



UNIVERSITY OF  
NOTRE DAME

Physical Chemistry for Chemical Engineers  
(CHE 30324)

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*AS A MEMBER OF THE NOTRE DAME COMMUNITY, I WILL NOT  
PARTICIPATE IN OR TOLERATE ACADEMIC DISHONESTY*

SIGNED: \_\_\_\_\_

WRITE YOUR SOLUTIONS IN THE SPACE INDICATED, MAKING SURE  
YOUR APPROACH IS CLEAR. USE THE BACK OF THE TABLES PAGES  
IF YOU NEED ADDITIONAL SCRATCH SPACE. WRITE YOUR NETID IN  
THE UPPER RIGHT OF EACH PAGE.

**1 (80 pts) Put a Dot On It**

"Quantum dots" are tiny particles of silicon or similar elements small enough to exhibit discrete, quantum mechanical electronic states. The wavefunctions and energy states of an electron in a quantum dot can be approximated by a particle in a three-dimensional cubic box of edge length  $L$ .

- 1.1 (10 pts) Write down the Schrödinger equation for this quantum dot model. Include as much detail as possible, including the physical meaning of each term in your equation and the boundary conditions on the solutions.

$$V = \begin{cases} 0 & 0 < x, y, z < L \\ \infty & \text{otherwise} \end{cases}$$

$$-\frac{\hbar^2}{2m_e} \nabla^2 \psi(x, y, z) = E \psi(x, y, z)$$

$K E$   $\text{Total } E$

$$\psi(x, y, 0) = \psi(x, y, L) = 0$$

$$\psi(x, 0, z) = \psi(x, L, z) = 0$$

$$\psi(0, y, z) = \psi(L, y, z) = 0$$

- 1.2 (3 pts) In one phrase, what strategy would work to solve this partial differential equation?

