University of Washington
Department of Chemistry
Chemistry 553
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Lecture 9: Application of Conditional Probabilities: Correlation Function for a Two Site Jump
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A. Two Site Jump

- This is a simple example of the use of conditional probabilities. This particular example uses a two site jump to model the segmental motion of a polymer, but other applications are possible.
- In the limit of high barriers (i.e. >>10kT) and for large values of D=BkT, motion in a double well potential can be treated approximately as a two site exchange, that is, exchange between the two well minima.
- Suppose a C-H bond vector reorients between two angular orientations. $P_{eq}(\phi_0)$ is the probability that the C-H vector is located at ϕ_0 at equilibrium. The function $P(\phi_t|\phi_0,t)$ is the conditional probability and is obtained by applying initial conditions to the function $P(\phi_t,t)$. Designate the probability of being at site 1 $P_1(t)$ and similarly for site 2. The C-H vector jumps between the two sites $1 \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} 2$ and the equations of motion are

$$\begin{aligned} \frac{dP_1}{dt} &= -k_{12}P_1 + k_{21}P_2 \\ \frac{dP_2}{dt} &= k_{12}P_1 + -k_{21}P_2 \end{aligned} \tag{9.1}$$

This may also be written in vector notation…

$$\begin{aligned} &\frac{d}{dt}\begin{pmatrix} P_1 \\ P_2 \end{pmatrix} = \begin{pmatrix} -k_{12} & k_{21} \\ k_{12} & -k_{21} \end{pmatrix}\begin{pmatrix} P_1 \\ P_2 \end{pmatrix} = -\Gamma\begin{pmatrix} P_1 \\ P_2 \end{pmatrix} \\ &where\ \Gamma = \begin{pmatrix} k_{12} & -k_{21} \\ -k_{12} & k_{21} \end{pmatrix} \end{aligned} \tag{9.2}$$

The conditional probability is obtained from the equation

$$P(\phi_t|\phi_0,t) = e^{-\Gamma t}P(0) \tag{9.3}$$

where P(0) is called an initial condition. So we have to determine the operator $e^{-\Gamma t}$. To do this, determine the eigenvalues of Γ. Call these eigenvalues λ_1 and λ_2. Then construct the matrix $e^{-\Delta t}$ where $\Delta = \begin{pmatrix} \lambda_1 & 0 \\ 0 & \lambda_2 \end{pmatrix}$. Note: These calculations can and should be done analytically.

- Solve the determinant equation…

$$\begin{aligned} &\begin{vmatrix} k_{12} - \lambda & -k_{21} \\ -k_{12} & k_{21} - \lambda \end{vmatrix} = 0 \Rightarrow (k_{12} - \lambda)(k_{21} - \lambda) - k_{12}k_{21} = 0 \\ &\lambda^2 - \lambda(k_{12} + k_{21}) = 0 \Rightarrow \lambda_1 = 0 \ldots \lambda_2 = k_{12} + k_{21} \end{aligned} \tag{9.4}$$

- Determine the eigenvectors u_1 and u_2. Hint: Use the relationships $\Gamma u_{1,2} = \lambda_{1,2} u_{1,2}$

Using these results, derive the matrix T, whose columns are the eigenvectors. Prove that $\Gamma = T\Delta T^{-1}$ and calculate $e^{-\Gamma t} = Te^{-\Delta t}T^{-1}$. Note: you obviously have to determine the inverse matrix T^{-1}. This can and should be done analytically.

- Solve the equations $\Gamma u_{1,2} = \begin{pmatrix} k_{12} & -k_{21} \\ -k_{12} & k_{21} \end{pmatrix} \begin{pmatrix} u_{1,2}^1 \\ u_{1,2}^2 \end{pmatrix} = \lambda_{1,2} u_{1,2}$ and use the orthonormality properties of the eigenvectors. For example…

$$\begin{aligned} &\begin{pmatrix} k_{12} & -k_{21} \\ -k_{12} & k_{21} \end{pmatrix} \begin{pmatrix} u_1^1 \\ u_1^2 \end{pmatrix} = \lambda_1 u_1 = 0 \ and \ (u_1^1)^2 + (u_1^2)^2 = 1 \\ &\therefore \vec{u}_1 = \frac{1}{r} \begin{pmatrix} k_{21} \\ k_{12} \end{pmatrix} \ldots where \ r = \sqrt{k_{12}^2 + k_{21}^2} \end{aligned} \tag{9.5}$$

and similarly… $\vec{u}_2 = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix}$.

