Solutions

Problems of Chap. 1

1.1. Gaussian Polymer Model

(a)
$$\Delta\mathbf{r}_i = \mathbf{r}_i - \mathbf{r}_{i-1}, \quad i = 1, \ldots, N,$$

$$P(\Delta\mathbf{r}_i) = \frac{1}{b^3}\sqrt{\frac{27}{8\pi^3}}\exp\left\{-\frac{3(\Delta\mathbf{r}_i)^2}{2b^2}\right\}$$

is the normalized probability function with

$$\int_{-\infty}^{\infty} P(\Delta\mathbf{r}_i)\mathrm{d}^3\Delta\mathbf{r}_i = 1, \quad \int_{-\infty}^{\infty} \Delta\mathbf{r}_i^2 P(\Delta\mathbf{r}_i)\mathrm{d}^3\Delta\mathbf{r}_i = b^2.$$

(b)
$$\mathbf{r}_N - \mathbf{r}_0 = \sum_{i=1}^{N} \Delta\mathbf{r}_i,$$

$$P\left(\sum_{i=1}^{N}\Delta\mathbf{r}_i = \mathbf{R}\right)$$

$$= \int_{-\infty}^{\infty}\mathrm{d}^3\Delta\mathbf{r}_1 \cdots \int_{-\infty}^{\infty}\mathrm{d}^3\Delta\mathbf{r}_N \prod_{i=1}^{N} P(\Delta\mathbf{r}_i)\delta\left(\mathbf{R} - \sum_{i=1}^{N}\Delta\mathbf{r}_i\right)$$

$$= \int \frac{1}{(2\pi)^3}\mathrm{d}^3\mathbf{k}\mathrm{e}^{\mathrm{i}\mathbf{k}\mathbf{R}} \int_{-\infty}^{\infty}\mathrm{d}^3\Delta\mathbf{r}_1 \cdots \int_{-\infty}^{\infty}\mathrm{d}^3\Delta\mathbf{r}_N \left(\frac{1}{b^3}\sqrt{\frac{27}{8\pi^3}}\right)^N$$

$$\times \prod \exp\left\{-\frac{3\Delta\mathbf{r}_i^2}{2b^2} - \mathrm{i}\mathbf{k}\Delta\mathbf{r}_i\right\}$$

$$= \int \frac{1}{(2\pi)^3}\mathrm{d}^3\mathbf{k}\mathrm{e}^{\mathrm{i}\mathbf{k}\mathbf{R}}$$

$$\times \left[\left(\frac{1}{b^3}\sqrt{\frac{27}{8\pi^3}}\right)\int_{-\infty}^{\infty} \mathrm{d}^3\Delta\mathbf{r}\exp\left\{-\frac{3\Delta\mathbf{r}^2}{2b^2} - \mathrm{i}\mathbf{k}\Delta\mathbf{r}\right\}\right]^N$$

$$= \int \frac{1}{(2\pi)^3}\mathrm{d}^3\mathbf{k}\mathrm{e}^{\mathrm{i}\mathbf{kR}}\exp\left(-\frac{Nb^2}{6}\mathbf{k}^2\right)$$

$$= \frac{1}{b^3}\sqrt{\frac{27}{8\pi^3 N^3}}\exp\left\{-\frac{3\mathbf{R}^2}{2Nb^2}\right\}.$$

(c)
$$\exp\left\{-\frac{1}{k_{\mathrm{B}}T}\left(\frac{f}{2}\sum\Delta\mathbf{r}_i^2 - \kappa\sum\Delta\mathbf{r}_i\right)\right\}$$

$$= \prod_i \exp\left\{-\frac{1}{k_{\mathrm{B}}T}\left(\frac{f}{2}\Delta\mathbf{r}_i^2 - \kappa\Delta\mathbf{r}_i\right)\right\}$$

$$\frac{f}{2k_{\mathrm{B}}T} = \frac{3}{2b^2} \to f = \frac{3k_{\mathrm{B}}T}{b^2}.$$

(d)
$$x_N - x_0 = \frac{N\kappa}{f}, \quad y_N - y_0 = z_N - z_0 = 0,$$

$$L = x_N - x_0 = \frac{N\kappa b^2}{3k_{\mathrm{B}}T}.$$

1.2. Three-Dimensional Polymer Model

(a) Nb^2.

(b) $b^2\left(N\frac{1+x}{1-x} + \frac{2x(x^2-1)}{(1-x)^2}\right)$ with $x = \cos\theta$

$$\approx Nb^2\frac{1+\cos x}{1-\cos x}.$$

(c) $Nb^2\frac{(1+\cos\theta_1)(1+\cos\theta_2)}{1-\cos\theta_1\cos\theta_2}$.

(d) $N \gg a/b$ with the coherence length

$$a = b\frac{1+\cos x}{(1-\cos x)\cos(x/2)}.$$

(e) $Nb^2\left(\frac{4}{\theta^2} - 1\right) - b^2\left(\frac{4}{\theta^2} - \frac{8}{\theta^4}\right)$.

1.3. Two-Component Model

(a)
$$\kappa = -k_{\mathrm{B}}T\frac{1}{l_\alpha - l_\beta}\ln\left(\frac{Ml_\alpha - L}{L - Ml_\beta}\right)$$

$$-k_{\mathrm{B}}T\left(\frac{1}{2Ml_\alpha - 2L} + \frac{1}{2Ml_\beta - L} + \frac{l_\alpha - l_\beta}{12(L - Ml_\beta)^2} - \frac{l_\alpha - l_\beta}{12(Ml_\alpha - L)^2}\right).$$

The exact solution can be written with the digamma function Ψ which is well known by algebra programs as

$$\kappa = -k_{\mathrm{B}}T\frac{1}{l_\alpha - l_\beta}\left(-\Psi\left(\frac{L - Ml_\beta}{l_\alpha - l_\beta} + 1\right) + \Psi\left(\frac{Ml_\alpha - L}{l_\alpha - l_\beta}\right)\right).$$

The error of the asymptotic expansion is largest for $L \approx Ml_\alpha$ or $L \approx Ml_\beta$. The following table compares the relative errors of the Stirling's approximation and the higher-order asymptotic expansion for $M = 1{,}000$ and $l_\beta/l_\alpha = 2$:

L/l_α	Stirling	Asympt. expansion
1,000.2	0.18	0.13
1,000.5	0.11	0.009
1,001	0.065	0.00094
1,005	0.019	2.5×10^{-6}

(b)
$$Z(\kappa, M, T) = \left(\mathrm{e}^{\kappa l_\alpha/k_{\mathrm{B}}T} + \mathrm{e}^{\kappa l_\beta/k_{\mathrm{B}}T}\right)^M,$$

$$\overline{L} = M\frac{l_\alpha \mathrm{e}^{\kappa l_\alpha/k_{\mathrm{B}}T} + l_\beta \mathrm{e}^{\kappa l_\beta/k_{\mathrm{B}}T}}{\mathrm{e}^{\kappa l_\alpha/k_{\mathrm{B}}T} + \mathrm{e}^{\kappa l_\beta/k_{\mathrm{B}}T}},$$

$$\overline{L^2} = \overline{L}^2 + M\mathrm{e}^{\kappa(l_\alpha+l_\beta)/k_{\mathrm{B}}T}\left(\frac{l_\alpha - l_\beta}{\mathrm{e}^{\kappa l_\alpha/k_{\mathrm{B}}T} + \mathrm{e}^{\kappa l_\beta/k_{\mathrm{B}}T}}\right)^2,$$

$$\sigma^2 = M\mathrm{e}^{\kappa(l_\alpha+l_\beta)/k_{\mathrm{B}}T}\left(\frac{l_\alpha - l_\beta}{\mathrm{e}^{\kappa l_\alpha/k_{\mathrm{B}}T} + \mathrm{e}^{\kappa l_\beta/k_{\mathrm{B}}T}}\right)^2,$$

$$\frac{\sigma}{\overline{\overline{L}}} \sim \frac{1}{\sqrt{N}},$$

$$\frac{\partial\sigma}{\partial\kappa} = 0 \quad \text{for} \quad (l_\alpha + l_\beta) = 2\frac{l_\alpha \mathrm{e}^{\kappa l_\alpha/k_{\mathrm{B}}T} + l_\beta \mathrm{e}^{\kappa l_\beta/k_{\mathrm{B}}T}}{\mathrm{e}^{\kappa l_\alpha/k_{\mathrm{B}}T} + \mathrm{e}^{\kappa l_\beta/k_{\mathrm{B}}T}},$$

hence for

$$\kappa = 0$$

$$\frac{\partial^2\sigma^2}{\partial\kappa^2}(\kappa = 0) = -\frac{M}{k(k_{\mathrm{B}}T)^2}(l_\alpha - l_\beta)^2 < 0 \rightarrow \text{maximum}$$

also a maximum of σ since the square root is monotonous.

Problems of Chap. 2

2.1. Osmotic Pressure of a Polymer Solution

$$\mu_\alpha(P,T) - \mu_\alpha^0(P,T) = k_\mathrm{B}T\left(\ln(1-\phi_\beta) + \left(1-\frac{1}{M}\right)\phi_\beta + \chi\phi_\beta^2\right),$$

$$\mu_\alpha^0(P',T) - \mu_\alpha^0(P,T) = \mu_\alpha(P,T) - \mu_\alpha^0(P,T) = -\Pi\frac{\partial\mu_\alpha^0(P,T)}{\partial P},$$

$$\Pi = -\left(\frac{\partial\mu_\alpha^0(P,T)}{\partial P}\right)^{-1} k_\mathrm{B}T\left(\ln(1-\phi_\beta) + \left(1-\frac{1}{M}\right)\phi_\beta + \chi\phi_\beta^2\right).$$

For the pure solvent,

$$\mu_\alpha^0 = \frac{G}{N_\alpha},$$

$$\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}P + \mu_\alpha^0(P,T)\mathrm{d}N,$$

$$\left.\frac{\partial\mu_\alpha^0}{\partial P}\right|_{T,N_\alpha} = \frac{V}{N_\alpha},$$

$$\Pi = -\frac{N_\alpha}{V}k_\mathrm{B}T\left(-\phi_\beta - \frac{1}{2}\phi_\beta^2 - \frac{1}{3}\phi_\beta^3 + \cdots + \left(1-\frac{1}{M}\right)\phi_\beta + \chi\phi_\beta^2\right)$$

$$= \frac{N_\alpha k_\mathrm{B}T}{V}\left(\frac{1}{M}\phi_\beta + \left(\frac{1}{2}-\chi\right)\phi_\beta^2 + \cdots\right),$$

$$\chi = \frac{\chi_0 T_0}{T},$$

high T:

$$\frac{1}{2} - \chi > 0, \quad \Pi > 0 \text{ good solvent}$$

low T:

$\Pi < 0$ bad solvent, possibly phase separation.

