

Name \_\_\_\_\_ Student Number \_\_\_\_\_

## Midterm #4

Show your work clearly. I will give partial credit in some cases, but *only* to the extent that I can clearly understand your work. There is extra paper at the front of the room if you need it.

There are 8 questions (12 points each) on this midterm. There are two bonus questions. There are four “free points” since the exam is graded out of 100, but there is only the possibility of losing 96 points.

### Key integrals and identities:

$$\left(\frac{a}{2}\right)\delta_{mn} = \int_0^a \sin\left(\frac{n\pi x}{a}\right) \sin\left(\frac{m\pi x}{a}\right) dx$$

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$$\frac{a^2}{4} = \int_0^a \left(\sin\left(\frac{n\pi x}{a}\right)\right)^2 x dx$$

$$\left(\frac{a}{2\pi n}\right)^3 \left(\frac{4\pi^3 n^3}{3} - 2\pi n\right) = \int_0^a \left(\sin\left(\frac{n\pi x}{a}\right)\right)^2 x^2 dx$$

$$\frac{1}{2}\sqrt{\frac{\pi}{\alpha}} = \int_0^\infty e^{-\alpha x^2} dx$$

$$\left(\frac{1}{2}\sqrt{\frac{\pi}{\alpha}}\right) \left(\frac{(2n-1)(2n-3)\cdots(3)(1)}{(2\alpha)^n}\right) = \int_0^\infty x^{2n} e^{-\alpha x^2} dx \quad n = 1, 2, 3, \dots$$

$$\left(\frac{1}{2}\right) \left(\frac{n!}{\alpha^{n+1}}\right) = \int_0^\infty x^{2n+1} e^{-\alpha x^2} dx \quad n = 0, 1, 2, \dots$$

$$2 \sin(x) \sin(y) = \cos(x-y) - \cos(x+y) \quad \rightarrow \quad 2 \sin^2 x = 1 - \cos(2x)$$

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$$\sin(x+y) = \sin x \cos y + \cos x \sin y \quad \rightarrow \quad \sin(2x) = 2 \sin x \cos x$$

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# VALUES OF SOME PHYSICAL CONSTANTS

Constant	Symbol	Value
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Proton charge	$e$	$1.60219 \times 10^{-19} \text{ C}$
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	$\hbar$	$1.05459 \times 10^{-34} \text{ J}\cdot\text{s}$
Speed of light in vacuum	$c$	$2.997925 \times 10^8 \text{ m}\cdot\text{s}^{-1}$
Atomic mass unit	amu	$1.66056 \times 10^{-27} \text{ kg}$
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Molar gas constant	$R$	$8.31441 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
Permittivity of a vacuum	$\epsilon_0$	$8.854188 \times 10^{-12} \text{ C}^2\cdot\text{s}^2\cdot\text{kg}^{-1}\cdot\text{m}^{-3}$
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Rydberg constant (infinite nuclear mass)	$R_\infty$	$2.179914 \times 10^{-23} \text{ J}$
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First Bohr radius	$a_0$	$5.29177 \times 10^{-11} \text{ m}$
Bohr magneton	$\mu_B$	$9.27409 \times 10^{-24} \text{ J}\cdot\text{T}^{-1}$
Stefan-Boltzmann constant	$\sigma$	$5.67032 \times 10^{-8} \text{ J}\cdot\text{m}^{-2}\cdot\text{K}^{-4}\cdot\text{s}^{-1}$

# CONVERSION FACTORS FOR ENERGY UNITS

joule	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{eV}$	au	$\text{cm}^{-1}$	Hz
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1 $\text{kJ}\cdot\text{mol}^{-1}$ = $1.661 \times 10^{-21}$	1	$1.036 \times 10^{-2}$	$3.089 \times 10^{-4}$	83.60	$2.506 \times 10^{12}$
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1 Hz = $6.626 \times 10^{-34}$	$3.990 \times 10^{-13}$	$4.136 \times 10^{-15}$	$1.520 \times 10^{-16}$	$3.336 \times 10^{-11}$	1

