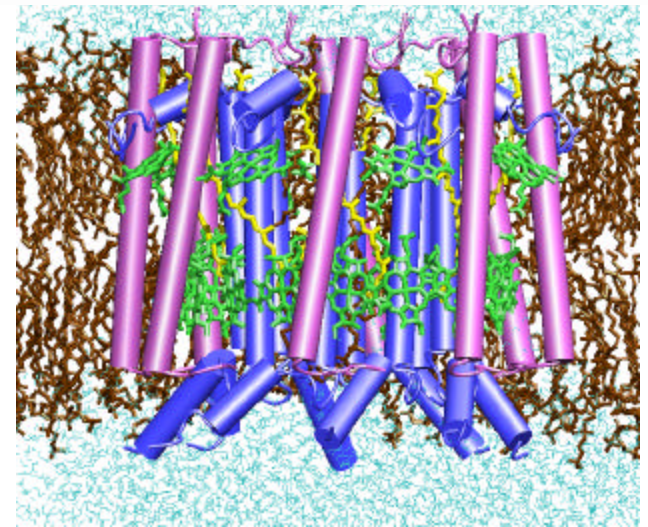
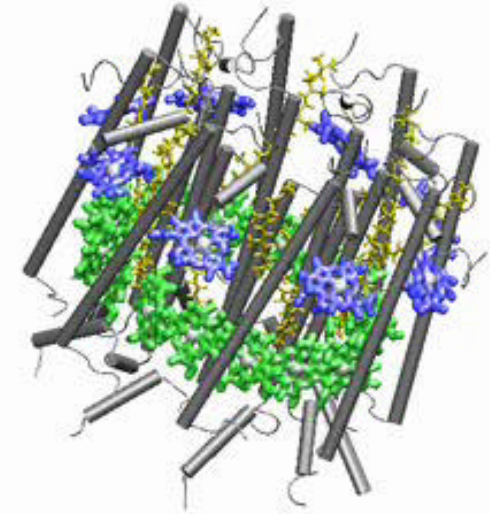
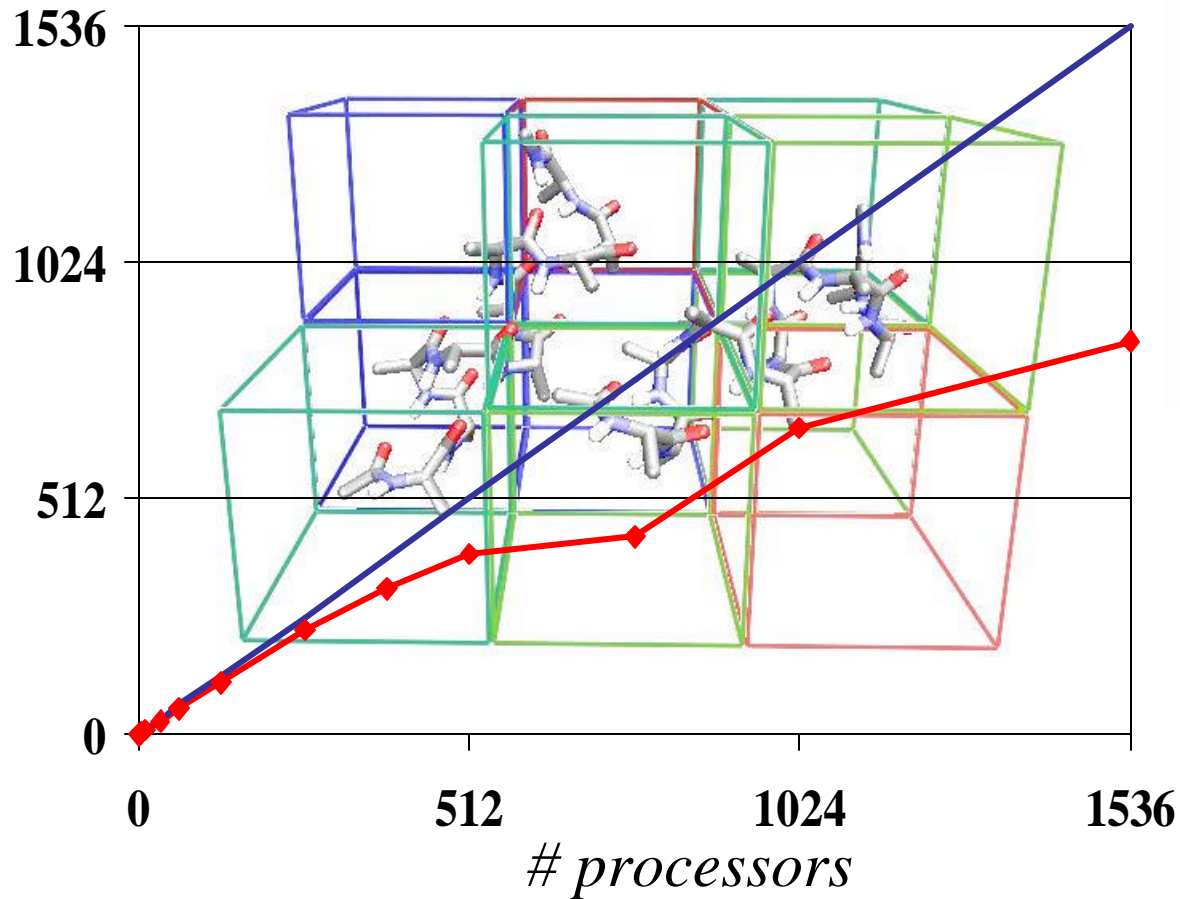


Simulating Conformational Fluctuations

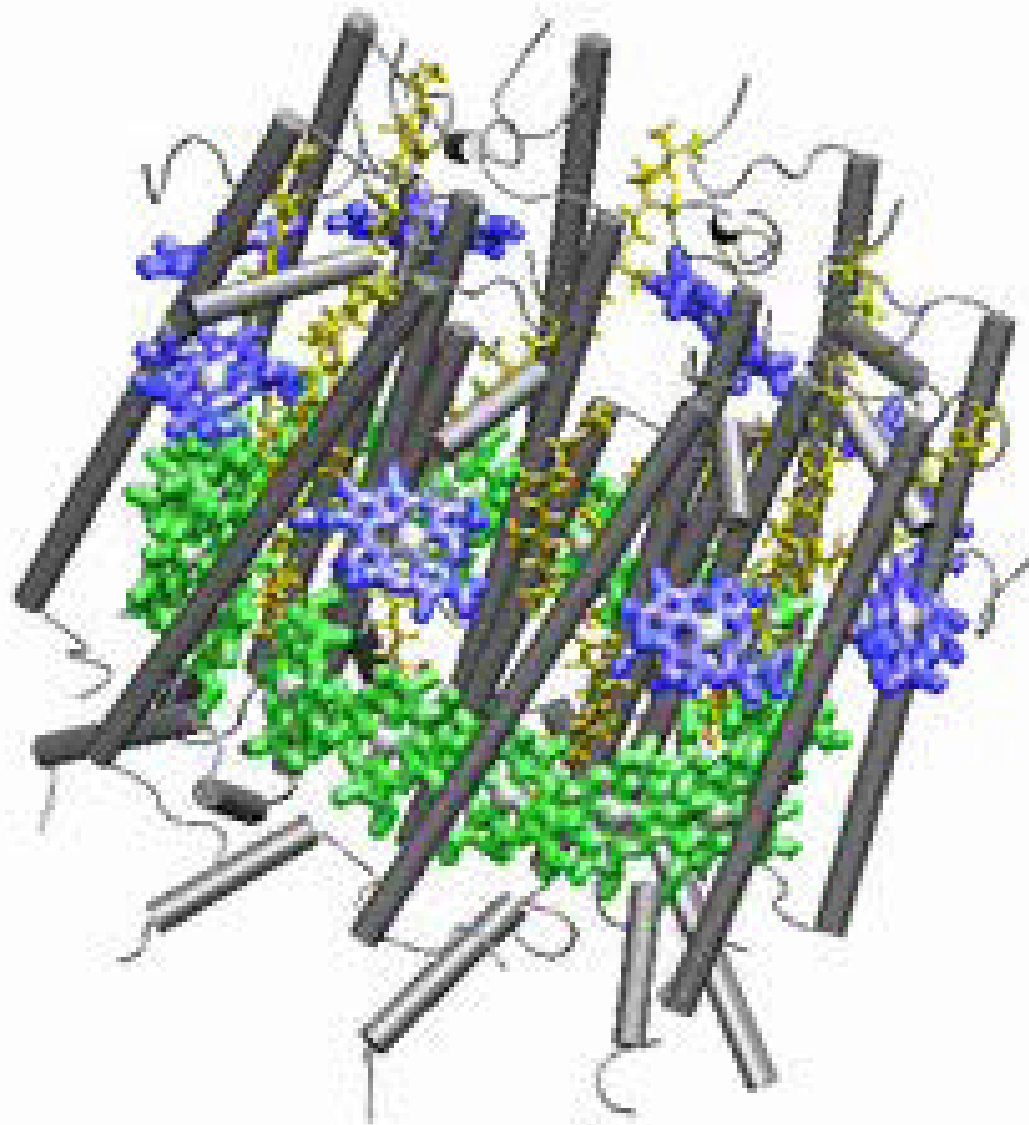
Molecular Dynamics Program NAMD



Kalé *et al.*, J. Comp. Phys., **151**, 283 (1999)