2.2. Polymer Mixture

$$\Delta F = Nk_\mathrm{B}T\left(\frac{\phi_1}{M_1}\ln\phi_1 + \frac{\phi_2}{M_2}\ln\phi_2 + \chi\phi_1\phi_2\right),$$

$$\phi_{2,\mathrm{c}} = \frac{1}{1+\sqrt{M_2/M_1}},$$

$$\chi_\mathrm{c} = \frac{1}{2}\left(\sqrt{M_1}+\sqrt{M_2}\right)\left(\frac{1}{M_2\sqrt{M_1}} + \frac{1}{M_1\sqrt{M_2}}\right),$$

symmetric case

$$\phi_c = \frac{1}{2}$$

$$\chi_c = \frac{2}{M} \text{ can be small, demixing possible.}$$

Problems of Chap. 4

4.1. Membrane Potential

$$\Phi_{\mathrm{I}} = B\mathrm{e}^{\kappa x}, \quad \Phi_{\mathrm{II}} = B\left(1 + \frac{\epsilon_W}{\epsilon_M}\kappa x\right), \quad \Phi_{\mathrm{III}} = V - B\mathrm{e}^{-\kappa(x-L)},$$

$$B = \frac{V}{2 + (\epsilon_w/\epsilon_M)\kappa L},$$

$$Q/A = \epsilon_W \kappa B \quad \text{per area} \quad A,$$

$$C/A = \frac{Q/A}{V} = \frac{\epsilon_W \kappa}{2 + (\epsilon_W/\epsilon_M)\kappa L} = \frac{1}{(2/\epsilon_w \kappa) + (L/\epsilon_M)}.$$

4.2. Ion Activity

$$k_\mathrm{B} T \ln \gamma^c = k_\mathrm{B} T \ln \frac{a}{c} = -\frac{Z^2 \mathrm{e}^2}{8\pi\epsilon} \frac{\kappa}{1 + \kappa R},$$

$$\ln \gamma^c_+ = \ln \gamma^c_- = -\frac{1}{k_\mathrm{B} T} \frac{Z^2 \mathrm{e}^2}{8\pi\epsilon} \frac{\kappa}{1 + \kappa R},$$

$$\ln \gamma^c_\pm = -\frac{1}{k_\mathrm{B} T} \frac{Z^2 \mathrm{e}^2}{16\pi\epsilon} \left(\frac{\kappa}{1 + \kappa R_+} + \frac{\kappa}{1 + \kappa R_-}\right),$$

$\kappa \to 0$ for dilute solution,

$$\ln \gamma^c_\pm \to -\frac{1}{k_\mathrm{B} T} \frac{Z^2 \mathrm{e}^2 \kappa}{8\pi\epsilon}.$$

Problems of Chap. 5

5.1. Abnormal Titration Curve

$$\begin{aligned}
\Delta G(\mathrm{B}, \mathrm{B}) &= 0, \\
\Delta G(\mathrm{BH}^+, \mathrm{B}) &= \Delta G_{1,\mathrm{int}}, \\
\Delta G(\mathrm{B}, \mathrm{BH}^+) &= \Delta G_{2,\mathrm{int}}, \\
\Delta G(\mathrm{BH}^+, \mathrm{BH}^+) &= \Delta G_{1,\mathrm{int}} + \Delta G_{2,\mathrm{int}} + W_{1,2},
\end{aligned}$$

$$
\begin{aligned}
\Xi &= 1 + \mathrm{e}^{-\beta(\Delta G_{1,\mathrm{int}}-\mu)} + \mathrm{e}^{-\beta(\Delta G_{2,\mathrm{int}}-\mu)} + \mathrm{e}^{-\beta(\Delta G_{1,\mathrm{int}}+\Delta G_{2,\mathrm{int}}-W+2\mu)},\\
\overline{s_1} &= \frac{\mathrm{e}^{-\beta(\Delta G_{1,\mathrm{int}}-\mu)} + \mathrm{e}^{-\beta(\Delta G_{1,\mathrm{int}}+\Delta G_{2,\mathrm{int}}-W+2\mu)}}{\Xi},\\
\overline{s_2} &= \frac{\mathrm{e}^{-\beta(\Delta G_{2,\mathrm{int}}-\mu)} + \mathrm{e}^{-\beta(\Delta G_{1,\mathrm{int}}+\Delta G_{2,\mathrm{int}}-W+2\mu)}}{\Xi}.
\end{aligned}
$$

Problems of Chap. 6

6.1. pH Dependence of Enzyme Activity

$$
\frac{r}{r_{\max}} = \frac{1}{1 + (1 + (c_{\mathrm{H}^+}/K))(K_M/c_{\mathrm{S}})},
$$

$$
K = \frac{c_{\mathrm{H}^+} c_{\mathrm{S}^-}}{c_{\mathrm{HS}}}, \quad c_s = c_{\mathrm{S}^-} + c_{\mathrm{HS}}.
$$

6.2. Polymerization at the End of a Polymer

$$
c_{iM} = K c_M c_{(i-1)M} = \cdots = \frac{(K c_M)^i}{K},
$$

$$
\langle i \rangle = \frac{\sum_{i=1}^{\infty} i (K c_M)^i}{\sum_{i=1}^{\infty} (K c_M)^i} = \frac{1}{1 - K c_M} \text{ for } K c_M < 1.
$$

6.3. Primary Salt Effect

$$
r = k_1 c_{\mathrm{X}},
$$

$$
K = \frac{c_{\mathrm{X}}}{c_{\mathrm{A}} c_{\mathrm{B}}} \exp\left\{ -\frac{Z_{\mathrm{A}} Z_{\mathrm{B}} \mathrm{e}^2 \kappa}{4\pi\epsilon k_{\mathrm{B}} T} \right\},
$$

$$
c_{\mathrm{X}} = K c_{\mathrm{A}} c_{\mathrm{B}} \exp\left\{ \frac{Z_{\mathrm{A}} Z_{\mathrm{B}} \mathrm{e}^2 \kappa}{4\pi\epsilon k_{\mathrm{B}} T} \right\}.
$$

Problems of Chap. 7

7.1. Smoluchowski Equation

$$
P(t + \Delta t, x) = \mathrm{e}^{\Delta t (\partial/\partial t)} P(t, x),
$$

$$
w^{\pm}(x \pm \Delta x) P(t, x \pm \Delta x) = \mathrm{e}^{\pm \Delta x (\partial/\partial x)} w^{\pm}(x) P(t, x),
$$

$$
\mathrm{e}^{\Delta t (\partial/\partial t)} P(t, x) = \mathrm{e}^{\Delta x (\partial/\partial x)} w^{+}(x) P(t, x) + \mathrm{e}^{-\Delta x (\partial/\partial x)} w^{-}(x) P(t, x),
$$

$$
P(t, x) + \Delta t \frac{\partial}{\partial t} P(t, x) + \cdots = (w^{+}(x) + w^{-}(x)) P(x, t)
$$

$$
+ \Delta x \frac{\partial}{\partial x} (w^{+}(x) - w^{-}(x)) P(x, t) + \frac{\Delta x^2}{2} \frac{\partial^2}{\partial x^2} (w^{+}(x) + w^{-}(x)) P(x, t) + \cdots,
$$

$$\frac{\partial}{\partial t}P(t,x) = \frac{\Delta x}{\Delta t}\frac{\partial}{\partial x}(w^+(x) - w^-(x))P(x,t) + \frac{\Delta x^2}{\Delta t}\frac{\partial^2}{\partial x^2}P(x,t) + \cdots,$$

$$D = \frac{\Delta x^2}{\Delta t}, \quad K(x) = -\frac{k_B T}{\Delta x}(w^+(x) - w^-(x)).$$

7.2. Eigenvalue Solution to the Smoluchowski Equation

$$-\frac{k_B T}{m\gamma}e^{-U/k_B T}\left(\frac{\partial}{\partial x}e^{U/k_B T}W\right)$$

$$= -\frac{k_B T}{m\gamma}e^{-U/k_B T}\left(e^{U/k_B T}\frac{\partial W}{\partial x} + e^{U/k_B T}W\frac{1}{k_B T}\frac{\partial U}{\partial x}\right)$$

$$= -\frac{k_B T}{m\gamma}\frac{\partial W}{\partial x} - \frac{1}{m\gamma}\frac{\partial U}{\partial x}W = S,$$

$$\mathfrak{L}_{\mathrm{FP}}W = -\frac{\partial}{\partial x}S = \frac{\partial}{\partial x}\frac{k_B T}{m\gamma}e^{-U/k_B T}\left(\frac{\partial}{\partial x}e^{U/k_B T}W\right),$$

$$\mathfrak{L}_{\mathrm{FP}} = \frac{k_B T}{m\gamma}\frac{\partial}{\partial x}e^{-U/k_B T}\frac{\partial}{\partial x}e^{U/k_B T},$$

$$\mathfrak{L} = e^{U/2k_B T}\mathfrak{L}_{\mathrm{FP}}e^{-U/2k_B T} = e^{U/2k_B T}\frac{k_B T}{m\gamma}\frac{\partial}{\partial x}e^{-U/k_B T}\frac{\partial}{\partial x}e^{U/2k_B T},$$

$$\mathfrak{L}^{\mathrm{H}} = e^{U/2k_B T}\left(-\frac{\partial}{\partial x}\right)e^{-U/k_B T}\left(-\frac{\partial}{\partial x}\right)\frac{k_B T}{m\gamma}e^{U/2k_B T} = \mathfrak{L},$$

since

$$\frac{k_B T}{m\gamma} = \text{constant}.$$

For an eigenfunction ψ of $\mathfrak{L}$, we have

$$\lambda\psi = \mathfrak{L}\psi = e^{U/2k_B T}\mathfrak{L}_{\mathrm{FP}}e^{-U/2k_B T}\psi.$$

