

Study guide for the second midterm

Chemistry 342, (01:160:342), Spring 2016 Physical Chemistry of Biochemical Systems

For the following, you should understand the concepts, know (have memorized) the key equations, understand what all the symbols mean, and be able to explain the equations in words and to appreciate their context. Please pay close attention to the summaries at the end of Chapters 12 and 13.

1 Chapter 12: Molecular structures and interactions

- Basic wavefunction for a two-electron bond: $\psi(1,2) = [\phi_A(1)\phi_B(2) + \phi_A(2)\phi_B(1)] [\alpha(1)\beta(2) - \alpha(2)\beta(1)]$. Note that for a closed-shell system, ϕ_A would be the same as ϕ_B .
- Combination of orbitals: if $\psi = c_A\phi_A + c_B\phi_B$, then one gets the following simultaneous equations:

$$\begin{aligned}(H_{AA} - ES_{AA})c_A + (H_{AB} - ES_{AB})c_B &= 0 \\ (H_{BA} - ES_{BA})c_A + (H_{BB} - ES_{BB})c_B &= 0\end{aligned}$$

The equation for the allowed values of E :

$$\det \begin{vmatrix} H_{AA} - ES_{AA} & H_{AB} - ES_{AB} \\ H_{BA} - ES_{BA} & H_{BB} - ES_{BB} \end{vmatrix} = 0$$

In the Huckel approximation, this becomes:

$$\det \begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} = 0 \Rightarrow E = \alpha \pm \beta$$

- Coulomb's law: $V = q_1q_2/4\pi\epsilon_0r$
- Lennard-Jones potential: $V_{ij} = B_{ij}/r^{12} - A_{ij}/r^6$
- dipole moments: $\mu_x = \sum_i q_i x_i$ or $\int \rho(x) x dx$

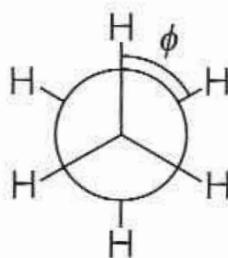
2 Chapter 13: Optical spectroscopy

- Beer-Lambert law: $A = \epsilon cl$, where $A = \log_{10}(I_0/I_t)$
- wave properties: $v\lambda = c$; $\tilde{\nu} = v/c = 1/\lambda$
- stimulated absorption and emission: $rate = NBI$; for spontaneous emission, $rate = NB(8\pi h\nu^3/c^3)$
- explain the nature of fluorescence and phosphorescence; natural lifetime for fluorescence: $\tau_0 = 1/k_f$

- quantum yield: $\phi_f = \frac{\text{number of photons fluoresced}}{\text{number of photons absorbed}} = \tau/\tau_0$
- transition dipole moment $\mu_{0A} = \int \psi_0 \mu \psi_A dV$
- fluorescence resonance energy transfer (FRET) efficiency: $E_{FRET} = r_0^6/(r_0^6 + r^6) = 1 - \tau_{D+A}/\tau_D$
- infrared frequencies: $\omega = 2\pi\nu = (k/\mu)^{1/2}$

3 Sample exam questions

1. Molecules (or atoms) with two unpaired electrons typically are found in singlet and triplet forms. Use the principles of quantum chemistry to explain this. You answer should define the terms singlet and triplet, and should contain approximate wavefunctions for each form. Is the triplet state generally higher or lower in energy than the singlet?
2. Arrange the species O_2^+ , O_2 , O_2^- and O_2^{2-} in order of increasing bond length.
3. We can explore bond torsions in ethane to understand the barrier to internal rotation of one bond relative to another in saturated carbon chains, such as those found in lipids. The potential energy of a CH₃ group in ethane as it is rotated around the C–C bond can be written $V = \frac{1}{2}V_0(1 + \cos 3\phi)$, where ϕ is the azimuthal angle and $V_0 = 11.6$ kJ/mol. What is the change in potential energy between the staggered and eclipsed conformations?



24 Ethane

4. The value of r_0 for FRET quenching of 1.5-I-AEDANS (a donor) and FITC (an acceptor) is 4.9 nm. One amino acid on the surface of a protein was labeled with this donor, and another with this acceptor. The fluorescence quantum yield of 1.5-I-AEDANS was decreased by 10% due to quenching by FITC. What is the distance between the amino acids?