ChemE 2200 - Physical Chemistry II for Engineers

Quiz 1 - January 29, 2025

Name: *Solution*

The transition is allowed if

$$\int \psi^*_{\text{final}} \hat{T} \psi_{\text{initial}} d\tau \neq 0$$

In one-dimensional systems, $\hat{T} = e E_x x$. Substitute the probability amplitudes and evaluate the integral.

$$\int \psi^*_2 \hat{T} \psi_0 d\tau = \int_{-\infty}^{\infty} \left(\frac{b}{4\pi}\right)^{1/4} (2bx^2 - 1)\, e^{-bx^2/2} (eE_x x) \left(\frac{b}{\pi}\right)^{1/4} e^{-bx^2/2} dx = eE_x \left(\frac{b}{2\pi}\right)^{1/2} \int_{-\infty}^{\infty} (2bx^3 - x) e^{-bx^2} dx$$

Consider the integrand; e^{-bx^2} is positive over the entire range of integration, $-\infty$ to $+\infty$. $2bx^3$ and x are odd functions; negative for $-\infty$ to 0 and positive for 0 to ∞. Thus the integral is zero. The transition is forbidden.

Alternatively, one may recall from Homework 2 that $\hat{T}\psi_0$ is proportional to ψ_1. Thus,

$$\int \psi^*_2 \hat{T} \psi_0 d\tau \propto \int \psi^*_2 \psi_1 d\tau = 0$$ because the eigenfunctions of a system are orthogonal.

Again we find that the transition is forbidden.

Grading Rubric:

Commonly forgot *, ok here b/c ψ_2 is real

$\int \psi_2^* \hat{T} \hat{\psi}_0 \, dx$: + 3

Note: $\int \psi_2^* \psi_1 \, d\tau$ also okay
↳ + 2 if had $\int \psi_2^* \hat{T} \psi_1$

$\hat{T} = e \mathcal{E}_x x$: + 2

Integral = 0 b/c { symmetry / pos + neg regions; even + odd explanation

- ↳ + 2 : correct evaluation & reasoning
- ↳ + 1 : correct reasoning (e.g. recognizing even/odd) w/ incorrect evaluation
- ↳ + 0 : incorrect evaluation & incorrect/no reasoning

Transition is forbidden/not allowed b/c { $\int \psi^*_{\text{final}} \hat{T} \psi_{\text{initial}} = 0$; No overlap in overlap integral

- ↳ + 3 : Correct answer & justification
- ↳ + 2 : Correct answer & incorrect/no justification
- ↳ + 1 : Incorrect answer but correct justification
- ↳ + 0 : incorrect answer & justification