Hence

$$\mathfrak{L}_{\mathrm{FP}}\left(e^{-U/2k_B T}\psi\right) = \lambda\left(e^{-U/2k_B T}\psi\right)$$

gives an eigenfunction of the Fokker–Planck operator to the same eigenvalue λ. A solution of the Smoluchowski equation is then given by

$$W(x,t) = e^{\lambda t}e^{-U/2k_B T}\psi(x).$$

The Hermitian operator is very similar to the harmonic oscillator in second quantization

$$\mathfrak{L} = \frac{k_B T}{m\gamma}\left(e^{U/2k_B T}\frac{\partial}{\partial x}e^{-U/2k_B T}\right)\left(e^{-U/2k_B T}\frac{\partial}{\partial x}e^{U/2k_B T}\right)$$

$$= \frac{k_B T}{m\gamma}\left(\frac{\partial}{\partial x} - \frac{1}{2k_B T}\frac{\partial U}{\partial x}\right)\left(\frac{\partial}{\partial x} + \frac{1}{2k_B T}\frac{\partial U}{\partial x}\right)$$

$$= \frac{k_\mathrm{B}T}{m\gamma}\left(\frac{\partial}{\partial x} - \frac{m\omega^2}{2k_\mathrm{B}T}x\right)\left(\frac{\partial}{\partial x} + \frac{m\omega^2}{2k_\mathrm{B}T}x\right)$$

$$= -\frac{\omega^2}{\gamma}\left(\sqrt{\frac{k_\mathrm{B}T}{m\omega^2}}\frac{\partial}{\partial x} - \frac{1}{2}\sqrt{\frac{m\omega^2}{k_\mathrm{B}T}}x\right)\left(\sqrt{\frac{k_\mathrm{B}T}{m\omega^2}}\frac{\partial}{\partial x} + \frac{1}{2}\sqrt{\frac{m\omega^2}{k_\mathrm{B}T}}x\right)$$

$$= -\frac{\omega^2}{\gamma}\left(\frac{\partial}{\partial \xi} - \frac{1}{2}\xi\right)\left(\frac{\partial}{\partial \xi} + \frac{1}{2}\xi\right) = -\frac{\omega^2}{\gamma}b^+b$$

with Boson operators

$$b^+b - bb^+ = 1.$$

From comparison with the harmonic oscillator, we know the eigenvalues

$$\lambda_n = -\frac{\omega^2}{\gamma}n, \quad n = 0, 1, 2, \ldots$$

The ground state obeys

$$a\psi_0 = \left(\frac{\partial}{\partial x} + \frac{1}{2k_\mathrm{B}T}\frac{\partial U}{\partial x}\right)\psi_0 = 0$$

with the solution

$$\psi_0 = \mathrm{e}^{-U(x)/2k_\mathrm{B}T}.$$

This corresponds to the stationary solution of the Smoluchowski equation:

$$W = \sqrt{\frac{m\omega^2}{2\pi k_\mathrm{B}T}}\mathrm{e}^{-U(x)/k_\mathrm{B}T}.$$

7.3. Diffusion Through a Membrane

$$k_\mathrm{AB} = k_\mathrm{A} + k_\mathrm{B},$$

$$0 = \frac{\mathrm{d}\overline{N}}{\mathrm{d}t} = \sum_{N=1}^{M}\frac{\mathrm{d}P_N}{\mathrm{d}t}N = -\sum_{N=1}^{M}k_\mathrm{AB}MNP_N + \sum_{N=1}^{N}(k_\mathrm{AB} - 2k_m)N^2P_N$$

$$+ \sum_{N=2}^{M}k_\mathrm{AB}MNP_{N-1} - \sum_{N=2}^{M}k_\mathrm{AB}(N-1)NP_{N-1}$$

$$+ \sum_{N=1}^{M-1}2k_mN(N+1)P_{N+1}$$

$$\approx -k_\mathrm{AB}M\overline{N} + (k_\mathrm{AB} - 2k_m)\overline{N^2} + k_\mathrm{AB}M(1+\overline{N}) - k_\mathrm{AB}(\overline{N^2} + \overline{N})$$

$$+2k_m(\overline{N^2} - \overline{N})$$

$$= k_{\mathrm{AB}}M - k_{\mathrm{AB}}\overline{N} - 2k_m\overline{N},$$

$$\overline{N} = M\frac{k_{\mathrm{A}} + k_{\mathrm{B}}}{k_{\mathrm{A}} + k_{\mathrm{B}} + 2k_m},$$

$$0 = \frac{\mathrm{d}\overline{N^2}}{\mathrm{d}t} = \sum N^2\frac{\mathrm{d}P_N}{\mathrm{d}t} = -\sum_{N=1}^{M} k_{\mathrm{AB}}MN^2P_N + \sum_{N=1}^{N}(k_{\mathrm{AB}} - 2k_m)N^3P_N$$

$$+ \sum_{N=2}^{M} k_{\mathrm{AB}}MN^2P_{N-1} - \sum_{N=2}^{M} k_{\mathrm{AB}}(N-1)N^2P_{N-1}$$

$$+ \sum_{N=1}^{M-1} 2k_mN^2(N+1)P_{N+1}$$

$$\approx -k_{\mathrm{AB}}M\overline{N^2} + (k_{\mathrm{AB}} - 2k_m)\overline{N^3} + k_{\mathrm{AB}}M(\overline{N^2} + 2\overline{N} + 1)$$

$$-k_{\mathrm{AB}}(\overline{N^3} + 2\overline{N^2} + \overline{N}) + 2k_m(\overline{N^3} - 2\overline{N^2} + \overline{N})$$

$$= k_{\mathrm{AB}}M(2\overline{N} + 1) - k_{\mathrm{AB}}(2\overline{N^2} + \overline{N}) + 2k_m(-2\overline{N^2} + \overline{N})$$

$$= k_{\mathrm{AB}}M + \overline{N}(2k_{\mathrm{AB}}M - k_{\mathrm{AB}} + 2k_m) - \overline{N^2}(2k_{\mathrm{AB}} + 4k_m)$$

$$\overline{N^2} = \frac{k_{\mathrm{AB}}M + (2k_{\mathrm{AB}}M - k_{\mathrm{AB}} + 2k_m)M\frac{k_{\mathrm{AB}}}{k_{\mathrm{AB}}+2k_m}}{2k_{\mathrm{AB}} + 4k_m}$$

$$= \frac{2k_{\mathrm{AB}}k_m}{(k_{\mathrm{AB}} + 2k_m)^2}M + \frac{k_{\mathrm{AB}}^2}{(k_{\mathrm{AB}} + 2k_m)^2}M^2,$$

and the variance is

$$\overline{N^2} - \overline{N}^2 = \frac{2k_mk_{\mathrm{AB}}}{(k_{\mathrm{AB}} + 2k_m)^2}M = \frac{2k_m}{k_{\mathrm{AB}}M}\overline{N}^2.$$

The diffusion current from A $\to$ B is

$$J = \frac{\mathrm{d}N_{\mathrm{A}}}{\mathrm{d}t} - \frac{\mathrm{d}N_{\mathrm{B}}}{\mathrm{d}t} = \sum_N (-k_{\mathrm{A}}(M-N)P_N + k_mNP_N)$$

$$-\sum_N (-k_{\mathrm{B}}(M-N)P_N + k_mNP_N)$$

$$= \sum_N (k_{\mathrm{B}} - k_{\mathrm{A}})(M-N)P_N = (k_{\mathrm{B}} - k_{\mathrm{A}})(M - \overline{N}).$$

Problems of Chap. 9

9.1. Dichotomous Model

$$\lambda_1 = 0,$$

$$\mathbf{L}_1 = (\,1\ 1\ 1\ 1), \quad \mathbf{R}_1 = \begin{pmatrix} 0 \\ 0 \\ \beta \\ \alpha \end{pmatrix}, \quad \frac{(\mathbf{L}_1\mathbf{P}_0)}{(\mathbf{L}_1\mathbf{R}_1)} = \frac{1}{\alpha+\beta}\,,$$

$$\lambda_2 = -(\alpha+\beta),$$

$$\mathbf{L}_2 = (\,\alpha\ -\beta\ \alpha\ -\beta), \mathbf{R}_2 = \begin{pmatrix} 0 \\ 0 \\ -1 \\ 1 \end{pmatrix}, \quad \frac{(\mathbf{L}_2\mathbf{P}_0)}{(\mathbf{L}_2\mathbf{R}_2)} = 0,$$

$$\lambda_{3,4} = -\frac{k_- + k_+ + \alpha + \beta}{2} \pm \frac{1}{2}\sqrt{(\alpha+\beta)^2 + (k_+ - k_-)^2 + 2(\beta-\alpha)(k_- - k_+)},$$

Fast fluctuations:

$$\lambda_3 = -\frac{\alpha}{\alpha+\beta}k_- - \frac{\beta}{\alpha+\beta}k_+ + O(k^2),$$

$$\mathbf{L}_3 \approx (1,1,0,0), \quad \mathbf{R}_3 \approx \begin{pmatrix} \beta \\ \alpha \\ -\beta \\ -\alpha \end{pmatrix},$$

$$\frac{(\mathbf{L}_3\mathbf{P}_0)}{(\mathbf{L}_3\mathbf{R}_3)} \approx \frac{1}{\alpha+\beta},$$

$$\lambda_4 = -(\alpha+\beta) - \frac{\alpha}{\alpha+\beta}k_+ - \frac{\beta}{\alpha+\beta}k_- + O(k^2),$$

$$\mathbf{L}_4 \approx (-\alpha,\beta,0,0), \quad \mathbf{R}_4 \approx \begin{pmatrix} 1 \\ -1 \\ 1 \\ -1 \end{pmatrix}, \quad \frac{(\mathbf{L}_4\mathbf{P}_0)}{(\mathbf{L}_4\mathbf{R}_1)} \approx 0,$$

$$\mathbf{P}(t) \approx \begin{pmatrix} 0 \\ 0 \\ \frac{\beta}{\alpha+\beta} \\ \frac{\alpha}{\alpha+\beta} \end{pmatrix} + \begin{pmatrix} \frac{\beta}{\alpha+\beta} \\ \frac{\alpha}{\alpha+\beta} \\ -\frac{\beta}{\alpha+\beta} \\ -\frac{\alpha}{\alpha+\beta} \end{pmatrix} \mathrm{e}^{\lambda_3 t} \rightarrow P(\mathrm{D}^*) = \mathrm{e}^{\lambda_3 t}.$$

Slow fluctuations:

$$\lambda_3 \approx -k_+ - \alpha,$$

$$\mathbf{L}_3 \approx (k_+ - k_-, -\beta, 0, 0), \quad \mathbf{R}_3 \approx \begin{pmatrix} k_+ - k_- \\ -\alpha \\ -(k_+ - k_-) \\ \alpha \end{pmatrix},$$

$$\frac{\mathbf{L}_3\mathbf{P}_0}{\mathbf{L}_3\mathbf{R}_3} \approx \frac{\beta}{\alpha+\beta}\frac{1}{k_+ - k_-},$$

$$\lambda_4 \approx -k_- - \beta,$$

$$\mathbf{L}_4 \approx (\alpha, k_+ - k_-, 0, 0),\ \mathbf{R}_4 \approx \begin{pmatrix} \beta \\ k_+ - k_- \\ -\beta \\ -(k_+ - k_-) \end{pmatrix},\ \frac{\mathbf{L}_4\mathbf{P}_0}{\mathbf{L}_4\mathbf{R}_4} \approx \frac{\alpha}{\alpha+\beta}\frac{1}{k_+ - k_-},$$

$$\mathbf{P}(t) \approx \begin{pmatrix} 0 \\ 0 \\ \frac{\beta}{\alpha+\beta} \\ \frac{\alpha}{\alpha+\beta} \end{pmatrix} + \frac{\beta}{\alpha+\beta}\begin{pmatrix} 1 \\ 0 \\ -1 \\ 0 \end{pmatrix} \mathrm{e}^{-(k_+ + \alpha)t} + \frac{\alpha}{\alpha+\beta}\begin{pmatrix} 0 \\ 1 \\ 0 \\ -1 \end{pmatrix} \mathrm{e}^{-(k_- + \beta)t},$$

$$P(\mathrm{D}^*) \approx \frac{\beta}{\alpha+\beta}\mathrm{e}^{-(k_+ + \alpha)t} + \frac{\alpha}{\alpha+\beta}\mathrm{e}^{-(k_- + \beta)t}.$$