# SOME MATHEMATICAL FORMULAS

Paul

$$\begin{aligned} \sin \alpha \sin \beta &= \frac{1}{2} \cos (\alpha - \beta) - \frac{1}{2} \cos (\alpha + \beta) \\ \cos \alpha \cos \beta &= \frac{1}{2} \cos (\alpha - \beta) + \frac{1}{2} \cos (\alpha + \beta) \\ \sin \alpha \cos \beta &= \frac{1}{2} \sin (\alpha + \beta) + \frac{1}{2} \sin (\alpha - \beta) \\ \sin (\alpha \pm \beta) &= \sin \alpha \cos \beta \pm \cos \alpha \sin \beta \\ \cos (\alpha \pm \beta) &= \cos \alpha \cos \beta \mp \sin \alpha \sin \beta \\ e^{\pm i \theta} &= \cos \theta \pm i \sin \theta \\ \cos \theta &= \frac{e^{i \theta} + e^{-i \theta}}{2} \\ \sin \theta &= \frac{e^{i \theta} - e^{-i \theta}}{2i} \\ f(x) &= f(a) + f'(a)(x-a) + \frac{1}{2!} f''(a)(x-a)^2 + \frac{1}{3!} f'''(a)(x-a)^3 + \dots \\ e^x &= 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \frac{x^4}{4!} + \dots \\ \cos x &= 1 - \frac{x^2}{2!} + \frac{x^4}{4!} - \frac{x^6}{6!} + \dots \\ \sin x &= x - \frac{x^3}{3!} + \frac{x^5}{5!} - \frac{x^7}{7!} + \dots \\ \frac{1}{1-x} &= 1 + x + x^2 + x^3 + x^4 + \dots \quad x^2 < 1 \\ (1 \pm xy)^n &= 1 \pm nx \pm \frac{n(n-1)}{2!} x^2 \pm \frac{n(n-1)(n-2)}{3!} x^3 \pm \dots \quad x^2 < \frac{1}{n} \\ \int_0^\infty x^n e^{-ax} dx &= \frac{n!}{a^{n+1}} \quad (n \text{ positive integer}) \\ \int_0^\infty e^{-ax^2} dx &= \left(\frac{\pi}{4a}\right)^{1/2} \\ \int_0^\infty x^{2n} e^{-ax^2} dx &= \frac{1 \cdot 3 \cdot 5 \cdot \dots \cdot (2n-1)}{2^{n+1} a^n} \left(\frac{\pi}{a}\right)^{1/2} \quad (n \text{ positive integer}) \\ \int_0^\infty x^{2n+1} e^{-ax^2} dx &= \frac{n!}{2a^{n+1}} \quad (n \text{ positive integer}) \\ \int_0^a \sin \frac{m\pi x}{a} \sin \frac{n\pi x}{a} dx &= \int_0^a \cos \frac{m\pi x}{a} \cos \frac{n\pi x}{a} dx = \frac{a}{2} \delta_{nm} \\ \int_0^a \cos \frac{m\pi x}{a} \sin \frac{n\pi x}{a} dx &= 0 \quad (m \text{ and } n \text{ integers}) \end{aligned}$$

$$1 \text{ J (oule)} = 1 \text{ kg}\cdot\text{m}^2/\text{s}^2 = 1 \text{ C (oulomb)}\cdot\text{V (olt)}$$

1. Write the electronic and nuclear Schrödinger equations for the neutral hydrogen molecule in SI units, showing the dependence on physical constants like the charge and mass of the electron.

electronic Schrödinger equation:

nuclear Schrödinger equation:

In Lithium Hydride, LiH, in the molecular orbital approximation, the ground state is predicted to be a singlet state, and the occupied molecular orbitals are both sigma orbitals. The electron configuration can then be written as  $1\sigma^2 2\sigma^2$ . Let  $\phi_{1\sigma}(\mathbf{r})$  and  $\phi_{2\sigma}(\mathbf{r})$  denote these molecular orbitals.

2. Write a Slater determinant for the  $1\sigma^2 2\sigma^2$  electron configuration of LiH. Write the determinant out in its entirety, showing all the occupied orbitals and the coordinates of all the electrons explicitly. Remember the normalization factor.