- Then T has as it columns the eigenvectors… $\vec{T} = \begin{pmatrix} \frac{k_{21}}{r} & \frac{1}{\sqrt{2}} \\ \frac{k_{12}}{r} & -\frac{1}{\sqrt{2}} \end{pmatrix}$. Now to invert T use the relationship…

$$\begin{aligned} &\vec{T} \cdot \vec{T}^{-1} = \vec{1} \Rightarrow \begin{pmatrix} \frac{k_{21}}{r} & \frac{1}{\sqrt{2}} \\ \frac{k_{12}}{r} & -\frac{1}{\sqrt{2}} \end{pmatrix} \begin{pmatrix} a & b \\ c & d \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \\ &Solving \ldots a = b = \frac{r}{k_{12} + k_{21}}, \ c = \frac{k_{12}\sqrt{2}}{k_{12} + k_{21}}, \ and \ d = -\frac{k_{21}\sqrt{2}}{k_{12} + k_{21}} \\ &\therefore T^{-1} = \frac{1}{k_{12} + k_{21}} \begin{pmatrix} r & r \\ k_{12}\sqrt{2} & -k_{21}\sqrt{2} \end{pmatrix} \end{aligned} \tag{9.6}$$

$$e^{-\Gamma t}=Te^{-\Delta t}T^{-1}=\begin{pmatrix}\frac{k_{21}}{r} & \frac{1}{\sqrt{2}}\\ \frac{k_{12}}{r} & -\frac{1}{\sqrt{2}}\end{pmatrix}\begin{pmatrix}1 & 0\\ 0 & e^{-(k_{12}+k_{21})t}\end{pmatrix}\frac{1}{k_{12}+k_{21}}\begin{pmatrix}r & r\\ k_{12}\sqrt{2} & -k_{21}\sqrt{2}\end{pmatrix}$$

$$=\frac{1}{k_{12}+k_{21}}\begin{pmatrix}\frac{k_{21}}{r} & \frac{e^{-(k_{12}+k_{21})t}}{\sqrt{2}}\\ \frac{k_{12}}{r} & -\frac{e^{-(k_{12}+k_{21})t}}{\sqrt{2}}\end{pmatrix}\begin{pmatrix}r & r\\ k_{12}\sqrt{2} & -k_{21}\sqrt{2}\end{pmatrix}=\frac{1}{\lambda}\begin{pmatrix}k_{21}+k_{12}e^{-\lambda t} & k_{21}-k_{21}e^{-\lambda t}\\ k_{12}-k_{12}e^{-\lambda t} & k_{12}+k_{21}e^{-\lambda t}\end{pmatrix} \quad (9.7)$$

$$\lambda=k_{12}+k_{21}$$

- Determine the conditional probabilities. Suppose we have the initial conditions $P_1(0)=\begin{pmatrix}1\\0\end{pmatrix}$ *and* $P_2(0)=\begin{pmatrix}0\\1\end{pmatrix}$. The vector $P_1(0)$ means all the C-H bonds are at site 1 at t=0 and $P_2(0)$ means all the C-H vectors are at site 2 at t=0. Generate the four conditional probabilities using the equation

$$P\left(\phi_t(1,2),t;\phi_0(1,2)\right)=e^{-\Gamma t}P_{1,2}(0) \quad (9.8)$$

.Performing this operation explicitly…

:

$$P\left(\phi_t(1,2),t;\phi_0(1)\right)=e^{-\Gamma t}P_1(0)=\frac{1}{\lambda}\begin{pmatrix}k_{21}+k_{12}e^{-\lambda t} & k_{21}-k_{21}e^{-\lambda t}\\ k_{12}-k_{12}e^{-\lambda t} & k_{12}+k_{21}e^{-\lambda t}\end{pmatrix}\begin{pmatrix}1\\0\end{pmatrix}$$

$$=\frac{1}{\lambda}\begin{pmatrix}k_{21}+k_{12}e^{-\lambda t}\\ k_{12}-k_{12}e^{-(k_{12}+k_{21})t}\end{pmatrix}$$

$$(9.9)$$

$$P\left(\phi_t(1,2),t;\phi_0(2)\right)=e^{-\Gamma t}P_2(0)=\frac{1}{\lambda}\begin{pmatrix}k_{21}+k_{12}e^{-\lambda t} & k_{21}-k_{21}e^{-\lambda t}\\ k_{12}-k_{12}e^{-\lambda t} & k_{12}+k_{21}e^{-\lambda t}\end{pmatrix}\begin{pmatrix}0\\1\end{pmatrix}$$

$$=\frac{1}{\lambda}\begin{pmatrix}k_{21}-k_{21}e^{-\lambda t}\\ k_{12}+k_{21}e^{-\lambda t}\end{pmatrix}$$

- Finally calculate the equilibrium probabilities by taking the infinite time limit of the conditional probability.

$$W=\begin{pmatrix}W(1)\\W(2)\end{pmatrix}=\underset{t\to\infty}{Lim}\,P\left(\phi_t(1,2),t;\phi_0(1)\right)=\underset{t\to\infty}{Lim}\,P\left(\phi_t(1,2),t;\phi_0(2)\right)=\frac{1}{k_{12}+k_{21}}\begin{pmatrix}k_{21}\\k_{12}\end{pmatrix} \quad (9.10)$$

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- As an application one can calculate the correlation function. See next homework set.

$$\left\langle e^{il\phi_0}e^{-il\phi_t}\right\rangle=\sum_{j=1,2}\sum_{k=1,2}e^{il\phi_0(j)}e^{-il\phi_t(k)}W\left(\phi_0(j)\right)P\left(\phi_t(k),t;\phi_0(j),t_0=0\right) \quad (9.11)$$