Problems of Chap. 10

10.1. Entropy Production

$$0 = \mathrm{d}H = T\,\mathrm{d}S + V\,\mathrm{d}p + \sum_k \mu_k \mathrm{d}N_k,$$

$$T\,\mathrm{d}S = -\sum_k \mu_k \mathrm{d}N_k = -\sum_j \sum_k \mu_k \nu_{kj} d\xi_j = \sum_j A_j d\xi_j,$$

$$\frac{\mathrm{d}S}{\mathrm{d}t} = \sum_j \frac{A_j}{T} r_j.$$

Problems of Chap. 11

11.1. ATP Synthesis

At chemical equilibrium,

$$0 = A = -\sum \nu_k \mu_k$$

$$
\begin{aligned}
&= \mu^0(\mathrm{ADP}) + k_\mathrm{B}T \ln c(\mathrm{ADP}) + \mu^0(\mathrm{POH}) + k_\mathrm{B}T \ln c(\mathrm{POH}) \\
&\quad +2k_\mathrm{B}T \ln c(H^+_\mathrm{out}) + 2e\Phi_\mathrm{out} \\
&\quad -\mu^0(\mathrm{ATP}) - k_\mathrm{B}T \ln c(\mathrm{ATP}) - \mu^0(\mathrm{H_2O}) - k_\mathrm{B}T \ln c(\mathrm{H_2O}) \\
&\quad -2k_\mathrm{B}T \ln c(H^+_\mathrm{in}) - 2e\Phi_\mathrm{in},
\end{aligned}
$$

$$
\begin{aligned}
k_\mathrm{B}T \ln K &= -\Delta G^0 = \mu^0(\mathrm{ADP}) - \mu^0(\mathrm{ATP}) + \mu^0(\mathrm{POH}) - \mu^0(\mathrm{H_2O}) \\
&= k_\mathrm{B}T \ln \frac{c(\mathrm{ATP})c(\mathrm{H_2O})c^2(H^+_\mathrm{in})}{c(\mathrm{ADP})c(\mathrm{POH})c^2(H^+_\mathrm{out})} + 2e(\Phi_\mathrm{in} - \Phi_\mathrm{out}) \\
&= k_\mathrm{B}T \ln \frac{c(\mathrm{ATP})c(\mathrm{H_2O})}{c(\mathrm{ADP})c(\mathrm{POH})} + 2k_\mathrm{B}T \ln \frac{c(H^+_\mathrm{in})}{c(H^+_\mathrm{out})} + 2e(\Phi_\mathrm{in} - \Phi_\mathrm{out}).
\end{aligned}
$$

Problems of Chap. 15

15.1. Transition State Theory

$$
\mathrm{A+B} \overset{K^\ddagger}{\leftrightharpoons} [\mathrm{AB}]^\ddagger \overset{k^\ddagger}{\rightarrow} \mathrm{P},
$$

$$
k = k^\ddagger c_{[\mathrm{AB}]^\ddagger} = k^\ddagger K^\ddagger c_\mathrm{A} c_\mathrm{B},
$$

$$
K^\ddagger = \frac{c_{[\mathrm{AB}]^\ddagger}}{c_\mathrm{A} c_\mathrm{B}} = \frac{q_{[\mathrm{AB}]^\ddagger}}{q_\mathrm{A} q_\mathrm{B}} \mathrm{e}^{-\Delta H^\ddagger/k_\mathrm{B}T} = q_x \frac{q^\ddagger_{[\mathrm{AB}]^\ddagger}}{q_\mathrm{A} q_\mathrm{B}} \mathrm{e}^{-\Delta H^\ddagger/k_\mathrm{B}T},
$$

$$
q_x = \frac{\sqrt{2\pi m k_\mathrm{B}T}}{h} \delta x,
$$

$$
k^\ddagger = \frac{v^\ddagger}{\delta x} = \frac{1}{\delta x} \sqrt{\frac{k_\mathrm{B}T}{2\pi m}},
$$

$$
\begin{aligned}
k &= \frac{1}{\delta x} \sqrt{\frac{k_\mathrm{B}T}{2\pi m}} \frac{\sqrt{2\pi m k_\mathrm{B}T}}{h} \delta x \frac{q^\ddagger_{[\mathrm{AB}]^\ddagger}}{q_\mathrm{A} q_\mathrm{B}} \mathrm{e}^{-\Delta H^\ddagger/k_\mathrm{B}T} c_\mathrm{A} c_\mathrm{B} \\
&= \frac{k_\mathrm{B}T}{h} \frac{q^\ddagger_{[\mathrm{AB}]^\ddagger}}{q_\mathrm{A} q_\mathrm{B}} \mathrm{e}^{-\Delta H^\ddagger/k_\mathrm{B}T} c_\mathrm{A} c_\mathrm{B}.
\end{aligned}
$$

15.2. Harmonic Transition State Theory

$$
\begin{aligned}
k &= v\langle \delta(x - x^\ddagger) \rangle = \sqrt{\frac{k_\mathrm{B}T}{2\pi m}} \frac{\int_{-\infty}^{\infty} \mathrm{e}^{-m\omega^2 x^2/2k_\mathrm{B}T} \delta(x - x^\ddagger)}{\int_{-\infty}^{\infty} \mathrm{e}^{-m\omega^2 x^2/2k_\mathrm{B}T}} \\
&= \sqrt{\frac{k_\mathrm{B}T}{2\pi m}} \frac{\mathrm{e}^{-m\omega^2 x^{\ddagger 2}/2k_\mathrm{B}T}}{\sqrt{2\pi k_\mathrm{B}T/m\omega^2}} \\
&= \frac{\omega}{2\pi} \mathrm{e}^{-\Delta E/k_\mathrm{B}T}.
\end{aligned}
$$

Problems of Chap. 16

16.1. Marcus Cross Relation

$$\mathrm{A{+}A^- \rightarrow A^-{+}A}, \qquad \lambda_\mathrm{A} = 2\Delta E(A_\mathrm{eq} \rightarrow A^-_\mathrm{eq}),$$

$$\mathrm{D{+}D^+ \rightarrow D^+{+}D}, \qquad \lambda_\mathrm{D} = 2\Delta E(D_\mathrm{eq} \rightarrow D^+_\mathrm{eq}),$$

$$\mathrm{A{+}D \ \rightarrow A^-{+}D^+},\ \lambda_\mathrm{AD} = \Delta E(\mathrm{A_{eq}} \rightarrow \mathrm{A^-_{eq}}) + \Delta E(\mathrm{D_{eq}} \rightarrow \mathrm{D^+_{eq}}) = \tfrac{\lambda_\mathrm{A}+\lambda_\mathrm{D}}{2},$$

$$k_\mathrm{A} = \frac{\omega_\mathrm{A}}{2\pi}\mathrm{e}^{-\lambda_\mathrm{A}/4k_\mathrm{B}T},$$

$$k_\mathrm{B} = \frac{\omega_\mathrm{B}}{2\pi}\mathrm{e}^{-\lambda_\mathrm{B}/4k_\mathrm{B}T},$$

$$K_\mathrm{AD} = \mathrm{e}^{-\Delta G/k_\mathrm{B}T},$$

$$\begin{aligned} k_\mathrm{AD} &= \frac{\omega_\mathrm{AD}}{2\pi}\exp\left\{-\frac{(\lambda_\mathrm{AD}+\Delta G)^2}{4\lambda_\mathrm{AD}k_\mathrm{B}T}\right\} \\ &= \frac{\omega_\mathrm{AD}}{2\pi}\exp\left\{-\frac{\lambda_\mathrm{A}+\lambda_\mathrm{D}}{8k_\mathrm{B}T} - \frac{\Delta G}{2k_\mathrm{B}T} - \frac{\Delta G^2}{4\lambda_\mathrm{AD}k_\mathrm{B}T}\right\} \\ &= \sqrt{k_\mathrm{A}k_\mathrm{B}K_\mathrm{AD}}\sqrt{\frac{\omega_\mathrm{AD}^2}{\omega_\mathrm{A}\omega_\mathrm{D}}}\exp\left\{-\frac{\Delta G^2}{4\lambda_\mathrm{AD}k_\mathrm{B}T}\right\}. \end{aligned}$$

Problems of Chap. 18

18.1. Absorption Spectrum

$$\begin{aligned} \alpha &= \frac{1}{2\pi\hbar}\int \mathrm{d}t \sum_{i,f} \mathrm{e}^{\mathrm{i}\omega t}\left\langle i\middle| \sum \frac{\mathrm{e}^{-\beta H}}{Q}\mathrm{e}^{-\mathrm{i}\omega_i t}\mu f\right\rangle \mathrm{e}^{\mathrm{i}\omega_f t}\langle f\mu i\rangle \\ &= \frac{1}{2\pi\hbar}\int \mathrm{d}t\, \mathrm{e}^{\mathrm{i}\omega t}\langle \mathrm{e}^{-\mathrm{i}Ht/\hbar}\mu \mathrm{e}^{\mathrm{i}Ht/\hbar}\mu\rangle \\ &= \frac{1}{2\pi\hbar}\int \mathrm{d}t\, \mathrm{e}^{\mathrm{i}\omega t}\langle \mu(0)\mu(t)\rangle \\ &\approx \frac{|\mu_\mathrm{eg}|^2}{2\pi\hbar}\int \mathrm{d}t\, \mathrm{e}^{\mathrm{i}\omega t}\langle \mathrm{e}^{-\mathrm{i}H_\mathrm{g}t/\hbar}\mathrm{e}^{\mathrm{i}H_\mathrm{e}t/\hbar}\rangle_\mathrm{g}. \end{aligned}$$

Problems of Chap. 20

20.1. Motional Narrowing

$$(s+\mathrm{i}\omega_1)(s+\mathrm{i}\omega_2)+(\alpha+\beta)(s+\mathrm{i}\overline{\omega})$$
$$=-\left(\Omega+\frac{\Delta\omega}{2}\right)\left(\Omega-\frac{\Delta\omega}{2}\right)-\mathrm{i}\omega_c\Omega,$$
$$\Omega=\omega-\overline{\omega},$$
$$\Omega^2-\frac{\Delta\omega^2}{4}+\mathrm{i}\omega_c\Omega=0,$$
$$\left(\Omega+\frac{\mathrm{i}\omega_c}{2}\right)^2=\frac{\Delta\omega^2}{4}-\frac{\omega_c^2}{4}.$$

For $\omega_c \ll \Delta\omega$, the poles are approximately at

$$\Omega_p=-\frac{\mathrm{i}\omega_c}{2}\pm\frac{\Delta\omega}{2}$$

and two lines are observed centered at the unperturbed frequencies $\overline{\omega}\pm\Delta\omega/2$ and with their width determined by ω_c. For $\omega_c=\Delta\omega$, the two poles coincide at

$$\Omega_p=-\frac{\mathrm{i}\omega_c}{2}$$

and a single line at the average frequency $\overline{\omega}$ appears. For $\omega_c \gg \Delta\omega$, one pole approaches zero according to

$$\Omega_p=-\mathrm{i}\frac{\Delta\omega^2}{4\omega_c},$$

which corresponds to a sharp line at the average frequency $\overline{\omega}$. The other pole approaches infinity as

$$\Omega_p=-\mathrm{i}\omega_c.$$

It contributes a broad line at $\overline{\omega}$ which vanishes in the limit of large ω_c (Fig. 32.1).