<http://www.ks.uiuc.edu/Research/namd/>

LH2 in membrane: **85,000 atoms**;
simulated for 2ns with NAMD2;
NpT ensemble; **periodic boundary condition**; **full electrostatics (PME)**



$$I(j) = \frac{2}{\pi} \text{Re}(0 | [2i(\mathbf{J} - j) - \mathbf{1}]^{-1} | 0)$$

$$\mathbf{J} = \text{diag}(J_1, J_2, \dots, J_6).$$

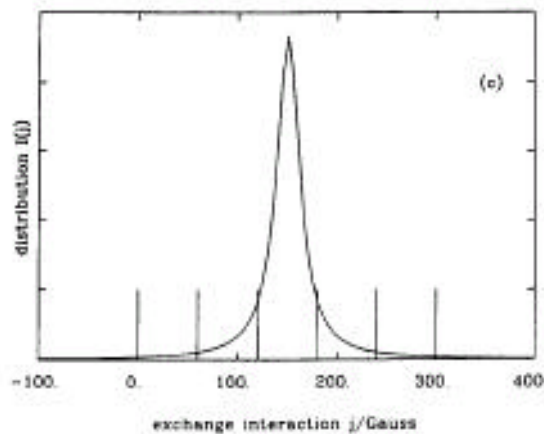
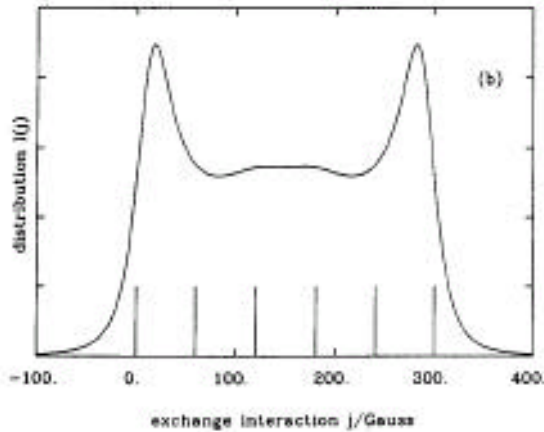
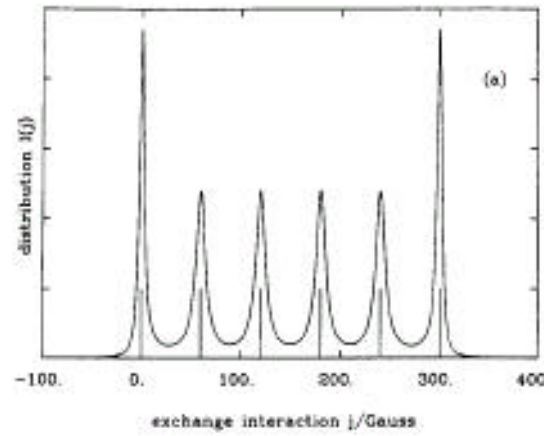
**Kubo
line shape
function**

slow

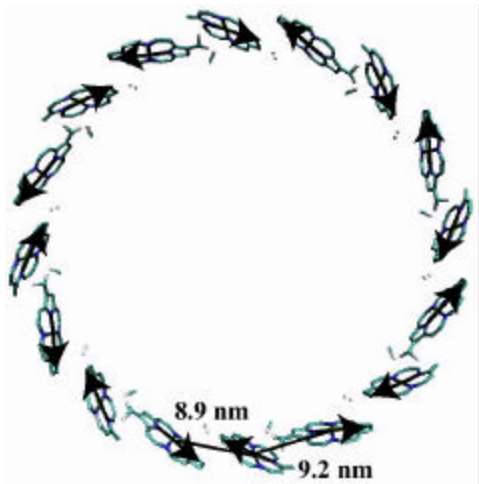
term project

medium

fast



The Effect of Static Disorder

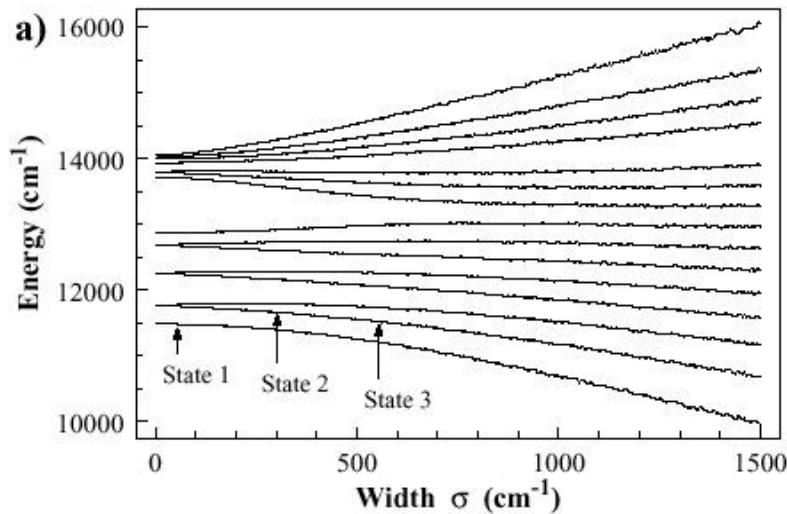


Stochastic Hamiltonian

$$\hat{H}_{rand} = \begin{pmatrix} \epsilon_1 & v_1 & & & & & & & & v_2 \\ & v_1 & \epsilon_2 & & & & & & & \\ & & & \ddots & & & & & & \\ & & & & W_{ij} & & & & & \\ & & & & & \ddots & & & & \\ & & & & & & W_{ij} & & & \\ & & & & & & & \ddots & & \\ & & & & & & & & v_1 & \epsilon_N \\ v_2 & & & & & & & & & \end{pmatrix}$$

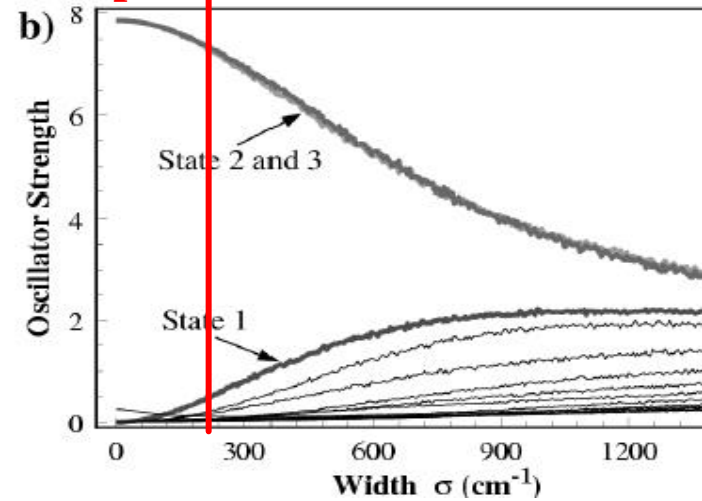
$$p(\epsilon_\alpha) = \frac{1}{\sqrt{2\pi}\sigma} \exp \left[-(\epsilon_\alpha - \epsilon)^2 / 2\sigma^2 \right]$$

