Quantum Mechanics and Spectroscopy
CHEM 3PA3
Assignment 23 **Name:** _____

1. One of the observed absorption lines in the spectrum of the Scandium atom ($[\mathrm{Ar}]4s^2 3d^1$) corresponds to excitation of an electron from the $3d$ orbital to the $5s$ orbital. Which of the following approximations is inadequate to explain this process?

   (a) long-wavelength approximation
   (b) weak-field approximation
   (c) long-time approximation

2. Which of the following transitions are electric-dipole allowed?

   (a) $1s \to 2s$
   (b) $1s \to 2p$
   (c) $2p \to 3d$
   (d) $3s \to 5d$
   (e) $3s \to 5p$

3. Consider a particle with unit mass and unit charge confined to a 3-dimensional box, with potential,

$$V_{3D-box}(x,y,z) = V_{1D-box}(x) + V_{1D-box}(y) + V_{1D-box}(z)$$

$$V_{1D-box}(i) = \begin{cases} +\infty, & i \leq 0 \\ 0 & 0 < i < a \\ -\infty, & i \geq a \end{cases}$$

   We place this box in linearly polarized light, which induces a time-dependent potential with the form $V_{light}(x,y,z,t) = -2Vx\sin(wt - kz)$.

   (a) What is the time-dependent Schrödinger equation for this system, using atomic units (so $\hbar = 1$)?
   (b) What whould $V_{light}(x,y,z,t)$ be if the long-wavelength approximation was assumed to be true?
   (c) Assume that the light propagates in the positive z direction, that the light is linearly polarized with its electric field oscillating in the x direction. What is the formula for the transition frequencies, ω_{fi}, of the electric-dipole-allowed (E1) transitions and electric-quadrupole-allowed (E2) transitions?
   (d) The intensity of the electric-quadrupole-allowed transitions is observed to be much weaker than that of the electric-dipole-allowed transitions. Why?

4. Consider the ground state of the Phosphorous atom, with electron configuration $[\mathrm{Ne}]3s^2 3p^3$.

   (a) What is the ground-state term symbol for this atom? (You do not need to worry about the J quantum number.)

(b) What are all the term symbols associated with the excited state of the Phosphorous atom with configuration [Ne]$3s^2 3p^2 3d^1$?

(c) Assume that only electric-dipole-allowed transitions are observed (E1 selection rules). List the term symbols of the excited states in part b that are E1-allowed transitions from the ground state term symbol in part (a).

(d) Draw the "multiplication" of the initial and final orbitals and show an example of a forbidden and an allowed E1 transition.