Problems of Chap. 21

21.1. Crude Adiabatic Model

$$\frac{\partial C}{\partial Q}=\begin{pmatrix}-s & c\\ -c & -s\end{pmatrix}\frac{\partial\zeta}{\partial Q},\quad C^\dagger\frac{\partial C}{\partial Q}=\begin{pmatrix}0 & 1\\ -1 & 0\end{pmatrix}\frac{\partial\zeta}{\partial Q},$$
$$\frac{\partial^2 C}{\partial Q^2}=\begin{pmatrix}-s & c\\ -c & -s\end{pmatrix}\frac{\partial^2\zeta}{\partial Q^2}-C\left(\frac{\partial\zeta}{\partial Q}\right)^2,$$

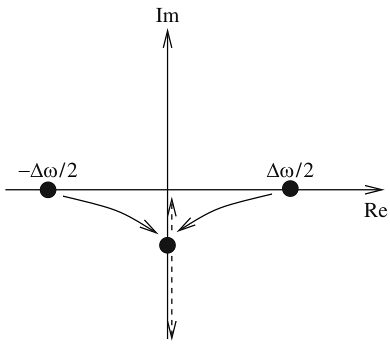

Fig. 32.1. Poles of the lineshape function

$$C^\dagger \frac{\partial^2 C}{\partial Q^2} = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} \frac{\partial^2 \zeta}{\partial Q^2} - \left(\frac{\partial \zeta}{\partial Q}\right)^2,$$

$$\int \mathrm{d}r\, C^\dagger \Phi^\dagger \frac{\partial^2}{\partial Q^2} \Phi C = C^\dagger \frac{\partial^2 C}{\partial Q^2} + 2C^\dagger \frac{\partial C}{\partial Q}\frac{\partial}{\partial Q} + \frac{\partial^2}{\partial Q^2}$$

$$= \frac{\partial^2}{\partial Q^2} + \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} \frac{\partial^2 \zeta}{\partial Q^2} - \left(\frac{\partial \zeta}{\partial Q}\right)^2 + 2\begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} \frac{\partial \zeta}{\partial Q}\frac{\partial}{\partial Q},$$

$$\int \mathrm{d}r\, C^\dagger \Phi^\dagger (T_{\mathrm{el}} + V_0 + \Delta V)\Phi C$$

$$= C^\dagger E C + C^\dagger \int \mathrm{d}r\, \Phi^\dagger \Delta V \Phi, \quad C = C^\dagger \begin{pmatrix} \overline{E}(Q) - \frac{\Delta E(Q)}{2} & V(Q) \\ V(Q) & \overline{E}(Q) + \frac{\Delta E(Q)}{2} \end{pmatrix} C,$$

$$\int \mathrm{d}r\, C^\dagger \Phi^\dagger H\, \Phi\, C$$

$$= -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial Q^2} + C^\dagger \begin{pmatrix} \overline{E}(Q) - \frac{\Delta E(Q)}{2} & V(Q) \\ V(Q) & \overline{E}(Q) + \frac{\Delta E(Q)}{2} \end{pmatrix} C + \frac{\hbar^2}{2m}\left(\frac{\partial \zeta}{\partial Q}\right)^2$$

$$-\frac{\hbar^2}{2m}\begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}\left(\frac{\partial^2 \zeta}{\partial Q^2} + 2\frac{\partial \zeta}{\partial Q}\frac{\partial}{\partial Q}\right),$$

$$\cos\zeta \sin\zeta = \frac{V(Q)}{\sqrt{4V(Q)^2 + \Delta E(Q)^2}},$$

$$\cos\zeta^2 - \sin\zeta^2 = \frac{\Delta E(Q)}{\sqrt{4V(Q)^2 + \Delta E(Q)^2}},$$

$$\frac{\partial}{\partial Q}(cs)^2 = 2cs(c^2 - s^2)\frac{\partial \zeta}{\partial Q} = \frac{2V\Delta E}{4V^2 + \Delta E^2}\frac{\partial \zeta}{\partial Q},$$

$$\frac{\partial}{\partial Q}(cs)^2 = \frac{\partial}{\partial Q}\frac{V^2}{4V^2+\Delta E^2}$$

$$= \frac{2V}{4V^2+\Delta E^2}\frac{\partial V}{\partial Q} - \frac{V^2}{(4V^2+\Delta E^2)^2}\left(2\Delta E\frac{\partial \Delta E}{\partial Q} + 8V\frac{\partial V}{\partial Q}\right),$$

$$\frac{\partial \zeta}{\partial Q} = \frac{\Delta E}{4V^2+\Delta E^2}\frac{\partial V}{\partial Q} - \frac{V}{4V^2+\Delta E^2}\frac{\partial \Delta E}{\partial Q} \approx \frac{1}{\Delta E}\frac{\partial V}{\partial Q},$$

$$\frac{\partial^2 \zeta}{\partial Q^2} = \frac{\Delta E\frac{\partial^2 V}{\partial Q^2} - V\frac{\partial^2 \Delta E}{\partial Q^2}}{4V^2+\Delta E^2} - \left(\Delta E\frac{\partial V}{\partial Q} - V\frac{\partial \Delta E}{\partial Q}\right)\frac{2\Delta E\frac{\partial \Delta E}{\partial Q} + 8V\frac{\partial V}{\partial Q}}{(4V^2+\Delta e^2)^2}$$

$$\approx \frac{1}{\Delta E}\frac{\partial^2 V}{\partial Q^2} - \frac{2}{\Delta E^2}\frac{\partial \Delta E}{\partial Q}\frac{\partial V}{\partial Q},$$

$$\widetilde{H} \approx -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial Q^2} + \begin{pmatrix} \overline{E} - \sqrt{4V^2+\Delta E^2} & \\ & \overline{E} + \sqrt{4V^2+\Delta E^2} \end{pmatrix}$$

$$+\frac{\hbar^2}{2m}\frac{1}{\Delta E^2}\left(\frac{\partial V}{\partial Q}\right)^2$$

$$-\frac{\hbar^2}{2m}\begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}\left(\frac{1}{\Delta E}\frac{\partial^2 V}{\partial Q^2} - \frac{2}{\Delta E^2}\frac{\partial \Delta E}{\partial Q}\frac{\partial V}{\partial Q} + \frac{2}{\Delta E}\frac{\partial V}{\partial Q}\frac{\partial}{\partial Q}\right).$$

Problems of Chap. 22

22.1. Ladder Model

$$\mathrm{i}\hbar\dot{C}_0 = V\sum_{j=1}^{n} C_j,$$

$$\mathrm{i}\hbar\dot{C}_j = E_j C_j + V C_0,$$

$$C_j = u_j \mathrm{e}^{(E_j/\mathrm{i}\hbar)t},$$

$$\mathrm{i}\hbar\dot{u}_j \mathrm{e}^{(E_j/\mathrm{i}\hbar)t} = V C_0,$$

$$u_j = \frac{V}{\mathrm{i}\hbar}\int_0^t \mathrm{e}^{-(E_j/\mathrm{i}\hbar)t'} C_0(t')\mathrm{d}t',$$

$$C_j = \frac{V}{\mathrm{i}\hbar}\int_0^t \mathrm{e}^{\mathrm{i}(E_j/\hbar)(t-t')} C_0(t')\mathrm{d}t',$$

$$E_j = \alpha + j^*\hbar\Delta\omega,$$

$$\dot{C}_0 = \frac{V}{\mathrm{i}\hbar}\sum_{j=1}^{n} C_j = -\frac{V^2}{\hbar^2}\sum\int_0^t \mathrm{e}^{\mathrm{i}(j\Delta\omega+\alpha/\hbar)(t-t')} C_0(t')\mathrm{d}t',$$

$$\omega = j\Delta\omega + \frac{\alpha}{\hbar},$$

$$\sum_{j=-\infty}^{\infty} e^{i(j\Delta\omega+\alpha/\hbar)(t-t')}\Delta j \;\rightarrow\; \int_{-\infty}^{\infty} e^{i\omega(t-t')}\frac{d\omega}{\Delta\omega} = \frac{2\pi}{\Delta\omega}\delta(t-t'),$$

$$\dot{C}_0 = -\frac{2\pi V^2}{\Delta\omega}C_0 = -\frac{2\pi V^2}{\hbar}\rho(E)C_0,$$

$$\rho(E) = \frac{1}{\hbar\Delta\omega} = \frac{1}{\Delta E}.$$

Problems of Chap. 23

23.1. Hückel Model with Alternating Bonds

(a)
$$\alpha e^{ikn} + \beta e^{i(kn+\chi)} + \beta' e^{i(kn+k+\chi)} = e^{ikn}\left(\alpha + \beta e^{i\chi} + \beta' e^{i(k+\chi)}\right),$$

$$\alpha e^{i(kn+\chi)} + \beta' e^{i(kn-k)} + \beta e^{ikn} = e^{i(kn+\chi)}\left(\alpha + \beta' e^{-i(k+\chi)} + \beta e^{-i\chi}\right).$$

