UNIVERSITY OF MARYLAND
Chemical Physics Program
College Park, Maryland

CHEMICAL PHYSICS
QUALIFYING EXAMINATION – Part I

August 29, 2013 **9:00 AM – 1:00 PM**

Do three (3) problems.
Problems I.A and I.B are **required**.
Choose one additional problem from I.1, I.2, I.3, or I.4. If more than three problem solutions are turned in, only **three** will be graded.

Within each problem the points assigned to each part reflect the **relative** weight of the parts within the problem. In the determination of your final grade for the examination, each of the three problems that you complete will count equally.

Put all answers on your answer sheets. Be sure your Qualifying Examination ID Number is at the top right corner of each sheet turned in.

ONLY THREE (3) PROBLEMS WILL BE GRADED
PROBLEMS I.A AND I.B ARE REQUIRED

Problem I.A – Quantum Chemistry

Huckel theory forms a good qualitative approach to the energies of conjugated π electron systems. Consider the cyclobutadiene molecule (C_4H_4), which is a four-membered ring, with one H atom attached to each carbon. As in benzene, each carbon atom contributes one π electron. Within Huckel theory, if one considers just the π electrons, the matrix of the electronic Hamiltonian can be written in terms of the one-center integral

$$\alpha = \langle 2p_i | \, \hat{H}_{el} \, | 2p_i \rangle$$

and the two-center integral

$$\beta = \langle 2p_i | \, \hat{H}_{el} \, | 2p_j \rangle$$

where i and j designate any two carbon atoms and where the j^{th} atom is connected to the i^{th} atom. All other matrix elements of $\hat{H}_{el}$ are zero. Furthermore, the $2p$ orbitals are assumed normalized and all overlap integrals are set to zero, namely

$$1 = \langle 2p_i \, | 2p_i \rangle$$

and

$$0 = \langle 2p_i \, | 2p_{\mathrm{j}\neq\mathrm{i}} \rangle$$

(a) [2 pts] Write down a simple stick representation of the structure of the cyclobutadiene molecule, indicating the bonds. Assume that (a) all C–C bonds are equal in length, (b) the molecule lies in the xy plane, (c) the origin lies at the center of the molecule, and (d) the atoms are placed in the center of the four quadrants, so that the x and y axes each bisect two C–C bonds. Make sure to number the C atoms.

(b) [3 pts] Write down the Huckel matrix. You can set $\alpha = 0$ (which is just a shift in the total energy).

(c) [6 pts] Consider the xz and yz reflection operators $\hat{\sigma}_{xz}$ and $\hat{\sigma}_{yz}$. The π molecular orbitals of cyclobutane can be written as linear combinations of the $2p_z$ atomic orbitals on the four carbons

$$\pi_N = \sum_i C_{Ni} 2p_{zi}$$

where N indexes the molecular orbitals. Because of the symmetry of the molecule, the π

orbitals must all be eigenfunctions, with eigenvalues equal to $\pm$ 1, of $\hat{\sigma}_{xz}$ and $\hat{\sigma}_{yz}$. What are these linear combinations? The most compact way to answer this question would be with a table indicating (a) the linear combination and (b) the reflection symmetries.

(d) [6 pts] Identify the linear algebra procedure that will allow you to obtain the Huckel matrix in the basis of the molecular orbitals which diagonalize $\hat{\sigma}_{xz}$ and $\hat{\sigma}_{yz}$? Then, obtain this matrix.

(e) [3 pts] How does the total π electron energy of cyclobutadiene compare with that of two ethylene molecules?

Problem I.B – Thermodynamics

1. A particular metal has a molar heat capacity that at low temperature is given by $c_v(T) = BT$ with B a constant. A block containing *one mole* of this material at temperature T_c is placed in thermal contact in a rigid adiabatic enclosure with a (generally different sized) block of the same material containing m moles and initially at a higher temperature T_h. The combined system comes to a new equilibrium at a final temperature T_f. Ignore any changes in the volumes of the blocks from thermal expansion, etc.

   (a) (5 points) Derive a general formula that allows T_f to be calculated as a function of T_c, T_h, and m. State the general thermodynamics principles you used to arrive at your result.

   (b) (3 points) Show that as $m \to \infty$, T_f tends to T_h and as $m \to 0$ T_f tends to T_c. Briefly explain why this behavior is to be expected and relate to the idea of a heat bath.

   (c) (3 points) Calculate T_f explicitly for $m = 1$ with $T_c = \sqrt{2}$ (degrees Kelvin) and $T_h = 4$. Does this agree with the "common sense" answer $T_f = (T_c + T_h)/2$? Briefly discuss.

   (d) (5 points) Calculate the change in entropy for *each* block for $m = 1$ with $T_c = \sqrt{2}$ and $T_h = 4$. What do you know in general about the sum of the entropy changes for both blocks?

