Problem Set 1
Physics 498TBP / Spring 2002
Solutions

Problem 1: Optical Properties of Ring of BChls

(a) Let us first construct the Hamiltonian in the basis of $\{|\alpha\rangle : \alpha = 1, \ldots, 2N\}$ where $N = 8$. The diagonal elements are assumed to be the same. The nearest-neighbor interaction energies are also the same because of the rotational symmetry of the ring structure. Thus, the Hamiltonian has the form of

$$H = \begin{pmatrix} \epsilon_0 & v & & & & v \\ v & \epsilon_0 & v & & & \\ & v & \epsilon_0 & & & \\ & & & \ddots & & \\ & & & & \epsilon_0 & v \\ v & & & & v & \epsilon_0 \end{pmatrix}. \tag{1}$$

The diagonal elements are $\epsilon_0 = 1.6\,\text{eV}$. We now calculate v:

$$v = \langle 1|H|2\rangle = \frac{\vec{d}_1 \cdot \vec{d}_2}{r_{12}^3} - \frac{3(\vec{r}_{12} \cdot \vec{d}_1)(\vec{r}_{12} \cdot \vec{d}_2)}{r_{12}^5}. \tag{2}$$

Here,

$$r_{12} = 2 \cdot 25\,\text{Å} \cdot \sin(\pi/2N) = 9.75\,\text{Å} \tag{3}$$

$$\vec{d}_1 \cdot \vec{d}_2 = -d_0^2 \cos(\pi/N) = -92.4\,\text{Debye}^2 \tag{4}$$

$$(\vec{r}_{12} \cdot \vec{d}_1)(\vec{r}_{12} \cdot \vec{d}_2) = -r_{12}^2 d_0^2 \cos^2(\pi/2N) = -9152.9\,\text{Debye}^2\text{Å}^2. \tag{5}$$

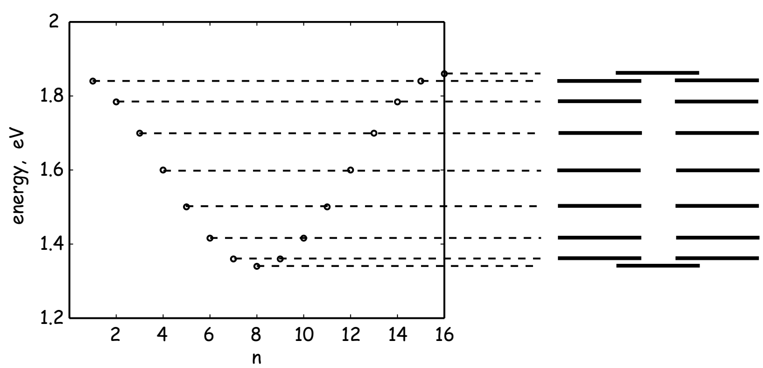
Plugging these values into Eq. 2 we find $v = 0.13\,\text{eV}$.

In class we have learned that the eigenstates (stationary states) of the Hamiltonian (Eq. 1) can be written as

$$|\tilde{n}\rangle = \frac{1}{\sqrt{2N}} \sum_{\alpha=1}^{2N} \mathrm{e}^{in\alpha\pi/N} |\alpha\rangle, \quad n = 1, \ldots, 2N. \tag{6}$$

The corresponding energies are

$$\epsilon_n = \epsilon_0 + 2v \cos\frac{n\pi}{N} = (1.6 + 2 \cdot 0.13 \cdot \cos\frac{n\pi}{8})\,\text{eV}. \tag{7}$$