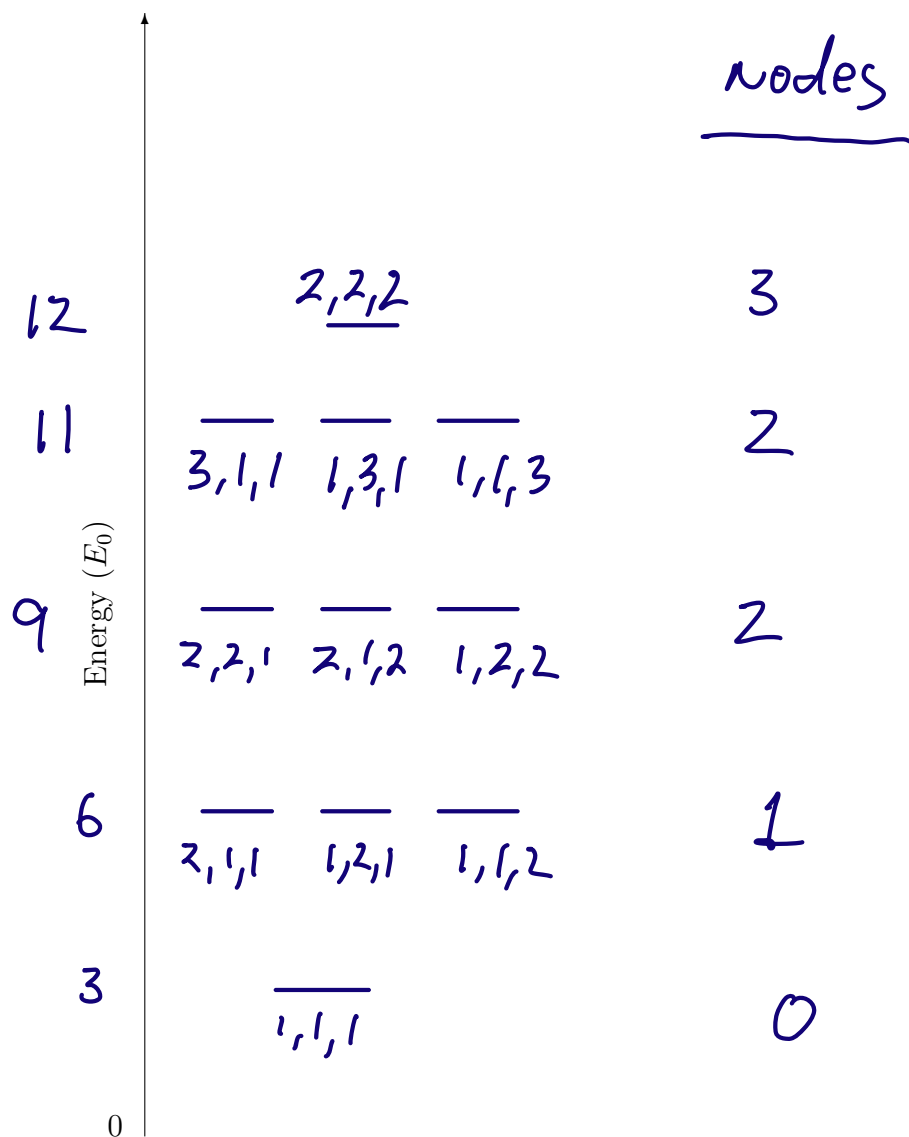
separation of variables

- 1.3 (5 pts) Do you expect the system to have a zero point energy? Very briefly, why?

Yes, because the electron is confined, we expect a ZPE. A consequence of uncertainty principle.

Upon solving, you find the energy states of the quantum dot are given by  $E = E_0(n_x^2 + n_y^2 + n_z^2)$ , where  $E_0 = 0.05 \text{ eV}$  for a value of  $L$  of interest and each quantum number can be any whole number greater than 0.

- 1.4 (15 pts) Fill in the energy level diagram below, including all states with energy less than  $13E_0$ . Indicate the corresponding quantum numbers and the degeneracy of each energy level.



- 1.5 (5 pts) Use your knowledge of wavefunctions in general and particle-in-a-box wavefunctions in particular, indicate on your plot above the number of *nodes* in the wavefunction of each energy state.

- 1.6 (6 pts) Write down the normalized wavefunction for the lowest energy state on your graph.

$$\psi(x, y, z) = \left(\frac{2}{L}\right)^{3/2} \sin \frac{\pi x}{L} \sin \frac{\pi y}{L} \sin \frac{\pi z}{L}$$

- 1.7 (4 pts) Suppose you were to observe the location of an electron in the wavefunction you just wrote. What is/are the most probable places you would find it? Provide coordinates.

the center

$$\left(\frac{L}{2}, \frac{L}{2}, \frac{L}{2}\right)$$

- 1.8 (6 pts) Suppose a quantum dot is at thermal equilibrium at 290 K. Calculate the relative likelihood that the electron is in the second relative to the first energy level. Note  $k_B T = 0.025$  eV at this temperature.

$$\begin{aligned} \frac{P(6E_0)}{P(3E_0)} &= \frac{3e^{-6E_0/kT}}{e^{-3E_0/kT}} \\ &= 3e^{-3(0.05)/0.025} \\ &= 3e^{-6} \quad \text{very small} \end{aligned}$$

- 1.9 (15 pts) You measure the spectrum of this 290 K, one-electron quantum dot using a spectrometer with a spectral range of 2000 to 8000 nm. In the table below, describe the spectrum you see. Indicate wavelengths of each absorption feature and the initial and final states that contribute to that feature. The specific selection rule is that at least one of  $\Delta n_x$ ,  $\Delta n_y$ ,  $\Delta n_z$  must be odd.