   (e) (4 points) Now suppose that, instead of allowing the blocks to exchange heat spontaneously under adiabatic conditions, a device can in principle be constructed to transfer heat *reversibly* from the hot block to the cold block, until the two blocks have reached a common final temperature. (For instance, imagine a heat engine that operates repeatedly between the two blocks. Without focusing on details of this device, use very general thermodynamic principles to answer the following questions.) In this idealized situation, what is the final temperature, T_f, as an function of the initial temperatures T_h and T_c? How much work would the device deliver during this process? For simplicity, take $m = 1$ for this part of the problem. **Bonus** (not graded but extra credit if you have a good idea!) Can you describe in more detail a device that could do this?

Problem I.1

Consider a particle of mass m confined to a two-dimensional plane with polar coordinates (r, ϕ), in the presence of an upside-down harmonic oscillator potential $V(r) = -\frac{1}{2}\kappa r^2$.

(a) **[5 points]** Identify two conserved quantities for the particle's motion, and write expressions for them.

(b) **[5 points]** Now assume the particle has an electric charge q, and there is a uniform and time-independent magnetic field of strength B, normal to the plane of motion. Write the Lagrangian L and the energy E for the particle as functions of $(r, \dot{r}, \phi, \dot{\phi})$. [A convenient vector potential for the magnetic field in this problem is $\boldsymbol{A} = (Br/2)\hat{\phi}$.]

(c) **[5 points]** Identify the conserved quantities for the motion, and write expressions for them.

Find the effective potential $V_{\text{eff}}(r)$ for the radial motion in the presence of the magnetic field, for any fixed value of the conserved variable p_ϕ conjugate to the angle ϕ.

Sketch $V_{\text{eff}}(r)$ in the limit of small and of large B.

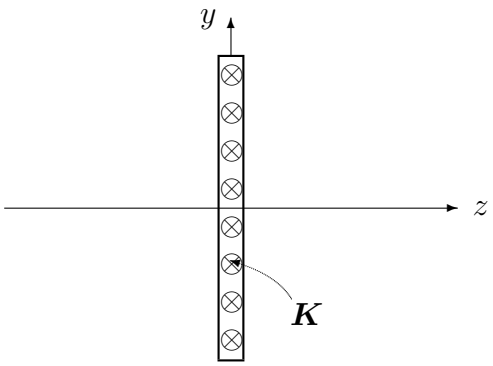
(d) **[5 points]** Show that the motion is stable (i.e. the particle remains for all time within a fixed distance from the origin) provided $|B|$ is larger than some minimum value B_0, and find that value.

(e) **[5 points]** Find the particle position (r, ϕ) as a function of time t for all trajectories that pass through the origin at time $t = 0$, assuming

(i) $|B| < B_0$,
(ii) $|B| = B_0$, and
(iii) $|B| > B_0$.

Problem I.2

An infinite conducting, current-carrying plate lies in the x-y plane (see Figure). Suppose there is a steady current in the plate in the $+x$ direction. Let the current per unit y-length be K.



(a) **[3 points]** Using Ampère's Law, $\oint \boldsymbol{B}\cdot\boldsymbol{dl} = \mu_0 I_{enc}$, find the steady magnetic field B_y in terms of K on either side of the plate. Assume that the fields associated with the current are appropriately reflection symmetric about the plate. Make a sketch of $\boldsymbol{B}$ for all z, using the Figure as reference.

Now suppose instead that there is time dependence: the current and fields vanish for $t < 0$, and K is turned on suddenly at $t = 0$. That is, $K = K_0\Theta(t)$ where Θ is the step function, $\Theta(t) = \begin{cases} 0 & t<0 \\ 1 & t>0 \end{cases}$. Consider now a snapshot of the system at some time $t > 0$:

(b) **[4 points]** *Using only qualitative reasoning*, in particular using causality, make a sketch of the snapshot of $\boldsymbol{B}$ in the Figure at time $t > 0$. Mark clearly any characteristic lengths in your sketch. (Note that the plate is of infinite extent; thus, the problem is still one-dimensional in z, but the $\boldsymbol{B}$ field may have structure in that direction.)

(c) **[4 points]** Do you think the total energy stored in the electromagnetic fields increases or decreases with time? Based on this, consider *qualitatively* the Poynting flux and deduce if there should be any associated electric fields $\boldsymbol{E}$. If so, include $\boldsymbol{E}$ in your sketch, with the proper signs.

From Maxwell equations, the vector potential $\boldsymbol{A}(z,t)$ can be shown to satisfy the wave equation

$$\left(\partial_z^2 - \frac{1}{c^2}\partial_t^2\right)\boldsymbol{A} = -\mu_0\boldsymbol{j},$$

where the current density is

$$\boldsymbol{j} = K\delta(z)\Theta(t)\ \hat{x}.$$

for our problem above. The solution for $\boldsymbol{A}$ can be constructed from a Green function, $G(z,z',t,t')$, according to

$$\boldsymbol{A}(z,t) = -\mu_0\int_{-\infty}^{\infty}dt'\int_{-\infty}^{\infty}dz'\,G(z,z',t,t')\ \boldsymbol{j}(z',t').$$

The Green function, in turn, for outgoing wave boundary conditions (i.e., causality), can be found to be

$$G = \frac{c}{2}\Theta(t_r - t') \qquad \text{where} \quad t_r = t - \frac{|z-z'|}{c}.$$

(d) **[5 points]** Find the non-zero component of the vector potential $\boldsymbol{A}(z,t)$ for all (z,t). Leave your answer in terms of an integral over t'.