3. Write a reasonable expression for the *highest* (the  $2\sigma$ ) occupied molecular orbital in LiH.

$$\phi_{2\sigma}(\mathbf{r}) =$$

4. **Write an expression for the wavefunction of the Hydrogen molecule ( $H_2$ ) using molecular orbital theory and using valence bond theory.** Assume that only the 1s orbitals of the “left” and “right” Hydrogen atoms need to be used to accurately build the molecular wavefunction. You do not have to include the normalization constant.

**MO Theory:**

**VB Theory:**

5. Fermi's Golden rule gives an expression for the rate of transition from an initial state to a final state. **Write a form of Fermi's Golden Rule that is appropriate for electric-dipole (E1) transitions in a molecular system.**

6. **Which of the following approximations are necessary to derive Fermi's Golden rule? Circle all that apply.**

- |                                     |                                |
|-------------------------------------|--------------------------------|
| (a) Born-Oppenheimer approximation. | (b) weak-field approximation.  |
| (c) long-time approximation.        | (d) Heisenberg approximation.  |
| (e) Wenzel approximation.           | (f) Dirac delta approximation. |
| (g) long-wavelength approximation.  | (h) Born postulate.            |

7. Listed below are formulas for the frequencies of the dipole-allowed (E1) transitions for the **(A)** one-electron atom **(B)** the one-dimensional-harmonic oscillator, and **(C)** rigid rotation of a diatomic molecule (with a dipole moment). The letter  $R$  is just a constant, which (obviously) has different interpretations in all three cases. **Label the formulas below correctly.**

\_\_\_\_\_  $\omega_{fi} = R$  (only one transition frequency)

\_\_\_\_\_  $\omega_{fi} = Rn$   $n = 1, 2, \dots$  (equally spaced transitions)

\_\_\_\_\_  $\omega_{fi} = R \left( \frac{1}{n_2^2} - \frac{1}{n_1^2} \right)$   $n_1 = 1, 2, \dots$   $n_2 = 1, 2, \dots$   $n_1 > n_2$

8. **Label the following approximate (unnormalized) molecular orbitals using the  $\sigma, \pi, \delta, u, g$ , and  $+, -$  designations. Here, we denote the  $1s$  orbital on the “left-hand” atom as  $\psi_{1s}^{(l)}(\mathbf{r})$ , with the obvious generalization of notation to the other orbitals and the “right-hand” atom.**

Orbital Symmetry Label	Molecular Orbital
	$\psi_{2s}^{(l)}(\mathbf{r}) + \psi_{2s}^{(r)}(\mathbf{r})$
	$\psi_{2s}^{(l)}(\mathbf{r}) - \psi_{2s}^{(r)}(\mathbf{r})$
	$\psi_{2p_x}^{(l)}(\mathbf{r}) + \psi_{2p_x}^{(r)}(\mathbf{r})$
	$\psi_{2p_x}^{(l)}(\mathbf{r}) - \psi_{2p_x}^{(r)}(\mathbf{r})$
	$\psi_{2p_y}^{(l)}(\mathbf{r}) + \psi_{2p_y}^{(r)}(\mathbf{r})$
	$\psi_{2p_y}^{(l)}(\mathbf{r}) - \psi_{2p_y}^{(r)}(\mathbf{r})$
	$\psi_{2p_z}^{(l)}(\mathbf{r}) + \psi_{2p_z}^{(r)}(\mathbf{r})$
	$\psi_{2p_z}^{(l)}(\mathbf{r}) - \psi_{2p_z}^{(r)}(\mathbf{r})$

**Bonus** (5 points) One of the observed absorption lines in the spectrum of the Scandium atom ( $[\text{Ar}]4s^23d^1$ ) 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.