	Wavelength (nm)	Initial state ( $n_x, n_y, n_z$ )	Final state ( $n_x, n_y, n_z$ )
$\Delta E = 3E_0$	$\frac{\lambda_0}{3} = 8267$	111 outside range	112, 121, 2,1,1
$\Delta E = 6E_0$	$\frac{\lambda_0}{6} = 4133$	111	221, 212, 122


$$\lambda_0 = \frac{hc}{E_0} = \frac{1240 \text{ eV nm}}{0.05 \text{ eV}} = 2.48 \times 10^4 \text{ nm}$$

- 1.10 (5 pts) For practical reasons, you would really like a quantum dot that absorbs at 500 nm, in the visible. Suggest a strategy for adjusting the spectrum of a quantum dot.

change the size of the particle

- 1.11 (6 pts) Quantum dots are of interest because they emit light. Briefly, what is *spontaneous emission* and how might a quantum dot spontaneously emit? You may illustrate with a picture if you like.

relax from an excited state and emit a photon



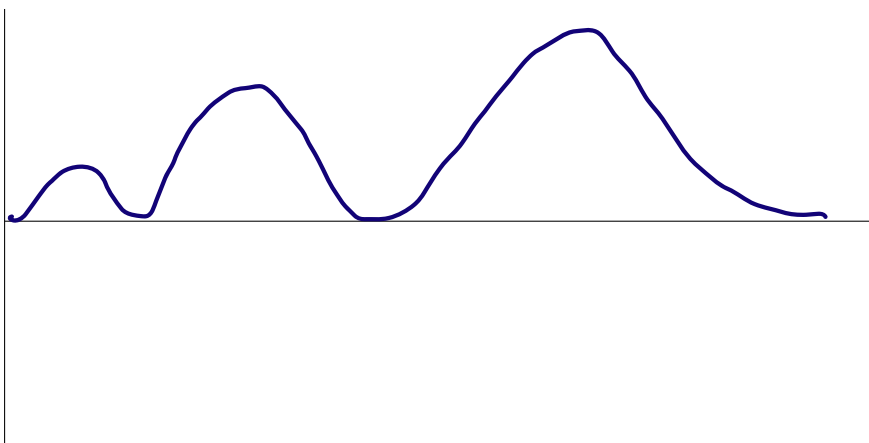
**2 Last hurrah (20 pts)**

The hydrogen atom is our last exactly solvable quantum mechanical problem. Consider an excited hydrogen atom with an electron in the 3p energy level.

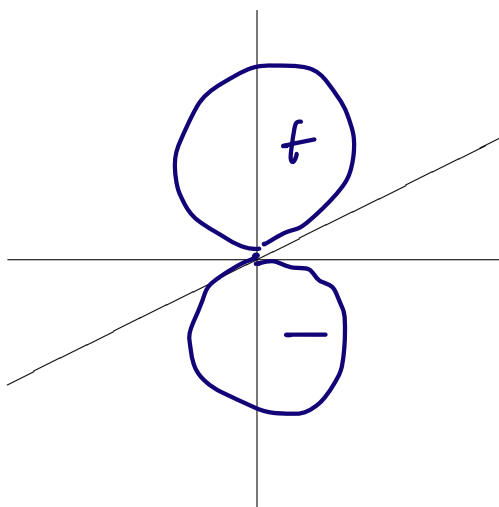
2.1 (4 pts) Provide **one possible set** of quantum numbers for this electronic state.

3 1 0  $\frac{1}{2}$

2.2 (5 pts) Sketch the radial probability function  $P_{31}(r)$  of this  $p$  electron.



2.3 (5 pts) Sketch a possible 3p electron angular wavefunction  $Y(\theta, \phi)$ . Be sure to indicate any nodes and to indicate the sign of the wavefunction as appropriate.



