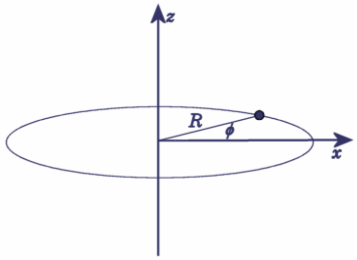
Problem Set 3
On Separation of Variables

1. 1. The Schrödinger equation for a particle of mass m (such as an electron) constrained to move on a circle with radius R (constrained by V = 0 on the circle, V=∞ everywhere else) is:



$$-(\hbar^2/2mR^2)\,(d^2/d\phi^2)\,\psi(\phi) = E\,\psi(\phi) \qquad \psi_k(\phi) = (1/\sqrt{2\pi})\exp[i\,k\phi]$$

Given the Hamiltonian for two non-interacting particles with masses M_1 and M_2 on the same circle of radius R:

$$\mathcal{H} = -(\hbar^2/2M_1R^2)\partial^2/\partial\phi_1^2 \; -(\hbar^2/2M_2R^2)\,\partial^2/\partial\phi_2^2$$

(a) Write the Schrödinger equation for this system.
(b) Solve the problem, that is, find the eigenfunctions and eigenvalues. [HINT: Use the method of separation of variables.]

2. If, in the system of above problem, instead of 1 or 2 particles, we have 6 non-interacting electrons on the circle, what would the Schrödinger equation for the 6-electron system be? (a) Write out the equation in detail, defining the symbols used. You may use $\Psi(\phi_1, \phi_2, \phi_3, \phi_4, \phi_5, \phi_6)$ to designate the eigenfunctions of the 6-electron system. How is Ψ related to $\psi_k(\phi)$?

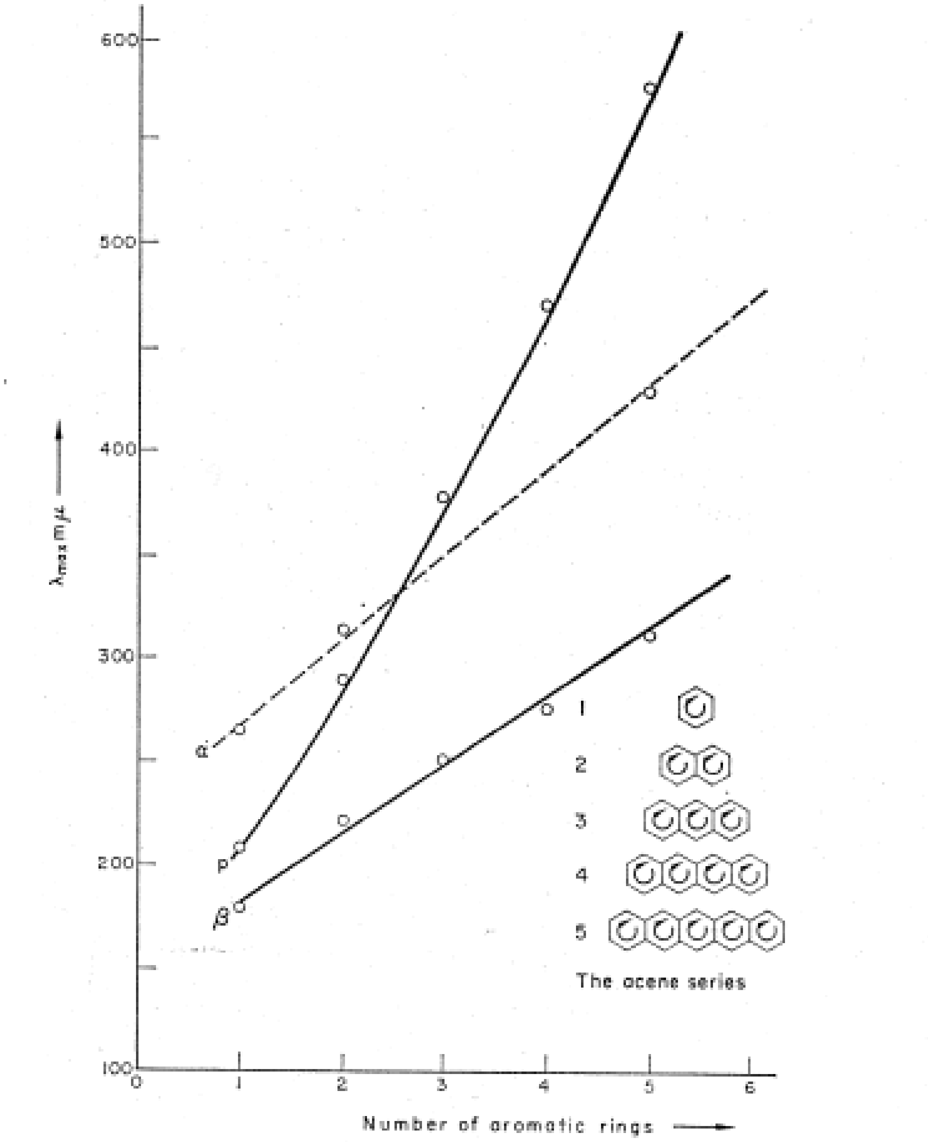
(b) Find the general forms of the eigenfunctions and eigenvalues of the 6 electron system. [HINT: Use the method of separation of variables.]