**Bonus:** (10 points) **What is the formula for the energies of the transitions allowed in a 3-dimensional particle in a box in the electric dipole (E1) and electric quadrupole (E2) approximation.** (I am asking for the analogue of the formulas in question #7.) Assume that the light propagates in the positive  $z$  directions, that the light is linearly polarized with its electric field oscillating in the  $x$  direction. The box is defined by the potential,

$$V(x, y, z) = \begin{cases} 0 & -\frac{1}{2}a_x < x < \frac{1}{2}a_x; \quad -\frac{1}{2}a_y < y < \frac{1}{2}a_y; \quad -\frac{1}{2}a_z < z < \frac{1}{2}a_z \\ +\infty & \text{otherwise} \end{cases}$$

Recall the eigenfunctions for a particle in a box of width  $a$  centered at the origin are:

$$\psi_n(x) = \begin{cases} \sqrt{\frac{2}{a}} \cos\left(\frac{n\pi x}{a}\right) & n = 1, 3, 5, \dots \\ \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right) & n = 2, 4, 6, \dots \end{cases}$$

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1. The electronic and nuclear Schrödinger equations for the neutral hydrogen molecule in SI units, showing the dependence on physical constants like the charge and mass of the electron.

In this case the atomic numbers of the two atoms are  $Z_1 = Z_2 = 1$ . And there are only two atoms and only two electrons. So the electronic Schrodinger equation is:

$$\left( \begin{aligned} &-\frac{\hbar^2}{2m_e} \nabla_{\mathbf{r}_1}^2 - \frac{\hbar^2}{2m_e} \nabla_{\mathbf{r}_2}^2 \\ &-\frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_1 - \mathbf{R}_1|} - \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_2 - \mathbf{R}_1|} \\ &-\frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_1 - \mathbf{R}_2|} - \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_2 - \mathbf{R}_2|} \\ &+\frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_1 - \mathbf{r}_2|} + \frac{e^2}{4\pi\epsilon_0 |\mathbf{R}_1 - \mathbf{R}_2|} \end{aligned} \right) \psi_e(\mathbf{r}_1, \mathbf{r}_2 | \mathbf{R}_1, \mathbf{R}_2) = U(\mathbf{R}_1, \mathbf{R}_2) \psi_e(\mathbf{r}_1, \mathbf{r}_2 | \mathbf{R}_1, \mathbf{R}_2)$$

and the nuclear Schrödinger equation is:

$$\left( -\frac{\hbar^2}{2M_H} \nabla_{\mathbf{R}_1}^2 - \frac{\hbar^2}{2M_H} \nabla_{\mathbf{R}_2}^2 + U(\mathbf{R}_1, \mathbf{R}_2) \right) \chi_n(\mathbf{R}_1, \mathbf{R}_2) = E \chi_n(\mathbf{R}_1, \mathbf{R}_2)$$

It would be OK to then separate out the translational/rotational components of the problem and then write something like:

$$\left( -\frac{\hbar^2}{2\mu_{H_2}} \nabla_{\mathbf{R}}^2 + U(R) \right) \chi_n(\mathbf{R}) = E \chi_n(\mathbf{R}) \quad \mu_{H_2} = \frac{1}{2} M_H \quad R = |\mathbf{R}_2 - \mathbf{R}_1|$$

or even:

$$\left( -\frac{\hbar^2}{2\mu_{H_2}} \left( \frac{1}{R^2} \frac{d}{dR} R^2 \frac{d}{dR} - \frac{\hat{L}^2}{R^2} \right) + U(R) \right) \chi_n(\mathbf{R}) = E \chi_n(\mathbf{R})$$

but this was not required for this problem.

In Lithium Hydride, LiH, in the molecular orbital approximation, the ground state is predicted to be a singlet state, and the occupied molecular orbitals are both sigma orbitals. The electron configuration can then be written as  $1\sigma^2 2\sigma^2$ . Let  $\phi_{1\sigma}(\mathbf{r})$  and  $\phi_{2\sigma}(\mathbf{r})$  denote these molecular orbitals.

