

Problem Set 2
Physics498:Theoretical Biophysics /Spring 2001
Professor Klaus Schulten

Problem 1: Semiclassical Theory of Electron Transfer

Consider electron transfer described in terms of a system coupled to a classical degree of freedom q (vibration). In the reactant state it has the energy

$$V_r(q) = \frac{1}{2}fq^2 \quad (1)$$

whereas in the product state the energy is

$$V_p(q) = \frac{1}{2}f(q - q_0)^2 + E_{\text{red}} \quad . \quad (2)$$

The rate for the transition $r \rightarrow p$ is described by the formula

$$k_{\text{cl}} = \frac{2\pi}{\hbar} |U|^2 S_{\text{cl}}(0) \quad (3)$$

where U is a coupling constant not considered here. $S_{\text{cl}}(E)$ is given by

$$S_{\text{cl}}(E) = p_0[q(E)] \left| \frac{dq}{dE} \right| \quad (4)$$

where $p_0(q)$ is the classical Boltzmann distribution corresponding to $V_r(q)$ and $q(E)$ is given by inverting

$$E(q) = V_p(q) - V_r(q) \quad . \quad (5)$$

a) Show ($\sigma_{\text{cl}} = k_B T / f$)

$$S_{\text{cl}}(E) = \frac{1}{\sqrt{2\pi\sigma_{\text{cl}}f^2q_0^2}} \exp \left[-\frac{(E_0 - E + \frac{1}{2}fq_0^2)^2}{2f^2q_0^2\sigma_{\text{cl}}} \right] \quad (6)$$

b) Plot k_{cl} as a function of T for values of your choice.

Describe now the initial distribution quantum mechanically. For this purpose define

$$k_{\text{qm}} = \frac{2\pi}{\hbar} |U|^2 S_{\text{qm}}(0) \quad (7)$$

where

$$S_{\text{qm}}(E) = p_{\text{qm}}[q(E)] \left| \frac{dq}{dE} \right| \quad . \quad (8)$$

Here the distribution $p_{\text{qm}}(q)$ is given by

$$p_{\text{qm}}(q') = \text{tr} \rho_0 \delta(q - q') \quad (9)$$

and $q(E)$ is as defined above. In this expression ρ_0 is the density matrix of the oscillator described by $V_r(q)$ and is defined in the basis of eigenstates

$$H_r |\tilde{n}\rangle = \hbar\omega(n + \frac{1}{2}) |\tilde{n}\rangle \quad (10)$$

where

$$H_r = \frac{\hat{p}^2}{2m} + \frac{1}{2} f \hat{q}^2 \quad (11)$$

and ω is the associated frequency $\sqrt{f/m}$.

(c) Show

$$[\rho_0]_{nm} = \delta_{nm} (1 - e^{-\frac{\hbar\omega}{k_B T}}) e^{\frac{\hbar\omega}{2k_B T}} e^{-\frac{\hbar\omega(n+\frac{1}{2})}{k_B T}} \quad (12)$$

(d) (difficult, extra credit)

To determine $p_{\text{qm}}(q)$ use

$$\delta(q - q') = \frac{1}{2\pi} \int_{-\infty}^{\infty} dx e^{ix(q-q')} \quad (13)$$

and then evaluate $\Phi(x)$ defined through

$$\begin{aligned} p_{\text{qm}}(q') &= \frac{1}{2\pi} \int_{-\infty}^{\infty} dx e^{-ixq'} \Phi(x) \\ \Phi(x) &= \text{tr} \rho_0 e^{ixq} \end{aligned} \quad (14)$$

Show

$$\Phi(x) = e^{-\frac{1}{2}\sigma_{\text{qm}}x^2} \quad (15)$$

where

$$\sigma_{\text{qm}} = \frac{\hbar}{2m\omega} \coth \frac{\hbar\omega}{2k_B T} \quad (16)$$

(e) Show that $S_{\text{qm}}(E)$ is given by eq. 6 where σ_{cl} is replaced by σ_{qm} as defined above.

