The Golden Rule in Four Acts

Dramatis Personae

- H_0 : Hamiltonian for which we know the eigenstates and which naturally define the initial and final states of a quantum evolution.
- $H_{\rm int}$: The perturbation responsible for transitions between eigenstates of H_0.
- $|\Psi(0)\rangle = |\Psi_i\rangle$: Initial quantum state and eigenstate of H_0 with energy E_i.
- $|\Psi_j\rangle \quad (j \neq i)$: Remaining eigenstates of H_0. Any quantum state of the system is a linear combination of these and $|\Psi_i\rangle$. Our system is confined to a finite box and the states therefore have a discrete index.
- $C_i(t)$ and $C_j(t)$: Complex amplitudes of the corresponding eigenstates. The boundary conditions are $C_i(0) = 1$, $C_j(0) = 0$.
- T : The final time in the quantum evolution.
- Γ : Rate of transitions to any final state.
- $d\Gamma/d\Omega$: Differential transition rate — transitions to final plane wave states within a particular element of spherical angle $d\Omega$.
- τ : The mean lifetime, equal to the inverse transition rate.

Act One

The future is determined by the time dependent Schrödinger equation:

$$i\hbar\frac{d}{dt}|\Psi\rangle = (H_0 + H_{\rm int})|\Psi\rangle \ .$$

Proceed by making the time evolution by H_0 explicit in the expansion of $|\Psi\rangle$:

$$|\Psi(t)\rangle = C_i(t)e^{-iE_it/\hbar}|\Psi_i\rangle + \sum_{j\neq i} C_j(t)e^{-iE_jt/\hbar}|\Psi_j\rangle \ .$$

Substitute into the Schrödinger equation and take the inner product with $\langle \Psi_f |$, where f is a particular choice of the indices j ($f \neq i$). Neglect doubly small terms, specifically $H_{\rm int} C_j(t)$, and make the approximation $C_i(t) \approx 1$ to obtain

$$|C_f(T)|^2 = \frac{1}{\hbar^2} |\langle \Psi_f | H_{\rm int} | \Psi_i \rangle|^2 \, F(T, E_f - E_i) \ ,$$

where

$$F(T, E_f - E_i) = \left| \int_0^T e^{i(E_f - E_i)t/\hbar} dt \right|^2 \ .$$

Act Two

Although each individual probability $|C_f(T)|^2$ oscillates with period $h/|E_f - E_i|$, the total transition probability, when summed over final states f, grows linearly with T when there is a quasi-continuum of states f with energy near E_i. As an important example of a quasi-continuum, consider plane-wave final states with wave-vectors $\mathbf{k}$. When defined in a volume V there are

$$\frac{V d^3 k}{(2\pi)^3}$$

distinct states in the wave-vector volume d^3k with normalized wavefunctions

$$\Psi_{\mathbf{k}}(\mathbf{r}) = \frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{\sqrt{V}} \ .$$

The sum over this quasi-continuum becomes an integral over $\mathbf{k}$. Since the transition probabilities depend sensitively on the energies of the final states through the function F, we transform to integration variables that exploit this fact. Changing notation from E_f to E_k, we have

$$d^3 k = d\Omega \, k^2 dk = d\Omega \, k^2 \left| \frac{dk}{dE_k} \right| dE_k \ ,$$

where Ω represents the spherical angles of $\mathbf{k}$.

To proceed, we note that both $k^2 |dk/dE_k|$ and $|\langle \Psi_{\mathbf{k}} | H_{\rm int} | \Psi_i \rangle|^2$ are smooth functions of $\mathbf{k}$ (and therefore E_k), whereas $F(T, E_k - E_i)$ becomes a strongly peaked function of E_k as T becomes large. We therefore treat the former as constants in the integral over E_k:

$$\sum_{f \neq i} |C_f(T)|^2 = \int d\Omega \frac{V}{(2\pi)^3} \, k^2 \left| \frac{dk}{dE_k} \right| \frac{1}{\hbar^2} |\langle \Psi_{\mathbf{k}} | H_{\rm int} | \Psi_i \rangle|^2 \left[\int dE_k F(T, E_k - E_i) \right] \ .$$

