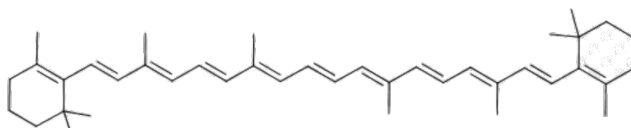


Lecture 7

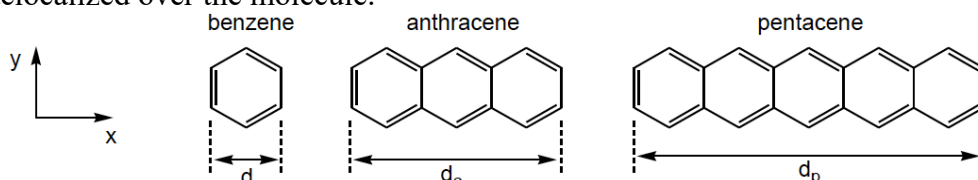
Question 1. Free particle confined in a 1D, 2D, or 3D box.

(1) Particle in a 1D box. When β -carotene (see the figure below) is oxidized in vivo, it breaks in half and forms two molecules of retinal (vitamin A), which is a precursor to the pigment in the retina responsible for vision. The conjugated system of retinal consists of 11 C atoms and one O atom. In the ground state of retinal, each level up to $n = 6$ is occupied by two electrons. Assuming an average internuclear distance of 140 pm, calculate the frequency of the radiation required to produce a transition between $n = 6$ (ground state) and $n = 7$ (the first excited state).

How does the absorption spectrum of a linear polyene shift as the number of conjugated atoms increase?



(2) Particle in a 2D box. Polycyclic aromatic hydrocarbons (PAHs) are atmospheric pollutants, components of organic light-emitting diodes and components of the interstellar medium. This problem deals with so-called linear PAHs, i.e., those being just one benzene ring wide whereas the length is varied. Specific examples are benzene, anthracene and pentacene, whose structures are shown below. Their physical and chemical properties depend on the extent to which the π -electron cloud is delocalized over the molecule.



(2a) The distance across the benzene ring is $d = 240$ pm. Use this information to estimate the distances along the horizontal axis for anthracene and pentacene, d_a and d_p , respectively.

(2b) Assume for simplicity that the π electrons of benzene can be modeled as being confined to a square. Within this model, the conjugated π electrons of longer PAHs may be considered as free particles in a 2D rectangular box in the plane. Note that for a particle in a 2D box, each energy level **may** consist of degenerate energy states. (If the two sides are unequal, then do you expect degeneracy?) Show the π -electron orbital energy diagram (with the values of the two quantum numbers for each state) qualitatively and calculate the energy gap ΔE (in Joules) between the highest occupied and lowest unoccupied energy levels (i.e., the LUMO-HOMO gap) for benzene, anthracene and pentacene.

(2c) Rank benzene, anthracene, and pentacene in order of increasing π -electron reactivity.

(2d) Rank benzene, anthracene, and pentacene in order of the wavelengths of absorption peaks in electronic absorption spectra qualitatively.

(3) Particle in a 3D box. Quantum mechanical effects need to be invoked in the description of the electronic properties of a metallic nanocrystal, here modeled as a 3D box.

(3a) Set up the eigenvalue equation for a particle of mass m in a 3D rectangular box with sides L_x , L_y , and L_z . Using separation of variables, solve for eigenfunctions and total energy.

(3b) Specialize the result from (3a) to an electron moving in a cubic box of side L and draw an energy diagram qualitatively (in the unit of $h^2/8mL^2$) showing the first 15 energy levels (with the values of quantum numbers for each state).

(3c) Compare the energy level diagram from (3b) with the energy level diagram for an electron in a 1D box of the same length L . Are the energy levels more or less sparsely distributed in the cubic box than in the 1D box? This practice gives you a feeling about the motion in 3D vs. 1D.

Lecture 8

Question 2. In this question, we will prove a very handy recipe for determining the relation between the expectation values of the kinetic energy and potential energy of stationary states without solving Schrodinger equation. From this recipe, you can analyze the contributions from the kinetic and potential energies to the total energy – the simplest energy-decomposition analysis.

(1) Let us start with a single particle in 1D space. Please show that the commutator $[\hat{H}, x\hat{p}_x]$ is equal to $i\hbar x \cdot (\partial V/\partial x) - i\hbar\hat{p}_x^2/m$

Hint: Use the algebraic properties of commutators to simplify your derivation. See, e.g., Problem Set 2, Q9, (2.3).

