MASSACHUSETTS INSTITUTE OF TECHNOLOGY

5.74 Quantum Mechanics II
Spring, 2004
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Problem Sets #8 and #9

DUE: At the start of Lecture on Wednesday, May 5.

Reading: HLB-RWF Section 9.3

Problems:

I. Intramolecular Vibrational Redistribution (IVR) and Isomerization.

Brooks Pate, at the University of Virginia, has performed ingenious infrared-microwave multiple resonance experiments designed to measure conformational isomerization rates in the presence of rapid IVR. [See *Int. Revs. Phys. Chem.* **19**, 363-407 (2000).] It is based on the concept of "motional narrowing" in NMR where two resolved transitions associated with chemically distinct spins broaden and merge into one transition (of width narrower than the separation between the previously resolved transitions) when the exchange rate between the chemically distinct sites becomes sufficiently rapid. This problem is my attempt to capture the essence of Pate's experiment in a simplified model.

A. IVR without Isomerization

Set up two 100×100 random matrices to represent the $J = 5$ and $J = 6$ rotational levels of isomer A, following the prescription:

(i) $\mathbf{H}_A(J = 5)$

$$5000 \text{ cm}^{-1} \leq \mathbf{H}^{(0)}_{An,An} / hc \leq 5010 \text{ cm}^{-1}$$

$$\rho^A_{vib} = 10 / \text{cm}^{-1} \qquad \text{(density of states, not density matrix)}$$

$$\left\langle \mathbf{H}^{(1)}_{An,Am} \right\rangle = 0$$

$$\sigma_A^{1/2} = \left[\left\langle \left(\mathbf{H}^{(1)}_{An,Am} / hc \right)^2 \right\rangle \right] = 0.20 \text{ cm}^{-1}.$$

You are to generate random numbers for both the diagonal and the off-diagonal matrix elements: two separate sets of random numbers.

(ii) $\mathbf{H}_A(J = 6)$

Construct this matrix by adding $12B = 12$ cm^{-1} to each of the diagonal elements in $\mathbf{H}_A(J = 5)$. Generate a new set of random numbers for the off-diagonal matrix elements, keeping $\sigma_A^{1/2} = 0.20$ cm^{-1}.

(iii)   The pure rotation spectrum is controlled by matrix elements of the electric dipole moment operator. For this problem, let

$$\mu_{nm}^A \langle A, J = 5, n | \mathbf{\mu} | A, J = 6, m \rangle = \mu_A \delta_{nm}.$$

In other words, the only allowed rotational transitions are between zero-order states that belong to the same vibrational quantum number.

(iv)   Compute the frequencies and intensities of the 10^4 eigenstate to eigenstate transitions in the pure rotational spectrum. Use the eigenvectors of $\mathbf{H}_A(J=5)$ and $\mathbf{H}_A(J=6)$. Plot the rotational spectrum (intensity vs. wavenumber) on an appropriately expanded cm^{-1} scale in the neighborhood of

$$\frac{E_{An}(6) - E_{An}(5)}{hc} = 12 \text{ cm}^{-1}.$$

"Edge effects" are minimized by retaining only the central 50% of the 10^4 transition frequencies.

(v)   Compute the Full Width at Half Maximum (FWHM) of the $J = 6 \leftarrow 5$ rotational spectrum. (You might want to convolve the infinite resolution spectrum that you have calculated with an appropriate lineshape function, say of FWHM ≈ 0.05 cm^{-1}, in order to get a smooth, symmetric, and hopefully near Lorentzian lineshape.)

(vi)   Increase and decrease $\left[\left\langle \left(\mathbf{H}_{An,Am}^{(1)} / hc \right)^2 \right\rangle \right]^{1/2}$ by a factor of 2 to verify that the FWHM of the pure rotation spectrum varies according to Fermi's Golden Rule Formula. This determines the IVR rate.

