

Problem Set 1 - Bonding

1. (a) i) de Broglie relation: $\lambda(ball)p(ball) = h$
 ii) momentum of the tennis ball: $p(ball) = m(ball)v(ball)$
 Thus $\lambda(ball) = h/(m(ball)v(ball))$

$$\lambda(ball) = \frac{6.626 \times 10^{-34} \text{ J.s}}{(0.057 \text{ kg}) \times (205 \times 1000/3600 \text{ m/s})} = 2.04 \times 10^{-34} \text{ m} \quad (1)$$

- (b) $\lambda(ball) = d(ball)$ on the condition that: $d(ball)m(ball)v(ball) = h$

$$m(ball) = \frac{h}{d(ball)v(ball)} = \frac{6.626 \times 10^{-34} \text{ J.s}}{(0.065 \text{ m}) \times (205 \times 1000/3600 \text{ m/s})} = 1.79 \times 10^{-34} \text{ kg} \quad (2)$$

2. 0) Cf. Reading Engel, Reid 16.3.

i) We model the molecules in the cone cells as infinite box of width a . The corresponding energies (eigenvalues of the Schrödinger equation) are $E_n = (h^2 n^2)/(8ma^2)$ (where $m = 9.11 \times 10^{-31} \text{ kg}$ is the electron mass).

Assuming that light absorption corresponds to a transition from the ground state ($n=1$) to the first excited state ($n=2$), the energy absorbed can be written as:

$$\Delta E = \frac{h^2}{8ma^2}(4^2 - 1^2) = \frac{3h^2}{8ma^2} \quad (3)$$

- ii) The energy absorbed is related to the wavelength $\lambda(light)$ through:

$$\Delta E = h\nu(light) = hc/\lambda(light) \quad (4)$$

(c =speed of light= $3.00 \times 10^8 \text{ m/s}$)

Consequently,

$$h \frac{c}{\lambda(light)} = \frac{3h^2}{8ma^2} \quad (5)$$

$$a = \sqrt{\frac{3\lambda(light)h}{8mc}} \quad (6)$$

$$(7)$$

The three molecular sizes are: $\left\{ \begin{array}{l} a_{red} = 713 \text{ pm} \\ a_{green} = 694 \text{ pm} \\ a_{blue} = 618 \text{ pm} \end{array} \right.$

3. Cf. Lecture 1 (slide “Interference in Action”)

An interface between two different light-transmitting media reflects a fraction of the incident wave. Consequently, spreading an organic thin film on the surface of a glass results in two reflected waves (one is due to the air/film interface; the other to the film/glass interface). By engineering the thickness and the composition of the film, it is possible to generate a destructive interference between the reflected waves (refer to the lecture slide showing two reflected waves out-of-phase with respect to one another). Glare is thus cut.

4. We can write the plane wave as $\psi(\vec{r}, t) = Ae^{i(\vec{k} \cdot \vec{r} - \omega t)}$. The square modulus of the wave is $\psi^*(\vec{r}, t)\psi(\vec{r}, t) = A^*A(\cos(\vec{k} \cdot \vec{r} - \omega t) - i \sin(\vec{k} \cdot \vec{r} - \omega t))(\cos(\vec{k} \cdot \vec{r} - \omega t) + i \sin(\vec{k} \cdot \vec{r} - \omega t)) = |A|^2(\cos^2(\vec{k} \cdot \vec{r} - \omega t) + \sin^2(\vec{k} \cdot \vec{r} - \omega t)) = |A|^2 = cst$.

The square modulus is a constant, its periodicity is thus zero.

5. (a) + case

The general solution of $d^2z(t)/dt^2 = +\omega^2z(t)$ can be written as:

$$z(t) = Ae^{\omega t} + Be^{-\omega t} \quad (8)$$

(b) - case

The general solution of $d^2z(t)/dt^2 = -\omega^2z(t)$ can be written as:

$$z(t) = Ae^{i\omega t} + Be^{-i\omega t} \quad (9)$$

or equivalently as:

$$z(t) = A \cos(\omega t) + B \sin(\omega t) \quad (10)$$

6. Cf Reading 16.1.

When E is in the energy range $-V_0 < E < 0$ and is not an eigenvalue, we observe that the solution of the S.S.E. is not well-behaved: the wavefunction $\psi(x)$ goes to $+\infty$ on the right part of the graph (that is, $x \rightarrow +\infty$). This behaviour is not physical: the probability of finding an electron at $x \rightarrow +\infty$ (which is given by $\lim_{x \rightarrow +\infty} \psi^*(x)\psi(x)$) can not be infinite. These solutions are not eigenstates of the S.S.E.

