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.
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4. **The sinc function is defined as**

   (a) $\operatorname{sinc}(x) \equiv x \cdot \sin(x)$
   (b) $\operatorname{sinc}(x) \equiv \sin(x)\, e^{x}$
   (c) $\operatorname{sinc}(x) \equiv x^{-1} \cdot \sin(x)$
   (d) $\operatorname{sinc}(x) \equiv \sin(x)\cos(x)$

   (e) $\operatorname{sinc}(x) \equiv \sin^2(x)\cos(x)$
   (f) $\operatorname{sinc}(x) \equiv x^2 \sin^2(x)$
   (g) $\operatorname{sinc}(x) \equiv \sin^2(x)\, e^{x}$
   (h) $\operatorname{sinc}(x) \equiv x^{-1} \cdot \sin^2(x)$

   (i) $\operatorname{sinc}(x) \equiv x \arcsin(x)$
   (j) $\operatorname{sinc}(x) \equiv x^2 \arcsin(x)$
   (k) $\operatorname{sinc}(x) = x(\sin(x))^{-1}$
   (l) $\operatorname{sinc}(x) = (x\sin(x))^{-1}$

5. **Write down the time-dependent Schrödinger Equation.**

6. **For a molecule in the kth 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.**

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

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?**

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? <u>Why?</u>**

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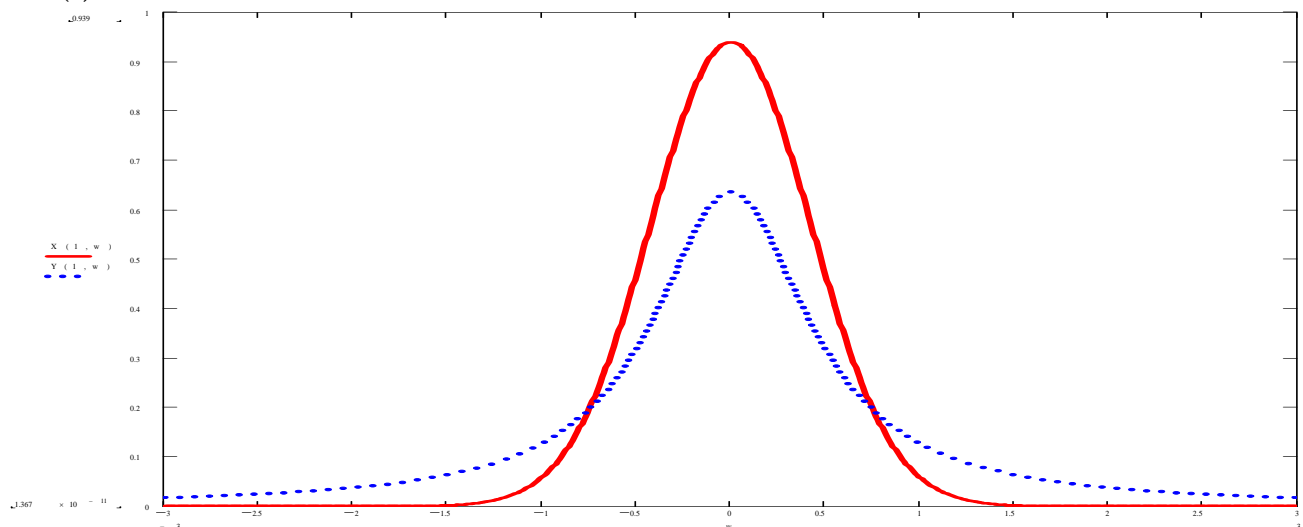
17. Write the equation for the lineshape in terms of the time-dependent transition dipole and the probability of occupying different states. That is, write the equation for the intensity versus frequency function, $I(\omega)$, in terms of fundamental entities like the wave function: <u>don't use the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

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

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1.   Write down Fermi's Golden rule.

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

2. $g\left(\hbar\omega \right)$ represents

   (a)   The amplitude of the electric field.

   (b)   The transition dipole moment.

