

## Problem Set PS05

ISSUED: 2/14/02 Due: 2/21/02

Prof. Darin J. Ulness

Name \_\_\_\_\_

**Instructions.** Complete all questions before class on the due date. You are encouraged to work together. Be sure to struggle with the problem before seeking help. Many of the exercises are very similar to problems in the book. Understanding the solution to these problems will be helpful in completing the assigned exercises.

### Mathematical Exercises

1. Evaluate the Fourier transform of  $f(t) = \Theta(t)e^{-\alpha t+i\omega t}$  by hand. Check your result using MATHEMATICA. Sketch a plot of the real and imaginary parts for both  $f(t)$  and  $\tilde{f}(\omega)$ .
2. Evaluate the Fourier transform of  $f(t) = e^{-\alpha|t|+i\omega t}$  by hand. Check your result using MATHEMATICA. Sketch a plot of both  $f(t)$  and  $\tilde{f}(\omega)$ .

### Exercises

3. We saw that for a vibration to be IR allowed the dipole must change during the vibration. In more mathematical terms, a transition is IR allowed if

$$\left| \int_{\text{space}} \psi_{\text{final}}^* \vec{x} \psi_{\text{initial}} d\Omega \right|^2 \neq 0.$$

It is IR forbidden if the above integral is equal to zero. For a one dimensional Harmonic oscillator this reduces to

$$\left| \int_{-\infty}^{\infty} \psi_{\text{final}}^* x \psi_{\text{initial}} dx \right|^2 \neq 0.$$

Convince yourself by means of a few examples that  $\Delta n = \pm 1$  is a selection rule for the harmonic oscillator. That is, show

$$\left| \int_{-\infty}^{\infty} \psi_{\text{final}}^* x \psi_{\text{initial}} dx \right|^2 = 0$$

when the final and initial states differ by more than one vibrational quanta.

4. In analogy with the previous problem deduce the selection rules for a particle in a box. A good way to do this is to set up a nested table in MATHEMATICA and then inspect the results to find a pattern.
5. Let's say we are interested in calculating the Franck–Condon factors for a transition from one box to another box. Taking the length of the ground state box to be  $a = 1$  and the length of the excited state box to be  $a = 3/4$ . Both boxes start at  $x = 0$ . Assume that before excitation the system is in the lowest energy level of the ground state box. Plot the Franck–Condon factors for this type of transition.
6. Repeat the above problem but now center the excited state box over the ground state box. That is the excited state box starts at  $x = 1/8$ .

## Conceptual Problems

7. An active area of research these days involves the theoretical and experimental investigation of spectral line broadening mechanisms in liquid phase spectroscopy. These studies provide much useful information including a deepening of our understanding of how molecules interact with their environment. There are two classes of line broadening mechanisms i) homogeneous and ii) inhomogeneous. These mechanisms are distinguished according to their time scales. Homogeneous broadening mechanisms are processes which occur much faster than the speed of the instrument making the measurement. Conversely Inhomogeneous mechanisms occur on a time scale much slower than the instrument making the measurement. In pure homogeneous process all the molecules that contribute to the observed signal rapidly sample many local environments. This broadens the contribution of each individual molecule. That is the signal arising from each molecule is itself broad and is very much like the signal from any other molecule. In the pure inhomogeneous case, each molecule is “frozen” in its own local environment. Therefore although the signal from any one molecule is rather narrow, the observed signal is the sum of the signals from all the molecules each of which has a slightly different central frequency. Thus the observed spectral line is broad. In real systems both mechanisms are at work, however many times one of the mechanisms dominate.

- (a) Based on the above discussion and your chemical intuition, how do think the relative contribution of homogeneous and inhomogeneous broadening goes with temperature.
- (b) Based on the above discussion and your chemical intuition, how do think the relative contribution of homogeneous and inhomogeneous broadening goes with viscosity.
- (c) A dye is embedded in plastic, which mechanism would you suspect contributes most the broadening
- (d) In a regular Raman experiment one of the strong vibrational line of liquid pyridine is about  $1\text{cm}^{-1}$  broad. In a SERS (surface enhanced Raman scattering) experiment the Raman signal is enormously enhanced when pyridine adsorbs to a rough silver surface. All one sees in the SERS spectrum is the signal coming from the absorbed pyridine molecules. The same line as seen in the regular Raman experiment is now about  $10\text{cm}^{-1}$  broad. Assuming an inhomogeneous broadening mechanism, what does this say about the kinetics of the adsorption process. That is, when a pyridine molecule sticks to the surface does it come off right a way and get replaced by a new pyridine or does it stay adsorbed for longer period of time?
- (e) Try to draw a picture that illustrates the difference between homogeneous and inhomogeneous broadening.