- 2.4 (6 pts) The 3p hydrogen is observed to spontaneously emit light. Provide a complete set of quantum numbers and corresponding energy of the emitted photon (in units of  $E_H$ ) for each of the possible final states.

$$E_n = -\frac{E_H}{2} \cdot \frac{1}{n^2}$$

$$\begin{aligned} 3p \rightarrow 2s \quad \Delta E &= -\frac{E_H}{2} \left( \frac{1}{3^2} - \frac{1}{2^2} \right) \\ &= \frac{5E_H}{2 \cdot 36} \end{aligned}$$

$$\begin{aligned} 3p \rightarrow 1s \quad \Delta E &= -\frac{E_H}{2} \left( \frac{1}{3^2} - \frac{1}{1^2} \right) \\ &= \frac{8E_H}{18} \end{aligned}$$

## 3 Tables

**Table 1:** Key units in Physical Chemistry

$N_{\text{Av}}$ :	$6.02214 \times 10^{23}$	$\text{mol}^{-1}$		
1 amu:	$1.6605 \times 10^{-27}$	kg		
$k_{\text{B}}$ :	$1.38065 \times 10^{-23}$	$\text{J K}^{-1}$	$8.61734 \times 10^{-5}$	$\text{eV K}^{-1}$
$R$ :	8.314472	$\text{J K}^{-1} \text{mol}^{-1}$	$8.2057 \times 10^{-2}$	$\text{l atm mol}^{-1} \text{K}^{-1}$
$\sigma_{\text{SB}}$ :	$5.6704 \times 10^{-8}$	$\text{J s}^{-1} \text{m}^{-2} \text{K}^{-4}$		
$c$ :	$2.99792458 \times 10^8$	$\text{m s}^{-1}$		
$h$ :	$6.62607 \times 10^{-34}$	$\text{J s}$	$4.13566 \times 10^{-15}$	$\text{eV s}$
$\hbar$ :	$1.05457 \times 10^{-34}$	$\text{J s}$	$6.58212 \times 10^{-16}$	$\text{eV s}$
$hc$ :	1239.8	$\text{eV nm}$		
$e$ :	$1.60218 \times 10^{-19}$	C		
$m_e$ :	$9.10938215 \times 10^{-31}$	kg	1: 0.5109989	$\text{MeV c}^{-2}$
$\epsilon_0$ :	$8.85419 \times 10^{-12}$	$\text{C}^2 \text{J}^{-1} \text{m}^{-1}$	$5.52635 \times 10^{-3}$	$e^2 \text{\AA}^{-1} \text{eV}^{-1}$
$e^2/4\pi\epsilon_0$ :	$2.30708 \times 10^{-28}$	$\text{J m}$	14.39964	$\text{eV \AA}$
$a_0$ :	$0.529177 \times 10^{-10}$	m	0.529177	$\text{\AA}$
$E_{\text{H}}$ :	1	Ha	27.212	eV

**Table 2:** Classical waves

The wave equation	$\frac{\partial^2 \Psi(x, t)}{\partial x^2} = \frac{1}{v^2} \frac{\partial^2 \Psi(x, t)}{\partial t^2}$
General solution	$\Psi(x, t) = A \sin(kx - \omega t)$
Wavelength (distance)	$\lambda = 2\pi/k$
Frequency (/time)	$\nu = 2\pi/\omega$
Speed	$v = \lambda\nu$
Amplitude (distance)	$A$
Energy	$E \propto A^2$
Standing wave	$\Psi(x, t) = A \sin(kx) \cos(\omega t), \quad k = n\pi/a$



**Table 3:** The new physics

Stefan-Boltzmann Law	$\int I(\lambda, T) d\lambda = \sigma_{\text{SB}} T^4$
Wien's Law	$\lambda_{\text{max}} T = 2897768 \text{ nm K}$
Rayleigh-Jeans eq	$I(\lambda, T) = \frac{8\pi}{\lambda^4} k_B T c$
Blackbody irradiance	$I(\lambda, T) = \frac{8\pi}{\lambda^5} \frac{hc^2}{e^{hc/\lambda k_B T} - 1}$
Einstein crystal	$C_v = 3R \left( \frac{h\nu}{k_B T} \right)^2 \frac{e^{h\nu/k_B T}}{(e^{h\nu/k_B T} - 1)^2}$
Photon energy	$\epsilon = h\nu$
Rydberg equation	$\nu = R_H c \left( 1/n^2 - 1/k^2 \right)$
Bohr equations	$l_n = n\hbar$
$n = 1, 2, \dots$	$r_n = n^2 \left( \frac{4\pi\epsilon_0 \hbar^2}{e^2 m_e} \right) = n^2 a_0$
	$E_n = -\frac{m_e e^4}{8\epsilon_0^2 \hbar^2} \frac{1}{n^2} = -\frac{E_H}{2} \frac{1}{n^2}$
	$p_n = \frac{e^2}{4\pi\epsilon_0} \frac{m_e}{\hbar} \frac{1}{n} = p_0 \frac{1}{n}$
de Broglie equation	$\lambda = h/p$