(2) Define $\hat{G} = \vec{r} \cdot \vec{p}$ for a particle in 3D, where the position vector $\vec{r} = (x, y, z)$ and the momentum vector $\vec{p} = (\hat{p}_x, \hat{p}_y, \hat{p}_z)$. Please generalize what you have in (1) to 3D:

$$[\hat{H}, \hat{G}] = i\hbar\vec{r} \cdot \nabla V - 2i\hbar\hat{T}$$

where \hat{T} is the kinetic energy operator, and ∇ the gradient operator in 3D.

(3) Show that for any stationary states $\Psi(\vec{r}, t) = \psi(\vec{r})e^{-iEt/\hbar}$, in which $\psi(\vec{r})$ is the eigenstate of \hat{H} with eigenvalue E , the expectation value $\langle [\hat{H}, \hat{G}] \rangle = 0$.

(4) Put (2) and (3) together, and show the relation between kinetic energy and potential energy follows $2 \cdot \langle \hat{T} \rangle = \langle \vec{r} \cdot \nabla V \rangle$ for any stationary states.

(5) Application 1: A chemical bond can be modeled by a 1D harmonic oscillator. The potential function $V(x) = kx^2/2$, where k is a constant (the so-called “force constant” of a bond), and x is the displacement. Please show that the kinetic energy $\langle \hat{T} \rangle$ and potential energy $\langle V \rangle$ contribute equally to the total energy of a 1D harmonic oscillator.

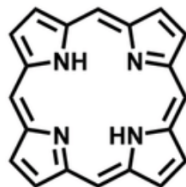
(6) Application 2: An electron moving in an H atom is under a central potential due to the attraction between the nucleus and the electron (we view the nuclear charge $Z = 1$ and set $e = 1$ unit below)

$$V(r) = -\frac{1}{4\pi\epsilon_0 r}$$

where r is the separation between the electron and the nucleus. We know that the ground-state energy of an electron in an H atom is 13.6 eV (which is the ionization energy of an H atom). What are the values of the kinetic energy $\langle \hat{T} \rangle$ and potential energy $\langle V \rangle$ at the ground state?

Lecture 9

Question 3.¹ The particle on a ring (2D) is a useful model for the motion of electrons around the porphyrin ring, the conjugated macrocycle that forms the structural basis of the haem group and the chlorophylls.



We may treat the group as a circular ring of radius 440 pm, with 22 electrons in the conjugated system moving along the perimeter of the ring. In the ground state of the molecule, each state is occupied by two electrons.

(1) Calculate the energy and angular momentum of an electron in the highest occupied orbital.

(2) Calculate the wavelength (in nm) of radiation that can induce a transition between the highest occupied and lowest unoccupied levels. Does this molecule have color to your eyes?

¹ Adapted from Atkins, the 9th edition, Chapter 8 – Problem 8.35.

Question 4.² Read Atkins (the 9th edition), section 8.7 “Rotation in three dimensions: the particle on a sphere”, subsections (a) and (b). Check McQuarrie, Chapter 8, section 8.4, if you need more math background information about spherical coordinates.

Particle **inside** a sphere with radius R is a reasonable starting point for the discussion of the electronic properties of spherical metal nanoparticles. Here, we justify the expression for the energy levels with the quantum number $l = 0$.

(1) (Optional – For bonus credits) The Hamiltonian for a free particle inside a sphere of radius R

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2$$

Show that the time-independent Schrodinger equation is separable into radial and angular components. That is, begin by writing $\psi(r, \theta, \phi) = u(r)Y(\theta, \phi)$, where $u(r)$ depends only on the distance of the particle away from the center of the sphere, and $Y(\theta, \phi)$ is a spheric harmonic function. Then show that the Schrodinger equation can be separated into two equations, one for u , the radial equation, and the other for Y , the angular equation:

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2 u(r)}{\partial r^2} + \frac{2}{r}\frac{\partial u(r)}{\partial r}\right) + \frac{l(l+1)\hbar^2}{2mr^2} \cdot u(r) = Eu(r)$$

$$\hat{\Lambda}^2 Y(\theta, \phi) = -l(l+1)Y(\theta, \phi)$$

(Please refer to section 8.7 (a) and (b) for the definition of the Legendrian operator $\hat{\Lambda}^2$.)