8. What is the Stokes shift?

9. Sketch the ground and first excited electronic energy levels for the following cases

Force Constant	Equilibrium Position
$k_{\text{ground}} > k_{\text{excited}}$	$R_{eq,\text{ground}} = R_{eq,\text{excited}}$
$k_{\text{ground}} > k_{\text{excited}}$	$R_{eq,\text{ground}} < R_{eq,\text{excited}}$
$k_{\text{ground}} < k_{\text{excited}}$	$R_{eq,\text{ground}} < R_{eq,\text{excited}}$
$k_{\text{ground}} > 0, k_{\text{excited}} = 0$	--

10. Does the following data for oxygen make sense? Explain

Electronic level	$R_{eq}$	$B_e$
ground	1.208Å	1.46cm <sup>-1</sup>
first excited	1.216Å	1.43cm <sup>-1</sup>
second excited	1.604Å	0.82cm <sup>-1</sup>

### Reflective Exercises

11. Read the following letter by Mark Friesel that appearing in the February 2001 issue of *Physics Today*. The writer of the letter categorizes rigorous intellectual pursuit into three categories: religion, philosophy and science and then discusses the fundamental underpinnings of each.

- What does the writer list as the fundamental aspects of religion, philosophy and science? Do you agree?
- How are these fundamental principles used to resolve a logic conflicts *within* the category?
- Is it possible to resolve logic conflicts *between* categories?
- Is there value in having three (or more) categories of rigorous intellectual pursuit? Can and should one category influence the other?
- Is it possible for a single individual to “exist” in more than one of these categories?

lar environment. This may have implications for the question of the origin of life.

## References

1. S. Kwok, K. Volk, B. J. Hrivnak, *Astrophys. J.* **345**, L51 (1989).
2. K. Volk, S. Kwok, B. J. Hrivnak, *Astrophys. J.* **516**, L99 (1999).
3. R. Papoular, *Astron. Astrophys.* **362**, L9 (2000).

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## Does Religion Prize Misdemeanors?

The Templeton Prize for Progress in Religion (see, for example, *PHYSICS TODAY*, May 2000, page 53) may have an undesirable consequence for science. The prize (with exceptions) goes to those who try to create commonality between religion and science, but it may also lead some scientists to compromise their integrity.

When scientists who never wrote a word about religion are suddenly writing books about “god particles” and the like, it indicates to me that the authors consider integrity to be a convenience, truth to be malleable, and both to be subservient to money. Why, then, should anyone trust their research?

The subjects of rigorous intellectual pursuit can be divided into three major categories: science, philosophy, and religion. Religion is based on belief in certain tenets: a god or gods with certain attributes, a priest or seer who can dictate the will of the deity, and perhaps a book of divine laws. Such beliefs do not preclude the use of logic by believers, and a rational investigation of the observable universe can be made based on these beliefs, as can attempts to address philosophical questions. However, if a conflict arises between religious beliefs and the rational implications of those beliefs, or between belief and observation, it is logic or observation that must be perceived as wrong. As an example, given what we know of human physiology, we understand that there is no virgin birth in humans because conception requires

the joining of sperm and egg. Yet Christians believe in virgin birth and therefore, to the believer such an occurrence must be possible, scientific considerations notwithstanding. Questioning the belief is not permitted. In brief, a defining principle of religion is that its fundamental tenets are accepted by its followers to be true beyond question.

In philosophy, axioms and rules of logic are fundamental. These may vary depending on the specific topic being addressed and may be investigated using yet other rules and axioms. The subject of an investigation may be religion and the observable universe, but if a conflict occurs then all elements—the beliefs, the rules of logic, and the axioms—may be questioned, because only the use of a logical system is fundamental to philosophy.