**Table 4:** Postulates of Non-relativistic Quantum Mechanics

**Postulate 1: The physical state of a system is completely described by its wavefunction**

$\Psi$ . In general,  $\Psi$  is a complex function of the spatial coordinates and time.  $\Psi$  is required to be:

Single-valued

continuous and twice differentiable

square-integrable ( $\int \Psi^* \Psi d\tau$  is defined over all finite domains)

For bound systems,  $\Psi$  can always be normalized such that  $\int \Psi^* \Psi d\tau = 1$

**Postulate 2:** To every physical observable quantity  $M$  there corresponds a Hermitian operator  $\hat{M}$ . **The only observable values of  $M$  are the eigenvalues of  $\hat{M}$ .**

Physical quantity	Operator	Expression
Position $x, y, z$	$\hat{x}, \hat{y}, \hat{z}$	$x, y, z$
Linear momentum $p_x, \dots$	$\hat{p}_x, \dots$	$-i\hbar \frac{\partial}{\partial x}, \dots$
Angular momentum $l_x, \dots$	$\hat{p}_x, \dots$	$-i\hbar \left( y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right), \dots$
Kinetic energy $T$	$\hat{T}$	$-\frac{\hbar^2}{2m} \nabla^2$
Potential energy $V$	$\hat{V}$	$V(\mathbf{r}, t)$
Total energy $E$	$\hat{H}$	$-\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}, t)$

**Postulate 3:** If a particular observable  $M$  is measured many times on many identical systems in a state  $\Psi$ , the average results will be the expectation value of the operator  $\hat{M}$ :

$$\langle M \rangle = \int \Psi^* (\hat{M} \Psi) d\tau$$

**Postulate 4:** The energy-invariant states of a system are solutions of the equation

$$\begin{aligned} \hat{H} \Psi(\mathbf{r}, t) &= i\hbar \frac{\partial}{\partial t} \Psi(\mathbf{r}, t) \\ \hat{H} &= \hat{T} + \hat{V} \end{aligned}$$

The time-independent, stationary states of the system are solutions to the equation

$$\hat{H} \Psi(\mathbf{r}) = E \Psi(\mathbf{r})$$

**Postulate 5: (The uncertainty principle.)** Operators that do not commute ( $\hat{A}(\hat{B}\Psi) \neq \hat{B}(\hat{A}\Psi)$ ) are called *conjugate*. Conjugate observables cannot be determined simultaneously to arbitrary accuracy. For example, the standard deviation in the measured positions and momenta of particles all described by the same  $\Psi$  must satisfy  $\Delta x \Delta p_x \geq \hbar/2$ .

**Table 5:** Particle-in-a-box model

$$V(x) = \begin{cases} 0 & 0 < x < L \\ \infty & x \leq 0 \text{ or } x \geq L \end{cases}$$

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$$

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2mL^2}, n = 1, 2, \dots$$

Selection Rule  
 $\Delta n = \text{odd}$

**Table 6:** Harmonic oscillator model

$$V(x) = \frac{1}{2}kx^2, -\infty < x < \infty$$

$$\psi_v(x) = N_v H_v(x/\alpha) e^{-x^2/2\alpha^2}, v = 0, 1, 2, \dots$$

$$\alpha = (\hbar^2/\mu k)^{1/4}, N_v = (2^v v! \alpha \sqrt{\pi})^{-1/2}$$

Hermite polynomials  
 $H_0(y) = 1$   
 $H_1(y) = 2y$   
 $H_2(y) = 4y^2 - 2$   
 $H_{n+1}(y) = 2yH_n(y) - 2nH_{n-1}(y)$

