

1. (10 pts total)

1. a) (5 pts) Global warming is a serious issue related to the absorption of IR radiation largely attributed to increases in CO₂ levels in the atmosphere. IR absorption results in the excitation of vibrational modes of the molecule such that global warming can be considered a quantum effect. Draw all the vibrational modes of CO₂ and label which ones are IR active.

b) (5pts) Earth's atmosphere is composed of a mixture of gases: primarily nitrogen (N₂; 78.6 percent), oxygen (O₂; 20.9 percent), water vapor (H₂O; 0.5 percent), and carbon dioxide (CO₂; 0.04 percent). Which of these 4 major constituents are greenhouse gases, and give a brief explanation? Which gas is the biggest contributor to IR absorption?

2. (15pts) Two water molecules labelled A and B are separated by 2.8 Å in liquid water, i.e., O – O separation under normal density for water.

a) (5pts) Use the equation for dipole-dipole interactions, i.e. $U = 2\mu_A\mu_B/4\pi\epsilon r^3$, to calculate the binding energy due to the dipole interaction between two water molecules. The dipole moment (μ) of water is 1.82 D or 6.072×10^{-30} Cm and ϵ for liquid H₂O is $7.1 \times 10^{-10} \text{ C}^2\text{N}^{-1}\text{m}^{-2}$ (i.e., using vacuum as reference $\epsilon_{\text{H}_2\text{O}}/\epsilon_0 = 80$).

b) (5 pts) Compare the interaction or binding energy you calculate in a) to the strength of a H-bond, which is typically 5-10 kJ/mole. Contrast H-bonds with dipole-dipole interactions to explain the difference and state which force is dominating in liquid water.

c) (5pts) Discuss the number of potential H bonds per water that contributes to the forces giving water its special properties. Specifically draw the hybridized orbitals for H₂O to show the hydrogen bonding with other waters.

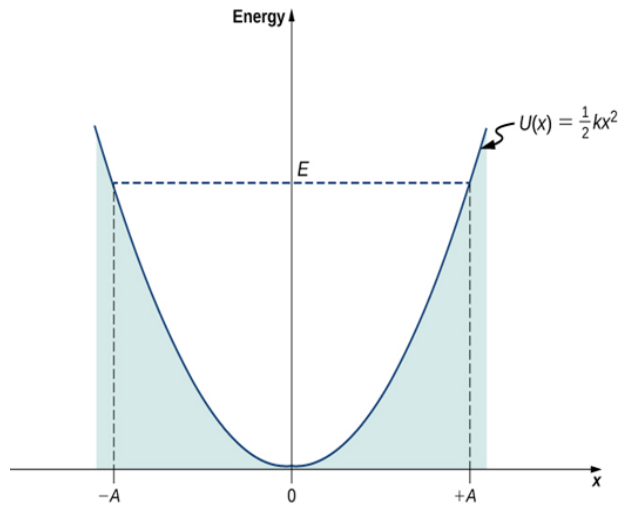
3. (10 pts) State whether the following statements are true or false.

- a) The order of binding energy for intermolecular forces goes as: ion-dipole > dipole-dipole > ion-induced dipole > dipole – induced dipole > induced dipole – induced dipole
- b) Van der Waals forces or dispersion forces are due to instantaneous fluctuations in electron density leading to induced dipole – induced dipole interactions.
- c) H-bonds only form in water.
- d) Molecules with three unpaired spins are stated to have triplet spin states.
- e) The selection rules for the absorption of light to excited electronic states requires a transition dipole moment, and $\Delta S=0$.
- f) Water has only 3 vibrational modes observed in IR spectra, which proves water is a linear molecule.
- g) Franck-Condon modes are forbidden
- h) Phosphorescence is slow or long lived, spin allowed, emission process.
- i) Fluorescence is a short lived, spin allowed, spontaneous emission process.
- j) Hydrophobic collapse refers to minimizing protein volume