(b) Transition dipole moments:

$$\begin{aligned}\langle 0|\vec{r}|\tilde{n}\rangle &= \frac{1}{4}\sum_{\alpha=1}^{16} \mathrm{e}^{in\alpha\pi/8}\langle 0|\vec{r}|\alpha\rangle \\ &= \frac{1}{4}\sum_{\alpha=1}^{16} \mathrm{e}^{in\alpha\pi/8}\vec{d}_\alpha/e \\ &= \frac{1}{4}\sum_{\alpha=1}^{16} \mathrm{e}^{in\alpha\pi/8}\frac{d_0}{e}(\hat{x}\cos\frac{9\pi\alpha}{8}+\hat{y}\sin\frac{9\pi\alpha}{8}),\end{aligned} \tag{8}$$

where $\hat{x}$ and $\hat{y}$ are the unit vectors in x and y direction, respectively. Evaluating this formula for $n = 1, \ldots, 16$, we find

$$\langle 0|\vec{r}|\tilde{n}\rangle = \begin{cases} (d_0/e)(2\hat{x}-2i\hat{y}) = (20/e)(\hat{x}-i\hat{y})\,\text{Debye}, & n=7 \\ (d_0/e)(2\hat{x}+2i\hat{y}) = (20/e)(\hat{x}+i\hat{y})\,\text{Debye}, & n=9 \\ 0, & \text{otherwise.} \end{cases} \tag{9}$$

Transition rates can be calculated from the transition dipole moments through the formula

$$k_{0\to\tilde{n}} = N_{\omega_n}\frac{4e^2\omega_n^3}{3c^3\hbar}|\langle 0|\vec{r}|\tilde{n}\rangle|^2, \tag{10}$$

where N_ω is the number of photons of energy $\hbar\omega$. Using the energy spectrum obtained in Eq. 7, we find

$$k_{0\to\tilde{n}} = \begin{cases} 0.32\,N_{\omega_7}/\text{ns}, & n=7 \\ 0.32\,N_{\omega_9}/\text{ns}, & n=9 \\ 0, & \text{otherwise.} \end{cases} \tag{11}$$

In fact, $k_{0\to\tilde{7}} = k_{0\to\tilde{9}}$ because $\omega_7 = \omega_9$.

Transition rate for individual BChls can be calculated in a similar way:

$$k_{0\to\alpha} = N_{\omega_0}\frac{4e^2\omega_0^3}{3c^3\hbar}|\langle 0|\vec{r}|\alpha\rangle|^2. \tag{12}$$

Here $\hbar\omega_0 = \epsilon_0 = 1.6\,\text{eV}$ and $|\langle 0|\vec{r}|\alpha\rangle|^2 = |\vec{d}_\alpha/e|^2 = (100/e^2)\,\text{Debye}$. Therefore,

$$k_{0\to\alpha} = 0.065\,N_{\omega_0}/\text{ns}. \tag{13}$$

Assuming $N_{\omega_{7,9}} \approx N_{\omega_0}$,

$$\frac{k_{0\to\tilde{7},\tilde{9}}}{k_{0\to\alpha}} \approx 4.9. \tag{14}$$

Problem 2: Semiclassical Theory of Electron Transfer

(a) $p_0(q)$ is the Boltzmann distribution corresponding to $V_r(q) = fq^2/2$:

$$p_0(q) = \sqrt{\frac{\beta f}{2\pi}}\,\mathrm{e}^{-\beta f q^2/2}, \tag{15}$$

where the prefactor was determined by the normalization condition, namely $\int_{-\infty}^{\infty} \mathrm{d}q\, p_0(q) = 1$. By inverting

$$E(q) = V_p(q) - V_r(q) = f(q-q_0)^2/2 + E_0 - fq^2/2, \tag{16}$$

we find

$$q(E) = \frac{1}{fq_0}\left(\frac{1}{2}fq_0^2 + E_0 - E\right) \tag{17}$$

and

$$\left|\frac{\mathrm{d}q}{\mathrm{d}E}\right| = \frac{1}{fq_0}. \tag{18}$$

Therefore,

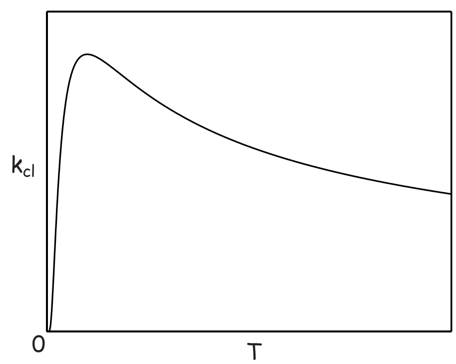
$$S_{\mathrm{cl}}(E) = p_0[q(E)]\left|\frac{\mathrm{d}q}{\mathrm{d}E}\right| \tag{19}$$