(b)
$$\beta e^{i\chi} + \beta' e^{i(k+\chi)} = \beta' e^{-i(k+\chi)} + \beta e^{-i\chi},$$

$$e^{2i\chi} = \frac{\beta' e^{-ik} + \beta}{\beta' e^{ik} + \beta} = e^{-ik}\frac{\beta' e^{-ik/2} + \beta e^{ik/2}}{\beta' e^{ik/2} + \beta e^{-ik/2}} = e^{-ik}\frac{\left(\beta' e^{-ik/2} + \beta e^{ik/2}\right)^2}{\beta'^2 + \beta^2 + 2\beta\beta'\cos k},$$

$$e^{i\chi} = \pm e^{-ik/2}\frac{\beta' e^{-ik/2} + \beta e^{ik/2}}{\sqrt{\beta'^2 + \beta^2 + 2\beta\beta'\cos k}},$$

$$\lambda = \alpha + \beta e^{i\chi} + \beta' e^{i(k+\chi)} = \alpha \pm \frac{\beta\beta' e^{-ik} + \beta^2 + \beta'^2 + \beta\beta' e^{ik}}{\sqrt{\beta'^2 + \beta^2 + 2\beta\beta'\cos k}}$$

$$= \alpha \pm \sqrt{\beta'^2 + \beta^2 + 2\beta\beta'\cos k}.$$

(c)
$$0 = \Im\left(e^{i\chi + i(N+1)k}\right) = \Im\left(\pm e^{-ik/2}\frac{\beta' e^{-ik/2} + \beta e^{ik/2}}{\sqrt{\beta'^2 + \beta^2 + 2\beta\beta'\cos k}}e^{i(N+1)k}\right)$$

$$= \pm\Im\left(\frac{\beta' e^{iNk} + \beta e^{i(N+1)k}}{\sqrt{\beta'^2 + \beta^2 + 2\beta\beta'\cos k}}\right),$$

$$0 = \beta'\sin(Nk) + \beta\sin(N+1)k.$$

(d) For a linear polyene with $2N-1$ carbon atoms, use again eigenfunctions

$$c_{2n} = \sin(kn) = \Im(e^{ikn}),$$

$$c_{2n-1} = \sin(kn+\chi) = \Im(e^{i(kn+\chi)}),$$

and chose the k-values such that

$$\Im(e^{iNk}) = \sin(Nk) = 0.$$

Problems of Chap. 25

25.1. Special Pair Dimer

$$\begin{pmatrix} c & -s \\ s & c \end{pmatrix} \begin{pmatrix} -\Delta/2 & V \\ V & \Delta/2 \end{pmatrix} \begin{pmatrix} c & s \\ -s & c \end{pmatrix}$$

is diagonalized if

$$(c^2 - s^2)V = cs\Delta$$

or with $c = \cos\chi$, $s = \sin\chi$

$$\tan(2\chi) = \frac{2V}{\Delta},$$

$$c^2 - s^2 = \cos 2\chi = \frac{1}{\sqrt{1 + (4V^2/\Delta^2)}} \geq 0,$$

$$2cs = \sin(2\chi) = \frac{1}{\sqrt{1 + (\Delta^2/4V^2)}} \geq 0.$$

The eigenvalues are (Fig. 32.2)

$$\begin{aligned} E_\pm &= \pm\left(\frac{\Delta}{2}(c^2 - s^2) + 2csV\right) \\ &= \pm\left(\frac{\Delta}{2}\frac{1}{\sqrt{1 + \frac{4V^2}{\Delta^2}}} + V\frac{1}{\sqrt{1 + \frac{\Delta^2}{4V^2}}}\right) = \pm\frac{1}{2}\sqrt{\Delta^2 + 4V^2}. \end{aligned}$$

The transition dipoles are

$$\mu_+ = s\mu_\mathrm{a} + c\mu_\mathrm{b},$$

$$\mu_- = c\mu_\mathrm{a} - s\mu_\mathrm{b},$$

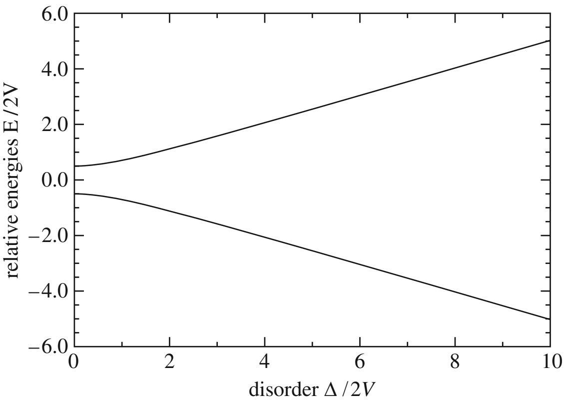

Fig. 32.2. Energy splitting of the two dimer bands

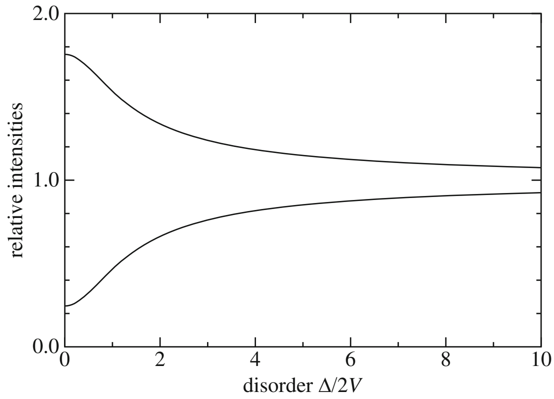

Fig. 32.3. Intensities of the two dimer bands

and the intensities (for $|\mu_{\mathrm{a}}| = |\mu_{\mathrm{b}}| = \mu$)

$$|\mu_{\pm}|^2 = \mu^2(1 \pm 2cs\cos\alpha) = \mu^2 \left(1 \pm \frac{\cos\alpha}{\sqrt{1 + (\Delta^2/4V^2)}}\right)$$

with (Fig. 32.3)

$$\cos\alpha = -0.755.$$

25.2. LH2

$$|n;\alpha\rangle = \frac{1}{3}\sum_k \mathrm{e}^{-\mathrm{i}kn}|k;\alpha\rangle,$$

$$\sum_{n=1}^{9} E_\alpha |n;\alpha\rangle\langle n;\alpha| = \sum_{n=1}^{9} E_\alpha \frac{1}{9}\sum_{k,k'} \mathrm{e}^{-\mathrm{i}(k-k')n}|k;\alpha\rangle\langle k';\alpha|$$

$$= \delta_{k,k'} E_\alpha |k;\alpha\rangle\langle k;\alpha|,$$

$$\sum_{n=1}^{9} E_\alpha |n;\beta\rangle\langle n;\beta| \sum_{n=1}^{9} E_\alpha \frac{1}{9}\sum_{k,k'} \mathrm{e}^{-\mathrm{i}(k-k')n}|k;\beta\rangle\langle k';\beta|$$

$$= \delta_{k,k'} E_\alpha |k;\beta\rangle\langle k;\beta|,$$

$$\sum_{n=1}^{9} V_{\mathrm{dim}} |n;\alpha\rangle\langle n;\beta| = \sum_{n=1}^{9} V_{\mathrm{dim}} \frac{1}{9}\sum_{k,k'} \mathrm{e}^{-\mathrm{i}(k-k')n}|k;\alpha\rangle\langle k';\beta|$$

$$= \delta_{k,k'} V_{\mathrm{dim}} |k;\alpha\rangle\langle k;\beta|,$$

$$\sum_{n=1}^{9} V_{\beta\alpha,1}|n;\alpha\rangle\langle n-1;\beta| = \sum_{n=1}^{9} V_{\beta\alpha,1}\mathrm{e}^{-\mathrm{i}k}\frac{1}{9}\sum_{k,k'}\mathrm{e}^{-\mathrm{i}(k-k')n}|k;\alpha\rangle\langle k';\beta|$$

$$= \delta_{k,k'}V_{\beta\alpha,1}\mathrm{e}^{-\mathrm{i}k}|k;\alpha\rangle\langle k;\beta|,$$

$$\sum_{n=1}^{9} V_{\beta\alpha,1}|n;\beta\rangle\langle n+1;\alpha| = \sum_{n=1}^{9} V_{\beta\alpha,1}\mathrm{e}^{\mathrm{i}k}\frac{1}{9}\sum_{k,k'}\mathrm{e}^{-\mathrm{i}(k-k')n}|k;\beta\rangle\langle k';\alpha|$$

$$= \delta_{k,k'}V_{\beta\alpha,1}\mathrm{e}^{\mathrm{i}k}|k;\beta\rangle\langle k;\alpha|,$$

$$\sum_{n=1}^{9} V_{\alpha\alpha,1}(|n;\alpha\rangle\langle n+1;\alpha| + \text{h.c.})$$

$$= \sum_{n=1}^{9} V_{\alpha\alpha,1}\mathrm{e}^{\mathrm{i}k}\frac{1}{9}\sum_{k,k'}\mathrm{e}^{-\mathrm{i}(k-k')n}|k;\alpha\rangle\langle k';\alpha| + \text{h.c.}$$

$$= \delta_{k,k'}2V_{\alpha\alpha,1}\cos k|k;\alpha\rangle\langle k;\alpha|,$$

$$H_{\alpha\alpha}(k) = E_\alpha + 2V_{\alpha\alpha 1}\cos k,$$

$$H_{\beta\beta}(k) = E_\beta + 2V_{\beta\beta 1}\cos k,$$

$$H_{\alpha\beta}(k) = V_{\text{dim}} + \mathrm{e}^{-\mathrm{i}k}V_{\beta\alpha,1},$$

$$H_{\beta\alpha}(k) = V_{\text{dim}} + \mathrm{e}^{\mathrm{i}k}V_{\beta\alpha,1},$$

$$H(k) = \begin{pmatrix} E_\alpha + 2V_{\alpha\alpha 1}\cos k & V + \mathrm{e}^{-\mathrm{i}k}W \\ V + \mathrm{e}^{\mathrm{i}k}W & E_\beta + 2V_{\beta\beta 1}\cos k \end{pmatrix}$$

$$= \overline{E}_k + \begin{pmatrix} -\Delta_k/2 & V + \mathrm{e}^{-\mathrm{i}k}W \\ V + \mathrm{e}^{\mathrm{i}k}W & \Delta_k/2 \end{pmatrix}.$$

Perform a canonical transformation with

$$S = \begin{pmatrix} c & -s\mathrm{e}^{-\mathrm{i}\chi} \\ s\mathrm{e}^{\mathrm{i}\chi} & c \end{pmatrix}.$$

$S^\dagger H S$ becomes diagonal if

$$c^2(V + \mathrm{e}^{\mathrm{i}k}W) - s^2\mathrm{e}^{2\mathrm{i}\chi}(V + \mathrm{e}^{-\mathrm{i}k}W) + cs\mathrm{e}^{\mathrm{i}\chi}\Delta_k = 0.$$

Chose χ such that

$$V + \mathrm{e}^{\mathrm{i}k}W = \operatorname{sign} V|V + \mathrm{e}^{\mathrm{i}k}W|\mathrm{e}^{\mathrm{i}\chi} = U(k)\mathrm{e}^{\mathrm{i}\chi}$$

and solve

$$(c^2 - s^2)U + cs\Delta_k = 0$$

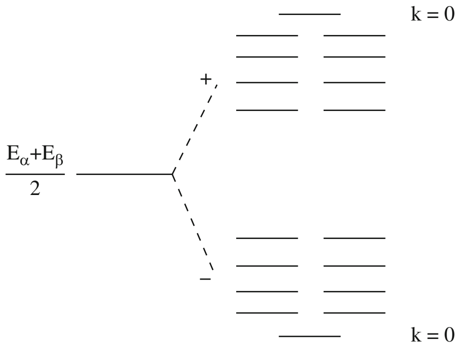

Fig. 32.4. Energy levels of LH2

by[1]

$$c^2 - s^2 = -\mathrm{sign}\left(\frac{U}{\Delta}\right)\frac{1}{\sqrt{1+(4U^2/\Delta^2)}}, \quad cs = \frac{|U/\Delta|}{\sqrt{1+(4U^2/\Delta^2)}}.$$