2. Write a Slater determinant for the  $1\sigma^2 2\sigma^2$  electron configuration of LiH.

$$|\Psi_{1\sigma^2 2\sigma^2}\rangle = \frac{1}{\sqrt{4!}} \begin{vmatrix} \phi_{1\sigma}(\mathbf{r}_1)\alpha(1) & \phi_{1\sigma}(\mathbf{r}_1)\beta(1) & \phi_{2\sigma}(\mathbf{r}_1)\alpha(1) & \phi_{2\sigma}(\mathbf{r}_1)\beta(1) \\ \phi_{1\sigma}(\mathbf{r}_2)\alpha(2) & \phi_{1\sigma}(\mathbf{r}_2)\beta(2) & \phi_{2\sigma}(\mathbf{r}_2)\alpha(2) & \phi_{2\sigma}(\mathbf{r}_2)\beta(2) \\ \phi_{1\sigma}(\mathbf{r}_3)\alpha(3) & \phi_{1\sigma}(\mathbf{r}_3)\beta(3) & \phi_{2\sigma}(\mathbf{r}_3)\alpha(3) & \phi_{2\sigma}(\mathbf{r}_3)\beta(3) \\ \phi_{1\sigma}(\mathbf{r}_4)\alpha(4) & \phi_{1\sigma}(\mathbf{r}_4)\beta(4) & \phi_{2\sigma}(\mathbf{r}_4)\alpha(4) & \phi_{2\sigma}(\mathbf{r}_4)\beta(4) \end{vmatrix}$$

3. Write a reasonable expression for the *highest* (the  $2\sigma$ ) occupied molecular orbital in LiH.

$$\phi_{2\sigma}(\mathbf{r}) = c\psi_{\text{Li-}2s}(\mathbf{r}) + \sqrt{1-|c|^2}\psi_{\text{H-}1s}(\mathbf{r})$$

You could reasonably expect that the orbital is “mostly” on the hydrogen (the more electronegative atom) so probably  $|c| < \frac{1}{\sqrt{2}}$ . You also could write this using the sp-hybrid orbital on the Lithium,

$$\phi_{2\sigma}(\mathbf{r}) = c\psi_{\text{Li-sp}}(\mathbf{r}) + \sqrt{1-|c|^2}\psi_{\text{H-}1s}(\mathbf{r})$$

4. Write an expression for the wavefunction of the Hydrogen molecule ( $\text{H}_2$ ) using molecular orbital theory and using valence bond theory. Assume that only the 1s orbitals of the “left” and “right” Hydrogen atoms need to be used to accurately build the molecular wavefunction.

**MO Theory:**

$$|\Psi_{\text{MO-H}_2}\rangle \propto (\psi_{1s}^{(l)}(\mathbf{r}_1) + \psi_{1s}^{(r)}(\mathbf{r}_1))(\psi_{1s}^{(l)}(\mathbf{r}_2) + \psi_{1s}^{(r)}(\mathbf{r}_2))[\alpha(1)\beta(2) - \alpha(2)\beta(1)]$$

**VB Theory:**

$$|\Psi_{\text{VB-H}_2}\rangle \propto (\psi_{1s}^{(l)}(\mathbf{r}_1)\psi_{1s}^{(r)}(\mathbf{r}_2) + \psi_{1s}^{(r)}(\mathbf{r}_1)\psi_{1s}^{(l)}(\mathbf{r}_2))[\alpha(1)\beta(2) - \alpha(2)\beta(1)]$$

5. Fermi’s Golden rule gives an expression for the rate of transition from an initial state to a final state. Write a form of Fermi’s Golden Rule that is appropriate for electric-dipole (E1) transitions in a molecular system.

$$W_{fi} = \frac{2\pi V^2 g(\hbar\omega_{fi})}{\hbar} \left| \langle \Phi_f | \mu_x | \Phi_i \rangle \right|^2$$

where

$$\mu_x = -\sum_{i=1}^N ex_i + \sum_{\alpha=1}^P (Z_{\alpha}e) X_{\alpha}$$

$$\hat{H}_{\text{mol}}\Phi_i = E_i\Phi_i$$

$$\omega_{fi} = \frac{E_f - E_i}{\hbar}$$

6. Which of the following approximations are necessary to derive Fermi’s Golden rule? Circle all that apply.

(a) Born-Oppenheimer approximation.

**(c) long-time approximation.**

(f) Wenzel approximation.

**(g) long-wavelength approximation.**

**(b) weak-field approximation.**

(d) Heisenberg approximation.

(f) Dirac delta approximation.

(h) Born postulate.