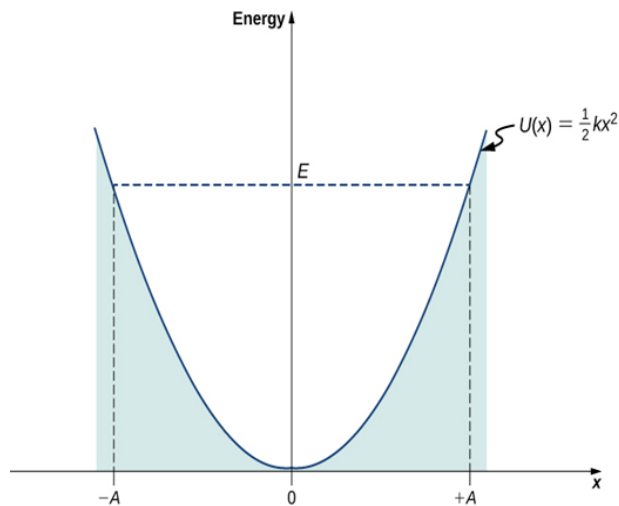
4. (20 pts total) Consider the wavefunctions for a harmonic oscillator.

a) (5 pts) Sketch below the wavefunctions, ψ , for the first 4 vibrational levels of the harmonic oscillator in the figure provided and explicitly show the energy difference between levels.

(Relevant equation $E = (n + \frac{1}{2})h\nu$; $n = 0, 1, 2, 3, \dots$).



b) (5 pts) In the figure below, now sketch the probability distributions, ψ^2 , for the wave function solutions to the harmonic oscillator. Indicate the classic turning points in the figure and discuss the probability of finding mass distribution displaced past this point where the energy is all potential energy. What is this effect called?



c) (5 pts) What are the selection rules for vibrational spectroscopy? Specifically state the mathematical form for the selection rule or describe the interaction with the light field that leads to the selection rules. Without doing the integrals, discuss how you can determine the selection rule for allowed transitions. (Hint: think symmetry in the wavefunctions of part a) and requirement for nonzero area for integration of this interaction with light.)

d) (5 pts) The nuclear probability of vibrational wavefunctions in b) are difficult to visualize as there are nodes in the internuclear separations. This expectation only manifests itself in measurement. The only current method to explore nuclear probability distributions of atomic motions is through Franck-Condon effects weighting the intensity of emission or strength of absorption of photons. Draw anharmonic potential energy surfaces, as in 4b, but for S_0 and S_1 electronic states of a molecule with these vibrational probability distributions. Show explicitly the photon transitions and explain the Franck-Condon factors or relations in terms of nuclear probability distributions that affect the probability for absorption or emission of a photon.

5. (20 pts) Levinthal's paradox is related to the enormous number of possible permutations in arrangements of atoms to form biologically active conformations or structures. The time to sufficiently sample a significant number of these permutations would be many orders of magnitude longer (longer than the age of life on earth) than the microsecond to few second times scales observed for protein folding to active conformations.

a) (2 pts) Consider a protein with 100 amino acids for which each amino acid could have 3 possible degenerate orientations about the amide linkages. What is the total number of possible permutations?

b) (2 pts) The answer to a) would seem to be an insurmountable number of configurations to sample. However, not all nuclear degrees of freedom are independent. How many possible permutations of nuclear configurations would there be if 10 amino acids formed secondary structures (e.g. helices) to give 10 independent secondary structures and each such secondary structure had 2 possible orientations relative to the other 9 similarly connected amino acids? (This speculative structure is close to the G-coupled Protein Receptor with 7 transmembrane helices and similar number of amino acids).

c) (4 pts) The number of possible configurations for the protein is enormously reduced by imposed secondary structures. Not all relevant motions are equivalent. There is always one class of motions that is rate limiting with respect to protein folding due to the exponential nature of statistical thermal sampling of different structures with energy costs or barriers (ΔE) to the rearrangement of atoms. The observation is that a particular protein folds on 1 millisecond timescale (10^{-3} seconds) at room temperature or 300 °K. For unimolecular processes, this rate, $k(\text{sec}^{-1})$, is given by:

$k = A \exp(-\Delta E/RT)$; R is the gas constant

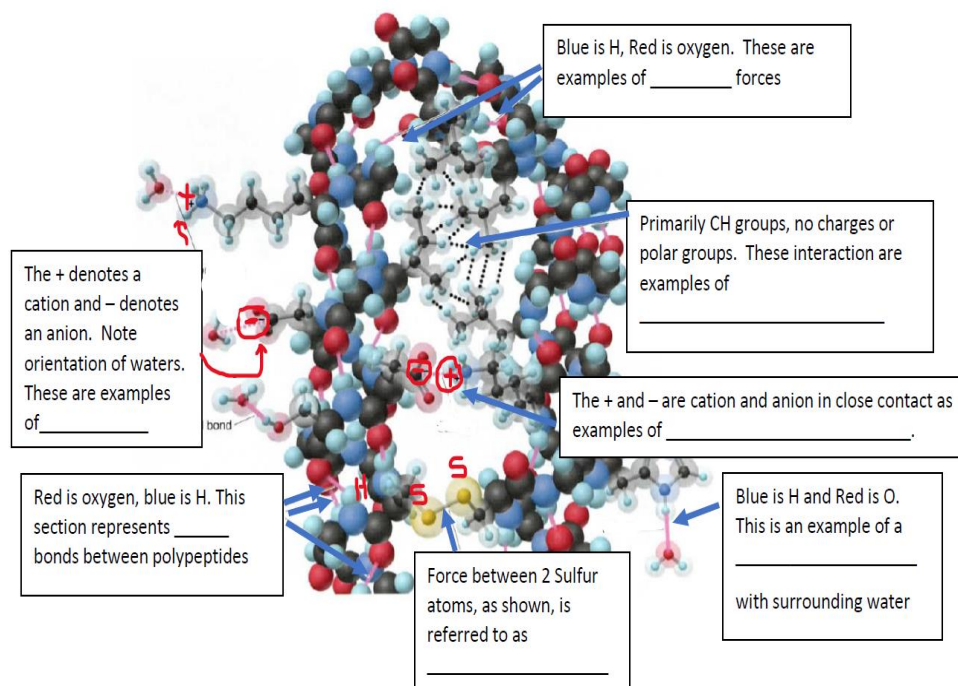
where A is the thermally driven sampling frequency. For helices comprised of 10 amino acids, this frequency is similar conceptually to molecular vibrations with a frequency $A = 10^{11} \text{ sec}^{-1}$.

For a typical folding time of 1 ms ($k = 10^3 \text{ sec}^{-1}$), calculate the maximum energy barrier that is limiting protein folding ($T=300 \text{ °K}$). Compare this energy to H bonds (approx. 10 kJ/mole) and

speculate on the number of H bonds rearranging to allow folding. You should find that very few H bonds need to be rearranged to direct protein folding.

5c) cont.

d) (7 pts) Protein folding to its active structure involves all the intramolecular as well as intermolecular forces that are quantum in origin and discussed in the course. Please list all the forces acting to guide protein folding. To help, please fill in the fields in the boxes of the figure given below (or write and use arrows to make clear which part of the protein you are referring).



e) (5 pts) Discuss the special role of water and hydrophobic core in guiding protein folding. It would be helpful to get across the basic concepts by including the funnel diagram for protein folding with different intermediate minima or conformations depicted in the potential energy landscape.

6. **Bonus question** (5pts). The Laser (Light Amplification by Stimulated Emitted Radiation) requires a population inversion, i.e., a higher population of excited states than the lower state involved in emission. It is impossible to base a laser on two level systems, i.e., just one ground state and one excited state. The net absorption or emission of light depends on the population of a given state. Also stimulated absorption (stimulated as it needs a photon) is identical in transition probability to stimulated emission by symmetry in the field interaction. For two level systems, as the population of excited states approaches 50% there is no way to go above 50% to have more excited states than ground states. Stimulated absorption = stimulated emission between 2 states = no gain in photons. Using the molecular energy level diagram below, show a scheme by which you could generate a population inversion (more excited states than lower states) to get more photons out by stimulated emission – get laser action.

There are many possible pathways. The stimulated emission leading to laser action should involve a strong, allowed, transition.

Use arrows to show the photon absorption, emission, and nonradiative relaxation pathways to create a 3 level or 4 level laser. Provide a brief description of your concept for laser action.