also term project



energy levels spread

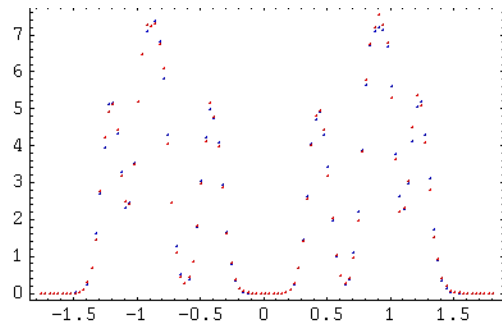
exp. value for static disorder



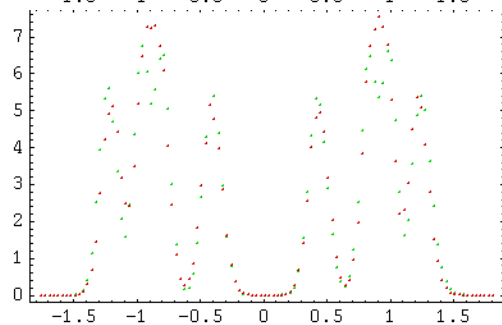
forbidden states become allowed

Random Matrix Theory (RMT) and Spectral Fluctuations

$$\begin{pmatrix} \epsilon & v_1 & 0 & 0 & \dots & v_2 \\ v_1 & \epsilon & v_2 & 0 & \dots & 0 \\ 0 & v_2 & \epsilon & v_1 & \dots & 0 \\ \dots & \dots & \dots & \dots & \dots & \dots \\ 0 & 0 & \dots & v_2 & \epsilon & v_1 \\ v_2 & 0 & \dots & 0 & v_1 & \epsilon \end{pmatrix} + \begin{pmatrix} & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \end{pmatrix} \left| \begin{array}{l} \mathbf{W}_{jk} \\ \text{(random)} \end{array} \right. \quad \text{RMT allows us to understand spectral fluctuations.}$$



blue: homogeneous
red: gaussian



red: homogenous
green: complex

Universality in RMT:

Spectral fluctuations are model independent.
(Reminiscent to *Central Limit Theorem*.)

- *Distribution* of \mathbf{W} is largely irrelevant. (i.e. a gaussian is as good as any other distribution.)
- *Symmetry class* of \mathbf{W} is largely irrelevant (for the spectral density only!) (i.e. \mathbf{W} can be real symmetric or complex hermitian.)

The *width* of \mathbf{W} needs to be carefully taken into account.

Spectral density for $2N=8$ (arbitrary units)

Analytical Computation of Spectral Density in Random Matrix Theory

also term project

Framework: *Supersymmetry Method*
(using *Harish-Chandra-Itzykson-Zuber Integrals*)

For finite N the final expressions can be evaluated with *Mathematica*.

Spectral density as sum over delta functions.

$$\rho(\lambda) = \left\langle \sum_i \delta(\lambda - \lambda_i) \right\rangle,$$

Representation of delta functions.

$$= \frac{1}{\pi} \text{Im} \left\langle \text{Tr} \frac{1}{\lambda - i\epsilon - (H_0 + W)} \right\rangle,$$

Representation of trace.

$$= \frac{1}{\pi} \text{Im} \frac{\partial}{\partial j} \Big|_{j=0} \mathcal{Z}(j)$$

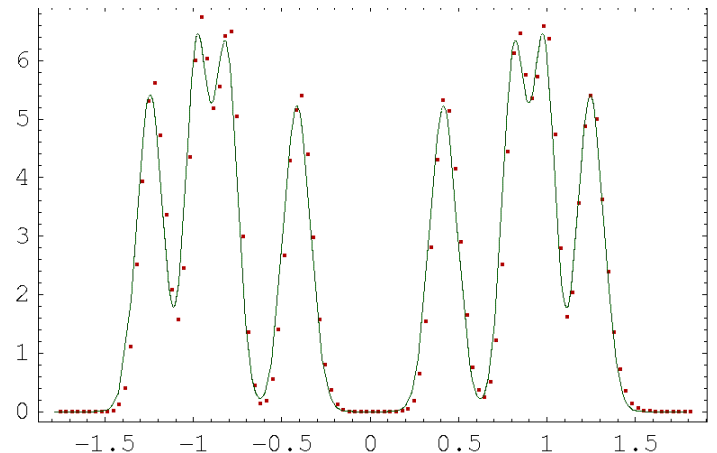
Supersymmetric partition function.

$$\mathcal{Z}(j) = \int d[W] P[W] \frac{\det(\lambda - i\epsilon - (H_0 + W) + j)}{\det(\lambda - i\epsilon - (H_0 + W) - j)},$$

Hubbard-Stratanovitch $(l+1) \times (l+1)$ supermatrix transformation.

$$= \int d[\sigma] P[\sigma] \prod_{i=1}^N \text{sdet}^{-1} \left[\begin{pmatrix} \lambda - i\epsilon - \gamma_i - j & 0 \\ 0 & \lambda - i\epsilon - \gamma_i + j \end{pmatrix} - \sigma \right].$$

$2N \times 2N$ matrix



Spectral density for $2N=8$
(arbitrary units)

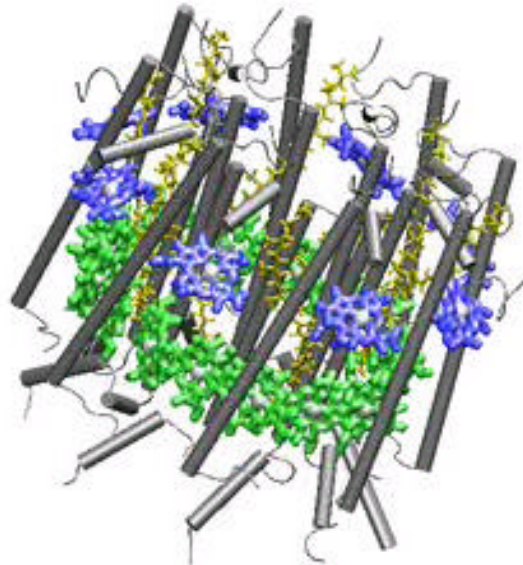
green curve: analytical
red dots: numerical

A big matrix integral is traded for an integral over a small supermatrix.

The Effect of Dynamic Disorder

Molecular Dynamics (MD) Simulation

Quantum Chemistry (QC) Calculations

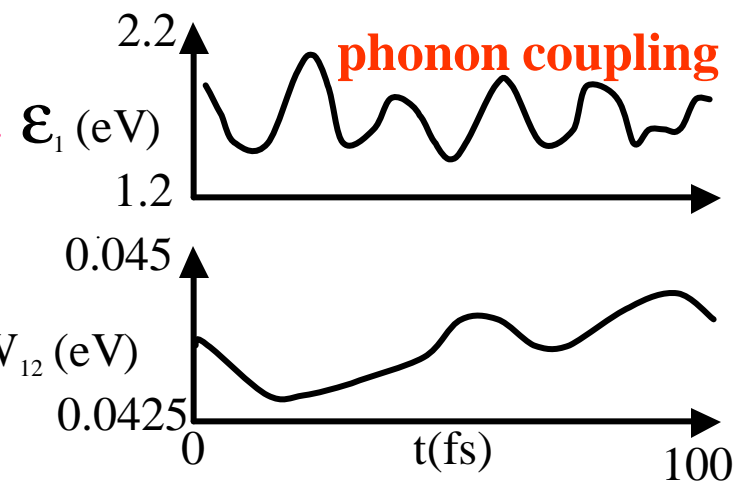
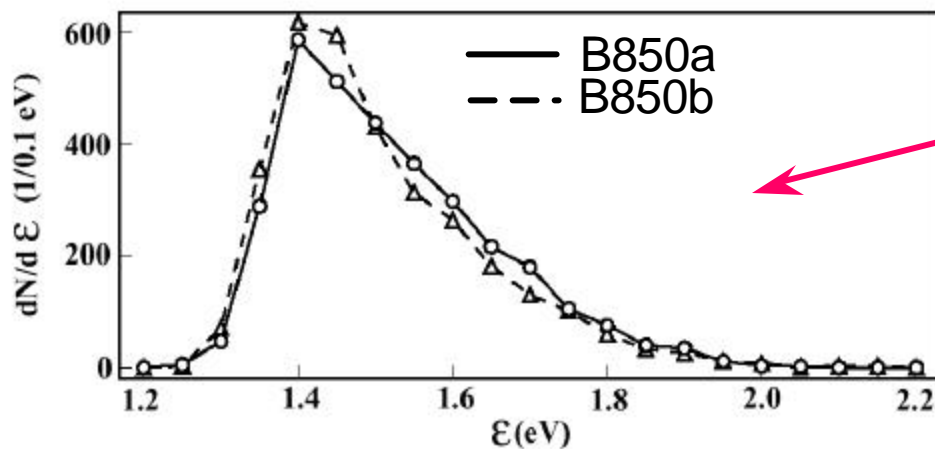