$$= \sqrt{\frac{\beta f}{2\pi}}\,\exp\left[-\frac{\beta f}{2(fq_0)^2}\left(E_0 - E + \frac{1}{2}fq_0^2\right)^2\right]\frac{1}{fq_0} \tag{20}$$

$$= \frac{1}{\sqrt{2\pi\sigma_{\mathrm{cl}}f^2q_0^2}}\,\exp\left[-\frac{(E_0 - E + fq_0^2/2)^2}{2f^2q_0^2\sigma_{\mathrm{cl}}}\right]. \tag{21}$$

(b)

$$k_{\mathrm{cl}} = \frac{2\pi}{\hbar}|U|^2 S_{\mathrm{cl}}(0) = \frac{2\pi}{\hbar}|U|^2\frac{1}{\sqrt{2\pi\sigma_{\mathrm{cl}}f^2q_0^2}}\,\exp\left[-\frac{(E_0 + fq_0^2/2)^2}{2f^2q_0^2\sigma_{\mathrm{cl}}}\right]. \tag{22}$$



(c) The density operator is

$$\rho_0 = \frac{1}{Z}\,\mathrm{e}^{-\beta H_r}, \tag{23}$$

where Z is the partition function. In the basis of energy eigenstates,

$$[\rho_0]_{nm} = \langle\tilde{n}|\frac{1}{Z}\,\mathrm{e}^{-\beta H_r}|\tilde{m}\rangle = \frac{1}{Z}\langle\tilde{n}|\tilde{m}\rangle\mathrm{e}^{-\beta\hbar\omega(m+1/2)} = \frac{1}{Z}\delta_{nm}\mathrm{e}^{-\beta\hbar\omega(n+1/2)}. \tag{24}$$

The partition function Z can be determined by the normalization condition:

$$1 = \mathrm{tr}\rho_0 = \sum_{n=0}^{\infty}[\rho_0]_{nn} = \frac{1}{Z}\sum_{n=0}^{\infty}\mathrm{e}^{-\beta\hbar\omega n}\mathrm{e}^{-\beta\hbar\omega/2} = \frac{1}{Z}\,\mathrm{e}^{-\beta\hbar\omega/2}\left(1 - \mathrm{e}^{-\beta\hbar\omega}\right)^{-1}. \tag{25}$$

Therefore,

$$Z = \left(\mathrm{e}^{\beta\hbar\omega/2} - \mathrm{e}^{-\beta\hbar\omega/2}\right)^{-1}, \tag{26}$$

and

$$[\rho_0]_{nm} = \delta_{nm}\left(1 - \mathrm{e}^{-\beta\hbar\omega}\right)\mathrm{e}^{\beta\hbar\omega/2}\mathrm{e}^{-\beta\hbar\omega(n+1/2)}. \tag{27}$$

(d)

$$p_{\rm qm}(q') = {\rm tr}[\rho_0\delta(q-q')] = {\rm tr}\left[\rho_0\frac{1}{2\pi}\int_{-\infty}^{\infty}{\rm d}x\,{\rm e}^{ix(q-q')}\right] = \frac{1}{2\pi}\int_{-\infty}^{\infty}{\rm d}x\,{\rm e}^{-ixq'}\Phi(x) \tag{28}$$

$$\Phi(x) \equiv {\rm tr}[\rho_0{\rm e}^{ixq}] = \left\langle{\rm e}^{ixq}\right\rangle_0, \tag{29}$$

where $\langle\cdot\rangle_0$ denotes the ensemble average with respect to the density operator ρ_0. We now turn to the second-quantization representation:

$$q = \sqrt{\frac{\hbar}{2m\omega}}(a+a^\dagger), \tag{30}$$

where a is the lowering operator and $a^\dagger$ is the raising operator. Introducing $\xi \equiv (\hbar/2m\omega)^{1/2}$ for simplicity, we have

$$\Phi(x) = \left\langle{\rm e}^{ix\xi(a+a^\dagger)}\right\rangle_0. \tag{31}$$

Using the identity,

$${\rm e}^A{\rm e}^B = {\rm e}^{A+B+[A,B]/2} \quad \text{if } [A,B] \text{ is a complex number}, \tag{32}$$

we factorize the exponential function:

$$\Phi(x) = {\rm e}^{-x^2\xi^2/2}\left\langle{\rm e}^{ix\xi a^\dagger}{\rm e}^{ix\xi a}\right\rangle_0 = {\rm e}^{-x^2\xi^2/2}\left\langle\sum_{m=0}^{\infty}\frac{1}{m!}(ix\xi a^\dagger)^m\sum_{n=0}^{\infty}\frac{1}{n!}(ix\xi a)^n\right\rangle_0, \tag{33}$$

where exponential functions were Taylor-expanded in the last step. Among the possible pairs of (m,n), only those satisfying $m=n$ survive the ensemble average:

$$\Phi(x) = {\rm e}^{-x^2\xi^2/2}\sum_{n=0}^{\infty}\frac{1}{n!n!}(ix\xi)^{2n}\left\langle a^{\dagger n}a^n\right\rangle_0. \tag{34}$$

By Wick's theorem, we have

$$\langle a^{\dagger n}a^n\rangle_0 = n!\langle a^\dagger a\rangle_0^n, \tag{35}$$

where the ensemble average $\langle a^\dagger a\rangle_0$ can be calculated in the energy eigenbasis:

$$\begin{aligned}
\langle a^\dagger a\rangle_0 &= \sum_{m=0}^{\infty}\langle\tilde{m}|\frac{1}{Z}{\rm e}^{-\beta H_r}a^\dagger a|\tilde{m}\rangle \\
&= \frac{1}{Z}\sum_m {\rm e}^{-\beta\hbar\omega(m+1/2)}m = \frac{1}{Z}\sum_m {\rm e}^{-\beta\hbar\omega(m+1/2)}\left(m+\frac{1}{2}-\frac{1}{2}\right) \\
&= \frac{1}{Z}\frac{\partial}{\partial(-\beta\hbar\omega)}\sum_m {\rm e}^{-\beta\hbar\omega(m+1/2)} - \frac{1}{2Z}\sum_m {\rm e}^{-\beta\hbar\omega(m+1/2)} \\
&= \frac{1}{Z}\frac{\partial}{\partial(-\beta\hbar\omega)}Z - \frac{1}{2} = \frac{1}{2}\left(\coth\frac{\beta\hbar\omega}{2}-1\right).
\end{aligned} \tag{36}$$

In the last step we used the partition function obtained in Eq. 26. Combining Eqs. 34, 35, and 36 we find

$$\begin{aligned}
\Phi(x) &= {\rm e}^{-x^2\xi^2/2}\sum_{n=0}^{\infty}\frac{1}{n!}(ix\xi)^{2n}\frac{1}{2^n}\left(\coth\frac{\beta\hbar\omega}{2}-1\right)^n \\
&= {\rm e}^{-x^2\xi^2/2}\exp\left[-\frac{x^2\xi^2}{2}\left(\coth\frac{\beta\hbar\omega}{2}-1\right)\right] = {\rm e}^{-\sigma_{\rm qm}x^2/2},
\end{aligned} \tag{37}$$

where

$$\sigma_{\rm qm} = \xi^2\coth\frac{\beta\hbar\omega}{2} = \frac{\hbar}{2m\omega}\coth\frac{\beta\hbar\omega}{2}. \tag{38}$$