7. Listed below are formulas for the frequencies of the dipole-allowed (E1) transitions for the **(A)** one-electron atom **(B)** the one-dimensional-harmonic oscillator, and **(C)** rigid rotation of a diatomic molecule (with a dipole moment). The letter  $R$  is just a constant, which (obviously) has different interpretations in all three cases. **Label the formulas below correctly.**

B(harm. osc.)  $\omega_{fi} = R$  (only one transition frequency)

C(rigid rotor)  $\omega_{fi} = Rn$   $n = 1, 2, \dots$  (equally spaced transitions)

A(1 el. atom)  $\omega_{fi} = R \left( \frac{1}{n_2^2} - \frac{1}{n_1^2} \right)$   $n_1 = 1, 2, \dots$   $n_2 = 1, 2, \dots$   $n_1 > n_2$

8. Label the following approximate (unnormalized) molecular orbitals using the  $\sigma, \pi, \delta$ ,  $u, g$ , and  $+, -$  designations. Here, we denote the  $1s$  orbital on the “left-hand” atom as  $\psi_{1s}^{(l)}(\mathbf{r})$ , with the obvious generalization of notation to the other orbitals and the “right-hand” atom.

Orbital Symmetry Label	Molecular Orbital
$\sigma_g^+$ *+ designation is optional for $\sigma$ -states.*	$\psi_{2s}^{(l)}(\mathbf{r}) + \psi_{2s}^{(r)}(\mathbf{r})$
$\sigma_u^+$	$\psi_{2s}^{(l)}(\mathbf{r}) - \psi_{2s}^{(r)}(\mathbf{r})$
$\pi_u^+$ (or -, but if you use - for $x$ you must use + for $y$ .)	$\psi_{2p_x}^{(l)}(\mathbf{r}) + \psi_{2p_x}^{(r)}(\mathbf{r})$
$\pi_g^+$	$\psi_{2p_x}^{(l)}(\mathbf{r}) - \psi_{2p_x}^{(r)}(\mathbf{r})$
$\pi_u^-$	$\psi_{2p_y}^{(l)}(\mathbf{r}) + \psi_{2p_y}^{(r)}(\mathbf{r})$
$\pi_g^-$	$\psi_{2p_y}^{(l)}(\mathbf{r}) - \psi_{2p_y}^{(r)}(\mathbf{r})$
$\sigma_u^+$	$\psi_{2p_z}^{(l)}(\mathbf{r}) + \psi_{2p_z}^{(r)}(\mathbf{r})$
$\sigma_g^+$	$\psi_{2p_z}^{(l)}(\mathbf{r}) - \psi_{2p_z}^{(r)}(\mathbf{r})$

**Bonus** (5 points) One of the observed absorption lines in the spectrum of the Scandium atom ( $[\text{Ar}]4s^23d^1$ ) 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?**

Because this is an electric quadrupole transition which is zero in the long-wavelength approx.

(a) long-wavelength approximation.

(b) weak-field approximation.

(c) long-time approximation.

**Bonus: (10 points) What is the formula for the energies of the transitions allowed in a 3-dimensional particle in a box in the electric dipole (E1) and electric quadrupole (E2) approximation.** (I am asking for the analogue of the formulas in question #7.) Assume that the light propagates in the positive  $z$  directions, that the light is linearly polarized with its electric field oscillating in the  $x$  direction. The box is defined by the potential,

$$V(x, y, z) = \begin{cases} 0 & -\frac{1}{2}a_x < x < \frac{1}{2}a_x; \quad -\frac{1}{2}a_y < y < \frac{1}{2}a_y; \quad -\frac{1}{2}a_z < z < \frac{1}{2}a_z \\ +\infty & \text{otherwise} \end{cases}$$

Recall the eigenfunctions for a particle in a one-dimensional box of width  $a$  centered at the origin are:

$$\psi_n(x) = \begin{cases} \sqrt{\frac{2}{a}} \cos\left(\frac{n\pi x}{a}\right) & n = 1, 3, 5, \dots \\ \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right) & n = 2, 4, 6, \dots \end{cases}$$