Science is based on observation. And a logical structure is created to describe and unite observations. A defining principle of science is that any conflict between observation and logic or between observation and religious belief, is resolved in favor of repeated observations.

I do not mean to propose that we have evolved religion, science, and philosophy in quarantine from each other or from other intellectual activity—art, for example. Yet it appears that science cannot and does not address religious questions at all. The truth of religious belief, by definition lacking any fundamental connection with observation, cannot be meaningfully evaluated by scientific methods. Nor can the truth or reality of scientific principles be meaningfully evaluated by applying the tenets of a religion, based as the latter is on belief.

Within each category, questions may arise that cannot be adequately answered by referral to the category's basic tenets. An individual may perhaps resolve such questions to his own satisfaction by taking refuge in other tenets. However, if a scientist chooses to accept as a matter of faith that Planck's constant is a fundamental quantity, this does not make science a religion, nor imply that religion and science share some fundamental commonality. A religious believer may similarly accept observations as true, but this does not make his religion a science.

Particularly in the context of ongoing attempts by American religious conservatives to infuse public

education with their religion, it seems to me that the Templeton Prize is little more than an incentive for them to continue such an effort. It also is a bribe—one that has successfully lured more than one well-known scientist into becoming a spokesman for the right-wing religious cause.

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## Szilard Endorsed Nuclear Medicine by Example

The excellent review of radionuclide therapy by Bert M. Coursey and Ravinder Nath (*PHYSICS TODAY*, April 2000, page 25) reminded me of a story I heard while conferring with the late Jonas Salk on his controversial idea of using an HIV vaccine to treat AIDS.

Leo Szilard, who is best known for obtaining an early patent on the fission bomb (as a method of “producing new elements”), was diagnosed with bladder cancer. Standard treatment consisted of surgery to debulk the tumor along with the *in situ* use of bacillus Calmette-Guérin (BCG), a tuberculosis vaccine, to stimulate the immune system. Apparently, Szilard declined this treatment and instead accepted radiation therapy. The way I heard it, Szilard consulted with Salk, celebrated for developing the first polio vaccine, and Szilard subsequently had a radioactive sliver implanted in his bladder. The procedure apparently helped cure his cancer.

I have no way of knowing how much of this story is accurate. But it would be interesting if the inventor of the atomic bomb had made a personal choice that served to encourage the medical use of radioactive isotopes. More recently, the term “nuclear magnetic resonance” had to be changed to “magnetic resonance imaging” because the public tends to think of anything “nuclear” as inherently dangerous. At least Szilard would have had a better perspective on what is and isn't dangerous.

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①  $\int_{-\infty}^{\infty} \delta(x) e^{-\alpha x + i\omega x} e^{i\omega x} dx = \int_0^{\infty} e^{-(\alpha - i(\omega_0 + \omega))x} dx$

$\frac{1}{\alpha - i(\omega_0 + \omega)}$

This differs from Mathematica by a factor of  $\frac{1}{\sqrt{2\pi}}$  because of the choice of convention

②  $\int_{-\infty}^{\infty} e^{-\alpha|t|} e^{i\omega t} e^{i\omega t} dt = \int_{-\infty}^0 e^{+\alpha t + i(\omega_0 + \omega)t} dt + \int_0^{\infty} e^{-\alpha t + i(\omega_0 + \omega)t} dt$

$= \frac{1}{\alpha + i(\omega_0 + \omega)} + \frac{1}{\alpha - i(\omega_0 + \omega)} = \frac{\alpha}{\alpha^2 + (\omega_0 + \omega)^2}$

③

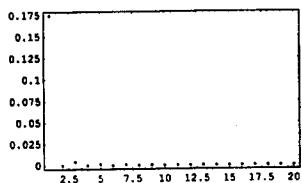
```
psi[n_, x_] := Exp[-(1/2) x^2] HermiteH[n, x]
Table[Integrate[psi[j, x] x psi[k, x], {x, -Infinity, Infinity}]^2,
{3, 0, 5}, {k, 0, 5}] // MatrixForm
```

0	π	0	0	0	0
π	0	16π	0	0	0
0	16π	0	576π	0	0
0	0	576π	0	36864π	0
0	0	0	36864π	0	3686400π
0	0	0	0	3686400π	0

