}})$ is per unit volume, in units $1/(\text{eV}\cdot\text{m}^3)$, as is standard in semiconductor physics. The scattering rate is linearly proportional to the density of scatterers. What is not immediately clear is how can we capture the effect of N scatterers by just multiplying the individual scatterer rate by N . This can be done if

the scatterers are uncorrelated, as will be discussed in the transport chapters. For now, note that the macroscopic volume has canceled out, as promised.

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