The eigenvalues are (Fig. 32.4)

$$E_\pm(k) = \overline{E}_k \pm \ \mathrm{sign}\, V \frac{1}{2}\sqrt{\Delta^2 + 4U^2}$$

$$= \frac{E_\alpha + E_\beta}{2} + (V_{\alpha\alpha 1} + V_{\beta\beta 1})\cos k$$

$$\pm \ \mathrm{sign}\, V \sqrt{\left(\frac{E_\alpha - E_\beta + 2(V_{\alpha\alpha 1} - V_{\beta\beta 1})\cos k}{2}\right)^2 + V^2 + W^2 + 2VW\cos k}$$

$$\mu_{k,+} = c\frac{1}{3}\sum_n \mathrm{e}^{ikn}\mu_{n\alpha} + s\mathrm{e}^{\mathrm{i}\chi}\frac{1}{3}\sum_n \mathrm{e}^{ikn}\mu_{n\beta}$$

$$= c\frac{1}{3}\sum_n \mathrm{e}^{ikn} S_9^n \mu_{0\alpha} + s\mathrm{e}^{\mathrm{i}\chi}\frac{1}{3}\sum_n \mathrm{e}^{ikn} S_9^n R_z(2\nu + \phi_\beta - \phi_\alpha)\mu_{0,\alpha}$$

$$= \frac{1}{3}\sum_n \mathrm{e}^{ikn}\begin{pmatrix} \cos\frac{2\pi}{9}n & -\sin\frac{2\pi}{9}n & \\ \sin\frac{2\pi}{9}n & \cos\frac{2\pi}{9}n & \\ & & 1 \end{pmatrix}$$

$$\times \left(c + s\mathrm{e}^{\mathrm{i}\chi}\begin{pmatrix} \cos\epsilon & -\sin\epsilon & \\ \sin\epsilon & \cos\epsilon & \\ & & 1 \end{pmatrix}\right)\mu_0 \begin{pmatrix} \sin\theta \\ 0 \\ \cos\theta \end{pmatrix}.$$

[1] The sign is chosen such that for $|\Delta| \ll |U|$, the solution becomes $c = s = 1/\sqrt{2}$.

The sum over n again gives the selection rules

$$k = 0 \quad z\text{-polarization},$$

$$k = \pm\frac{2\pi}{9} \quad \text{circular } xy\text{-polarization.}$$

The second factor gives for z-polarization

$$\mu = 3\mu_0(c + s\mathrm{e}^{\mathrm{i}\chi})\cos\theta,$$

$$|\mu|^2 = 9\mu_0^2(1 + 2cs\ \cos\chi)\cos^2\theta,$$

with

$$\cos^2\theta \approx 0.008$$

and for polarization in the xy-plane

$$\mu = 3\mu_0 \sin\theta \begin{pmatrix} c + s\mathrm{e}^{\mathrm{i}\chi}\cos\epsilon \\ s\mathrm{e}^{\mathrm{i}\chi}\sin\epsilon \end{pmatrix},$$

$$|\mu|^2 = 9\mu_0^2\sin^2\theta(1 + 2\cos\epsilon\, cs\cos\chi),$$

with

$$\sin^2\theta \approx 0.99, \quad \cos\epsilon \approx -0.952.$$

The intensities of the $(k, -)$ states are

$$|\mu_z|^2 = 9\mu_0^2(1 - 2cs\ \cos\chi)\cos^2\theta,$$

$$|\mu_\perp|^2 = 9\mu_0^2\sin^2\theta(1 - 2\cos\epsilon\, cs\cos\chi).$$

25.3. Exchange Narrowing

$$P(\delta E_k = X) = \int \mathrm{d}\delta E_1 \mathrm{d}\delta E_2 \cdots P(\delta E_1)P(\delta E_2)\cdots\delta\left(X - \frac{\sum\delta E_n}{N}\right),$$

$$P(\delta E_k = X) = \frac{1}{2\pi}\int \mathrm{d}t \int \delta E_1 \mathrm{d}\delta E_2 \cdots \frac{1}{\Delta\sqrt{\pi}}\mathrm{e}^{-\delta E_1^2/\Delta^2}\cdots\mathrm{e}^{\mathrm{i}t(X-\sum\delta E_n/N)}$$

$$= \frac{1}{2\pi}\int \mathrm{d}t\,\mathrm{e}^{\mathrm{i}tX}\left(\frac{1}{\Delta\sqrt{\pi}}\int \mathrm{d}t\,\delta E_1 \mathrm{e}^{-\delta E_1^2/\Delta^2 - \mathrm{i}t\delta E_1/N}\right)^N$$

$$= \frac{1}{2\pi}\int \mathrm{d}t\,\mathrm{e}^{\mathrm{i}tX}\mathrm{e}^{-\Delta^2 t^2/4N}$$

$$= \frac{\sqrt{N}}{\sqrt{\pi}\Delta}\mathrm{e}^{-X^2 N/\Delta^2}. \tag{32.19}$$

Problems of Chap. 28

28.1. Deviation from Equilibrium

$$\Omega = \mathrm{e}^{-\Delta U/k_\mathrm{B}T}(1-\mathrm{e}^{\Delta\mu/k_\mathrm{B}T})\frac{\alpha_2}{\alpha_2+\beta_2},$$

$$\Omega(x) = \mathrm{e}^{(\Delta\mu^0-\Delta U(x))/k_\mathrm{B}T}\frac{\alpha_2(x)}{\alpha_2(x)+\beta_2(x)}\left(K_\mathrm{eq}-\frac{C(\mathrm{ATP})}{C(\mathrm{ADP})C(\mathrm{P})}\right).$$

For $\Delta\mu \neq 0$ but $\Delta\mu \ll k_\mathrm{B}T$, Ω becomes a linear function of $\Delta\mu$

$$\Omega(x) \to -\mathrm{e}^{-\Delta U(x)/k_\mathrm{B}T}\frac{\alpha_2(x)}{\alpha_2(x)+\beta_2(x)}\frac{\Delta\mu}{k_\mathrm{B}T},$$

whereas in the opposite limit $\Delta\mu \gg k_\mathrm{B}T$ it becomes proportional to the concentration ratio:

$$\Omega(x) \to -\mathrm{e}^{-\Delta U(x)/k_\mathrm{B}T}\frac{\alpha_2(x)}{\alpha_2(x)+\beta_2(x)}\mathrm{e}^{\Delta\mu^0/k_\mathrm{B}T}\frac{C(\mathrm{ATP})}{C(\mathrm{ADP})C(\mathrm{P})}.$$

References

1. T.L. Hill, *An Introduction to Statistical Thermodynamics* (Dover, New York, 1986)
2. S. Cocco, J.F. Marko, R. Monasson, arXiv:cond-mat/0206238v1
3. C. Storm, P.C. Nelson, Phys. Rev. E **67**, 51906 (2003)
4. K.K. Mueller-Niedebock, H.L. Frisch, Polymer **44**, 3151 (2003)
5. C. Leubner, Eur. J. Phys. **6**, 299 (1985)
6. P.J. Flory, J. Chem. Phys. **10**, 51 (1942)
7. M.L. Huggins, J. Phys. Chem. **46**, 151 (1942)
8. M. Feig, C.L. Brooks III, Curr. Opin. Struct. Biol. **14**, 217 (2004)
9. B. Roux, T. Simonson, Biophys. Chem. **78**, 1 (1999)
10. A. Onufriev, Annu. Rep. Comput. Chem. **4**, 125 (2008)
11. M. Born, Z. Phys. **1**, 45 (1920)
12. D. Bashford, D. Case, Annu. Rev. Phys. Chem. **51**, 29 (2000)
13. W.C. Still, A. Tempczyk, R.C. Hawley, T. Hendrickson, JACS **112**, 6127 (1990)
14. G.D. Hawkins, C.J. Cramer, D.G. Truhlar, Chem. Phys. Lett. **246**, 122 (1995)
15. M. Schaefer, M. Karplus, J. Phys. Chem. **100**, 1578 (1996)
16. I.M. Wonpil, M.S. Lee, C.L. Brooks III, J. Comput. Chem. **24**, 1691 (2003)
17. F. Fogolari, A. Brigo, H. Molinari, J. Mol. Recognit. **15**, 377 (2002)
18. A.I. Shestakov, J.L. Milovich, A. Noy, J. Colloid Interface Sci. **247**, 62 (2002)
19. B. Lu, D. Zhang, J.A. McCammon, J. Chem. Phys. **122**, 214102 (2005)
20. P. Koehl, Curr. Opin. Struct. Biol. **16**, 142 (2006)
21. P. Debye, E. Hueckel, Phys. Z. **24**, 305 (1923)
22. G. Goüy, Comt. Rend. **149**, 654 (1909)
23. G. Goüy, J. Phys. **9**, 457 (1910)
24. D.L. Chapman, Philos. Mag. **25**, 475 (1913)
25. O. Stern, Z. Elektrochem. **30**, 508 (1924)
26. A.-S. Yang, M. Gunner, R. Sampogna, K. Sharp, B. Honig, Proteins **15**, 252 (1993)
27. P.W. Atkins, *Physical Chemistry* (Freeman, New York, 2006)
28. W.J. Moore, *Basic Physical Chemistry* (Prentice-Hall, New York, 1983)
29. M. Schaefer, M. Sommer, M. Karplus, J. Phys. Chem. B **101**, 1663 (1997)
30. R.A. Raupp-Kossmann, C. Scharnagl, Chem. Phys. Lett. **336**, 177 (2001)
31. H. Risken, *The Fokker–Planck Equation* (Springer, Berlin, 1989)
32. H.A. Kramers, Physica **7**, 284 (1941)