(2) Consider the case $l = 0$. Show by differentiation that the solution of the radial equation has the form

$$u(r) = (2\pi R)^{-1/2} \cdot \frac{\sin(n\pi r/R)}{r}$$

(3) Now go on to show that the allowed energies are given by

$$E_n = \frac{n^2 h^2}{8mR^2}$$

for $l = 0$ (the so-called “s state”).

Lecture 10

Question 5. Chemists use electrochemistry and electrocatalysis to synthesize new molecules with sustainable energy – electricity. An external electric field can certainly change the reactivity of a molecule or an ion.

A charged diatomic molecule (ion) in an external electric field can be modeled as (within the

1D harmonic approximation): $\hat{H} = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2 - q\epsilon x$, in which m is the reduced mass, ω is

the harmonic frequency, x is the displacement coordinate, q is the charge, and ϵ is the strength of the external uniform field. Solve for the exact energy levels.

Hint: Try to rewrite the Hamiltonian in terms of a new displacement coordinate such that the Hamiltonian is in the same form as a 1D harmonic oscillator.

Question 6. 1D Harmonic oscillator:

(1) Prove that the rising operator $(\hat{a}^+)^2$ increases the energy of the eigenstate $|n\rangle$ by $2\hbar\omega$.

(2) Evaluate $\langle n|x|n\rangle$, $\langle n|x^2|n\rangle$, $\langle n|\hat{p}_x|n\rangle$, $\langle n|\hat{p}_x^2|n\rangle$ and $\Delta x\Delta p_x$, by using the algebraic properties of the raising and lowering operators.

² Adapted from Atkins, the 9th edition, Chapter 8 – Problem 8.38.

Question 7. Isotope effect modeled by a 1D harmonic oscillator. The vibration of a diatomic molecule AB with the reduced mass $\mu = m_A m_B / (m_A + m_B)$ around its equilibrium geometry can be modeled by

$$\hat{H} = \frac{\hat{p}_x^2}{2\mu} + \frac{1}{2}\mu\omega^2 x^2$$

where ω is the vibrational angular frequency, and x the relative displacement.

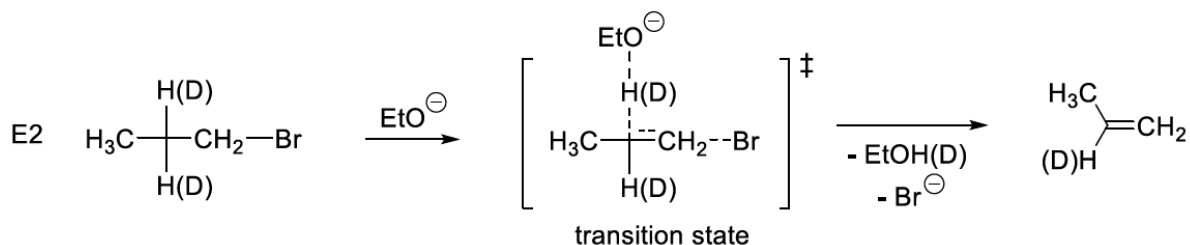
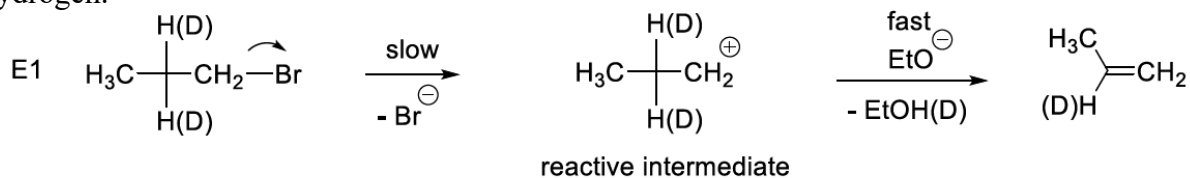
Various isotopes of a given atom obey the same chemical principles, but their different masses cause different behaviors in a dynamic sense. The kinetic isotope effect refers to a phenomenon wherein isotopically substituted molecules react at different rates. It was postulated in 1933 by Eyring and Polanyi and since then kinetic isotope effects have provided detailed information about mechanisms of many organic and biochemical reactions.