Problem I.2 (continued)

(e) **[3 points]** The electromagnetic fields can be calculated from $\boldsymbol{A}(z,t)$ according to the relations given below. (There is no scalar potential φ in this problem, so ignore it.) Calculate $B_y(z,t)$ [perform any differentiations by commuting across the integral]. Describe the waveform in z for given t clearly, and compare with your snapshot above.

Hint: Consider separately the cases $t_r < 0$ and $t_r > 0$.

(f) **[3 points]** Likewise, calculate $\boldsymbol{E}(z,t)$. Compare with your snapshot above.

(g) **[3 points]** For $z > 0$, calculate the energy per unit plate area stored in the electromagnetic fields at time t. Calculate the Poynting energy flux per unit plate area. Confirm that the power input into the electromagnetic energy equals the Poynting flux.

(Expressions for the electromagnetic energy density, u, and Poynting flux, $\boldsymbol{S}$, are given below.)

Useful equations

$$\Theta[f] = \begin{cases} 0 & f < 0 \\ 1 & f > 0 \end{cases} \qquad \frac{d}{dt}\Theta[f(t)] = \delta(f)\frac{df}{dt}$$

$$\boldsymbol{B} = \boldsymbol{\nabla} \times \boldsymbol{A}, \qquad \boldsymbol{E} = -\boldsymbol{\nabla}\varphi - \frac{\partial \boldsymbol{A}}{\partial t}$$

$$u = \frac{1}{2}\left(\epsilon_0 E^2 + \frac{B^2}{\mu_0}\right), \qquad \boldsymbol{S} = \frac{\boldsymbol{E} \times \boldsymbol{B}}{\mu_0}$$

Problem I.3 – Statistical Mechanics

Consider an ideal gas of indistinguishable particles near a surface.

(a) [6 pts] The translational partition function for the gas is given by

$$q_{trans} = \left(\frac{2\pi m k_B T}{h^2} \right)^{2/3} V .$$

The chemical potential is given by

$$\mu_{gas}(T,P) = -k_B T \left(\frac{\partial \ln Q_{gas}}{\partial N} \right)_{V,T}$$

Show that the chemical potential of the gas is given by

$$\mu_{gas}(T,P) = \mu_0(T) + k_B T \ln P,$$

where P is pressure. Give an explicit expression for μ_0.

(b) [6 pts] Now consider a surface on which adsorbed gas molecules are in equilibrium. We model the surface as a 2D lattice composed of m sites. The partition function of an unoccupied site is 1, and the partition function of an occupied site is $q(T)$. Based on this model, justify expressing the partition function for n adsorbed molecules as

$$Q_{surface}(n,m,T) = \frac{m!}{n!(m-n)!} q^n(T)$$

Use this result to derive the chemical potential of the adsorbed molecules on the surface.

(c) [8 pts] At equilibrium, the chemical potential of the gas and the adsorbed molecules are equal. Use this condition to derive the Langmuir adsorption isotherm:

$$\frac{\theta}{1-\theta} = q \exp\left(\frac{\mu_0(T)}{k_B T} \right) \cdot P,$$

where $\theta = n/m$ is the fractional coverage of the surface.

Problem I.4 – Inorganic Chemistry

The hypothetical RuH_5 complex has a trigonal bipyramidal structure with D_{3h} point symmetry. Each part is worth 5 points.

a) Construct a molecular orbital diagram showing the proper # of electrons and all symmetry labels.

b) If one of the axial hydride ligands were replaced by a chloride ligand, use you answer from above to reassign the symmetries of the orbitals under the correct symmetry of C_{3v}. Neglect (omit) chlorine lone pairs in this part.

c) Using C_{3v} point symmetry and symmetry labels, show how the chloride π-interactions would affect the MO diagram.

d) Could you use IR spectroscopy to differentiate between an axial or equatorial Cl ligand in the trigonal bipyramidal complex above? Be specific.

Character tables appear below:

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$	
A_1'	1	1	1	1	1	1	x^2+y^2, z^2
A_2'	1	1	-1	1	1	-1	R_z
E'	2	-1	0	2	-1	0	$(x^2-y^2, xy), (x,y)$
A_1''	1	1	1	-1	-1	-1	
A_2''	1	1	-1	-1	-1	1	z
E"	2	-1	0	-2	1	0	(R_x,R_y) (xz, yz)

C_{3v}	E	$2C_3$	$3\sigma_v$	
A_1'	1	1	1	z, x^2+y^2, z^2
A_2'	1	1	-1	R_z
E'	2	-1	0	$(x^2-y^2, xy), (x,y)$ $(R_x,R_y)(xz, yz)$