Act Three

Now consider in detail the integral over E_k:

$$\int dE_k\, F(T, E_k - E_i) = \int dE_k \left[\frac{\sin\left((E_k - E_i)T/2\hbar\right)}{(E_k - E_i)/2\hbar}\right]^2 .$$

As remarked in Act Two, the integrand is strongly peaked at $E_k = E_i$. We can think of this as approximate energy conservation: a discrepancy in $E_k - E_i$ of order $\hbar/T$, the width of the peak. If we think of T as the relatively long time associated with the detection of the final state by a macroscopic detector, then the energy scale $\hbar/T$ is certainly going to be much smaller than the energy scale on which microscopic quantities, the perturbation matrix element and the phase space factor in particular, have a significant variation. This justifies placing these outside of the energy integral.

In evaluating the energy integral we may extend the integration limits to $\pm\infty$ since the main contribution comes from the neighborhood of the peak:

$$\int_{-\infty}^{\infty} dE_k\, F(T, E_k - E_i) = 2\hbar T \int_{-\infty}^{\infty} dx \frac{\sin^2 x}{x^2} = 2\pi\hbar T .$$

When we substitute this back into the last expression in Act Two we must remember that all quantities associated with the final state are to be evaluated for wave-vectors that conserve energy, that is, for wave-vectors with magnitude $k(E_i)$:

$$\sum_{f\neq i} |C_f(T)|^2 = T\,\frac{2\pi}{\hbar} \int d\Omega \frac{V}{(2\pi)^3} \left[k^2 \left|\frac{dk}{dE_k}\right| |\langle\Psi_{\mathbf{k}}|H_{\text{int}}|\Psi_i\rangle|^2\right]_{k=k(E_i)} .$$

Act Four

At the end of the last Act we saw that the probability for the system to be measured in some final plane wave state grows linearly with the time T. The same linear behavior applies if we perform a partial sum, corresponding to a restriction on the range of spherical angles of the final states. A linearly growing probability (of an event having occurred) has the interpretation of a constant transition rate Γ (of the event happening) acting at all times:

$$\Gamma = \frac{1}{T} \sum_{f\neq i} |C_f(T)|^2 = \frac{2\pi}{\hbar} \int d\Omega \frac{V}{(2\pi)^3} \left[k^2 \left|\frac{dk}{dE_k}\right| |\langle\Psi_{\mathbf{k}}|H_{\text{int}}|\Psi_i\rangle|^2\right]_{k=k(E_i)} .$$

The differential transition rate,

$$\frac{d\Gamma}{d\Omega} = \frac{2\pi}{\hbar} \frac{V}{(2\pi)^3} \left[k^2 \left|\frac{dk}{dE_k}\right| |\langle\Psi_{\mathbf{k}}|H_{\text{int}}|\Psi_i\rangle|^2\right]_{k=k(E_i)} ,$$

gives the rate of transitions into final states with wave-vectors $\mathbf{k}$ within an element of spherical angle $d\Omega$. A more compact way of writing these expressions uses the delta function and the identity

$$\delta(f(x) - f(a)) = \frac{1}{|f'(a)|}\delta(x-a) \; ,$$

applied to the function E_k:

$$\begin{aligned} \int \frac{V d^3k}{(2\pi)^3}\, \delta(E_k - E_i)(\cdots) &= \int \frac{V d^3k}{(2\pi)^3} \left|\frac{dk}{dE_k}\right| \delta(k - k(E_i))(\cdots) \\ &= \int \frac{V d\Omega}{(2\pi)^3} \left[k^2 \left|\frac{dk}{dE_k}\right| (\cdots) \right]_{k=k(E_i)} \; . \end{aligned}$$

