Density Matrix – Second Order Spectra

BCMB/CHEM 8190
Operators in Matrix Notation

If we stay with one basis set, properties vary only because of changes in the coefficients weighting each basis set function

\[ \mu_x = \gamma \left( \frac{\hbar}{2\pi} \right) \langle \psi | \mathbf{I} x | \psi \rangle \]

\[ \psi = c_1 \alpha\alpha + c_2 \alpha\beta + c_3 \beta\alpha + c_4 \beta\beta = \sum_j c_j \phi_j \]

\[ \langle \psi | \mathbf{I} x | \psi \rangle = \sum_{j,k} c_j^* c_k \langle \phi_j | \mathbf{I} x | \phi_k \rangle \]

We need calculate \( \langle \phi_j | \mathbf{I} x | \phi_k \rangle \) only once if we stay with this basis set – these can be put in a \( n \times n \) matrix.

Matrix equivalent: \( \langle \psi | \mathbf{I} x | \psi \rangle = (c_1, c_2, \ldots)^* \begin{bmatrix} \mathbf{I} x \\ \mathbf{I} x \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \\ \cdot \end{bmatrix} \)
Special Case: Pauli Spin Matrices

\[ |I_x| = \begin{pmatrix} 0 & \frac{1}{2} \\ \frac{1}{2} & 0 \end{pmatrix} \]

Note: \( \langle \alpha | I_x | \alpha \rangle = \frac{1}{2} \) \( \langle \alpha | \beta \rangle = 0 \)

\( \langle \alpha | I_x | \beta \rangle = \frac{1}{2} \langle \alpha | \alpha \rangle = \frac{1}{2} \)

\[ |I_y| = \begin{pmatrix} 0 & -i\frac{1}{2} \\ i\frac{1}{2} & 0 \end{pmatrix} \]

\[ |I_z| = \begin{pmatrix} \frac{1}{2} & 0 \\ 0 & \frac{1}{2} \end{pmatrix} \]

How do they work? Try something we know: \( I_x | \alpha \rangle = \frac{1}{2} \beta \)

\[ \begin{pmatrix} 0 & \frac{1}{2} \\ \frac{1}{2} & 0 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} 0 \\ \frac{1}{2} \end{pmatrix} = \frac{1}{2} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \frac{1}{2} \beta \]

Operators are a matrix of numbers, Spin functions a vector of numbers
Larger Collections of Spin ½ Nuclei

\[ I_{Ax} = \begin{pmatrix}
\alpha\alpha & ? & ? & ? & ? \\
\beta\alpha & ? & ? & ? & ? \\
\alpha\beta & ? & ? & ? & ? \\
\beta\beta & ? & ? & ? & ? \\
\end{pmatrix} \]

\[ <\alpha\alpha| I_{Ax} |\beta\alpha> = \frac{1}{2} \]

\[ <\alpha\alpha | \frac{1}{2} | \alpha\alpha> = \frac{1}{2} \]

Easier way: direct products: \( E \otimes I_{Ax} \) with 2X2 matrices
Density Matrices and Observables for an Ensemble of Spins

Expectation values pertain to single spin properties; we observe net behavior of an ensemble of spins. For a particular system (two spin \( \frac{1}{2} \) nuclei) operator representations are the same; all variations are in basis set coefficients. We need to average over these coefficients.

\[
<\psi| I_x |\psi> = (c_1, c_2, \ldots)^* \begin{bmatrix} c_1 \\ I_x \\ c_2 \end{bmatrix} = \sum_{j,k} c_j^* c_k I_{x_{jk}}
\]

Products of averaged coefficients can also be collected and used in matrix form. This is called a density matrix, \( \rho \).

\[
<\psi| I_x |\psi> = \text{Tr} |c_j c_k^*| I_x | = \text{Tr} |\rho| I_x |
\]
Solving for the Time Dependence of $\rho$

Our observables are time dependent (magnetization precesses). All time dependence can also be put in basis set coefficients, or in coefficient products of the density matrix.

Schrodinger’s time dependent equation ($H \psi(t) = -i \frac{h}{2\pi} \frac{d}{dt}(\psi(t))$) Allows us to solve for $\frac{dc_j}{dt}$, $\frac{d}{dt}(c_j^*c_k) = c_j^*(\frac{dc_k}{dt}) + (\frac{dc_j}{dt})c_k$

Result in terms of a density matrix is Lioville – von Neuman eq.

$$\frac{d}{dt} |\rho| = \frac{i}{h/2\pi} \{ |\rho| |H| - |H| |\rho| \}$$

Implications: If we know $\rho$ at any time (equilibrium at time 0) and know the Hamiltonian ($H$), we can solve for $\rho$ at any time, and calculate any observable as the $\text{Tr} |\rho| |O|$ ($O$ is any operator).
Test: Does X Magnetization Precess in $B_0$?