(c) Suppose that we invoke the rule that no more than two electrons may have the same value of k (one with spin up the other with spin down). Write down the lowest energy eigenvalue and the corresponding eigenfunction (ground state) for this system of 6 electrons. Write down completely the energy eigenvalue and eigenfunction for each of the lowest two excited states. Starting with these 3 energies, draw an energy level diagram for the system of 6 non-interacting electrons constrained to move on the circle.

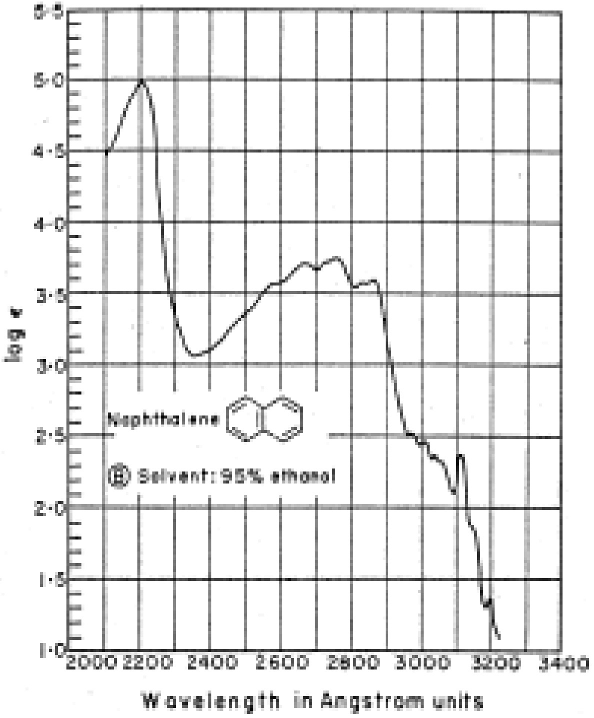
(d) Suppose that transitions between states can be induced by light of the appropriate wavelength. Suppose that the peak intensity for the k→k′ transition depends on the square of the integral $\int \psi_k^* \, x \, \psi_{k'} \, d\tau$ where $x = R\cos\phi$ (as shown in the figure). For which pairs of k and k′ is the intensity not zero (that is, when does the integral not vanish)? What two states of the 6-electron system are participating in the k→k′ transition? Describe what you mean, using diagrams, and identify the functions and energies involved.