This form generalizes readily to arbitrary quasi-continuum sets of final states. As an example, consider plane-wave final states in one dimension. When these are defined in a box of width W,

$$\begin{aligned} \Gamma &= \int_{-\infty}^{\infty} \frac{W dk}{2\pi}\, \delta(E_k - E_i) \frac{2\pi}{\hbar} |\langle \Psi_{\mathbf{k}} | H_{\rm int} | \Psi_i \rangle|^2 \\ &= \frac{W}{2\pi} \left|\frac{dk}{dE_k}\right|_{k=k(E_i)} \frac{2\pi}{\hbar} \left(|\langle \Psi_{k(E_i)} | H_{\rm int} | \Psi_i \rangle|^2 + |\langle \Psi_{-k(E_i)} | H_{\rm int} | \Psi_i \rangle|^2 \right) \; . \end{aligned}$$

The two (usually equal) terms correspond to there being two distinct plane wave states in one dimension for any particular energy (such as E_i). In two dimensions this sum over two terms becomes an integral over one angle, and in three dimensions, an integral over the solid angle Ω.

The final act ends with a formula you can actually remember, and one that applies in any number of dimensions. Here it is:

$$\Gamma = \frac{2\pi}{\hbar} \sum_f \delta(E_f - E_i)\, |\langle \Psi_f | H_{\rm int} | \Psi_i \rangle|^2 \; .$$

Start by checking the units and note that (apart from the 2π factor) this pretty much determines the whole formula! There is a complication buried in the summation that we already know about: the sum is actually an integral since the Golden Rule **always** assumes a quasi-continuum of states. Converting the sum into an integral involves the density of states in a box:

$$\text{1D} \;\; : \;\; \sum_f (\cdots) = \int \frac{W\, dk_f}{2\pi} (\cdots)$$

$$
\begin{aligned}
2\text{D} \quad &: \quad \sum_f (\cdots) = \int \frac{A\, dk_f^2}{(2\pi)^2} (\cdots) \\
3\text{D} \quad &: \quad \sum_f (\cdots) = \int \frac{V\, dk_f^3}{(2\pi)^3} (\cdots) \ .
\end{aligned}
$$

The width (W), area (A), or volume (V) of the box will disappear from the calculation since the squared normalization of the state $|\Psi_f\rangle$ has the same quantity in the denominator.

Another appealing feature of the compact formula for Γ is that it also makes sense when the sum is transferred to the initial states. In this form the Golden Rule describes an absorption process: energy from an initial continuum state is transferred to a discrete microstate.

Balancing Act

A deeper appreciation of the Golden Rule is gained through study of the balancing act required to select the appropriate quantum evolution time T. In Act Three it was emphasized that T could not be too small, since otherwise energy conservation of the quantum system was compromised. More to the point: When the microscopic system is probed through measurement at intervals of time T that correspond to energies $\hbar/T$ that are comparable to the micro-scale of energy, then the system effectively exchanges energy with its environment and is therefore no longer truly isolated. On the other hand, there is also an upper limit on the size of T. From the conservation of probability we must have

$$
1 \geq \sum_{f \neq i} |C_f(T)|^2 = \Gamma\, T \ .
$$

In fact we really want the stronger condition $\Gamma\, T \ll 1$, since in Act One we assumed $C_i(T) \approx 1$. Compatibility of the upper and lower bounds on T hinges ultimately on the smallness of H_{int}. If we define the mean lifetime by $\tau = 1/\Gamma$, then the validity of our derivation ends at times T that are much smaller than τ.

So what can we say about times T that are comparable or even longer than τ? This is subtle and naturally leads to the topic of measurement. We can idealize our detector of the final state particle as executing a sequence of measurements at regular intervals T. The outcome of each measurement is a definite state: either the transition has occurred (particle detected) or not (no particle detected). In the latter case, we know the microscopic system is definitely in the state $|\Psi_i\rangle$, that is, $C_i = 1$ and $C_j = 0$ $(j \neq i)$. If we call this an unsuccessful measurement, then it is legitimate to restart the quantum evolution from our original initial conditions after every unsuccessful measurement. The probability that any of the sequential measurements is successful is ΓT, and is reliably given by the Golden Rule calculation, provided of course $\Gamma T \ll 1$. But this is really just the statement that there is a constant transition rate that applies to every interval in a fine subdivision of an arbitrarily long period of time.