from QC \rightarrow $\epsilon_2(t)$

from MD \rightarrow $W_{ij}(t)$

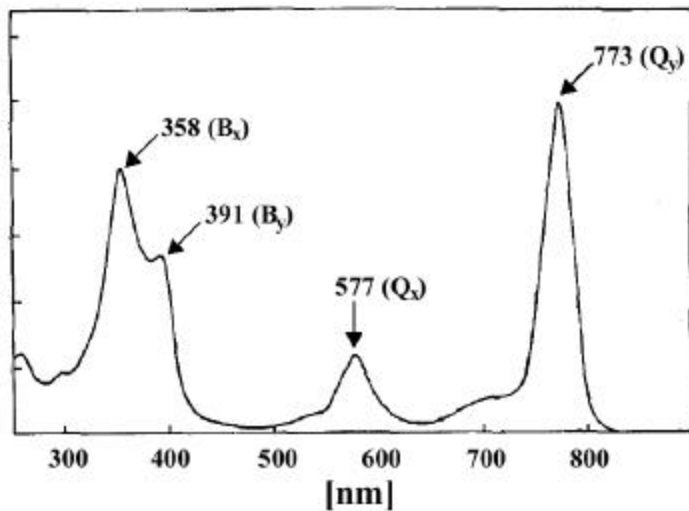
$$\hat{H}(t)^{exc} = \begin{pmatrix} \epsilon_1(t) & & & & \\ & \epsilon_2(t) & & & \\ & & W_{ij}(t) & & \\ & & & \ddots & \\ & & & & \epsilon_{16}(t) \end{pmatrix}$$

$$W_{jk} = C \left(\frac{\vec{d}_j \cdot \vec{d}_k}{r_{jk}^3} - \frac{3(\vec{r}_{jk} \cdot \vec{d}_j)(\vec{r}_{jk} \cdot \vec{d}_k)}{r_{jk}^5} \right)$$

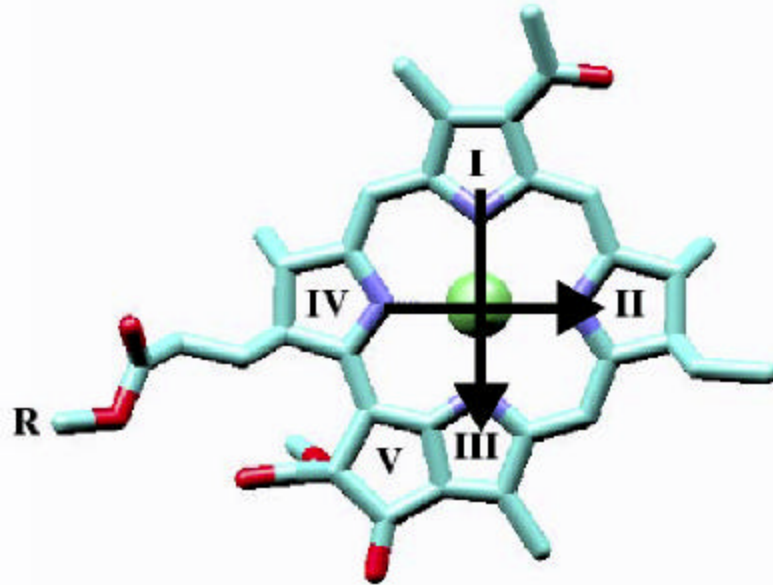


\Rightarrow apply the polaron model

Excitations of Individual Chlorophyll



Absorption spectrum of monomeric BChl a in ether. The spectrum shows four peaks, corresponding to the Q_y transition at 773 nm, the Q_x transition at 577 nm, and the B_y and B_x transitions at 391 and 358 nm, respectively.

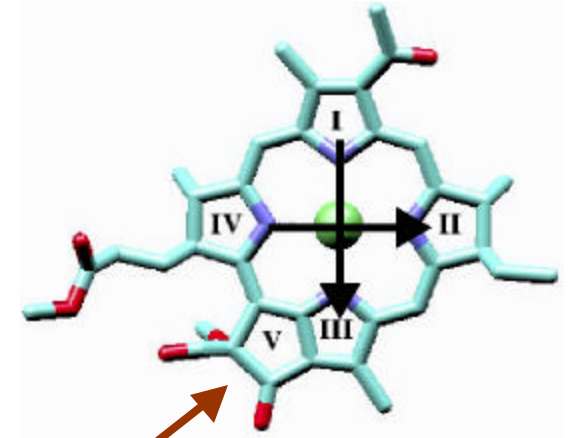


Structure of BChl a. R denotes the phytyl tail of BChl. The arrows indicate the transition dipole moments for the Q_y (from pyrrole ring II to IV) and the Q_x (from pyrrole ring I to III) transitions.

Two State QM System Coupled to Vibrational Mode

First case: Coupling to a single oscillator

$$\text{Hamiltonian} \quad \hat{H}_{\text{qo}}^{(s)} = \begin{pmatrix} \hat{H}_r^{(s)} & v \\ v & \hat{H}_p^{(s)} + E \end{pmatrix}$$

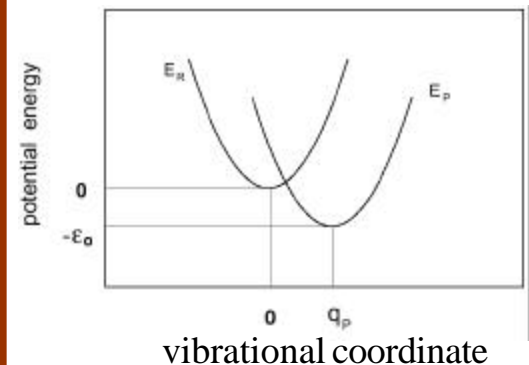


Protein matrix is a bath of oscillators linearly coupled to the electron transfer according to

$$\hat{H}_r^{(s)} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2 q^2$$

$$\hat{H}_p^{(s)} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2 \left(q - \frac{c}{m\omega^2} \right)^2$$

only a single oscillator considered at present!



Eigenstates and Propagator of (Shifted) Oscillator

oscillator

$$\hat{H}_r^{(s)} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2 q^2$$

shifted oscillator

$$\hat{H}_p^{(s)} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2 \left(q - \frac{c}{m\omega^2} \right)^2$$

oscillator

$$\langle q|n\rangle^{(r)} = \phi_n^{(r)}(q) = \left(\frac{\lambda}{\pi} \right)^{\frac{1}{4}} (2^n n!)^{-\frac{1}{2}} H_n(\sqrt{\lambda}q) e^{-\frac{1}{2}\lambda q^2}$$

eigenstates

$$\epsilon_n^{(r)} = \hbar\omega \left(n + \frac{1}{2} \right) \quad \lambda = m\omega/\hbar$$

$$\langle q|n\rangle^{(p)} = \phi_n^{(p)}(q) = \left(\frac{\lambda}{\pi} \right)^{\frac{1}{4}} (2^n n!)^{-\frac{1}{2}} H_n(\sqrt{\lambda}(q - \frac{c}{m\omega^2})) e^{-\frac{1}{2}\lambda(q - c/m\omega^2)^2}$$

shifted oscillator

$$\epsilon_n^{(p)} = \hbar\omega \left(n + \frac{1}{2} \right) \quad q_0 = c/m\omega^2$$

propagators

$$\langle q'|e^{-iH_r^{(s)}(t-t_0)/\hbar}|q\rangle = \left[\frac{m\omega}{2i\pi\hbar \sin\omega(t-t_0)} \right]^{\frac{1}{2}} \times \exp \left\{ \frac{im\omega}{2\hbar \sin\omega(t-t_0)} [(q'^2 + q^2) \cos\omega(t-t_0) - 2q'q] \right\}$$

oscillator

shifted oscillator

$$\langle q'|e^{-iH_p^{(s)}(t-t_0)/\hbar}|q\rangle = \left[\frac{\lambda}{2\pi \sinh\xi} \right]^{\frac{1}{2}} \times \exp \left\{ -\frac{\lambda}{4} \left[(q' + q)^2 \tanh\frac{\xi}{2} + (q' - q)^2 \coth\frac{\xi}{2} \right] \right\}$$

$$\xi = i\omega(t-t_0).$$

The reactant states (57) are occupied in thermal equilibrium with probability

$$p_n^{(r)} = x^n (1 - x), \quad x = e^{-\hbar\omega/kT},$$

a result which is well-known from elementary statistical mechanics. The corresponding equilibrium state density matrix of the reactant state oscillator $\rho_o^{(r)}$ has the matrix elements

$$[\hat{\rho}_o^{(r)}]_{mn} = p_n^{(r)} \delta_{nm}.$$

The density matrix can also be written

$$\hat{\rho}_o^{(r)} = 2 \sinh(\hbar\omega/2kT) e^{-H^{(r)}/kT}.$$

The transitions from reactant to product states are induced through the matrix elements v in (54). In case of electron transfer in proteins, the coupling is induced through electron tunneling between prosthetic groups in the protein. The corresponding energy values v are very small, usually of the order of 10^{-4} eV. As a result, reactant states $|n\rangle^{(r)}$ and product states $|m\rangle^{(p)}$ couple only when they are essentially degenerate.