B.   The Other Isomer

Repeat parts (i) - (v) for isomer B. Since isomer B is less stable than isomer A, the levels of isomer B in the neighborhood of

$$\mathbf{H}^{(0)}_{Bn,Bn}/hc = 5005 \text{ cm}^{-1}$$

have smaller values of

$$\rho^{B}_{vib} = 5/\text{cm}^{-1}$$

$$\left[\left\langle\left(\mathbf{H}^{(1)}_{Bn,Bm}\right)^2\right\rangle\right]^{1/2} = 0.10 \text{ cm}^{-1}.$$

According to the Golden Rule Formula, the FWHM of the isomer B transition should be narrower than that for isomer A by a factor of 8. Let

$$\mu_A = \mu_B$$
$$B_B = 0.95 \ B_A.$$

The low-resolution $J = 6 \leftarrow 5$ pure rotation spectrum of the thermal isomer A + B mixture should consist of two composite lines, that for isomer-B centered at 11.4 cm^{-1}, a factor of 8 narrower and with integrated intensity a factor of 2 smaller than that for the isomer-A line centered at 12.0 cm^{-1}.

If overlap between the isomer A and B lines obscures the shape of either line, you should reduce B_B to 0.9 B_A.

C.   Conformational Isomerization

(i)   Combine the isomer-A and isomer-B $\mathbf{H}(J+5)$ matrices into a 200 × 200 super-matrix. The $\mathbf{H}_A$ and $\mathbf{H}_B$ matrices are centered at the same average energy:
$$E/hc = 5005 \text{ cm}^{-1}.$$

(ii)   Introduce off-diagonal matrix elements between the isomer-A and isomer-B blocks using random numbers with

$$\left\langle\mathbf{H}^{(1)}_{An,Bm}\right\rangle = 0$$

$$\sigma^{1/2}_{AB} = \left[\left\langle\left(\mathbf{H}^{(1)}_{An,Bm}\right)^2\right\rangle\right] = 0.5 \text{ cm}^{-1}.$$

Note that you will have 10^4 nonzero matrix elements between the $\mathbf{H}_A(J=5)$ and $\mathbf{H}_B(J=5)$ blocks.

(iii) Do the same for the isomer-A and isomer-B $J = 6$ blocks. Use a new set of random numbers with $\sigma_{AB}^{1/2} = 0.5$ cm^{-1} for the off-diagonal matrix elements. Since the isomer-A and isomer-B blocks do not span the same range of zero-order energies, you should discard the eigen-energies that fall outside the 5013 cm$^{-1} \leq E \leq 5020.6$ cm^{-1} region.

(iv) Diagonalize the two 200×200 $\mathbf{H}(J{=}5)$ and $\mathbf{H}(J{=}6)$ matrices. Compute the pure rotation spectrum in the region

$$8.4 \text{ cm}^{-1} \leq \frac{E(J = 6) - E(J - 5)}{hc} \leq 15 \text{ cm}^{-1}$$

using the eigenvectors of $\mathbf{H}(6)$ and $\mathbf{H}(5)$ and transition moment matrix

$$\boldsymbol{\mu} = \boldsymbol{\mu}^{A} + \boldsymbol{\mu}^{B}.$$

Note that transitions between basis states that belong to different isomers are forbidden
$$\langle An|\boldsymbol{\mu}|Bm\rangle = \mu_A \delta_{AB}\delta_{mn}.$$

(v) Vary $\sigma_{AB}^{1/2} = \left[\left\langle \left(\mathbf{H}_{An,Bm}^{(1)}\right)^2 \right\rangle\right]^{1/2}$ in factor of 3 steps until you can follow the evolution from a spectrum consisting of two distinct isomer-A and isomer-B lines (low value of $\sigma_{AB}^{1/2}$) to a spectrum containing a single "motionally narrowed" line (high value of $\sigma_{AB}^{1/2}$).

II. <u>Interaction between Sharp and Broad Quasi-Eigenstates</u>

You are going to approach this problem in two ways. First you will consider the interaction between two clusters of eigenstates. Next you will replace the cluster of individual eigenstates by a single broad quasi-engenstate. The spectral properties of the two approaches had better be very similar.

A. Use $\mathbf{H}_A(J{=}5)$ and $\mathbf{H}_B(J{=}6)$ from problem IA(i) and IB. You want two clusters, each composed of 100 eigenstates. The two clusters should have Fermi Golden Rule widths different by approximately a factor of 10. The two clusters should have $\langle E_A \rangle = \langle E_B \rangle$.

