Study guide for the final exam

Chemistry 342, Spring 2016
Wednesday, May 11, 8-11am
Physical Chemistry of Biochemical Systems

Key concepts and equations

The final exam will be comprehensive, with some extra emphasis on material since the second midterm. 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 *Summary* and the *Mathematics Needed* sections at the end of the chapters. Please bring a calculator to the exam. Be sure to *show your work* for each problem.

1 Chapter 10: Enzyme kinetics

- Michaelis-Menten kinetics: initial rate $v_0 = V_{max}[S]/(K_M + [S])$, where $V_{max} = k_2[E]_0$
- Form of a Lineweaver-Burke plot

2 Chapter 11: Basics of quantum mechanics

- Bohr frequency relationship: $\Delta E = h\nu$
- de Broglie relation: $\lambda = h/p$
- Schrodinger equation: $-(\hbar^2/2m)(d^2\psi/dx^2) + U(x)\psi = E\psi$
- Harmonic oscillator: $E_n = (n + \frac{1}{2})h\nu$, where $\nu = \frac{1}{2\pi}\left(\frac{k}{\mu}\right)^{1/2}$
- Coulomb's law: $(q_1 q_2)/(4\pi\varepsilon_0 r)$

3 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: $V = q_1q_2/4\pi\varepsilon_0 r$
- Lennard-Jones potential: $V_{ij} = B_{ij}/r^{12} - A_{ij}/r^6$
- dipole moments: $\mu_x = \sum_i q_i x_i$ or $\int \rho(x)xdx$

4 Chapter 13: Optical spectroscopy

- Beer-Lambert law: $A = \varepsilon cl$, where $A = \log_{10}(I_0/I_t)$
- wave properties: $\nu\lambda = c$; $\tilde{\nu} = \nu/c = 1/\lambda$
- stimuated 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: $\phi_f = \frac{number\, of\, photons\, fluoresced}{number\, of\, photons\, absorbed} = \tau/\tau_0$
- 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: $\omega = 2\pi\nu = (k/\mu)^{1/2}$

5 Chapter 14: Magnetic resonance spectroscopy

- Larmor frequency: $\Delta E = h\nu_L = \gamma\hbar B_0$
- chemical shift: $\delta = \sigma - \sigma_{ref} = [(\nu - \nu_{ref})/\nu] \times 10^6$
- dependence of spin-spin coupling constants on torsion angle: $J = A + B\cos\phi + C\cos(2\phi)$
- inversion recovery experiments: $M(t) = M_0(1 - 2e^{-t/T_1}$
- spin-spin relaxations: $T_2 = 1/(\pi LW)$, where LW=peak width at half height
- Bloch equations: $d\mathbf{M}/dt = -\gamma\mathbf{B}\times\mathbf{M}$; be able to analyze simple pulse sequences, precision, rotating frame descriptions

6 Chapter 15: Macromolecular structure and X-ray diffraction

- von Laue equations: $a(\cos\alpha - \cos\alpha_0) = h\lambda$; similar for Miller indices k and ℓ
- Bragg's law: $n\lambda = 2d_{hkl}\sin\theta$
- structure factors: $F(h,k,l) = \sum_j f_j \exp(2\pi i(hX_j + kY_y + lZ_j) = \int dX \int dY \int dZ \rho(X,Y,Z) \exp(2\pi i(hX + kY + lZ))$
- electron density, by inverse Fourier transform of the structure factors: $\rho(X,Y,Z) = \frac{1}{V}\sum_{hkl} F(h,k,l)\exp(-2\pi i(hX + kY + lZ))$
- understand the basic ideas of molecular replacement and X-ray refinement
- de Broglie wavelength for an electron: $\lambda = h/(2m_e V_c)^{1/2}$, where $V_c = V\left(1 + \frac{eV}{2m_e c^2}\right)$