(f) Plot k_{qm} as a function of T . Explain why the value does not vanish for $T \rightarrow 0$ by inspecting $p_{\text{qm}}(q')$ for $T \rightarrow 0$. What is $p_{\text{qm}}(q')$ at $T = 0$?

Problem 2: Average over Radiation Field

Following the class notes '*Interaction of Radiation with matter*', section '*Absorption of Thermal Radiation*' derive that the average $\langle u_\alpha u_\beta \rangle_{\text{rad}}$ is given by

$$\langle u_\alpha u_\beta \rangle_{\text{rad}} = \frac{2}{3} \delta_{\alpha\beta} \quad . \quad (17)$$

Problem 3: Spectrum of Polyenes

Using the web form available at www.ks.uiuc.edu/~ritz/form1.html carry out and analyse a mean field single configuration interaction calculation for polyenes with six $2p_z$ orbitals and six electrons. Assume for the Coulomb interaction between electrons that they repel each other when two electrons 'collide' in one $2p_z$ atomic orbital with repulsion energy $5eV$. For the single electron states assume a Hamiltonian matrix (note: only elements $t_{jk}, j \leq k, t_{jk} \neq 0$ need to be specified in the web form)

$$H = \begin{pmatrix} \epsilon_1 & t & 0 & 0 & 0 & 0 \\ t & \epsilon_2 & t & 0 & 0 & 0 \\ 0 & t & \epsilon_3 & t & 0 & 0 \\ 0 & 0 & t & \epsilon_4 & t & 0 \\ 0 & 0 & 0 & t & \epsilon_5 & t \\ 0 & 0 & 0 & 0 & t & \epsilon_6 \end{pmatrix} \quad (18)$$

where $t = -2.5eV$.

(a) Use the web form to describe hexatriene using $\epsilon_1 = \epsilon_2 = \dots = \epsilon_6 = 0$. Compare the molecular orbital energies and molecular orbital coefficients with the results from a diagonalisation of H in analytical form.

(b) Describe the symmetry of the orbitals in terms of symmetry with respect to rotation around the center of the molecule.

(c) The configurations of electrons in which electrons are excited from an occupied orbital j to an unoccupied orbital k are denoted in the output as $0j0k$. These configurations contain, e.g., in the case of excitation 0304 the single electron orbitals $\Phi_1\Phi_1\Phi_2\Phi_2\Phi_3\Phi_4$ (the ground state is $\Phi_1\Phi_1\Phi_2\Phi_2\Phi_3\Phi_3$, denoted in our output as 0000). State how the excited configurations are classified in two symmetry classes similar to those symmetry classes of the

single electron orbitals. Argue why the Hamiltonian

$$\langle\langle I||H||J\rangle\rangle \quad (19)$$

where

$$\begin{aligned} ||I\rangle\rangle = & \text{ground state, excitations } 3 \rightarrow 4, 3 \rightarrow 5, 3 \rightarrow 6 \\ & 2 \rightarrow 4, 2 \rightarrow 5, 2 \rightarrow 6, 1 \rightarrow 4, 1 \rightarrow 5, 1 \rightarrow 6 \end{aligned} \quad (20)$$

has block diagonal form

$$H = \begin{pmatrix} H_{00} & 0 & 0 \\ 0 & H_{11} & 0 \\ 0 & 0 & H_{22} \end{pmatrix} \quad (21)$$

where H_{00} is a 1×1 -matrix, H_{11} is a 5×5 - matrix and H_{22} is a 4×4 -matrix. Which configurations $||I\rangle\rangle$ are involved in the matrices H_{00} , H_{11} and H_{22} ?

(d) Which excitations, those of H_{11} or those of H_{22} do you expect to have non-vanishing transition dipole moments (TDM) and why?

(e) Design yourself a molecule by varying t , to make hexatrien absorb blue, green and red light.

Due Tuesday March 20th in class