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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 kth 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.

$$\Psi\left(\mathbf{r}_1, \ldots, \mathbf{r}_N; t \right) = \psi_k\left(\mathbf{r}_1, \ldots, \mathbf{r}_k \right) \times \left[e^{-\frac{iE_k t}{\hbar}} \right]$$

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?

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

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? <u>Why?</u>

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 that electric quadrupole transitions.

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

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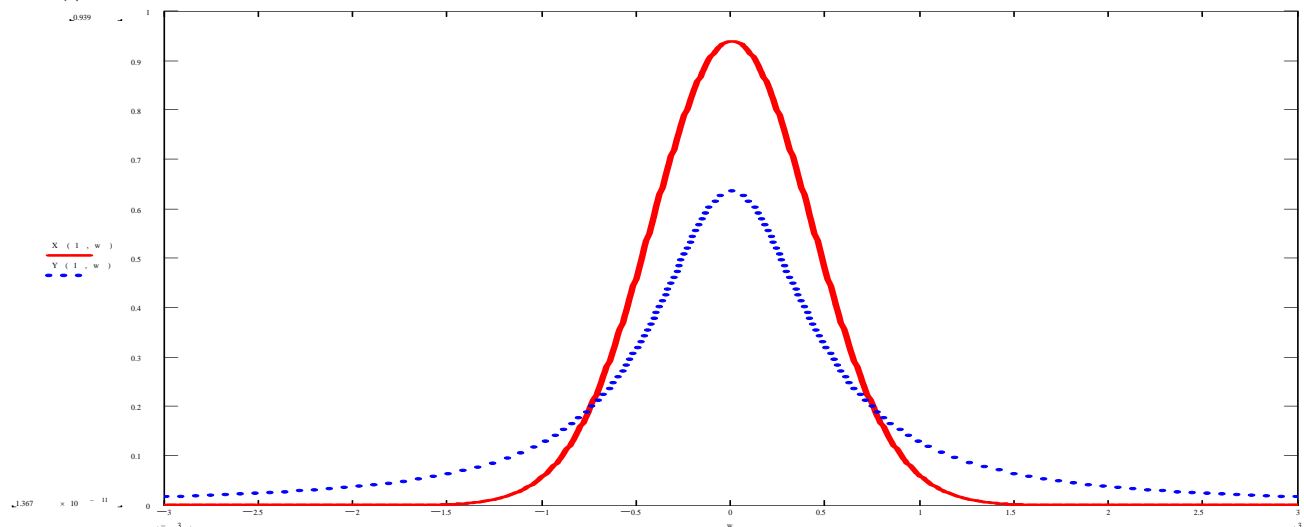**This is allowed. Multiplying these two orbitals together gives a "dipole" shape:**
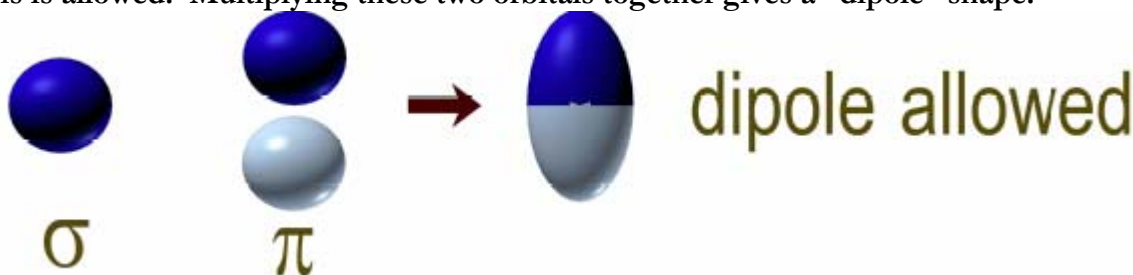
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$$I(\omega) = \int_{-\infty}^{\infty} \left(\sum_{i=0}^{\infty} p_i \left\langle \Phi_i \left| \hat{\mu}(0) \cdot \hat{\mu}(t) \right| \Phi_i \right\rangle e^{-i\omega t} \right) dt$$

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