A solution is admissible on the condition that E is an eigenvalue of the S.S.E.: the wavefunction goes to zero at the boundaries when this condition is satisfied.

7. i) classical quantity: $\frac{p^3}{3m}$

ii) correspondence principle: $p \rightarrow -i\hbar \frac{d}{dx}$

iii) quantum operator

$$\frac{\hat{p}^3}{3m}\psi(x) = \frac{1}{3m} \left[-i\hbar \frac{d}{dx} \left\{ -i\hbar \frac{d}{dx} \left(-i\hbar \frac{d}{dx} \psi(x) \right) \right\} \right] = (-i\hbar)^3 \frac{d^3}{dx^3} \psi(x) = i\hbar^3 \frac{d^3}{dx^3} \psi(x)$$

Finally

$$\underline{\underline{\frac{\hat{p}^3}{3m} = i\hbar^3 \frac{d^3}{dx^3}}} \quad (11)$$

8. The eigenfunctions and eigenvalues for a particle in a two-dimensional box of size $a \times a$ are: $\psi_{l,m}(x, y) = A \sin(\frac{l\pi x}{a}) \sin(\frac{m\pi y}{a})$ and $E_{l,m} = \frac{h^2}{8ma^2} (l^2 + m^2)$.

Consequently, the three lowest-energy eigenfunctions are

$$\begin{cases} \psi_{l=1,m=1}(x, y) = A_1 \sin(\frac{\pi x}{a}) \sin(\frac{\pi y}{a}) & (E_{l=1,m=1} = \frac{h^2}{4ma^2}) \\ \psi_{l=1,m=2}(x, y) = A_2 \sin(\frac{\pi x}{a}) \sin(\frac{2\pi y}{a}) & (E_{l=1,m=2} = \frac{5h^2}{8ma^2}) \\ \psi_{l=2,m=1}(x, y) = A_3 \sin(\frac{2\pi x}{a}) \sin(\frac{\pi y}{a}) & (E_{l=2,m=1} = \frac{5h^2}{8ma^2}) \end{cases} \quad (\text{see graphs on next page})$$

(a) orthogonality - analytically

The orthogonality condition between $\psi_{l=1,m=1}(x, y)$ and $\psi_{l=1,m=2}(x, y)$ is:

$$\int_{x=0}^{x=a} \int_{y=0}^{y=a} \left\{ A_1 \sin(\frac{\pi x}{a}) \sin(\frac{\pi y}{a}) \right\}^* A_2 \sin(\frac{\pi x}{a}) \sin(\frac{2\pi y}{a}) dx dy = 0 \quad (12)$$

which we can rewrite as:

$$\left(\int_{x=0}^{x=a} \sin(\frac{\pi x}{a}) \sin(\frac{\pi x}{a}) dx \right) \left(\int_{y=0}^{y=a} \sin(\frac{\pi y}{a}) \sin(\frac{2\pi y}{a}) dy \right) = 0 \quad (13)$$

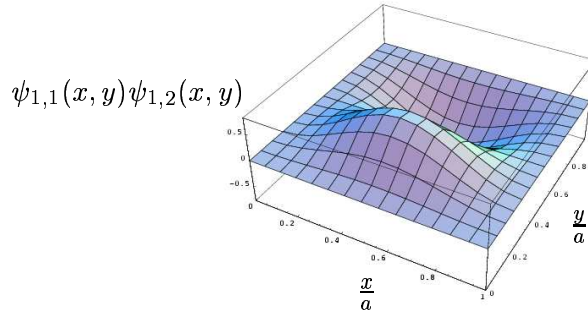
Using mathematica or maple, each integral can be calculated.

In particular, $\int_{y=0}^{y=a} \sin(\frac{\pi y}{a}) \sin(\frac{2\pi y}{a}) dy = 0$.

Thus, $\psi_{l=1,m=1}(x, y)$ and $\psi_{l=1,m=2}(x, y)$ are orthogonal.

