?
?
?

$$k_{Marcus} = \frac{2\pi}{\hbar}|V_{ab}|^2 \frac{1}{\sqrt{4\pi k_B T \lambda}} e^{-(\lambda+\Delta G^o)^2/4\lambda k_B T}, \tag{1}$$

k_{Marcus}
ΔG^o
λ
?
?
?
V_{ab}
?
ab initio
?
?
?
?
??
?
?
?
?
?
?
?
N

$$H_{dia} = \begin{pmatrix} \epsilon_1 & V_{12} \\ V_{21} & \epsilon_2 \end{pmatrix} + \begin{pmatrix} \mathbf{g}_{11} & \mathbf{g}_{12} \\ \mathbf{g}_{21} & \mathbf{g}_{22} \end{pmatrix} \cdot \mathbf{q} + \frac{\mathbf{p}^2}{2} + \frac{1}{2}\mathbf{q}^T \cdot \mathbf{\Omega} \cdot \mathbf{q}. \tag{2}$$

ϵ_1
ϵ_2
V_{ij}
$\mathbf{q}$
$\mathbf{\Omega}$
ω_j^2
$\mathbf{g}_{11}$
$\mathbf{g}_{22}$
$\mathbf{g}_{12}$
$\mathbf{g}_{21}$

$$H_{dia} = \begin{pmatrix} \epsilon_1 & V_{12} \\ V_{21} & \epsilon_2 \end{pmatrix} + \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix} \mathbf{g}_{22} \cdot \mathbf{q} + H_{osc} \tag{3}$$

H_{osc}
?
θ

$$H_{dia,e} = \begin{pmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{pmatrix} \begin{pmatrix} \epsilon_1 & 0 \\ 0 & \epsilon_2 \end{pmatrix} \begin{pmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{pmatrix}. \tag{4}$$

$$V_{12} = \frac{1}{2}\sin 2\theta\,(\epsilon_2 - \epsilon_1) \tag{5}$$

$$\begin{aligned} H &= U^T H_{dia} U \\ &= \begin{pmatrix} E_1 & 0 \\ 0 & E_2 \end{pmatrix} + \begin{pmatrix} \sin^2\theta & \frac{1}{2}\sin 2\theta \\ \frac{1}{2}\sin 2\theta & \cos^2\theta \end{pmatrix} \mathbf{g}_{22} \cdot \mathbf{q} \\ &\quad + H_{osc}. \end{aligned} \tag{6}$$

E_1
E_2
H_{osc}
θ
??
??
?

$$H = \begin{pmatrix} \epsilon_1 & 0 \\ 0 & \epsilon_2 \end{pmatrix} + \begin{pmatrix} \mathbf{g}_{11} & \mathbf{g}_{12} \\ \mathbf{g}_{21} & \mathbf{g}_{22} \end{pmatrix} \cdot \mathbf{q} + \frac{\mathbf{p}^2}{2} + \frac{1}{2}\mathbf{q}^T \cdot \mathbf{\Omega} \cdot \mathbf{q} \tag{7}$$

?
?
?

$$\begin{aligned} U &= e^{-\sum_{ni} \frac{g_{nni}}{\hbar\omega_i} |n\rangle\langle n| (a_i^\dagger - a_i)} \\ &= \sum_n |n\rangle\langle n| e^{-\sum_i \frac{g_{nni}}{\hbar\omega_i}(a_i^\dagger - a_i)} \end{aligned} \tag{8}$$

$C_{nm}(t)$
$V_{nm}(t)$
$C(t)$
k_{nm}
?
$\mathbf{g}_{22}$
??
?
$\mathbf{v}_1 =$
$\mathbf{g}_{22}$
k

$$\mathbf{P}_k = \mathbf{v}_k \otimes \mathbf{v}_k \quad (13)$$

$\mathbf{Q}_k =$
$\mathbf{I} -$
$\mathbf{P}_k$

$$\mathbf{p} = \sum_k (\mathbf{P}_k) \quad (14)$$

$k \leq$
N
$\mathbf{\Omega}$
viz.

$$\mathbf{\Omega}_p = \mathbf{P}_k \cdot \mathbf{\Omega} \cdot \mathbf{P}_k \;\&\; \mathbf{\Omega}_q = \mathbf{Q}_k \cdot \mathbf{\Omega} \cdot \mathbf{Q}_k \quad (15)$$

$\{\alpha_p, \mathbf{M}_p\}$
$\{\alpha_q, \mathbf{M}_q\}$
$\mathbf{\Omega}_p$
$\mathbf{\Omega}_q$
$N \times$
N
$N -$
k

$$\mathbf{M}_k = \{\mathbf{M}_p, \mathbf{M}_q\} \quad (16)$$

$\mathbf{\Omega}$
$N \times$
N
$\mathbf{\Omega}'$
$\mathbf{\Omega}'$
$k \times$
k
-1
$C =$
C
??
??
π
??
D_{2h}
C_s
C_1
C_{2v}

$$w_i = \frac{\left\langle \overrightarrow{M_i} | \overrightarrow{PLM} \right\rangle^2}{\sqrt{\sum_i \left\langle \overrightarrow{M_i} | \overrightarrow{PLM} \right\rangle^2}}$$

$\overrightarrow{M_i}$
i
A_g
A_1
??
??
A_u
$B_{2g})$
??
??
$\overrightarrow{\pi}$
??
??
?
??
B_{2u}
x
y
??
??
B_{2u}
??
A_g
A_g
B_{2u}
A_g
B_{2u}
xy