(e) We calculate $p_{\rm qm}(q')$ and then $S_{\rm qm}(E)$. From Eq. 28,

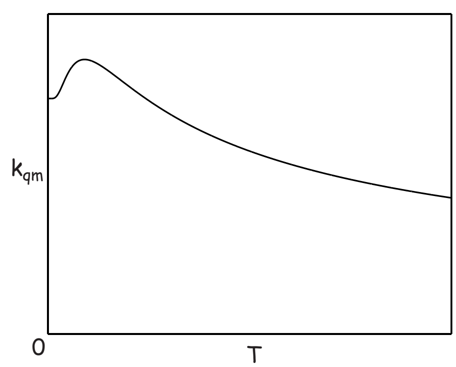
$$\begin{aligned} p_{\rm qm}(q') &= \frac{1}{2\pi}\int_{-\infty}^{\infty} {\rm d}x\, {\rm e}^{-ixq'}{\rm e}^{-\sigma_{\rm qm}x^2/2} \\ &= \frac{1}{2\pi}\int_{-\infty}^{\infty} {\rm d}x\, \exp\left[-\frac{\sigma_{\rm qm}}{2}\left(x+\frac{iq'}{\sigma_{\rm qm}}\right)^2 - \frac{q'^2}{2\sigma_{\rm qm}}\right] \\ &= (2\pi\sigma_{\rm qm})^{-1/2}\exp\left[-\frac{q'^2}{2\sigma_{\rm qm}}\right]. \end{aligned} \tag{39}$$

Combining Eqs. 17, 18, and 39 leads to

$$\begin{aligned} S_{\rm qm}(E) &= p_{\rm qm}[q(E)]\left|\frac{{\rm d}q}{{\rm d}E}\right| \\ &= (2\pi\sigma_{\rm qm})^{-1/2}\exp\left[-\frac{1}{2\sigma_{\rm qm}}\frac{1}{f^2q_0^2}(fq_0^2/2+E_0-E)^2\right]\frac{1}{fq_0} \\ &= (2\pi\sigma_{\rm qm}f^2q_0^2)^{-1/2}\exp\left[-\frac{(E_0-E+fq_0^2/2)^2}{2f^2q_0^2\sigma_{\rm qm}}\right]. \end{aligned} \tag{40}$$

(f)

$$\begin{aligned} k_{\rm qm} &= \frac{2\pi}{\hbar}|U|^2 S_{\rm qm}(0) = \frac{\sqrt{2\pi}}{\hbar}\frac{|U|^2}{\sqrt{\sigma_{\rm qm}f^2q_0^2}}\exp\left[-\frac{(E_0+fq_0^2/2)^2}{2f^2q_0^2\sigma_{\rm qm}}\right] \\ &= \frac{\sqrt{2\pi}}{\hbar}\frac{|U|^2}{|fq_0|}\left(\frac{\hbar}{2m\omega}\coth\frac{\hbar\omega}{2k_BT}\right)^{-1/2}\exp\left[-\frac{(E_0+fq_0^2/2)^2}{2f^2q_0^2}\left(\frac{\hbar}{2m\omega}\coth\frac{\hbar\omega}{2k_BT}\right)^{-1}\right]. \end{aligned} \tag{41}$$



Take $T\to 0$ limit of Eqs. 38 and 39:

$$\sigma_{\rm qm} \to \frac{\hbar}{2m\omega} \tag{42}$$

$$p_{\rm qm}(q') \to \left(\frac{m\omega}{\pi\hbar}\right)^{1/2}\exp\left[-\frac{m\omega q'^2}{\hbar}\right] = |\psi_0(q')|^2, \tag{43}$$

where ψ_0 is the ground-state wave function for the harmonic oscillator representing the reactant state. The quantum mechanical transition rate $k_{\rm qm}$ does not vanish at $T=0$ because there exists quantum mechanical fluctuation even at zero temperature; the ground-state wave function is not a delta function.

