

Name:

When you hand in your quizzes,

- get a copy of the answer key from James.
- get a copy of the evaluation form.

You can decide whether you want to return the form to Josie Petrie (in the main chemistry office) or give them to James to return.

The exam is on April 10th. I am trying to schedule it for the afternoon, so you can ask me last-minute questions in the morning.

The exam will be about 30-40 short answer/multiple choice plus some problems/derivations. It is very similar to what you've been seeing on the mid-terms.

If it would help you to replace your test grades and your quiz grade with your exam grade, I will replace them. (However, either *everything* counts or *nothing* counts; you can't pick and choose, and drop two tests but not the quizzes!)

You get one drop grade: either the lowest test score, the quiz average, or half the final exam (which counts the same as the two tests, combined).

There are *four* drop grades for quizzes. That is, your top *seven* scores count.

Homework is due by noon on April 12th.

Extra credit homework is due one week after the exam.

Good luck!

Quiz 10,11

Chemistry 3BB3; Winter 2006

1. Write down Fermi's Golden rule.

2. $g \hbar \omega$ represents

- (a) The amplitude of the electric field.
- (b) The transition dipole moment.
- (c) The probability that the light that is shining on the molecule with frequency ω .

3. $\left\langle \Phi_f \left| \sum_{j=1}^N -e \left(\frac{x_j + y_j + z_j}{2} \right) + \sum_{\alpha=1}^P Z_{\alpha} e \left(\frac{X_{\alpha} + Y_{\alpha} + Z_{\alpha}}{2} \right) \right| \Phi_i \right\rangle$ represents

- (a) The amplitude of the electric field.
- (b) The transition dipole moment.
- (c) The probability that the light that is shining on the molecule with frequency ω .

4. The sinc function is defined as

- | | | |
|---|---|---|
| (a) $\text{sinc } x \equiv x \cdot \sin x$ | (e) $\text{sinc } x \equiv \sin^2 x \cos x$ | (i) $\text{sinc } x \equiv x \arcsin x$ |
| (b) $\text{sinc } x \equiv \sin x e^x$ | (f) $\text{sinc } x \equiv x^2 \sin^2 x$ | (j) $\text{sinc } x \equiv x^2 \arcsin x$ |
| (c) $\text{sinc } x \equiv x^{-1} \cdot \sin x$ | (g) $\text{sinc } x \equiv \sin^2 x e^x$ | (k) $\text{sinc } x = x \sin x^{-1}$ |
| (d) $\text{sinc } x \equiv \sin x \cos x$ | (h) $\text{sinc } x \equiv x^{-1} \cdot \sin^2 x$ | (l) $\text{sinc } x = x \sin x^{-1}$ |

5. Write down the time-dependent Schrödinger Equation.

6. For a molecule in the k^{th} excited state of a system, the spatial part of the wave function solves $\hat{H}\psi_k = E_k\psi_k$. Complete the following equation by filling in the "time dependence" of the wave function.

$$\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N; t) = \psi_k(\mathbf{r}_1, \dots, \mathbf{r}_k) \times \left[\right]$$

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7. You want to excite a molecule from an initial state with energy E_i to a final state with energy E_f . What is the *wavelength* of the light that you should shine on the molecule?

- 8,9. Allowed or Forbidden: Is the excitation from the 1S ground state of Beryllium ($1s^2 2s^2$ electron configuration) to the lowest energy 1P state ($1s^2 2p^1 3p^1$ electron configuration) allowed for forbidden? Why?

- 10-14. For each of the following statements, indicate whether the result follows from the weak-field approximation (W), long-time approximation (T), long-wavelength approximation (L), or the Condon approximation (C). (Select all that apply).

_____ Perturbation theory can be used to describe the interaction of radiation with a molecule.

_____ Nonlinear optical effects are not very important.

_____ Vibronic coupling is not very important.

_____ Electric dipole transitions are much more intense than electric quadrupole transitions.

_____ In the absence of broadening, the absorption spectrum of a molecule is a collection of delta-function peaks.

- 15,16. Allowed or Forbidden: Will there be a spectral line associated with the excitation from a π_u^+ orbital to the σ_g^+ orbital in the Carbon Dimer? Why or why not?