(b) orthogonality - graphically

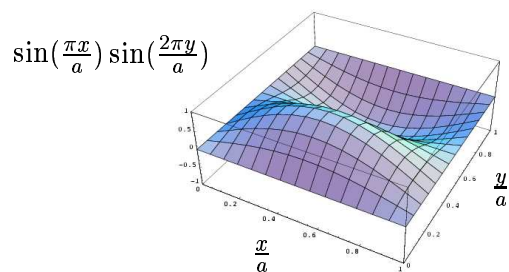
We want to prove that $\int_{x=0}^{x=a} \int_{y=0}^{y=a} \psi_{l=1,m=1}^*(x, y) \psi_{l=1,m=2}(x, y) dx dy$ equals zero. Graphically, this integral is the volume between the plane $z = 0$ and the surface representing the function $\psi_{l=1,m=1}^*(x, y) \psi_{l=1,m=2}(x, y)$. We can plot this function:



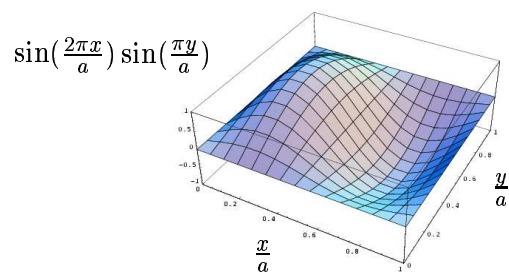
From the graph, it can be seen that $\psi_{l=1,m=1}^*(x, y) \psi_{l=1,m=2}(x, y)$ is symmetric with respect to the plane $y = a/2$. Hence, in the integral $\int_{x=0}^{x=a} \int_{y=0}^{y=a} \psi_{l=1,m=1}^*(x, y) \psi_{l=1,m=2}(x, y) dx dy$

“the negative part exactly cancels the positive part”. The integral is thus zero: $\psi_{l=1,m=1}(x,y)$ and $\psi_{l=1,m=2}(x,y)$ are orthogonal.

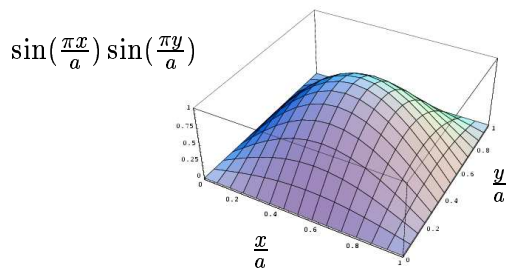
Similarly, one can show that $\psi_{1,1}(x,y)$ is orthogonal to $\psi_{2,1}(x,y)$, and that $\psi_{1,2}(x,y)$ is orthogonal to $\psi_{2,1}(x,y)$.



(a) energy = $\frac{5h^2}{8ma^2}$



(b) energy = $\frac{5h^2}{8ma^2}$



(c) energy = $\frac{h^2}{4ma^2}$

of them with its corresponding eigenfunction. Can you describe what is happening for E lesser than zero ? Do we still have eigenstates ? What happens when E is not an eigenvalue ? Note that the applet starts its numerical integration from left to the right.

7. In a parallel universe, the kinetic energy of a particle is $p^3/(3m)$. What would be the corresponding quantum mechanical operator ?
8. Sketch the graph of the three lowest energy eigenfunctions of a particle in a 2-dimensional box. Show graphically and analytically that they are orthogonal (Use the method of separation of variables to write the ground-state wavefunction of this 2-dimensional problem using the 1-dimensional solutions). What are the three lowest-energy states ?

THERMODYNAMICS

9. **Thermodynamic Variables.** We have described two classes of thermodynamic variables: intensive (such as temperature and pressure) and extensive (such as volume).
 - a. What class would the variable mass (let's use the symbol M for mass) fall into- intensive or extensive?

Mass is an **extensive** variable: it depends linearly on the size of the system: if I double the number of moles of some material, I double the mass of that material.

- b. What about variables that are derived from other variables? Consider density: We define density as the mass of a material per unit volume:

$$\rho = \frac{M}{V}$$

Can density be classified simply as an intensive or extensive variable? Explain your answer. (Hint: Look carefully at the definitions!)

