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1. Consider a two–level system with the Hamiltonian being

$$H = \varepsilon_0|0\rangle\langle 0| + \varepsilon_1|1\rangle\langle 1| + V(|0\rangle\langle 1| + |1\rangle\langle 0|). \tag{1}$$

Here $|a\rangle$ $(a = 0, 1)$ are two complete orthonormal basis and ε_a and V are real constants. Setting $\hbar = 1$[1], the Schrödinger equation reads

$$\frac{\mathrm{d}}{\mathrm{d}t}|\psi(t)\rangle = -iH|\psi(t)\rangle. \tag{2}$$

(a) Given initial state $|\psi(t_0)\rangle = |0\rangle$, show that up to the first order perturbation of V, the solution reads

$$|\psi(t)\rangle = e^{-i\varepsilon_0(t-t_0)}|0\rangle - Ve^{-i(\varepsilon_1 t-\varepsilon_0 t_0)}|1\rangle\frac{e^{i\omega_{10}t} - e^{i\omega_{10}t_0}}{\omega_{10}} + \mathcal{O}(V^2), \tag{3}$$

with $\omega_{10} \equiv \varepsilon_1 - \varepsilon_0$. Further prove the transition probability from $|0\rangle$ to $|1\rangle$ is

$$P_{0\to 1}(t) \equiv |\langle 1|\psi(t)\rangle|^2 = \frac{4V^2}{\omega_{10}^2}\sin^2\left[\frac{\omega_{10}}{2}(t-t_0)\right] \tag{4}$$

and the rate constant is

$$k_{0\to 1} \equiv \lim_{t_0\to-\infty}\frac{\mathrm{d}}{\mathrm{d}t}P_{0\to 1} = 2\pi V^2\delta(\omega_{10}). \tag{5}$$

This is the famous Fermi's golden rule.

(b) (Optional, just for your information) Now turn to the electron transfer (or charge/energy transfer) process.[2] The Hamiltonian is a generalization of Eq. (1),

[1] For convenient, we often set $\hbar$ as unit. In this case, we have unit relations,

$$[\text{Energy}] = [\text{Time}]^{-1} = [\text{Frequency}].$$

[2] More on the electron transfer can be found in Y. Wang, Y. Su, R. X. Xu, X. Zheng, and Y. J. Yan, *Chin. J. Chem. Phys.* **34**, 462 (2021). On the energy transfer: Z. H. Chen, Y. Wang, R. X. Xu, and Y. J. Yan, *J. Chem. Phys.* **154**, 244105 (2021).

reading

$$H_{\mathrm{T}} = H + \hat{V}, \tag{6}$$

with

$$H = \sum_j \varepsilon_j |0; j\rangle\langle 0; j| + \sum_j \varepsilon'_j |1; j\rangle\langle 1; j| \equiv H_0 + H_1 \tag{7}$$

and

$$\hat{V} = \sum_{jk} V_{jk}(|0; j\rangle\langle 1; k| + |1; k\rangle\langle 0; j|). \tag{8}$$

Suppose the initial state is given by

$$\hat{\rho}_{\mathrm{T}}(t_0) = \sum_j P_j |0; j\rangle\langle 0; j|. \tag{9}$$

Thus the rate is counted by averaging the initial state and summing over the final state, namely

$$k_{\mathrm{ET}} = \sum_{jk} 2\pi V_{jk}^2 P_j \delta(\varepsilon_j - \varepsilon'_k). \tag{10}$$

Show that

$$k_{\mathrm{ET}} = 2\mathrm{Re} \int_0^{\infty} \mathrm{d}t \, \langle \hat{V}(t)\hat{V}(0)\rangle_0, \tag{11}$$

by defining $\hat{V}(t) \equiv e^{iHt}\hat{V}e^{-iHt}$ and

$$\langle (\cdot) \rangle_0 \equiv \mathrm{Tr}_0[(\cdot)e^{-\beta H_0}]/\mathrm{Tr}\, e^{-\beta H_0} = \sum_j \langle 0; j|(\cdot)e^{-\beta H_0}|0; j\rangle/\mathrm{Tr}\, e^{-\beta H_0}. \tag{12}$$