Equations for Quantum Mechanics Part	Comment
$E = h\nu$	Photon energy
$E_n = -\frac{m_e Z^2 e^4}{8h^2 \epsilon_0^2} \frac{1}{n^2} = -Z^2 E_R / n^2$; $E_R = 13.6 \text{ eV}$	Energy of hydrogen ($Z=1$) and Hydrogen like atom with atomic number Z
$h\nu = \Phi + \frac{1}{2} m_e v^2$	Einstein Photoemission relation
$\Delta E = E_f - E_i = h\nu$	Photon transitions between quantized levels
$\psi_n(x) = N_n e^{-\beta^2 x^2 / 2} H_n(\beta x)$, $n = 0, 1, 2, 3, \dots$	QM Harmonic Oscillator wave functions
$E = \frac{1}{2} m v^2$	Kinetic energy
$f = m_e v^2 / r$	Centripetal force
$\Delta x \Delta p \geq \frac{h}{4\pi}$	Uncertainty Principle in momentum/position
$F(\nu) = (8\pi \nu^3 / c^3) h\nu / (e^{h\nu/kT} - 1)$	Blackbody emission/spectral density
$U = -Z_{\text{eff}} k e^2 / r$ where $Z_{\text{eff}} \rightarrow Z$ as $r \rightarrow 0$ and $Z_{\text{eff}} \rightarrow 1$ as $r \rightarrow \infty$	IPA potential, extrapolation of limits in Z_{eff} from Gauss's law
$E = (n + \frac{1}{2}) h\nu$; $n = 0, 1, 2, 3, \dots$	Quantum Harmonic Oscillator Energies
$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} = \frac{2M}{\hbar^2} [U - E] \psi$	Three Dimensional Schroedinger equation for a single particle of mass M .
$\Delta E \Delta t \geq \frac{h}{4\pi}$	Uncertainty Relation for time/energy
$f = Ze^2 / 4\pi \epsilon_0 r^2 = ke^2 / r^2$; $U = -Zke^2 / r$	Coulomb force for charge Z protons and 1 e; Coulomb potential energy for Z protons and 1 electron
$\lambda = \frac{h}{mv} = \frac{h}{p}$	De Broglie relation
$\mu_{mn} = \{ \int \psi_m \mu \psi_n d\tau_e \} \{ \int \psi_m(\nu) \psi_n(\nu') d\tau_\nu \}$	Molecular Electronic Transition Probability weighted by Franck Condon Factors $\int \psi_m(\nu) \psi_n(\nu') d\tau_\nu$
$\mu_{mn} = \int \psi_n \mu \psi_m d\tau$;	Transition Probability for absorption of light. Depends on dipole moment or induced dipole moment via light interaction
$-(\hbar^2 / 8\pi^2 m) d^2/dx^2 (\psi) = E\psi$; $U(x) = 0$; $0 < x < L$; $U(x) = \infty$ for $x < 0$ or $x > L$	Schroedinger eq. for 1D Box
$\psi = (2/L)^{1/2} \sin(n\pi/L)x$; $E = n^2 \hbar^2 / 8mL^2$	Solutions to 1D Particle in the Box
$U = -Zke^2 / r$; $U = +ke^2 / r$	Attractive potential of nucleus; repulsive e-e
$\Delta E = m \mu_B B$; $m = 0, 1, \dots, \pm l$	Zeeman (mag. field B) effect re: Orbital angular momentum
$\Delta E = \pm \frac{e\hbar}{2m_e} B = \pm \mu_B B$	Zeeman effect (B) re: spin magnetic moment
$L = \sqrt{l(l+1)}\hbar$; $S = \sqrt{s(s+1)}\hbar$	Quantized orbital angular; spin momentum $l = 0, 1, 2, 3, \dots$; $m_s = \pm \frac{1}{2}$; $L_z = m \hbar$ and $S_z = m_s \hbar$