Density is a variable formed by the ratio of two other extensive variables. But is density extensive? Suppose I have system A with mass M_A and volume V_A , and I combine it with system B with mass M_B and volume V_B . Then the density of the composite system is, by definition:

$$\rho_{A+B} = \frac{M_{A+B}}{V_{A+B}} = \frac{M_A + M_B}{V_A + V_B} = \frac{V_A}{V_A + V_B} \rho_A + \frac{V_B}{V_A + V_B} \rho_B$$

Comparing this result to a linear addition of the densities of A and B:

$$\rho_A + \rho_B = \frac{M_A}{V_A} + \frac{M_B}{V_B}$$

Density is neither explicitly intensive nor extensive- the density of a composite system is the weighted average of the densities of the individual subsystems.

10. **Thinking about systems and boundaries.** Read the descriptions below of some thermodynamic systems (any macroscopic material can be a thermodynamic system!)

undergoing various changes and identify the type of system (open, closed, etc.). Explain in one sentence for each case why your choice is appropriate- state your assumptions to defend your choice.

- (a) The system is a liter of hot coffee placed inside a high-quality, sealed thermos that has an evacuated space between an inner rigid cylinder where the liquid is placed and the outside walls of the container.

Based on the given information, which is that the system (the coffee) is stored in a rigid, sealed volume that restricts heat transfer, we could state that this is approximately an isolated system. Of course, as with any real system, the isolation is not perfect... the coffee eventually gets cold as heat slowly escapes the container.

- (b) If the thermos described above had flexible rather than perfectly rigid walls, what kind of system would we have?

If the walls of the container are flexible, then the volume of the system is not forced to be constant- and a system that restricts heat transfer but can change volume (allowing work to be done on/by the system) is an adiabatic system.

- (c) The system is a puddle of water on the sidewalk.

Because water molecules can evaporate or condense on the puddle, and the puddle could be heated or cooled depending on its surroundings, this is an open system.

- (d) You have a glass jar of strawberry jam and the metal screw-top lid is stuck (the jam is your system). You really want a peanut butter and jelly sandwich, so you place the jar under a stream of hot water to loosen the lid.

You have a closed system (jam can't get out of the jar, but heat is clearly going to pass through the glass walls of the jar).

- (e) You are the system. You're on a ski trip at Killington and you are wearing a high-tech insulated parka, hood, and snow pants to keep you warm. It's -10°C on the ski slope, but as you trudge up to the ski lift, you are getting warm.

Assuming your parka is a perfect (or at least very good) insulator, we could state that you are an isolated system. (If you assume the parka isn't a good insulator, then you are a closed system.) The fact that you feel warmer after exerting yourself is due to the transformation of internal chemical energy stored in your body into some waste heat during the process of walking to the ski lift. This fact might further suggest that the parka is a good insulator and no heat is transferring out of you into the surroundings (in practice of course, some heat is always leaking into the surroundings).

11. **Using the First Law.** We introduced the theoretical concept of an ideal gas in lecture- 'ideal' because real gases only approach ideal behavior under select conditions. Recall that the two key thermodynamic characteristics of an ideal gas are an equation of state $PV = nRT$ and that the internal energy is only a function of temperature ($U = 1.5nRT$). Suppose we have 1 mole of an ideal gas confined in a cylinder with a movable piston top, which allows the volume of the gas to be controlled. The gas starts at an initial volume $V_0 = 10\text{ L}$ at a pressure of 1 atm. We want to consider the effect of two different two-step processes, each of which starts with the gas in the same initial state and ends with the gas in the same final state:

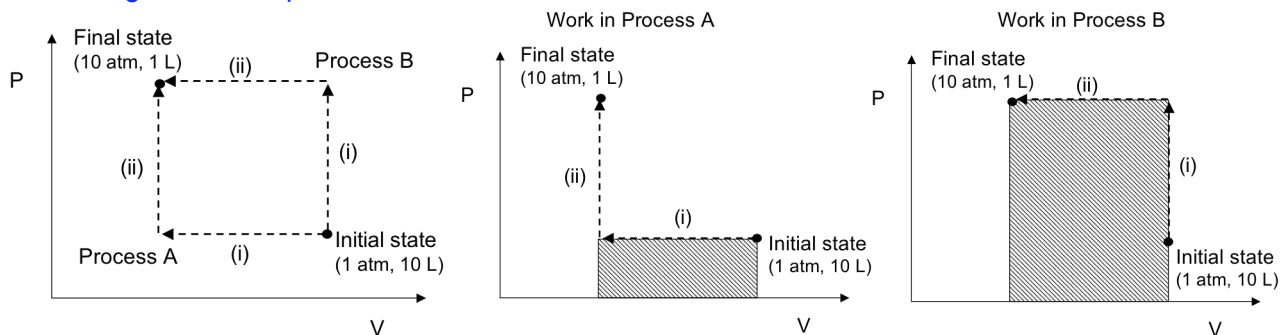
Process A: (i) The gas is compressed to a volume of 1 L at constant pressure ($P = 1\text{ atm}$). (ii) The pressure is then slowly increased from 1 atm to 10 atm at constant volume.