(e) The above model can be used, and has been used, to interpret the ultraviolet spectrum of benzene and catacondensed hydrocarbons such as anthracene, etc. In this model, the circle on which the electrons are constrained is taken to be of such radius that the perimeter of the circle equals the outer C-C perimeter of the hydrocarbon. Using this model for benzene, (C-C bond lengths are 1.394 Å) designate the possible transitions which could be assigned to the <u>longest wavelength</u> band in the UV spectrum of benzene.

(f) The observed wavelengths of the three ultraviolet bands observed for the acenes are shown to the right. The wavelength is shown to vary linearly with the number of rings. <u>Demonstrate</u> that this observation is (or is not) in accordance with the results of the above model. In other words, derive a relationship between the number of rings and the wavelength from the above model. The spectra of the first three members of the acene series are shown on the next page.



The variation in wavelength of the three ultra-violet bands of the acenes with the number of rings. The weaker α-band is swamped by the stronger p-band for $n = 3, 4$. [Data taken from Clar[8], solvents: an alcohol or benzene.]



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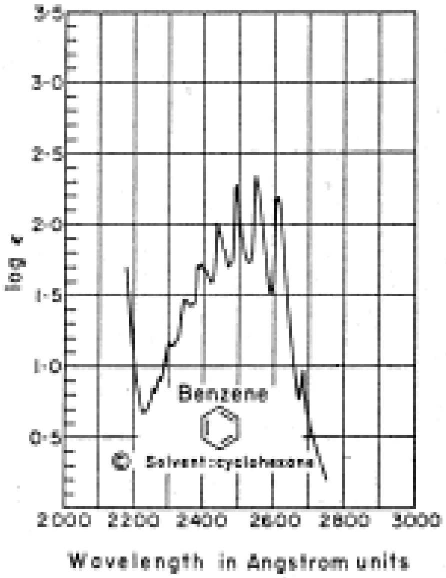
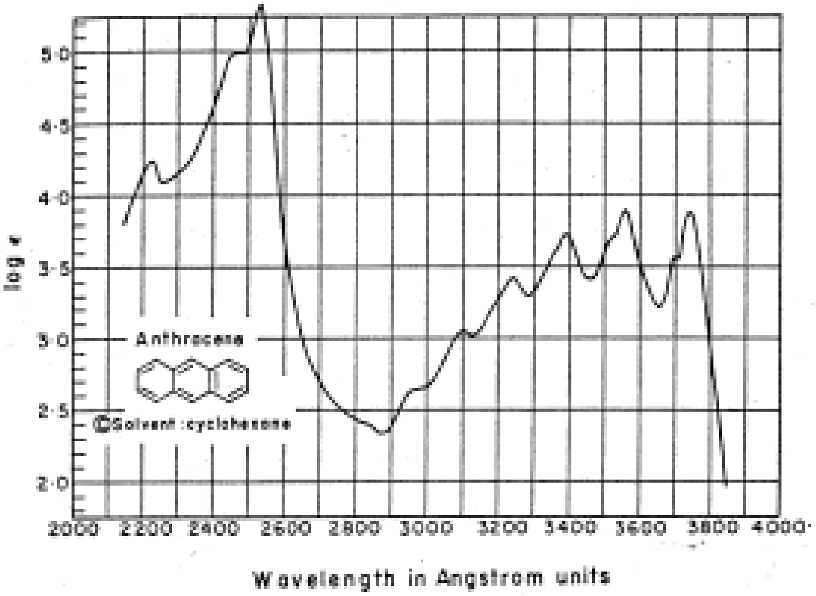


(2)