The eigenfunctions and eigenvalues of the particle in a box are:

$$\psi_{n_x n_y n_z}(x, y, z) = \psi_{n_x}(x) \psi_{n_y}(y) \psi_{n_z}(z)$$

$$E_{n_x n_y n_z} = \frac{h^2}{8m} \left( \frac{n_x^2}{a_x^2} + \frac{n_y^2}{a_y^2} + \frac{n_z^2}{a_z^2} \right)$$

where we have used the solutions for the 1-dimensional particle in a box. The transition from state  $(n_x, n_y, n_z)$  to state  $(n'_x, n'_y, n'_z)$  is dipole allowed if

$$\begin{aligned} 0 \neq \langle \psi_{n'_x n'_y n'_z} | x | \psi_{n_x n_y n_z} \rangle &= \int_{-\frac{1}{2}a_x}^{\frac{1}{2}a_x} \int_{-\frac{1}{2}a_y}^{\frac{1}{2}a_y} \int_{-\frac{1}{2}a_z}^{\frac{1}{2}a_z} \psi_{n'_x n'_y n'_z}(x, y, z) x \psi_{n_x n_y n_z}(x, y, z) dz dy dx \\ &= \frac{8}{a_x a_y a_z} \int_{-\frac{1}{2}a_x}^{\frac{1}{2}a_x} \int_{-\frac{1}{2}a_y}^{\frac{1}{2}a_y} \int_{-\frac{1}{2}a_z}^{\frac{1}{2}a_z} x \psi_{n_x}(x) \psi_{n_y}(y) \psi_{n_z}(z) \psi_{n'_x}(x) \psi_{n'_y}(y) \psi_{n'_z}(z) dz dy dx \\ &= \frac{8}{a_x a_y a_z} \underbrace{\left[ \int_{-\frac{1}{2}a_x}^{\frac{1}{2}a_x} x \psi_{n_x}(x) \psi_{n'_x}(x) dx \right]}_{\substack{f(x)=x \text{ is an odd function} \\ \psi_{n_x}(x) \text{ is odd if } n_x \text{ is even} \\ \text{and even if } n_x \text{ is odd.}}} \underbrace{\left[ \int_{-\frac{1}{2}a_y}^{\frac{1}{2}a_y} \psi_{n_y}(y) \psi_{n'_y}(y) dy \right]}_{\substack{\text{zero unless } n_y = n'_y \text{ because eigenvectors} \\ \text{are orthogonal}}} \underbrace{\left[ \int_{-\frac{1}{2}a_z}^{\frac{1}{2}a_z} \psi_{n_z}(z) \psi_{n'_z}(z) dz \right]}_{\substack{\text{zero unless } n_z = n'_z \text{ because eigenvectors} \\ \text{are orthogonal}}} \\ &= \frac{8}{a_x a_y a_z} (\text{zero unless } n_x + n'_x \text{ is odd}) (\text{zero unless } n_y = n'_y) (\text{zero unless } n_z = n'_z) \end{aligned}$$

This allows us to write the energy of the allowed transitions as:

$$\begin{aligned} E_{n'_x n'_y n'_z} - E_{n_x n_y n_z} &= \frac{h^2}{8m} \left( \frac{n_x'^2}{a_x^2} + \frac{n_y'^2}{a_y^2} + \frac{n_z'^2}{a_z^2} \right) - \frac{h^2}{8m} \left( \frac{n_x^2}{a_x^2} + \frac{n_y^2}{a_y^2} + \frac{n_z^2}{a_z^2} \right) \\ &= \frac{h^2}{8ma_x^2} \left( (n'_x)^2 - n_x^2 \right) & n'_x = n_x + 1, n_x + 3, \dots \\ &= \frac{h^2}{8ma_x^2} \left( (n_x + k)^2 - n_x^2 \right) & k = 1, 3, 5, \dots \\ &= \frac{h^2}{8ma_x^2} (2kn_x + k^2) & k = 1, 3, 5, \dots; n_x = 1, 2, 3, \dots \end{aligned}$$

The frequencies of the allowed transitions are:

$$\begin{aligned}
 \omega_{fi} &= \frac{E_{n'_x n'_y n'_z} - E_{n_x n_y n_z}}{\hbar} \\
 &= \frac{h^2}{8ma_x^2} (2kn_x + k^2) & k=1,3,5,\dots; n_x=1,2,3,\dots \\
 &= \frac{2\pi h}{8ma_x^2} (2kn_x + k^2) & k=1,3,5,\dots; n_x=1,2,3,\dots
 \end{aligned}$$