The overall rate of transfer from reactant states R to product states P is then

$$k_{qo}(R \rightarrow P) = \frac{2\pi}{\hbar^2} v^2 \mathcal{S}_{qo}(E)$$

where

$$\mathcal{S}_{qo}(E) = \sum_{n,m=0}^{\infty} p_n^{(r)} |{}^{(r)}\langle n|m \rangle^{(p)}|^2 \delta \left(\frac{E + \epsilon_m^{(p)} - \epsilon_n^{(r)}}{\hbar} \right)$$

is the so-called spectral line shape function.

We seek to express the line shape function (70) in a more compact form. For this purpose we use the identity

$$\delta \left(\frac{E + \epsilon_m^{(p)} - \epsilon_n^{(r)}}{\hbar} \right) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt e^{itE/\hbar} e^{-it\epsilon_n^{(r)}/\hbar} e^{it\epsilon_m^{(p)}/\hbar}$$

Employing the definition of the density matrix $[\hat{\rho}_o^{(r)}]_{mn} = p_n^{(r)} \delta_{nm}$ one can write

$$\mathcal{S}_{qo}(E) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt e^{itE/\hbar} \sum_{n,m=0}^{\infty} {}^{(r)}\langle n | \hat{\rho}_o^{(r)} e^{-it\hat{H}_r^{(s)}/\hbar} | m \rangle^{(p)(p)} \langle m | e^{it\hat{H}_p^{(s)}/\hbar} | n \rangle^{(r)}$$

or, equivalently, using $\hat{\rho}_o^{(r)} = 2 \sinh(\hbar\omega/2kT) e^{-H^{(r)}/kT}$

$$\mathcal{S}_{qo}(E) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt e^{itE/\hbar} 2 \sinh \frac{\hbar\omega}{2kT} \text{tr} \left(e^{-\hat{H}_r^{(s)}/kT} e^{-it\hat{H}_r^{(s)}/\hbar} e^{it\hat{H}_p^{(s)}/\hbar} \right)$$

Expressing the trace as an integral over q' we conclude that the spectral line shape function is

$$\mathcal{S}_{qo}(E) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt e^{itE/\hbar} 2 \sinh \frac{\hbar\omega}{2kT} \int_{-\infty}^{+\infty} dq \int_{-\infty}^{+\infty} dq' \langle q' | e^{-i(t - \hbar/kT)\hat{H}_r^{(s)}/\hbar} | q \rangle \langle q | e^{it\hat{H}_p^{(s)}/\hbar} | q' \rangle$$

The propagator (64) allows one to evaluate the line shape function (74). One employs

$$\begin{aligned} \langle q | e^{it\hat{H}_p^{(s)}/\hbar} | q' \rangle &= \left[\frac{\lambda}{2\pi \sinh \eta_1} \right]^{\frac{1}{2}} \times \\ &\times \exp \left\{ -\frac{\lambda}{4} \left[(q' + q - 2q_o)^2 \tanh \frac{\eta_1}{2} + (q' - q)^2 \coth \frac{\eta_1}{2} \right] \right\} \\ \eta_1 &= -i\omega t . \end{aligned}$$

and, displacing time into the complex plane to account for the equilibrium (temperature T) density matrix,

$$\begin{aligned} \langle q' | e^{-i(t - \hbar/kT)\hat{H}_r^{(s)}/\hbar} | q \rangle &= \left[\frac{\lambda}{2\pi \sinh \eta_2} \right]^{\frac{1}{2}} \times \\ &\times \exp \left\{ -\frac{\lambda}{4} \left[(q' + q)^2 \tanh \frac{\eta_2}{2} + (q' - q)^2 \coth \frac{\eta_2}{2} \right] \right\} \\ \eta_2 &= i\omega t - \hbar\omega/kT . \end{aligned}$$

Inserting (75–78) into (74) results in the expression

$$\mathcal{S}_{q_0}(E) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt e^{itE/\hbar} \frac{\lambda \sinh\left(\frac{\hbar\omega}{2kT}\right)}{\pi \sqrt{\sinh\eta_1 \sinh\eta_2}} I(t)$$

where

$$I(t) = \int_{-\infty}^{+\infty} dq \int_{-\infty}^{+\infty} dq' \exp \left[-\alpha(t)(q + q')^2 - \beta(q + q' - 2q_0)^2 - \gamma(q - q')^2 \right]$$

$$\alpha = \frac{\lambda}{4} \tanh \frac{\eta_2}{2}$$

$$\beta = \frac{\lambda}{4} \tanh \frac{\eta_1}{2}$$

$$\gamma = \frac{\lambda}{4} \left(\tanh \frac{\eta_1}{2} + \tanh \frac{\eta_2}{2} \right)$$

Expression (79–83) for the spectral line shape function played an important role in the theory of spectral transitions of so-called F-centers in solids as reviewed in [21]. The expression can be further simplified [21]. For this purpose one transforms to new integration variables $u = q + q'$ and $u' = q - q'$. Noting that for the Jacobian holds $\partial(u, u')/\partial(q, q') = 2$, the integral (80) reads

$$I(t) = \frac{1}{2} \int_{-\infty}^{+\infty} du \int_{-\infty}^{+\infty} du' \exp[-\alpha(t)u^2 - \beta(u - 2q_0)^2] \exp[-\gamma u'^2] .$$

Completion of the square in the first exponent results in the expression

$$I(t) = \frac{1}{2} \exp\left[-4q_0^2 \left(\beta - \frac{\beta^2}{\alpha + \beta}\right)\right] \times \\ \times \int_{-\infty}^{+\infty} du' \exp[-\gamma u'^2] \int_{-\infty}^{+\infty} du \exp[-(\alpha + \beta)(u - s)^2] .$$

where

$$s = 2\beta q_0 / (\alpha + \beta) .$$

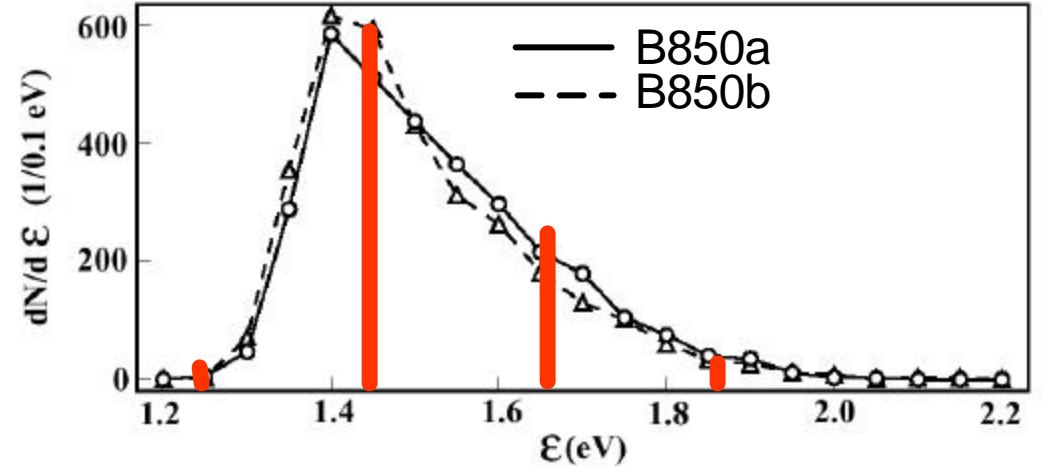
a few more steps of Gaussian integration ...