Process B: (i) The pressure is slowly increased from 1 atm to 10 atm at constant volume ($V = V_0$). (ii) The gas is then compressed from 10 L to 1 L at constant pressure ($P = 10\text{ atm}$).

Assume the changes occur slowly enough for the gas to remain in equilibrium at all times (reversible processes).

- a. By which composite process, **A** or **B**, is more work done by the gas? Show why using a P vs. V diagram and also quantitatively by calculation.

A P-V diagram of this process looks like:



Mathematically, the work in each composite process is:

Process A: (i) $dw = -P_{ext}dV$ $w = - \int_{V_0}^{V_{final}} P_{ext} dV = -(1\text{ atm})(1\text{ L} - 10\text{ L}) = 9\text{ L} \cdot \text{atm}$

Note that to put this result in more conventional units of energy (Joules), we can use the following conversion factor (which is just a ratio of the gas constant R in two different units- something readily memorizable!):

$$(9\text{ L} \cdot \text{atm}) \left(\frac{8.3144\text{ J}}{0.082057\text{ L} \cdot \text{atm}} \right) = 911\text{ J}$$

The work is positive: work is done **on** the system.

(ii) $dw = 0$ ($dV = 0$, no volume change so no hydrostatic work is performed).

Total work: 911 J

Process B: (i) $dw = 0$ no volume change in the first step

$$(ii) w = - \int_{V_o}^{V_{final}} P_{ext} dV = -(10 atm)(1L - 10L) = 90L \cdot atm \left(\frac{8.3144J}{0.082057L \cdot atm} \right) = 9,119J$$

Total work: 9,119 J

Thus, more work is performed in process B.

- b. Is the change in internal energy of the gas the same for each composite process? Why?

Yes. Internal energy is a state function, and thus changes in internal energy do not depend on the path taken, only the identity of the initial and final states. Since the initial and final states of the system undergoing each process are the same, the change in internal energy must be the same.

- c. With the given information, can you calculate the heat transferred into/out of the gas during process A? Why or why not? If yes, show your calculation.

The internal energy change in process A can be determined, using the given expression for internal energy:

$$\Delta U_{process_A} = U_{final} - U_{initial} = 1.5nR(T_{final} - T_{initial})$$

We can determine the temperature at the initial and final states using the given information and the ideal gas equation of state:

$$PV = nRT$$

$$T_{initial} = \frac{PV}{nR} = \frac{(1atm)(10L)}{(0.082057 \frac{L \cdot atm}{K \cdot mole})} = 121.9K$$

$$T_{final} = \frac{PV}{nR} = \frac{(10atm)(1L)}{(0.082057 \frac{L \cdot atm}{K \cdot mole})} = 121.9K$$

We have calculated the work in this process above. Using these two calculations and the first law, we can obtain the heat transfer:

$$\Delta U_{process_A} = 1.5nR(T_{final} - T_{initial}) = 0 = q + w = q + 911J$$

$$\therefore q = -911J$$

Thus, 911 J of heat **leaves** the system.

Suppose now we carry out a four-step process: Starting in the initial state ($V = V_o$, $P = 1 atm$), we perform composite process A, followed by composite process B in reverse.

- d. What is the total internal energy change for the gas after all 4 steps?

The composite process described is a cycle- the initial and final states are the same; therefore, the change in internal energy is zero.

- e. Can you determine the total heat transferred into/out of the gas for this 4-step composite process? If yes, show your calculation.

Yes: applying the first law as in part c:

$$\Delta U_{process} = w_A + q_A + w_B + q_B = 0$$

$$q_{total} = q_A + q_B$$

$$\Delta U_{process} = 911 - 9119 + q_{total} = 0$$

$$\therefore q_{total} = 8,208J$$