Named Constants

Atomic mass unit:	$1\text{u} = \frac{1}{12}m(^{12}\text{C atom})$ $= 1.66 \times 10^{-27} \text{ kg}$ $= 931.5 \text{ MeV}/c^2$
Avogadro's constant:	$N_A = 6.02 \times 10^{23} \text{ particles/mole}$
Bohr magneton:	$\mu_B = e\hbar/(2m_e)$ $= 5.79 \times 10^{-5} \text{ eV/T}$ $= 9.27 \times 10^{-24} \text{ J/T (or } \text{A} \cdot \text{m}^2)$
Bohr radius:	$a_B = \hbar^2/(ke^2m_e)$ $= 5.29 \times 10^{-11} \text{ m}$
Boltzmann's constant:	$k_B = 8.62 \times 10^{-5} \text{ eV/K}$ $= 1.38 \times 10^{-23} \text{ J/K}$
Coulomb force constant:	$k = 1/(4\pi\epsilon_0) = \mu_0 c^2/(4\pi)$ $= 8.99 \times 10^9 \text{ N} \cdot \text{m}^2/\text{C}^2$
Electron Compton wavelength:	$\lambda_c = h/(m_e c)$ $= 2.43 \times 10^{-12} \text{ m}$
Electron volt:	$1 \text{ eV} = 1.60 \times 10^{-19} \text{ J}$
Elementary charge:	$e = 1.60 \times 10^{-19} \text{ C}$
Fine-structure constant:	$\alpha = ke^2/(\hbar c)$ $= 7.30 \times 10^{-3} \approx 1/137$
Gas constant:	$R = 8.31 \text{ J/(mole} \cdot \text{K)}$ $= 0.0821 \text{ liter} \cdot \text{atm/(mole} \cdot \text{K)}$
Gravitational constant:	$G = 6.67 \times 10^{-11} \text{ N} \cdot \text{m}^2/\text{kg}^2$
Mass of electron:	$m_e = 5.49 \times 10^{-4} \text{ u}$ $= 9.11 \times 10^{-31} \text{ kg}$ $= 0.511 \text{ MeV}/c^2$
Mass of proton:	$m_p = 1.007 \text{ u}$ $= 1.673 \times 10^{-27} \text{ kg}$ $= 938.3 \text{ MeV}/c^2$
Mass of neutron:	$m_n = 1.009 \text{ u}$ $= 1.675 \times 10^{-27} \text{ kg}$ $= 939.6 \text{ MeV}/c^2$
Nuclear magneton:	$\mu_N = e\hbar/(2m_p)$ $= 3.15 \times 10^{-8} \text{ eV/T}$ $= 5.05 \times 10^{-27} \text{ J/T}$
Permeability of space:	$\mu_0 = 4\pi \times 10^{-7} \text{ N/A}^2$ $= 1.26 \times 10^{-6} \text{ N/A}^2$
Permittivity of space:	$\epsilon_0 = 1/(\mu_0 c^2)$ $= 8.85 \times 10^{-12} \text{ C}^2/(\text{N} \cdot \text{m}^2)$

Planck's constants:	$h = 6.63 \times 10^{-34} \text{ J} \cdot \text{s}$ $= 4.14 \times 10^{-15} \text{ eV} \cdot \text{s}$ $\hbar = h/2\pi$ $= 1.05 \times 10^{-34} \text{ J} \cdot \text{s}$ $= 6.58 \times 10^{-16} \text{ eV} \cdot \text{s}$
Rydberg constant:	$R = m_e k^2 e^4 / (4\pi\hbar^3)$ $= 1.10 \times 10^{-2} \text{ nm}^{-1}$
Rydberg energy:	$E_R = \hbar c R = m_e k^2 e^4 / (2\hbar^2)$ $= 13.6 \text{ eV}$
Speed of light:	$c = 3.00 \times 10^8 \text{ m/s}$

Useful Combinations

$hc = 1240 \text{ eV} \cdot \text{nm} = 1240 \text{ MeV} \cdot \text{fm}$
$\hbar c = 197 \text{ eV} \cdot \text{nm} = 197 \text{ MeV} \cdot \text{fm}$
$ke^2 = 1.44 \text{ eV} \cdot \text{nm} = 1.44 \text{ MeV} \cdot \text{fm}$
$N_A \times (1 \text{ u}) = 1 \text{ gram}$
$k_B T = 0.0252 \text{ eV}$ at room temperature (293 K)

Conversion Factors

Area:	$1 \text{ barn} = 10^{-28} \text{ m}^2$
Energy:	$1 \text{ cal} = 4.184 \text{ J}$ $1 \text{ eV} = 1.60 \times 10^{-19} \text{ J}$
Length:	$1 \text{ \AA} = 1 \text{ angstrom}$ $= 10^{-10} \text{ m}$ $1 \text{ ft} = 30.48 \text{ cm}$ $1 \text{ in} = 2.54 \text{ cm}$ $1 \text{ mi} = 1609 \text{ m}$
Mass:	$1 \text{ lb(mass)} = 0.454 \text{ kg}$ $1 \text{ MeV}/c^2 = 1.074 \times 10^{-3} \text{ u}$ $= 1.783 \times 10^{-30} \text{ kg}$ $1 \text{ u} = \frac{1}{12} m(^{12}\text{C atom})$ $= 931.5 \text{ MeV}/c^2$ $= 1.66 \times 10^{-27} \text{ kg}$
Momentum:	$1 \text{ MeV}/c = 5.34 \times 10^{-22} \text{ kg} \cdot \text{m/s}$