Combining Eqs. (62, 79, 87, 88, 91) results in

$$\mathcal{S}_{q_0}(E) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt \exp\left[itE/\hbar - \frac{c^2}{2m\hbar\omega^3} \coth\frac{\hbar\omega}{2kT} (1 - \cos\omega t) + i \frac{c^2}{2m\hbar\omega^3} \sin\omega t \right]$$

$$k_{q_0}(R \rightarrow P) = \frac{2\pi}{\hbar^2} v^2 \mathcal{S}_{q_0}(E) \quad |$$

Final Result



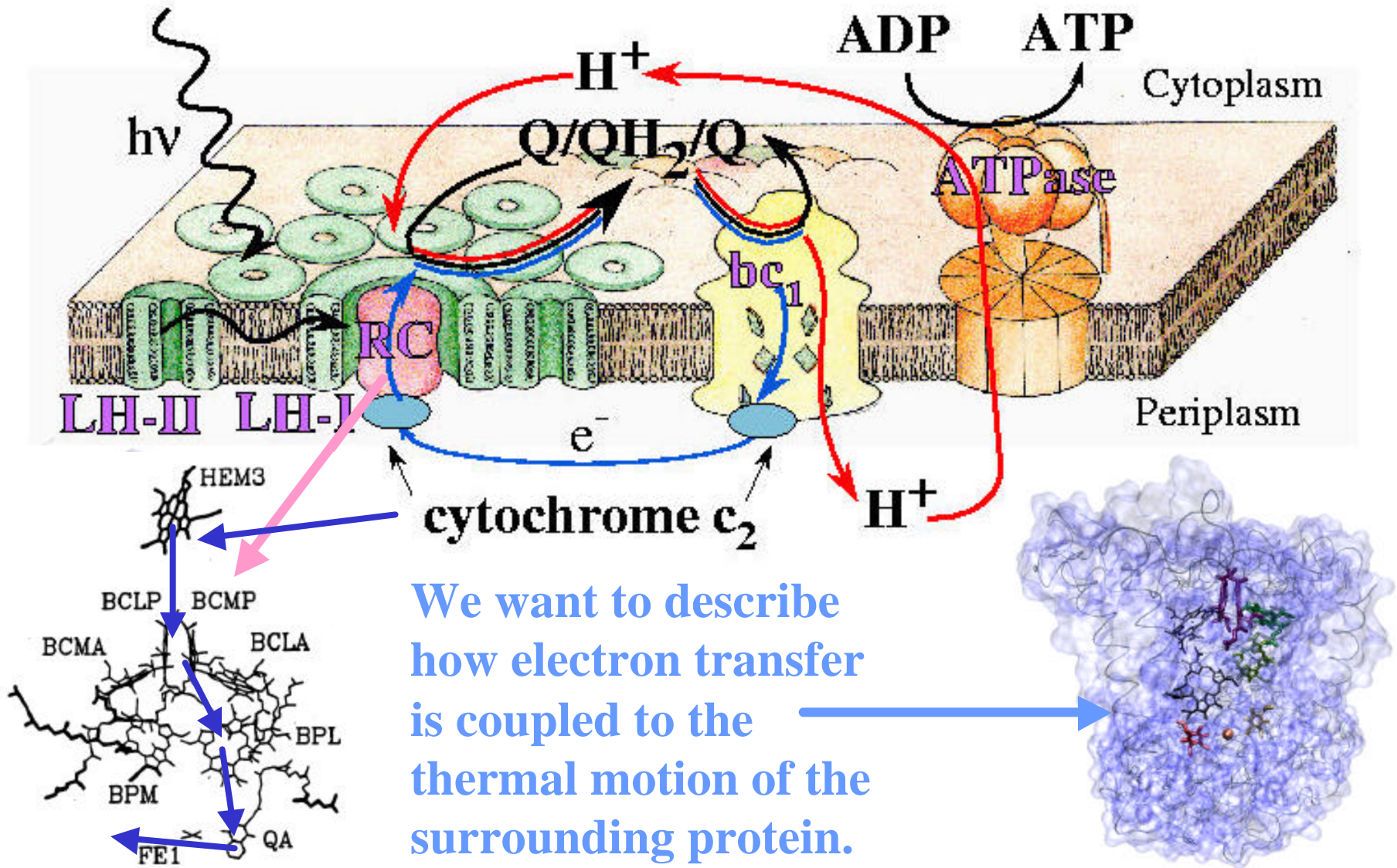
$$\mathcal{S}_{qo}(E) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt \exp \left[itE/\hbar - \frac{c^2}{2m\hbar\omega^3} \coth \frac{\hbar\omega}{2kT} (1 - \cos\omega t) + i \frac{c^2}{2m\hbar\omega^3} \sin\omega t \right] \quad (92)$$

The integral in (92) can be carried out and the line shape function expressed as a series of regular, modified Bessel functions $I_k(x)$ [21]. The result is

$$\mathcal{S}_{qo}(E) = \frac{e^{-\Lambda(1+2n_o)}}{\omega} \left(\frac{n_o + 1}{n_o} \right)^{s_j/2} \sum_{k=-\infty}^{\infty} \delta(k - s(E)) I_k \left(2\Lambda \sqrt{n_o(n_o + 1)} \right) \quad (94)$$

where $\Lambda = \frac{1}{2}m\omega^2 q_o^2/\hbar\omega = c^2/2m\hbar\omega^3$ is the so-called reorganization energy in units of vibrational quanta $\hbar\omega$, $n_o = e^{-\hbar\omega/kT}/(1 - e^{-\hbar\omega_j/kT})$ is the average number of quanta thermally excited in the oscillator, and $s(E) = (E - \frac{1}{2}\hbar\omega)/\hbar\omega$ counts the number of oscillator levels up to energy E . The summation in (93) is over integers k such that one and only one term in the sum contributes anytime that $s(E)$ assumes an integer value.

Electron Transfer in the Photosynthetic Reaction Center



Two State QM System Coupled to Protein Matrix

First case: Coupling to a single oscillator

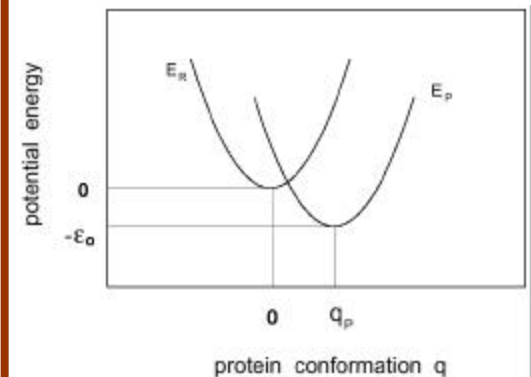
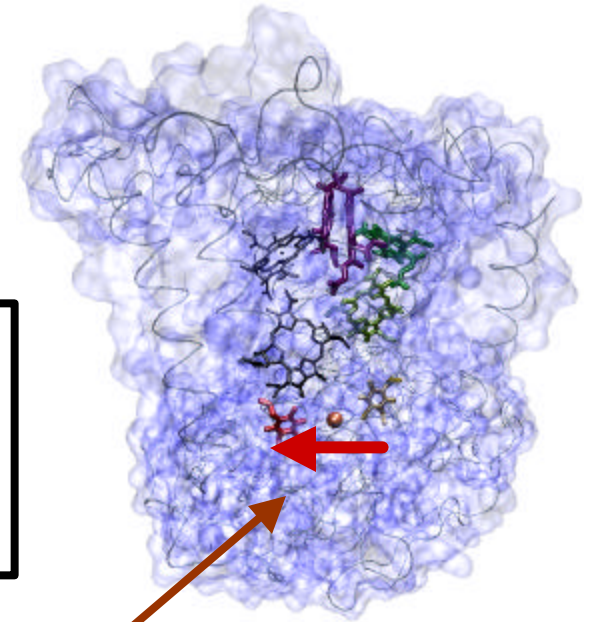
$$\text{Hamiltonian} \quad \hat{H}_{\text{qo}}^{(s)} = \begin{pmatrix} \hat{H}_r^{(s)} & v \\ v & \hat{H}_p^{(s)} + E \end{pmatrix}$$

Protein matrix is a bath of oscillators linearly coupled to the electron transfer according to

$$\hat{H}_r^{(s)} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2 q^2$$

$$\hat{H}_p^{(s)} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2 \left(q - \frac{c}{m\omega^2} \right)^2$$

only a single oscillator considered at present!