(1) Isotopic substitution does not change the potential-energy surface of a molecule. Therefore, the force constant ($\mu\omega^2$) remains unaffected. Given the vibrational wavenumbers of $^1\text{H}^A\text{X}$ (2439.0 cm^{-1}) and $^2\text{D}^{A+2}\text{X}$ (1734.8 cm^{-1}), determine the unknown element X.

Note: ^1H and ^2D are the isotopes of hydrogen; ^AX and ^{A+2}X are the isotopes of the unknown element X with atomic mass A and $A+2$, respectively.

(2) Zero-point vibrational energy is the key contributor to the kinetic isotope effect. If we assume that the bond is fully broken at the transition state and only the ground vibrational state is populated, the difference in activation energies has the same absolute value as the difference in zero-point vibrational energies. The wave numbers of the C–H and C–D stretches are 2900 cm^{-1} and 2100 cm^{-1} , respectively. Calculate the ratio of the rate constants $k(\text{C–H})/k(\text{C–D})$ for the cleavage of the C–H/D bond at 300 K, taking into account only the difference in zero-point vibrational energies.

(3) Kinetic isotope effects provide insight into the rate-determining step of a reaction mechanism. The ratio of $k_{\text{H}}/k_{\text{D}}$ for the formation of propene from 1-bromopropane and 1-bromo-2,2-dideuteriopropene in basic solution is 6.5. Does the reaction proceed by E1 or E2 mechanism? E1 takes place in two steps: formation of the carbocation intermediate followed by loss of H^+ . E2 occurs in a single step involving removal of the halide at the same time as the neighboring hydrogen.



(4) Let us consider the formation of the corresponding alkene from 2-bromo-3,3-dideuterio-2-methylbutane and its light-hydrogen analog upon heating in ethanol. How significant would the kinetic isotope effect be in this case?

Lecture 11

Question 8.³ Many biological electron-transfer reactions, such as those associated with biological energy conversion, may be visualized as arising from electron tunneling between protein-bound co-factors, such as cytochromes, quinones, flavins, and chlorophylls. This tunneling occurs over distances that are often greater than 1.0 nm, with sections of protein separating electron donor from the acceptor. For a specific combination of donor and acceptor, the rate of electron tunneling is proportional to the transmission probability, with the absolute value of the electron's wave vector being 7 nm^{-1} in the tunneling region. Estimate that by what factor does the rate of electron tunneling between two co-factors increase as the distance between them changes from 2.0 nm to 1.0 nm?

Question 9. Consider a particle with mass m in a 1D finite well, in which the potential $V(x)$:

$$V(x) = \begin{cases} 0 & (|x| > \frac{L}{2}) \\ -V_0 & (-\frac{L}{2} \leq x \leq \frac{L}{2}) \end{cases}$$

where V_0 is a positive constant, and L is the length of the box.

(1) For the bound states (i.e., $E < 0$, in which the particle stays inside the trap), show that the energy levels satisfy $\alpha = \beta \tan(\beta L / 2)$ (for the *even* $\psi(x)$ in $-\frac{L}{2} \leq x \leq \frac{L}{2}$) or $\alpha = -\beta \cot(\beta L / 2)$

(for the *odd* $\psi(x)$ in $-\frac{L}{2} \leq x \leq \frac{L}{2}$), where $\alpha = \frac{\sqrt{-2mE}}{\hbar}$ and $\beta = \frac{\sqrt{2m(E+V_0)}}{\hbar}$.

Hint: In 1D, if the potential function is an even function, then the wavefunctions of the eigenstates must be either odd or even.

(2) (Optional – For bonus credits) Are you guaranteed to have bound states (i.e., $E < 0$) inside the finite well for any positive value of V_0 ($V_0 > 0$), i.e., a trap with some finite depth?

(3) For the scattering states (i.e., a particle with the energy $E > 0$ is shooting from the left side of the potential), show that in general, the transmission probability $T \leq 1$.

$T < 1$ is called the *non-classical reflection*. Imagine you throw a golf ball *above* your desk, and the ball hits your face! What does the energy E need to be (the so-called *resonance* energy) in order to let the well become perfectly transparent, i.e., $T = 1$?

Lecture 12

Question 10.⁴ H atom: Eigenfunctions and eigenvalues. Explicit expressions for hydrogenic orbitals are given in Table 9.1 and 8.2 (Atkins, the 9th ed.).

(1) What is the most probable point (not radius) at which a $2p$ electron will be found in the hydrogen atom?