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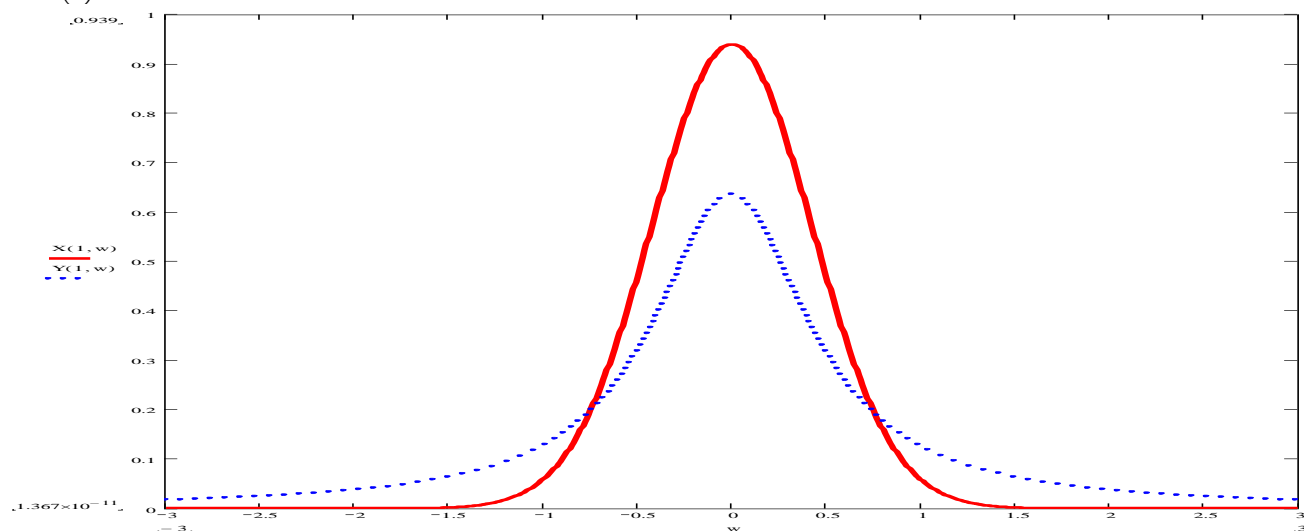
17. Write the equation for the lineshape in terms of the time-dependent transition dipole and the probability of occupying different states. That is, write the equation for the intensity versus frequency function, $I(\omega)$, in terms of fundamental entities like the wave function: don't use the time-correlation function.

18. A Gaussian lineshape is associated with _____ broadening.

- (a) inhomogeneous
- (b) homogeneous

19. One of the following curves is a Gaussian; the other is a Lorentzian. The Gaussian is the

- (a) solid curve.
- (b) dotted curve.



20. These days, a lot of people are interested in doing experiments in ionic liquids, in which the solvent molecules are actually cations and anions. These are not innocuous solvents: because the solvent molecules are ions, they often interact with the solute very strongly. Consequently, the mechanism and/or properties of chemical reactions in an ionic liquid are sometimes very different from the analogous results for a conventional solvent.

But that's complicated. This question is simple. If you measured the spectrum of a molecule dissolved in an ionic liquid, you would expect to observe a _____ lineshape.

- (a) Gaussian
- (b) Lorentzian

Quiz 10,11

Chemistry 3BB3; Winter 2006

1. Write down Fermi's Golden rule.

$$W_{fi} = \frac{2\pi V^2}{\hbar} \left| \langle \Phi_f | \hat{\mu}_x | \Phi_i \rangle \right|^2 g_{\hbar\omega_{fi}} + g_{\hbar\omega_{if}}$$

2. $g_{\hbar\omega}$ represents

- (a) The amplitude of the electric field.
(b) The transition dipole moment.

(c) The probability that the light that is shining on the molecule with frequency ω .

3. $\left\langle \Phi_f \left| \sum_{j=1}^N -e \left(\frac{x_j + y_j + z_j}{2} \right) + \sum_{\alpha=1}^P Z_{\alpha} e \left(\frac{X_{\alpha} + Y_{\alpha} + Z_{\alpha}}{2} \right) \right| \Phi_i \right\rangle$ represents

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5. Write down the time-dependent Schrödinger Equation.

$$\hat{H}\Psi = i\hbar \frac{\partial \Psi}{\partial t}$$

6. For a molecule in the k^{th} excited state of a system, the spatial part of the wave function solves $\hat{H}\psi_k = E_k\psi_k$. Complete the following equation by filling in the "time dependence" of the wave function.

$$\Psi(r_1, \dots, r_N; t) = \psi_k(r_1, \dots, r_k) \times \left[e^{-\frac{iE_k t}{\hbar}} \right]$$

7. You want to excite a molecule from an initial state with energy E_i to a final state with energy E_f . What is the *wavelength* of the light that you should shine on the molecule?

$$\lambda = \frac{c}{\nu} = \frac{2\pi c}{\omega_{fi}} = \frac{2\pi c}{\left(\frac{E_f - E_i}{\hbar} \right)} = \frac{2\pi\hbar c}{E_f - E_i} = \frac{hc}{E_f - E_i}$$

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- 8,9. Allowed or Forbidden: Is the excitation from the 1S ground state of Beryllium ($1s^2 2s^2$ electron configuration) to the lowest energy 1P state ($1s^2 2p^1 3p^1$ electron configuration) allowed for forbidden? Why?