We start from the previously derived result

$$\mathcal{S}_{qo}(E) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt \exp \left[itE/\hbar - \frac{c^2}{2m\hbar\omega^3} \coth \frac{\hbar\omega}{2kT} (1 - \cos\omega t) + i \frac{c^2}{2m\hbar\omega^3} \sin\omega t \right] \quad (92)$$

$$k_{qo}(R \rightarrow P) = \frac{2\pi}{\hbar^2} v^2 \mathcal{S}_{qo}(E) \quad |$$

Two State QM System Coupled to Protein Matrix

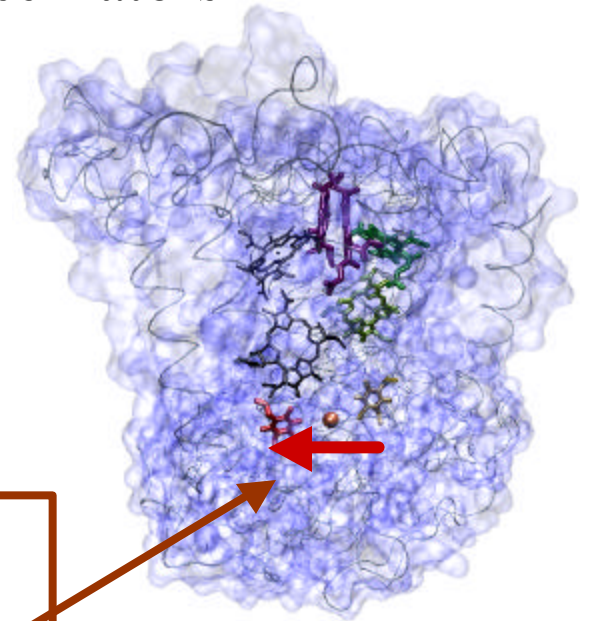
Second case: Coupling to an ensemble of oscillators

Hamiltonian

$$\hat{H}_{\text{qo}}^{(s)} = \begin{pmatrix} \hat{H}_r^{(s)} & v \\ v & \hat{H}_p^{(s)} + E \end{pmatrix}$$

Protein matrix is a bath of oscillators linearly coupled to the electron transfer according to

$$\hat{H}_r = \sum_j \left(\frac{\hat{p}_j^2}{2M_j} + \frac{1}{2}M_j\omega_j^2 q_j^2 \right)$$
$$\hat{H}_p = \sum_j \left(\frac{\hat{p}_j^2}{2M_j} + \frac{1}{2}M_j\omega_j^2 \left(q_j - \frac{c_j}{M_j\omega_j^2} \right)^2 \right)$$



Electron Transfer Process Coupled to the Protein Matrix

Rate for an ensemble of oscillators

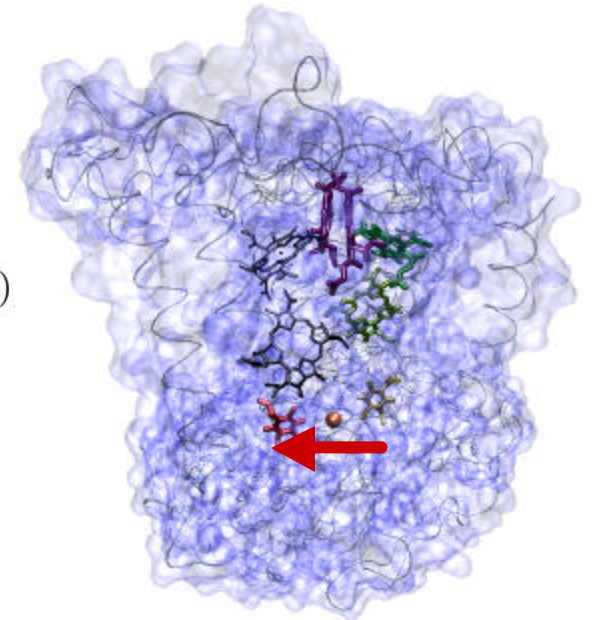
$$k_{qb}(R \rightarrow P) = \frac{v^2}{\hbar^2} \int_{-\infty}^{+\infty} dt e^{itE/\hbar} e^{iQ_1(t)/\pi\hbar} e^{-Q_2(t)/\pi\hbar}$$

Relaxation rate

$$k_{\text{rel}} = \frac{2v^2}{\hbar^2} \int_0^{+\infty} dt \cos(-itE/\hbar) \cos(Q_1(t)/\pi\hbar) e^{-Q_2(t)}$$

$$Q_1(t) = \frac{\pi}{2} \sum_j \frac{c_j^2}{\hbar\omega_j^3} \sin\omega_j t$$

$$Q_2(t) = \frac{\pi}{2} \sum_j \frac{c_j^2}{\hbar\omega_j^3} \coth\frac{\hbar\omega_j}{2kT} [1 - \cos(\omega_j t)]$$



But we don't know all the coupling constants c_j ? All we need to know is

$$J(\omega) = \frac{\pi}{2} \sum_j \frac{c_j^2}{\omega_j} \delta(\omega - \omega_j) \quad \begin{aligned} Q_1(t) &= \int_0^\infty d\omega \omega^{-2} J(\omega) \sin\omega t \\ Q_2(t) &= \frac{\pi}{2} \int_0^\infty d\omega \omega^{-2} J(\omega) \coth\frac{\hbar\omega}{2kT} (1 - \cos\omega t) \end{aligned}$$

Solution of Rate Equation

$$\frac{d}{dt} \begin{pmatrix} p_R(t) \\ p_P(t) \end{pmatrix} = \begin{pmatrix} -k_{qb}(R \rightarrow P) & k_{qb}(P \rightarrow R) \\ k_{qb}(R \rightarrow P) & -k_{qb}(P \rightarrow R) \end{pmatrix} \begin{pmatrix} p_R(t) \\ p_P(t) \end{pmatrix}$$

$$\begin{pmatrix} p_R(t) \\ p_P(t) \end{pmatrix} = \frac{1}{k_{qb}(R \rightarrow P) + k_{qb}(P \rightarrow R)} \left[\begin{pmatrix} k_{qb}(P \rightarrow R) \\ k_{qb}(R \rightarrow P) \end{pmatrix} + \begin{pmatrix} k_{qb}(R \rightarrow P) \\ -k_{qb}(R \rightarrow P) \end{pmatrix} \exp \{ - [k_{qb}(R \rightarrow P) + k_{qb}(P \rightarrow R)] t \} \right]$$

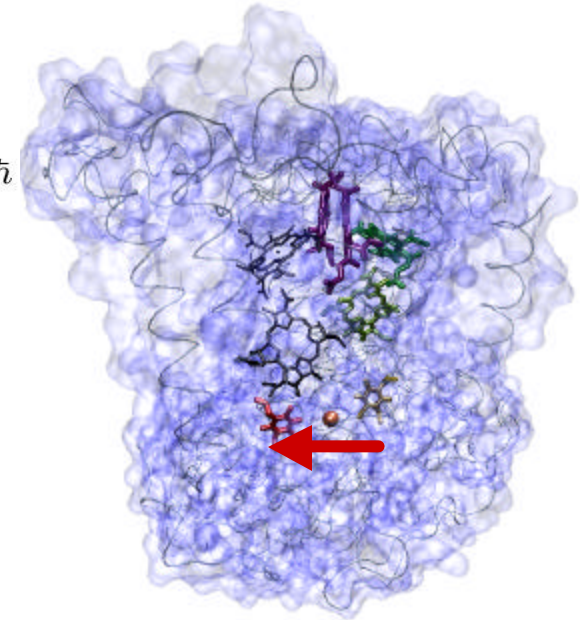
Electron Transfer Process Coupled to the Protein Matrix

Relaxation rate

$$k_{\text{rel}} = \frac{2v^2}{\hbar^2} \int_0^{+\infty} dt \cos(-itE/\hbar) \cos(Q_1(t)/\pi\hbar) e^{-Q_2(t)/\pi\hbar}$$

$$Q_1(t) = \int_0^{\infty} d\omega \omega^{-2} J(\omega) \sin\omega t$$

$$Q_2(t) = \frac{\pi}{2} \int_0^{\infty} d\omega \omega^{-2} J(\omega) \coth\frac{\hbar\omega}{2kT} (1 - \cos\omega t)$$



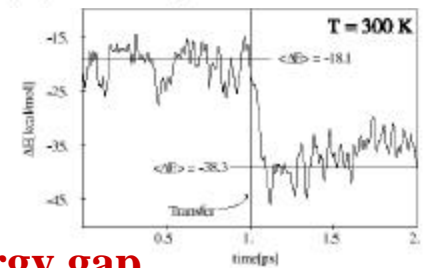
$$\frac{J(\omega)}{\omega} = \frac{\sigma^2}{k_B T} \int_0^{\infty} dt C(t) \cos\omega t \quad \text{1994}$$

$$C_{\epsilon\epsilon}(t) = \frac{\langle (\epsilon(t) - \langle \epsilon \rangle) (\langle \epsilon(0) - \langle \epsilon \rangle) \rangle}{\langle \epsilon(0) - \langle \epsilon \rangle \rangle^2}$$