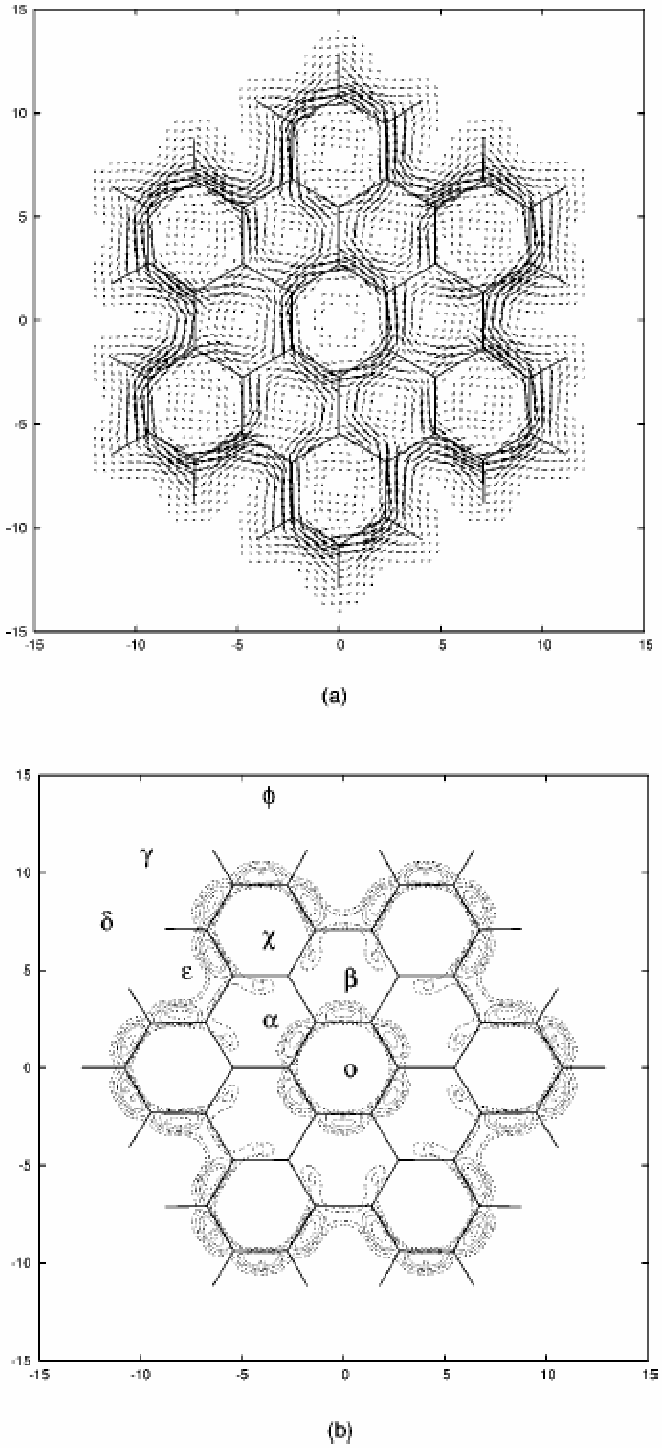
(4)

Some ultra-violet spectra of the acene-series.

Some condensed ring systems, especially peri-condensed ring systems where some carbon atoms are shared by 3 or more rings, are highly carcinogenic agents. Ultraviolet photoelectron spectroscopy, fluorescence (UV excitation followed by emission) studies, and quantum-mechanical calculations have been used by Prof. Pierre LeBreton's research group to study DNA binding of benzo[a]pyrene and benz[a]anthracene at intercalation sites.

Additional notes for problem 2:

In the Journal of Chemical Physics, 1 September, 2004 vol. 121, p. 3952, is an article by J. Juselius, D. Sundholm, and J. Gauss on the calculations of current densities using state of the art level of quantum mechanical calculations (the so-called coupled cluster singles doubles and triples which includes electron correlation) and large basis sets (something we will explain later in this course when we get to the variational method). I attach a page out of that paper to show you that *the assumption you make in Problem Set 3*, to treat catacondensed aromatic hydrocarbons, such as naphthalene to tetracene, in terms of non-interacting *electrons on a circle*, the perimeter of the circle being $2\pi R$ = sum of the *outer* C-C bond lengths, is not too far-fetched. The attached page from the current issue of J. Chem. Phys. clearly shows in Fig. 5(b) at 1 bohr above the molecular plane of hexabenzocoronene the main current pathways are one around the central benzene ring, and another is along the outer edges of the molecule. The current strengths are greatest along the molecular edge around the whole molecule and also, incidentally, the benzene ring at the molecular center.