The transition from state  $(n_x, n_y, n_z)$  to state  $(n'_x, n'_y, n'_z)$  is quadrupole allowed if

$$\begin{aligned}
 0 \neq \langle \psi_{n'_x n'_y n'_z} | xz | \psi_{n_x n_y n_z} \rangle &= \int_{-\frac{1}{2}a_x}^{\frac{1}{2}a_x} \int_{-\frac{1}{2}a_y}^{\frac{1}{2}a_y} \int_{-\frac{1}{2}a_z}^{\frac{1}{2}a_z} \psi_{n'_x n'_y n'_z}(x, y, z) xz \psi_{n_x n_y n_z}(x, y, z) dz dy dx \\
 &= \frac{8}{a_x a_y a_z} \int_{-\frac{1}{2}a_x}^{\frac{1}{2}a_x} \int_{-\frac{1}{2}a_y}^{\frac{1}{2}a_y} \int_{-\frac{1}{2}a_z}^{\frac{1}{2}a_z} xz \psi_{n_x}(x) \psi_{n_y}(y) \psi_{n_z}(z) \psi_{n'_x}(x) \psi_{n'_y}(y) \psi_{n'_z}(z) dz dy dx \\
 &= \frac{8}{a_x a_y a_z} \underbrace{\left[ \int_{-\frac{1}{2}a_x}^{\frac{1}{2}a_x} x \psi_{n_x}(x) \psi_{n'_x}(x) dx \right]}_{\substack{f(x)=x \text{ is an odd function} \\ \psi_{n_x}(x) \text{ is odd if } n_x \text{ is even} \\ \text{and even if } n_x \text{ is odd.}}} \underbrace{\left[ \int_{-\frac{1}{2}a_y}^{\frac{1}{2}a_y} \psi_{n_y}(y) \psi_{n'_y}(y) dy \right]}_{\substack{\text{zero unless } n_y = n'_y \text{ because eigenvectors} \\ \text{are orthogonal}}} \underbrace{\left[ \int_{-\frac{1}{2}a_z}^{\frac{1}{2}a_z} z \psi_{n_z}(z) \psi_{n'_z}(z) dz \right]}_{\substack{f(z)=z \text{ is an odd function} \\ \psi_{n_z}(z) \text{ is odd if } n_z \text{ is even} \\ \text{and even if } n_z \text{ is odd.}}} \\
 &= \frac{8}{a_x a_y a_z} (\text{zero unless } n_x + n'_x \text{ is odd}) (\text{zero unless } n_y = n'_y) (\text{zero unless } n_z + n'_z \text{ is odd})
 \end{aligned}$$

and so

$$\begin{aligned}
 E_{n'_x n'_y n'_z} - E_{n_x n_y n_z} &= \frac{h^2}{8m} \left( \frac{n_x'^2}{a_x^2} + \frac{n_y'^2}{a_y^2} + \frac{n_z'^2}{a_z^2} \right) - \frac{h^2}{8m} \left( \frac{n_x^2}{a_x^2} + \frac{n_y^2}{a_y^2} + \frac{n_z^2}{a_z^2} \right) \\
 &= \frac{h^2}{8m} \left( \frac{(n_x + k_x)^2 - n_x^2}{a_x^2} + \frac{(n_z + k_z)^2 - n_z^2}{a_z^2} \right) & k_x, k_z = 1, 3, 5, \dots \\
 &= \frac{h^2}{8m} \left( \frac{2n_x k_x + k_x^2}{a_x^2} + \frac{2n_z k_z + k_z^2}{a_z^2} \right) & \begin{aligned} k_x, k_z &= 1, 3, 5, \dots \\ n_x, n_z &= 1, 2, 3, \dots \end{aligned}
 \end{aligned}$$

and finally

$$\omega_{fi} = \frac{2\pi h}{8m} \left( \frac{2n_x k_x + k_x^2}{a_x^2} + \frac{2n_z k_z + k_z^2}{a_z^2} \right) \quad \begin{aligned} k_x, k_z &= 1, 3, 5, \dots \\ n_x, n_z &= 1, 2, 3, \dots \end{aligned}$$