33. P.O.J. Scherer, Chem. Phys. Lett. **214**, 149 (1993)
34. E.W. Montroll, H. Scher, J. Stat. Phys. **9**, 101 (1973)
35. E.W. Montroll, G.H. Weiss, J. Math. Phys. **6**, 167 (1965)
36. A.A. Zharikov, P.O.J. Scherer, S.F. Fischer, J. Phys. Chem. **98**, 3424 (1994)
37. A.A. Zharikov, S.F. Fischer, Chem. Phys. Lett. **249**, 459 (1995)
38. S.R. de Groot, P. Mazur, *Irreversible Thermodynamics* (Dover, New York, 1984)
39. D.G. Miller, Faraday Discuss. Chem. Soc. **64**, 295 (1977)
40. R. Paterson, Faraday Discuss. Chem. Soc. **64**, 304 (1977)
41. D.E. Goldman, J. Gen. Physiol. **27**, 37 (1943)
42. A.L. Hodgkin, A.F. Huxley, J. Physiol. **117**, 500 (1952)
43. J. Kenyon, How to solve and program the Hodgkin–Huxley equations (http://134.197.54.225/department/Faculty/kenyon/Hodgkin&Huxley/pdfs/HH.Program.pdf)
44. J. Vreeken, A friendly introduction to reaction–diffusion systems, Internship Paper, AILab, Zurich, July 2002
45. E. Pollak, P. Talkner, Chaos **15**, 026116 (2005)
46. F.T. Gucker, R.L. Seifert, *Physical Chemistry* (W.W. Norton, New York, 1966)
47. S. Glasstone, K.J. Laidler, H. Eyring, *The Theory of Rate Processes* (McGraw-Hill, New York, 1941)
48. K.J. Laidler, *Chemical Kinetics*, 3rd edn. (Harper & Row, New York, 1987)
49. G.A. Natanson, J. Chem. Phys. **94**, 7875 (1991)
50. R.A. Marcus, Annu. Rev. Phys. Chem. **15**, 155 (1964)
51. R.A. Marcus, N. Sutin, Biochim. Biophys. Acta **811**, 265 (1985)
52. R.A. Marcus, Angew. Chem. Int. Ed. Engl. **32**, 1111 (1993)
53. A.M. Kuznetsov, J. Ulstrup, *Electron Transfer in Chemistry and Biology* (Wiley, Chichester, 1998), p. 49
54. P.W. Anderson, J. Phys. Soc. Jpn. **9**, 316 (1954)
55. R. Kubo, J. Phys. Soc. Jpn. **6**, 935 (1954)
56. R. Kubo, in *Fluctuations, Relaxations and Resonance in Magnetic Systems*, ed. by D. ter Haar (Plenum, New York, 1962)
57. T.G. Heil, A. Dalgarno, J. Phys. B **12**, 557 (1979)
58. L.D. Landau, Phys. Z. Sowjetun. **1**, 88 (1932)
59. C. Zener, Proc. R. Soc. Lond. A **137**, 696 (1932)
60. E.S. Kryachko, A.J.C. Varandas, Int. J. Quant. Chem. **89**, 255 (2001)
61. E.N. Economou, *Green's Functions in Quantum Physics* (Springer, Berlin, 1978)
62. H. Scheer, W.A. Svec, B.T. Cope, M.H. Studler, R.G. Scott, J.J. Katz, JACS **29**, 3714 (1974)
63. A. Streitwieser, *Molecular Orbital Theory for Organic Chemists* (Wiley, New York, 1961)
64. J.E. Lennard-Jones, Proc. R. Soc. Lond. A **158**, 280 (1937)
65. B.S. Hudson, B.E. Kohler, K. Schulten, in *Excited States*, ed. by E.C. Lin (Academic, New York, 1982), pp. 1–95
66. B.E. Kohler, C. Spangler, C. Westerfield, J. Chem. Phys. **89**, 5422 (1988)
67. T. Polivka, J.L. Herek, D. Zigmantas, H.-E. Akerlund, V. Sundstrom, Proc. Natl. Acad. Sci. USA **96**, 4914 (1999)
68. B. Hudson, B. Kohler, Synth. Met. **9**, 241 (1984)
69. B.E. Kohler, J. Chem. Phys. **93**, 5838 (1990)

70. W.T. Simpson, J. Chem. Phys. **17**, 1218 (1949)
71. H. Kuhn, J. Chem. Phys. **17**, 1198 (1949)
72. M. Gouterman, J. Mol. Spectrosc. **6**, 138 (1961)
73. M. Gouterman, J. Chem. Phys. **30**, 1139 (1959)
74. M. Gouterman, G.H. Wagniere, L.C. Snyder, J. Mol. Spectrosc. **11**, 108 (1963)
75. C. Weiss, *The Porphyrins*, vol. III (Academic, New York, 1978), p. 211
76. D. Spangler, G.M. Maggiora, L.L. Shipman, R.E. Christofferson, J. Am. Chem. Soc. **99**, 7470 (1977)
77. B.R. Green, D.G. Durnford, Annu. Rev. Plant Physiol. Plant Mol. Biol. **47**, 685 (1996)
78. H.A. Frank et al., Pure Appl. Chem. **69**, 2117 (1997)
79. R.J. Cogdell et al., Pure Appl. Chem. **66**, 1041 (1994)
80. H. van Amerongen, R. van Grondelle, J. Phys. Chem. B **105**, 604 (2001)
81. T. Förster, Ann. Phys. **2**, 55 (1948)
82. T. Förster, Disc. Faraday Trans. **27**, 7 (1965)
83. D.L. Dexter, J. Chem. Phys. **21**, 836 (1953)
84. F.J. Kleima, M. Wendling, E. Hofmann, E.J.G. Peterman, R. van Grondelle, H. van Amerongen, Biochemistry **39**, 5184 (2000)
85. T. Pullerits, M. Chachisvilis, V. Sundström, J. Phys. Chem. **100**, 10787 (1996)
86. R.C. Hilborn, Am. J. Phys. **50**, 982 (1982), revised 2002
87. S.H. Lin, Proc. R. Soc. Lond. A **335**, 51 (1973)
88. S.H. Lin, W.Z. Xiao, W. Dietz, Phys. Rev. E **47**, 3698 (1993)
89. MOLEKEL 4.0, P. Fluekiger, H.P. Luethi, S. Portmann, J. Weber, Swiss National Supercomputing Centre CSCS, Manno Switzerland, 2000
90. J. Deisenhofer, H. Michel, Science **245**, 1463 (1989)
91. J. Deisenhofer, O. Epp, K. Miki, R. Huber, H. Michel, Nature **318**, 618 (1985)
92. J. Deisenhofer, O. Epp, K. Miki, R. Huber, H. Michel, J. Mol. Biol. **180**, 385 (1984)
93. H. Michel, J. Mol. Biol. **158**, 567 (1982)
94. E.W. Knapp, P.O.J. Scherer, S.F. Fischer, BBA **852**, 295 (1986)
95. P.O.J. Scherer, S.F. Fischer, in *Chlorophylls*, ed. by H. Scheer (CRC, Boca Raton, 1991), pp. 1079–1093
96. R.J. Cogdell, A. Gall, J. Koehler, Q. Rev. Biophys. **39**, 227 (2006)
97. M. Ketelaars et al., Biophys. J. **80**, 1591 (2001)
98. M. Matsushita et al., Biophys. J. **80**, 1604 (2001)
99. K. Sauer, R.J. Cogdell, S.M. Prince, A. Freer, N.W. Isaacs, H. Scheer, Photochem. Photobiol. **64**, 564 (1996)
100. A. Freer, S. Prince, K. Sauer, M. Papitz, A. Hawthorntwaite-Lawless, G. McDermott, R. Cogdell, N.W. Isaacs, Structure **4**, 449 (1996)
101. M.Z. Papiz, S.M. Prince, A. Hawthorntwaite-Lawless, G. McDermott, A. Freer, N.W. Isaacs, R.J. Cogdell, Trends Plant Sci. **1**, 198 (1996)
102. G. McDermott, S.M. Prince, A. Freer, A. Hawthorntwaite-Lawless, M. Papitz, R. Cogdell, Nature **374**, 517 (1995)
103. N.W. Isaacs, R.J. Cogdell, A. Freer, S.M. Prince, Curr. Opin. Struct. Biol. **5**, 794 (1995)
104. E.E. Abola, F.C. Bernstein, S.H. Bryant, T.F. Koetzle, J. Weng, in *Crystallographic Databases – Information Content, Software Systems, Scientific Applications*, ed. by F.H. Allen, G. Bergerhoff, R. Sievers (Data Commission of the International Union of Crystallography, Cambridge, 1987), p. 107

105. F.C. Bernstein, T.F. Koetzle, G.J.B. Williams, E.F. Meyer Jr., M.D. Brice, J.R. Rodgers, O. Kennard, T. Shimanouchi, M. Tasumi, J. Mol. Biol. **112**, 535 (1977)
106. R. Sayle, E.J. Milner-White, Trends Biochem. Sci. **20**, 374 (1995)
107. Y. Zhao, M.-F. Ng, G.H. Chen, Phys. Rev. E **69**, 032902 (2004)
108. A.M. van Oijen, M. Ketelaars, J. Köhler, T.J. Aartsma, J. Schmidt, Science **285**, 400 (1999)
109. C. Hofmann, T.J. Aartsma, J. Köhler, Chem. Phys. Lett. **395**, 373 (2004)
110. S.E. Dempster, S. Jang, R.J. Silbey, J. Chem. Phys. **114**, 10015 (2001)
111. S. Jang, R.J. Silbey, J. Chem. Phys. **118**, 9324 (2003)
112. K. Mukai, S. Abe, Chem. Phys. Lett. **336**, 445 (2001)
113. R.G. Alden, E. Johnson, V. Nagarajan, W.W. Parson, C.J. Law, R.G. Cogdell, J. Phys. Chem. B **101**, 4667 (1997)
114. V. Novoderezhkin, R. Monshouwer, R. van Grondelle, Biophys. J. **77**, 666 (1999)
115. M.K. Sener, K. Schulten, Phys. Rev. E **65**, 31916 (2002)
116. A. Warshel, S. Creighton, W.W. Parson, J. Phys. Chem. **92**, 2696 (1988)
117. M. Plato, C.J. Winscom, in *The Photosynthetic Bacterial Reaction Center*, ed. by J. Breton, A. Vermeglio (Plenum, New York, 1988), p. 421
118. P.O.J. Scherer, S.F. Fischer, Chem. Phys. **131**, 115 (1989)
119. L.Y. Zhang, R.A. Friesner, Proc. Natl. Acad. Sci. USA **95**, 13603 (1998)
120. M. Gutman, Structure **12**, 1123 (2004)
121. P. Mitchell, Biol. Rev. Camb. Philos. Soc. **41**, 445 (1966)
122. H. Luecke, H.-T. Richter, J.K. Lanyi, Science **280**, 1934 (1998)
123. R. Neutze et al., BBA **1565**, 144 (2002)
124. D. Borgis, J.T. Hynes, J. Chem. Phys. **94**, 3619 (1991)
125. F. Juelicher, in *Transport and Structure: Their Competitive Roles in Biophysics and Chemistry*, ed. by S.C. Müller, J. Parisi, W. Zimmermann. Lecture Notes in Physics (Springer, Berlin, 1999)
126. A. Parmeggiani, F. Juelicher, A. Ajdari, J. Prost, Phys. Rev. E **60**, 2127 (1999)
127. F. Jülicher, A. Ajdari, J. Prost, Rev. Mod. Phys. **69**, 1269 (1997)
128. F. Jülicher, J. Prost, Progr. Theor. Phys. Suppl. **130**, 9 (1998)
129. H. Qian, J. Math. Chem. **27**, 219 (2000)
130. M.E. Fisher, A.B. Kolomeisky, arXiv:cond-mat/9903308v1
131. N.D. Mermin, J. Math. Phys. **7**, 1038 (1966)
132. M.W. Schmidt, K.K. Baldridge, J.A. Boatz, S.T. Elbert, M.S. Gordon, J.J. Jensen, S. Koseki, N. Matsunaga, K.A. Nguyen, S. Su, T.L. Windus, M. Dupuis, J.A. Montgomery J. Comput. Chem. **14**, 1347 (1993)

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