(a)

(b)

FIG. 5. The induced current density (a) and the modulus of the current density (b) for hexabenzocoronene calculated at the DFT-BP86/TZP level. The current density is displayed in a plane parallel to the molecular framework and 1 bohr above it with the magnetic field chosen perpendicular to the molecular plane. The symbols are used to define the cut planes for the numerical integration of the currents.

3. The Schrödinger equation for a particle of mass m (such as an electron) constrained to move on a line of length L (constrained by $V = 0$ on the line, $V=\infty$ everywhere else) is:

$$-(\hbar^2/2m)\,(d^2/dx^2)\,\psi(x) = E\,\psi(x) \qquad \psi_n(x) = (2/L)^{1/2}\sin[n\pi x/L] \qquad \text{for } 0 \le x \le L$$

(This model system is otherwise known as a particle in a one-dimensional box, or a particle in an infinite potential well). When the model is extended to several non-interacting electrons on the line, and the condition is imposed that no more than two electrons (one with spin up, the other with spin down) may be permitted to have the same value of n, then the model can be used to interpret the ultraviolet spectra of ‘linear’ (all-trans conjugated) polyenes.
The length L may be taken as $(n_C+1)r_{CC}$, where n_C is the number of carbon atoms, and r_{CC} is an average bond length (1.40 Å), because the electron density in the real system extends somewhat beyond the end carbon atoms.

(a) Consider four non-interacting electrons on a line that is a model for the pi system of butadiene. Derive the general expressions for energy eigenvalues and the eigenfunctions for the model system. [HINT: Use separation of variables.] Invoking the condition that no more than two electrons may be permitted to have the same value of n, find the energy eigenvalue associated with the ground state of this model system. What is the eigenfunction?

(b) Suppose that transitions between states can be induced by light of the appropriate wavelength. Suppose that the peak intensity for the n→n′ transition depends on the square of the integral $\int \psi_n^* \, x \, \psi_{n'} \, dx$. For which pairs of n and n′ is the intensity not zero (that is, when does the integral not vanish)? Derive the general result, and fill in the table of integrals.
HINT: $(2/L)\int_0^L x\bullet\sin(n\pi x/L)\bullet\sin(n'\pi x/L)\,dx$ is evaluated by changing variables $\pi x/L = s$, which means that the upper limit of integration becomes $s = \pi$ and the lower limit is $s=0$.
Use the identity $2\bullet\sin(ns)\bullet\sin(n's) = \cos[(n - n')s] - \cos[(n + n')s]$,
and do $(n - n')$, $(n + n')$ = even, separately from odd.

n \ n′	1	2	3	4	5	6	7	...
1	0		0		0		0	
2		0		0		0		0
3	0		0		0		0	
4		0		0		0		0
5	0		0		0		0	
6		0		0		0		0
7	0		0		0		0	
...		0		0		0		0

(c) What two states of the 4-electron system are participating in the n→n′ transition? Describe what you mean, using diagrams, and identify the functions and energies involved.
Predict the wavelengths of the first UV band of butadiene.

(d) Apply the model to hexatriene and octatriene and predict those as well.
Compare with the experimentally observed absorption bands in the ultraviolet spectra: butadiene 217 nm; hexatriene 251 nm; octatriene 304 nm.

Some conjugated polyenes of biochemical importance are carotenoids. For example β carotene is a “linear” polyene of 18 carbons terminated by two partially saturated rings.