(2) Verify both that the $3p_x$ orbital is normalized and that $3p_x$ and $3d_{xy}$ are mutually orthogonal.

(3) Determine the positions of both the radial nodes and nodal planes of the $3s$, $3p_x$, and $3d_{xy}$ orbitals.

(4) Draw a graph of the radial distribution function for $3s$, $3p_x$, and $3d_{xy}$ orbitals.

(5) Determine whether the p_x and p_y orbitals are eigenfunctions of \hat{L}_z . If not, does a linear combination exist that is an eigenfunction of \hat{L}_z ?

³ Adapted from Atkins, the 9th edition, Chapter 8 – Problem 8.32.

⁴ Adapted from Atkins, the 9th edition, Chapter 9 – Problems.

(6) (Optional – For bonus credits) The “size” of an atom is sometimes considered to be measured by the radius of a sphere that contains 90 per cent of the charge density of the electrons in the outermost occupied orbital. Calculate the “size” of a hydrogen atom in its ground state according to this definition.

Go on to explore how the “size” varies as the definition is changed to other percentages, and plot your conclusion.

(7) Some atomic properties depend on the average value of $1/r$ rather than the average value of r itself. Compute the expectation value of $1/r$ for **(a)** 1s orbital, **(b)** 2s orbital, and **(c)** 2p orbital.

Lecture 13

Question 11. Work with angular momentum operator in spherical coordinates. Check McQuarrie, Chapter 8, section 8.4, if you need more math background information about spherical coordinates.

(1) Start from the definition of angular momentum operator $\hat{L} = -i\hbar\hat{r} \times \nabla$ with the gradient operator in spherical coordinates $\nabla = e_r \frac{\partial}{\partial r} + e_\theta \frac{1}{r} \frac{\partial}{\partial \theta} + e_\phi \frac{1}{r \sin \theta} \frac{\partial}{\partial \phi}$, prove:

$$\hat{L}^2 = -\hbar^2 \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right]$$

(2) Validate $[\hat{L}_x, \hat{L}_y] = i\hbar\hat{L}_z$ with the spherical-coordinate representation.

(3) Eigenfunction and eigenvalue.

(a) Validate that the function $f(\theta, \phi) = \sin^3 \theta \cos(3\phi)$ is an eigenfunction of \hat{L}^2 . What is the corresponding eigenvalue?

(b) Is this function also an eigenfunction of \hat{L}_z ?

(c) Normalize $f(\theta, \phi)$.

Question 12. When describing the quantum states of multielectron atoms, we use the term symbol. (We will cover term symbol in the later lecture.) What one does is to consider the “addition” (a better word would be “coupling”) of various angular momenta from different electrons. We will need to use the following bra-kets (or matrix elements):

$$(a) \langle l', m' | \hat{L}_z | l, m \rangle = m\hbar \delta_{ll'} \delta_{mm'} \quad \langle l', m' | \hat{L}^2 | l, m \rangle = l(l+1)\hbar^2 \delta_{ll'} \delta_{mm'}$$

$$(b) \langle l', m' | \hat{L}_+ | l, m \rangle = \hbar \sqrt{l(l+1) - m(m+1)} \delta_{ll'} \delta_{m', m+1}$$

$$\langle l', m' | \hat{L}_- | l, m \rangle = \hbar \sqrt{l(l+1) - m(m-1)} \delta_{ll'} \delta_{m', m-1}$$

$$(c) \langle l', m' | \hat{L}_x | l, m \rangle = \frac{\hbar}{2} \left[\sqrt{l(l+1) - m(m+1)} \delta_{ll'} \delta_{m', m+1} + \sqrt{l(l+1) - m(m-1)} \delta_{ll'} \delta_{m', m-1} \right]$$

$$\langle l', m' | \hat{L}_y | l, m \rangle = -\frac{i\hbar}{2} \left[\sqrt{l(l+1) - m(m+1)} \delta_{ll'} \delta_{m', m+1} - \sqrt{l(l+1) - m(m-1)} \delta_{ll'} \delta_{m', m-1} \right]$$

in which the Dirac notation for a spherical harmonic function $Y_{l,m}(\theta, \phi)$ with quantum numbers l and m is $|l, m\rangle$, and $\delta_{ll'}$, $\delta_{mm'}$, etc. are the Kronecker deltas for orthonormal relations.

Use the properties of angular momentum operators and the associated eigenequations, prove the above bra-kets (a), (b), and (c).