B. Pick one zero-order state in each cluster which lies closest to $E^{(0)}/hc = 5005.0\,\mathrm{cm}^{-1}$, $\psi_{A,\text{middle}}^{(0)}$ and $\psi_{B,\text{middle}}^{(0)}$. Plot the fractional character of $\psi_{A,\text{middle}}^{(0)}$ and $\psi_{B,\text{middle}}^{(0)}$ in each of the eigenstates vs. eigen-energy. The plot of fractional character vs. energy should be approximately Lorentzian with FWHM predicted by the Fermi Golden Rule Formula. The lineshape can be made clearer by convoluting the stick spectrum with a suitable lineshape function.

C. Construct an $\mathbf{H}_A(J{=}5) + \mathbf{H}_B(J{=}6)$ super matrix. The off-diagonal elements in this matrix will be given by a constant, H_{AB}, times the product of the amplitudes of $\psi_{A,\text{middle}}^{(0)}$ and $\psi_{B,\text{middle}}^{(0)}$ in each eigenstate of $\mathbf{H}_A(J{=}5)$ and $\mathbf{H}_B(J{=}6)$, respectively. Choose $H_{AB} = \tfrac{1}{2}\Gamma_B$, where Γ_B is the Fermi Golden Rule width of cluster B (the narrower cluster).

D. Find the eigen-energies and eigen-vectors of the $\mathbf{H}_A(J{=}5) + \mathbf{H}_B(J{=}6)$ super matrix. Compute the fractional $\psi_{A,\text{middle}}^{(0)}$ and $\psi_{B,\text{middle}}^{(0)}$ character in each of the 200 eigenstates of the super matrix and plot the fractional character vs. eigen-energy as in part (ii).

E Repeat steps C and D for values of H_{AB} increased each time by a factor of ~3 until $H_{AB} \approx 4\Gamma_A$ (A is the broader cluster). You should see a qualitative change in the distribution of $\psi_{A,\text{middle}}^{(0)}$ and $\psi_{B,\text{middle}}^{(0)}$ character vs. energy. Describe this qualitative change.

III. Complex $\mathbf{H}^{\text{eff}}$ formalism for interaction between sharp and broad quasi–eigenstates. This is a much more compact and convenient method than the random matrix method you used in problem 2.

A. Strong Coupling Limit

$$E \equiv \varepsilon - i\Gamma/2$$

For the zero-order states A and B

$$\bar{\varepsilon} = \frac{\varepsilon_A + \varepsilon_B}{2} = 0$$
$$\Gamma_A/hc = 9 \ \mathrm{cm}^{-1}$$
$$\Gamma_B/hc = 1 \ \mathrm{cm}^{-1}$$
$$H_{AB}/hc = 20 \ \mathrm{cm}^{-1}$$
$$E_\pm \equiv \varepsilon_\pm - i\Gamma_\pm/2 \qquad \left(\text{by definition, } \varepsilon_+ \geq \varepsilon_- \right).$$

Plot ε_+, ε_-, Γ_+, Γ_- vs. $\varepsilon_A - \varepsilon_B$ over the region

$$-50 \ \mathrm{cm}^{-1} \leq \frac{\varepsilon_A - \varepsilon_B}{hc} \leq 50 \ \mathrm{cm}^{-1}.$$

Make special note of $\varepsilon_+ - \varepsilon_-$, and $\Gamma_+ - \Gamma_-$ at $\varepsilon_A - \varepsilon_B = 0$. Explain your observations in the context of ordinary 2-state non-degenerate and quasi–degenerate perturbation theory.

B. Repeat the calculations and plots in Part A for all parameters the same except

$$\Gamma_A/hc = \Gamma_B/hc = 5 \ \mathrm{cm}^{-1}.$$

C. Weak Coupling Limit. Repeat the calculations and plots in Part A for all parameters the same as in Part A except

$$H_{AB}/hc = 0.5 \ \mathrm{cm}^{-1}.$$

Make special note of $\varepsilon_+ - \varepsilon_-$ and $\Gamma_+ - \Gamma_-$ at $\varepsilon_A - \varepsilon_B = 0$. What, if anything, is surprising?

D. Repeat the calculations and plots in Part C except

$$\Gamma_A/hc = \Gamma_B/hc = 5 \ \mathrm{cm}^{-1}.$$

E. Does the transition between the strong and weak coupling limits depend on the magnitude of H_{AB} relative to $\dfrac{|\Gamma_A - \Gamma_B|}{2}$ or $\dfrac{|\Gamma_A + \Gamma_B|}{2}$? Discuss.