Forbidden; this is a double excitation, so it will be a weak transition.

- 10-14. For each of the following statements, indicate whether the result follows from the weak-field approximation (W), long-time approximation (T), long-wavelength approximation (L), or the Condon approximation (C). (Select all that apply).

___W___ Perturbation theory can be used to describe the interaction of radiation with a molecule.

___W___ Nonlinear optical effects are not very important.

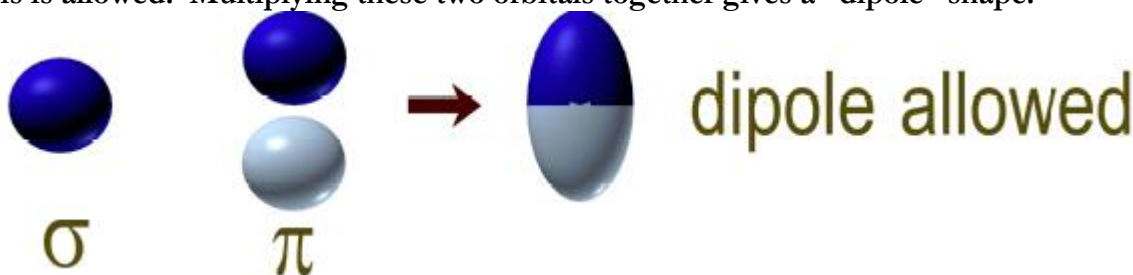
___C___ Vibronic coupling is not very important.

___L___ Electric dipole transitions are much more intense than electric quadrupole transitions.

___T___ In the absence of broadening, the absorption spectrum of a molecule is a collection of delta-function peaks.

- 15,16. Allowed or Forbidden: Will there be a spectral line associated with the excitation from a π_u^+ orbital to the σ_g^+ orbital in the Carbon Dimer? Why or why not?

This is allowed. Multiplying these two orbitals together gives a “dipole” shape:



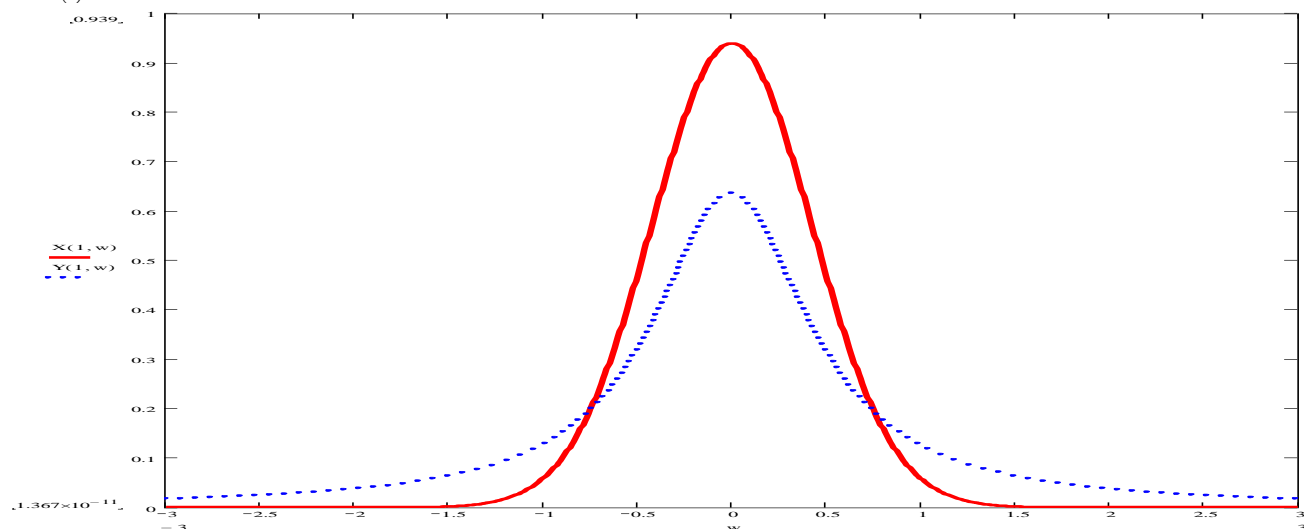
17. Write the equation for the lineshape in terms of the time-dependent transition dipole and the probability of occupying different states. That is, write the equation for the intensity versus frequency function, $I(\omega)$, in terms of fundamental entities like the wave function: don't use the time-correlation function.

$$I(\omega) = \int_{-\infty}^{\infty} \left(\sum_{i=0}^{\infty} p_i \langle \Phi_i | \hat{\mu}(0) \cdot \hat{\mu}(t) | \Phi_i \rangle e^{-i\omega t} \right) dt$$

18. A Gaussian lineshape is associated with _____ broadening.
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