Problem 3: End-End Reaction of One-Dimensional Polymer

(a) Let a_i be the orientation of ith segment. It takes the value of either $+1$ or -1 with probability 1/2. The end-to-end distance x is then given as $x = b\sum_{i=1}^{2N} a_i$. Since a_i are independent random variables, we can apply the central limit theorem. The theorem states that as $N \to \infty$ the distribution for x becomes Gaussian.

In order to determine the actual formula for the Gaussian distribution, we need only the mean and the variance:

$$\langle x \rangle = b\sum_i \langle a_i \rangle = 0 \tag{44}$$

$$\langle x^2 \rangle = b^2 \sum_i \sum_j \langle a_i a_j \rangle = b^2 \sum_i \langle a_i^2 \rangle = 2Nb^2. \tag{45}$$

Here we have used the independence, namely $\langle a_i a_j \rangle = \delta_{ij} \langle a_i^2 \rangle = \delta_{ij}$. The Gaussian distribution with the above mean and variance is

$$p_0(x) = \left(4\pi b^2 N\right)^{-1/2} \exp\left(-x^2/4b^2N\right). \tag{46}$$

(b) Any probability distribution that makes the right-hand side of the Smoluchowski equation vanish is stationary. It is straightforward to show that $p_0(x)$ makes the right-hand side vanish:

$$\begin{aligned} &(4Nb^2\partial_x^2 + 2\partial_x x)p_0(x) \\ &= (4\pi b^2 N)^{-1/2}\left[4Nb^2\left(-\frac{1}{2b^2N} + \frac{x^2}{4b^4N^2}\right) + 2 - \frac{x^2}{b^2N}\right]\exp\left(-\frac{x^2}{4b^2N}\right) \\ &= 0. \end{aligned} \tag{47}$$

The distribution $p_0(x)$ is therefore a stationary solution.

(c)

$$p(x,t|x_0,t_0) = [4b^2N\pi S(t,t_0)]^{-1/2} \exp\left[-\frac{(x - x_0 \mathrm{e}^{-2(t-t_0)/\tau})^2}{4b^2NS(t,t_0)}\right] \tag{48}$$

$$S(t,t_0) = 1 - \mathrm{e}^{-4(t-t_0)/\tau}. \tag{49}$$

A little algebra leads to

$$\begin{aligned} &\tau\partial_t p(x,t|x_0,t_0) = (4Nb^2\partial_x^2 + 2\partial_x x)p(x,t|x_0,t_0) \\ &= -\frac{2b^2NS(t,t_0) + xx_0(\mathrm{e}^{-2(t-t_0)/\tau} + \mathrm{e}^{2(t-t_0)/\tau}) - (x^2 + x_0^2)}{2b^3N^{3/2}\pi^{1/2}S(t,t_0)^{5/2}\mathrm{e}^{4(t-t_0)/\tau}} \exp\left[-\frac{(x - x_0\mathrm{e}^{-2(t-t_0)/\tau})^2}{4b^2NS(t,t_0)}\right], \end{aligned} \tag{50}$$

which means that $p(x,t|x_0,t_0)$ satisfies the Smoluchowski equation. We now show that it also satisfies the initial condition. First, it is normalized at any time t later than t_0: $\int_{-\infty}^{\infty} \mathrm{d}x\, p(x,t|x_0,t_0) = 1$. Second, as t approaches t_0, $p(x,t|x_0,t_0)$ gets vanishingly small for $x \neq x_0$:

$$\lim_{t\to t_0} p(x,t|x_0,t_0) = \lim_{S\to 0^+} (4b^2N\pi S)^{-1/2} \exp\left[-\frac{(x-x_0)^2}{4b^2NS}\right] = 0. \tag{51}$$

These two properties imply that $\lim_{t\to t_0} p(x,t|x_0,t_0) = \delta(x - x_0)$. This completes the proof.

As $t \to \infty$, $S(t,t_0) \to 1$ and the solution $p(x,t|x_0,t_0)$ indeed relaxes to the equilibrium distribution $p_0(x)$.