⑥

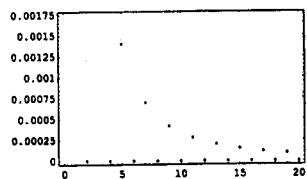
```
In[5] := f02 = N[Table[Integrate[psi[j, x - 1/8, 3/4] psi[k, x, 1], {x, 1/8, 7/8}]^2, {3, 1, 20}]];
```

```
In[6] := ListPlot[Chop[f02], PlotRange -> All, Frame -> True]
```



Out[6] - Graphics -

```
In[8] := ListPlot[Chop[f02], Frame -> True]
```



Blow up of

④

```
psi[n_, x_] := Sin[n Pi x / a]
```

```
Table[Integrate[psi[j, x] x psi[k, x], {x, 0, a}]^2, {3, 1, 7}, {k, 1, 7}] // MatrixForm
```

$\frac{4}{15}$	$\frac{64}{315}$	0	$\frac{2048}{30315}$	0	$\frac{32768}{1300455}$	0
$\frac{64}{315}$	$\frac{4}{15}$	$\frac{224}{225}$	0	$\frac{14080}{110115}$	0	$\frac{11008}{110115}$
0	$\frac{224}{225}$	$\frac{4}{15}$	$\frac{2204}{2205}$	0	$\frac{64}{15}$	0
$\frac{2048}{30315}$	0	$\frac{2204}{2205}$	$\frac{4}{15}$	$\frac{6400}{33015}$	0	$\frac{11008}{110115}$
0	$\frac{64}{15}$	0	$\frac{6400}{33015}$	$\frac{4}{15}$	$\frac{14080}{110115}$	0
$\frac{32768}{1300455}$	0	$\frac{64}{15}$	0	$\frac{14080}{110115}$	$\frac{4}{15}$	$\frac{11008}{110115}$
0	$\frac{11008}{110115}$	0	$\frac{11008}{110115}$	0	$\frac{11008}{110115}$	$\frac{4}{15}$

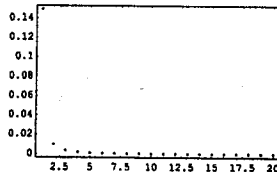
⑤

```
In[1] := psi[n_, x_, a_] := Sin[n Pi x / a]
```

```
In[2] := f0 = Table[Integrate[psi[j, x, 3/4] psi[k, x, 1], {x, 0, 3/4}]^2, {3, 1, 20}]
```

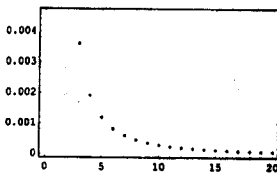
```
Out[2] = { $\frac{72}{49\pi^2}$ ,  $\frac{288}{3025\pi^2}$ ,  $\frac{8}{225\pi^2}$ ,  $\frac{1152}{81009\pi^2}$ ,  $\frac{1800}{132881\pi^2}$ ,  $\frac{32}{3989\pi^2}$ ,  $\frac{3528}{600625\pi^2}$ ,  $\frac{4608}{1030225\pi^2}$ ,  $\frac{72}{7200}$ ,  $\frac{8712}{8112}$ ,  $\frac{128}{128}$ ,  $\frac{12168}{14112}$ ,  $\frac{20449\pi^2}{2531281\pi^2}$ ,  $\frac{3713329\pi^2}{3713329\pi^2}$ ,  $\frac{65025\pi^2}{65025\pi^2}$ ,  $\frac{7263025\pi^2}{9778129\pi^2}$ ,  $\frac{200}{18432}$ ,  $\frac{20808}{288}$ ,  $\frac{25992}{28800}$ ,  $\frac{159201\pi^2}{16703569\pi^2}$ ,  $\frac{21298225\pi^2}{330625\pi^2}$ ,  $\frac{33258289\pi^2}{33258289\pi^2}$ ,  $\frac{40844801\pi^2}{40844801\pi^2}$ }
```

```
In[3] := ListPlot[f0, PlotRange -> All, Frame -> True]
```



Out[3] - Graphics -

```
In[4] := ListPlot[f0, Frame -> True]
```



Out[4] - Graphics -

blow up of

⑦ see last year's answers

⑧ your words

⑨ see last year's answers

⑩ see last year's answers

⑪ your words