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國立臺灣大學97學年度碩士班招生考試試題

科目:物理化學(B)

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1. For a quantum mechanical system that has a particle in a 1-D infinite-depth box, the general solution to the Schrodinger equation is shown to be: $w = Ae^{ix\sqrt{2mE}/\hbar} + Be^{-ix\sqrt{2mE}/\hbar}$

$$\psi = Ae^{\frac{n^2\pi^2\hbar^2}{4mE^2\hbar^2}} + Be^{-\frac{n^2\pi^2\hbar^2}{4mE^2\hbar^2}}$$
(a) Show that the energy of the particle is quantized, as given by $E_n = \frac{n^2\pi^2\hbar^2}{2mL^2}$ $n = 1, 2, ...$

where L is the length of the box and m is the mass of the particle.

(8 points)

(b) The system's wavefunction is given by:
$$\psi = \left(\frac{2}{L}\right)^{1/2} \sin nx$$

In the state with n = 1, if the momentum of the particle is measured, how many possible values will there be? What are they? What is the probability of getting each of the possible values? (8 points)

(c) If the system that is measured in (b) is measured again for the particle's position, how many possible values will there be?

(8 points)

(d) If the system that is measured in (c) is measured again for the particle's momentum, how many possible values will there be? (8 points)

2. Consider that the particle in Problem 1 is irradiated with a plane-polarized light. The polarization is such that the electric field of the radiation is only in the x direction, which is along the length of the box. Neglect the effect of the magnetic filed. Assume that the first-order approximation by the time-dependent perturbation method is adequate.

(a) What is the requirement of the particle if it is to be influenced by the light?

(8 points)

(b) Suppose the particle meets the requirement in (a). Which of the following transitions are allowed: $1\rightarrow 2$, $1\rightarrow 3$, $1\rightarrow 4$? Prove your answer. (15 points)

You may find SOME of the information given below useful in solving the exam problems:

$$\int x \cos \frac{nx}{a} dx = \frac{\cos(nx/a)}{8n^2/a^2} + \frac{x \sin(nx/a)}{4n/a} \qquad \int x \sin^2 \frac{nx}{a} dx = \frac{x^2}{4} - \frac{x \sin(2nx/a)}{4n/a} - \frac{\cos(2nx/a)}{8n^2/a^2}$$

$$\int x \sin \frac{\pi x}{a} \sin \frac{n\pi x}{a} dx = \frac{1}{2} \left[\frac{a^2 \cos \frac{(n-1)\pi x}{a}}{(n-1)^2 \pi^2} + \frac{(n-1)ax \sin \frac{(n-1)\pi x}{a}}{(n-1)\pi} \right]$$
$$-\frac{1}{2} \left[\frac{a^2 \cos \frac{(n+1)\pi x}{a}}{(n+1)^2 \pi^2} + \frac{ax \sin \frac{(n+1)\pi x}{a}}{(n+1)\pi} \right]$$

3. Decide whether the following equations of state lead to critical behavior, and decide whether gases following each of the equations would undergo liquefication. (8 points each)

(a)
$$pV_m = RT(1 + \frac{b}{V_m})$$
 (b) $p(V_m - b) = RT$

4. Consider a gas A2 that adsorbs dissociatively onto a surface M as represented by

A₂ (g) + 2 M (surface) \leftrightarrow 2 AM (surface) It is assumed that the adsorption process follows the Langmuir isotherm, i.e. $\theta = \frac{(Kp)^{1/2}}{1 + (Kp)^{1/2}}$

where θ = fractional coverage and p = partial pressure of A_2 above M.

(a) State the 3 assumptions leading to the formulation of the Langmuir isotherm. (9 points

(b) Derive the above expression of Langmuir isotherm for the adsorption process in question. (10 points)

(c) Design an experiment such that it will enable you to confirm whether the adsorption process in question follows the Langmuir isotherm. (10 points)