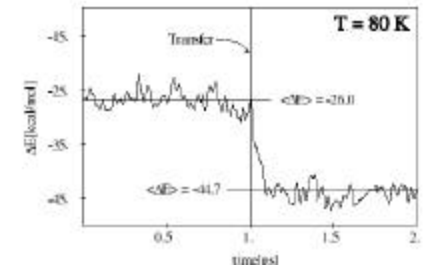
energy gap correlation function

σ **rms deviation of energy gap**

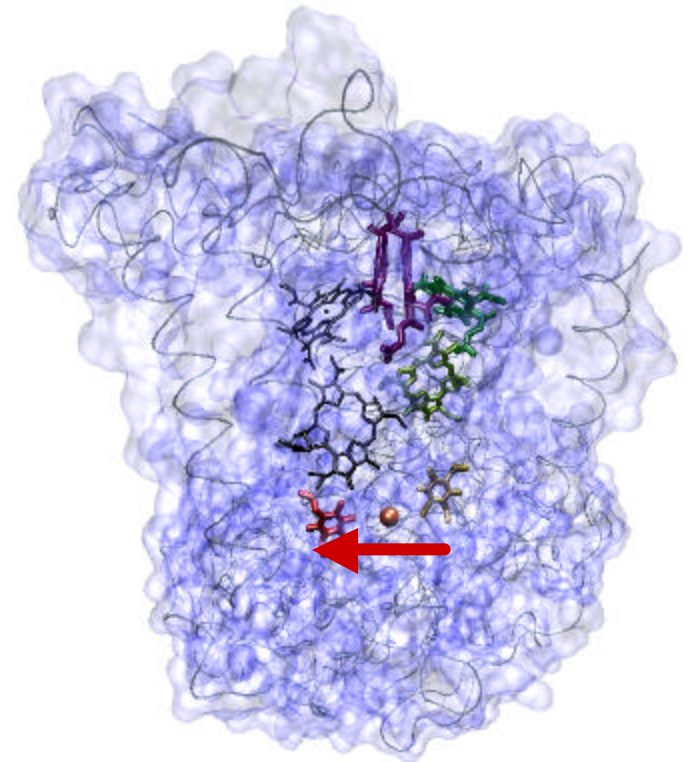
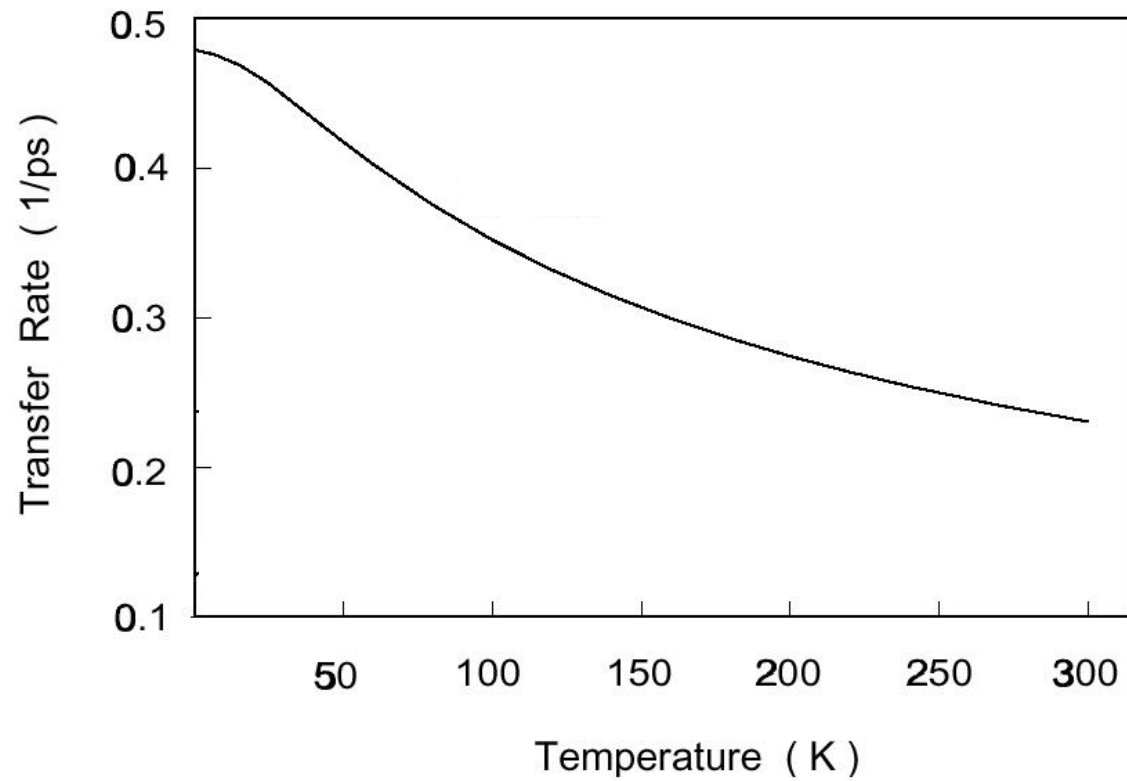
$$\epsilon(t) = \hat{H}_p - \hat{H}_r + E$$



energy gap



Temperature Dependence of Electron Transfer Rate



Classical (High Temperature) Limit of Electron Transfer

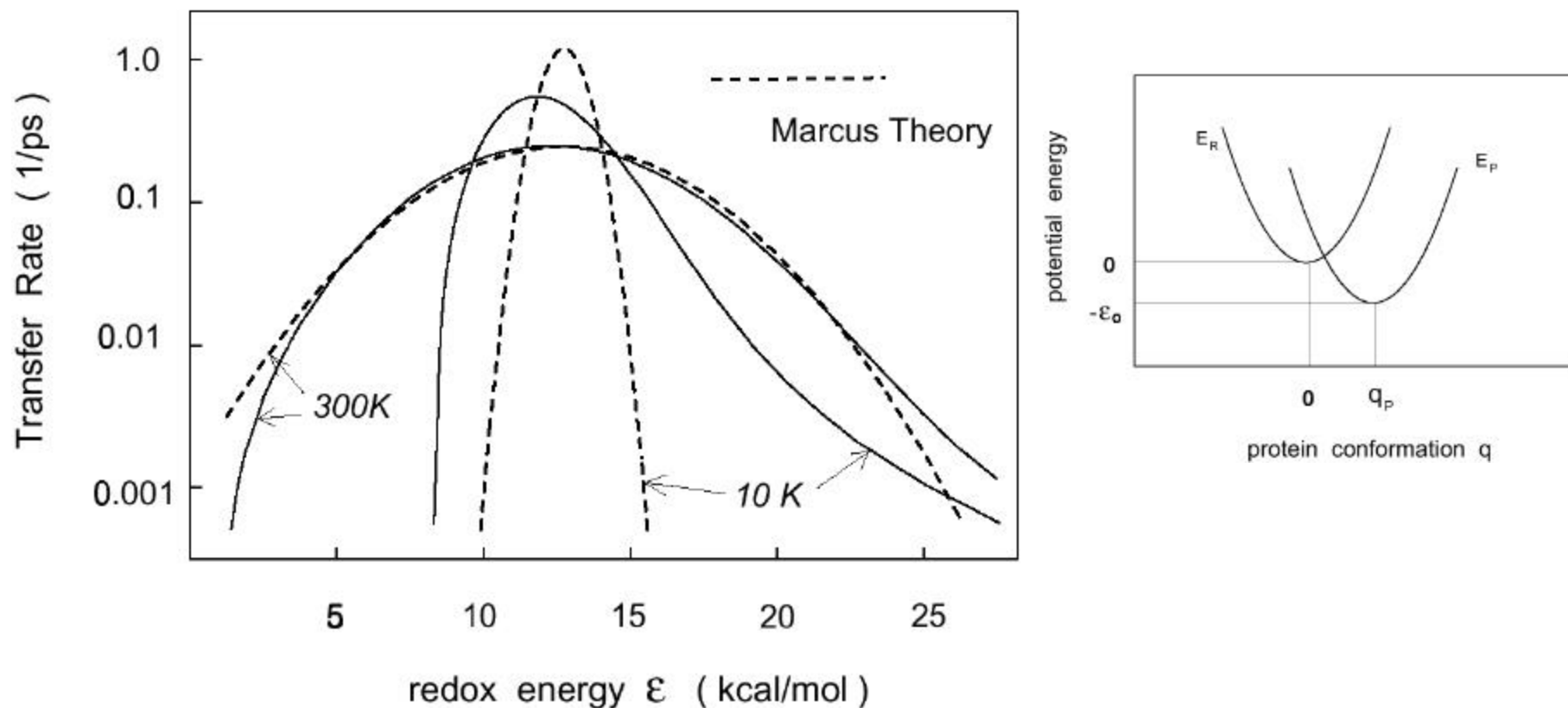


Figure 2: Comparison of electron transfer rates $k(\epsilon, T)$ shown as a function of ϵ evaluated in the framework of the spin-boson model (solid lines) and by Marcus theory (dashed lines) at temperatures 10 K and 300 K. The functions are centered approximately around ϵ_m . From [3].