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

$$E_v = (v + \frac{1}{2})h\nu, v = 0, 1, 2, \dots$$

Selection Rule  
 $\Delta v = \pm 1$

**Table 7:** 2-D rigid rotor model

$$\begin{aligned}
 V(\phi) &= 0, 0 \leq \phi \leq 2\pi \\
 \hat{H} &= -\frac{\hbar^2}{2I} \frac{\partial^2}{\partial \phi^2}, \quad I = \mu R^2 \\
 \psi_{m_l}(\phi) &= \frac{1}{\sqrt{2\pi}} e^{-im_l \phi}, m_l = 0, \pm 1, \pm 2, \dots \\
 E_{m_l} &= \frac{\hbar^2}{2I} m_l^2 \\
 L_z &= m_l \hbar \\
 \text{Selection Rules} \\
 \Delta m_l &= \pm 1
 \end{aligned}$$

**Table 8:** 3-D rigid rotor model

$$\begin{aligned}
 V(\theta, \phi) &= 0, 0 \leq \phi \leq 2\pi, 0 \leq \theta < \pi \\
 \hat{L}^2 &= -\hbar^2 \left[ \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) \right] \\
 \hat{H}_{\text{rot}} &= \frac{1}{2I} \hat{L}^2 \\
 Y_{lm_l}(\theta, \phi) &= N_l^{|m_l|} P_l^{|m_l|}(\cos(\theta)) e^{im_l \phi} \\
 l &= 0, 1, 2, \dots, \quad m_l = 0, \pm 1, \dots, \pm l \\
 E_l &= \frac{\hbar^2}{2I} l(l+1) \\
 |L| &= \hbar \sqrt{l(l+1)}, L_z = m_l \hbar \\
 \text{Selection Rules} \\
 \Delta l &= \pm 1, \quad \Delta m_l = 0
 \end{aligned}$$

**Table 9:** Hydrogen atom

$$V(r) = -\frac{e^2}{4\pi\epsilon_0} \frac{1}{r}, 0 < r < \infty$$

$$\hat{H} = -\frac{\hbar^2}{2m_e} \frac{1}{r^2} \left[ \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \hat{L}^2 \right] + V(r)$$

$$\psi(r, \theta, \phi) = R(r) Y_{l, m_l}(\theta, \phi)$$

$$\left\{ -\frac{\hbar^2}{2m_e} \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d}{dr} \right) + \frac{\hbar^2 l(l+1)}{2m_e r^2} - \frac{e^2}{4\pi\epsilon_0} \frac{1}{r} \right\} R(r) = E R(r)$$

$$R_{nl}(r) = N_{nl} e^{-x/2} x^l L_{nl}(x), \quad x = \frac{2r}{na_0}$$

$$P_{nl}(r) = r^2 R_{nl}^2$$

$$n = 1, 2, \dots, \quad l = 0, \dots, n-1 \quad m_l = 0, \pm 1, \dots, \pm l$$

$$N_{nl} = \sqrt{\left( \frac{2}{na_0} \right)^3 \frac{(n-l-1)!}{2n(n+l)!}}$$

$$L_{10} = L_{21} = L_{32} = \dots = 1 \quad L_{20} = 2 - x \quad L_{31} = 4 - x$$

$$E_n = -\frac{1}{2} \frac{\hbar^2}{m_e a_0^2} \frac{1}{n^2} = -\frac{E_H}{2} \frac{1}{n^2}$$

$$|L| = \hbar \sqrt{l(l+1)}, L_z = m_l \hbar$$

$$\langle r \rangle = \left\{ \frac{3}{2} n^2 - \frac{1}{2} l(l+1) \right\} \frac{a_0}{Z}$$

Selection Rules

$$\Delta l = \pm 1, \quad \Delta m_l = 0, \pm 1 \quad \Delta m_s = 0$$