• What elements of $\rho$ dictate $x$ magnetization?

$$<I_x> = \text{Tr} \left[ \rho \right] \left[ I_x \right]$$ 
- examine spin $\frac{1}{2}$ case

$$= \text{Tr} \begin{bmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{bmatrix} \begin{bmatrix} 0 & 1/2 \\ 1/2 & 0 \end{bmatrix} = 1/2\rho_{12} + 1/2\rho_{21}$$

• Therefore, consider $\rho(0) = \begin{bmatrix} 0 & \rho_{12} \\ \rho_{21} & 0 \end{bmatrix}$

• What is $H$?, 

$$H = -(\gamma h B_0/(2\pi))I_z = -(\gamma h B_0/(2\pi)) \begin{bmatrix} 1/2 & 0 \\ 0 & -1/2 \end{bmatrix}$$

• $$\frac{d}{dt} \begin{bmatrix} 0 & \rho_{12} \\ \rho_{21} & 0 \end{bmatrix} = \frac{i}{\hbar} (-\gamma h B_0) \begin{bmatrix} 0 & \rho_{12} \\ \rho_{21} & 0 \end{bmatrix} \begin{bmatrix} 1/2 & 0 \\ 0 & -1/2 \end{bmatrix} - \begin{bmatrix} 1/2 & 0 \\ 0 & -1/2 \end{bmatrix} \begin{bmatrix} 0 & \rho_{12} \\ \rho_{21} & 0 \end{bmatrix}$$
Consider evolution of one element

- \((d/dt)\rho_{12}(t) = i\gamma B_0 (-\frac{1}{2} \rho_{12}(t) - \frac{1}{2} \rho_{12}(t)) = i\omega_0 \rho_{12}(t)\)
  
- Solution: \(\rho_{12}(t) = \rho_{12}(0) \exp(-i\omega_0 t)\) or:
  \[= \rho_{12}(0) (\cos(\omega_0 t) - i \sin(\omega_0 t))\]

- Same happens for \(\rho_{21}(t)\)

- Hence elements corresponding to x magnetization precess

\[t = 0\]

\[t = 1\]
Density Matrix Simulation of 2nd Order Spectra

- For two spins basis set is: $\alpha\alpha$, $\alpha\beta$, $\beta\alpha$, $\beta\beta$

$$\rho = \begin{bmatrix} \rho_{11} & \rho_{12} & \rho_{13} \\ \rho_{21} & \rho_{22} & . \\ \rho_{31} & . & . \\ . & . & . \end{bmatrix}$$

- $\rho_{12}, \rho_{21}, ...$ are associated with lines in an AX spectrum

- Don’t have to have a 1:1 association if $\psi$ is not an eigen function of $H$.

- $c_i \phi_i + c_i \phi_i$ may evolve coherently as one line – ie $\rho_{12}, \rho_{21}$, are mixed

- Calculation of $Mx$ still works!
Second Order Spectrum Example: Acetonitrile

- Twelve lines, all equal intensities
- $J_{AB} = -2$ Hz, $\delta_C = 5.6$ ppm
- $J_{AC} = 11$ Hz, $\delta_B = 6.1$ ppm
- $J_{BC} = 16$ Hz, $\delta_A = 6.3$ ppm
- Actual spectrum is more complex, field dependent
Field dependence of second order spectra

60 MHz

90 MHz

250 MHz

490 MHz
Line intensities: density matrix elements and transition probabilities

• \( \rho_{kl} = c_k^* c_l \); \( c_k^* c_l \) is the probability of being in state \( k \)
• \( c_k^* c_k c_l^* c_l \) is the probability of starting in \( k \) and ending in \( l \)
• If we know we start in \( k \), \( c_k^* c_k = 1 \), and just need \( c_l \)
• from Schrodinger equation: \( \frac{dc_l}{dt} \propto \langle \phi_l | H' | \phi_k \rangle \)
• Integrating from \( t = 0 \) and combining with \( c_l^* \)
• \( P_{k \to l} \propto |\langle \phi_l | H' | \phi_k \rangle|^2 \) … gives line intensities
Understanding second order spectra

- $A_2$ vs AX or $H_2O$  vs  HF

- For HF ..

- $P_{\beta\beta\rightarrow\alpha\beta} \propto |<\beta\beta|\gamma B_1(I_{x1} + I_{x2})|\alpha\beta>|^2$;  $I_x = (I_+ + I_-)/2$

- this is finite and same for all $P_{ij}$

- implies same line intensities
For an $A_2$ system:

- $\alpha\alpha$, $\alpha\beta$, $\beta\alpha$, $\beta\beta$ are not good wave functions
- Imply distinguishability
- Use: $\alpha\alpha$, $(\alpha\beta+\beta\alpha)/\sqrt{2}$, $(\alpha\beta-\beta\alpha)/\sqrt{2}$, $\beta\beta$
- $<\beta\beta|B_1(I_{x1} + I_{x2})| (\alpha\beta+\beta\alpha)/\sqrt{2} > = (1/2 + 1/2)/\sqrt{2}$
- $<\beta\beta|B_1(I_{x1} + I_{x2})| (\alpha\beta-\beta\alpha)/\sqrt{2} > = (1/2 - 1/2 )/\sqrt{2} =0$
- Outer transitions are not allowed
Intermediate behavior of 2\textsuperscript{nd} order spectra

- H\textsubscript{2}O
- AB
- HF

Outer lines are not observed. Couplings still exist.
Second order effects can be important

- Coupling of H4 and H5, H5’ protons in ribose rings – an ABX system
- Karplus equation might be used to deduce torsion angle, but can couplings be measured from multiplet?
- For degenerate H5, H5’, see a triplet, but splitting is \((J_{45} + J_{45'})/2\)
- Cannot conclude that \(J_{45} = J_{45'}\)
- Answer: simulate spectra