

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

5.61 Physical Chemistry
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FIFTY MINUTE EXAMINATION II **ANSWER KEY**

I. Short Answer Questions

(40 Points)

A. (20 points) Rotational Spectrum of HCl

$$m_H = 1.0078 \text{ g/mol}$$

$$m_{^{35}\text{Cl}} = 34.9689 \text{ g/mol}$$

$$m_{^{37}\text{Cl}} = 36.9659 \text{ g/mol}$$

$$\mu(\text{H}^{35}\text{Cl}) = 0.97957 \text{ g/mol}$$

$$\mu(\text{H}^{37}\text{Cl}) = 0.98105 \text{ g/mol}$$

$$B_e(\text{H}^{35}\text{Cl}) = 10.593416 \text{ cm}^{-1}$$

$$\alpha_e(\text{H}^{35}\text{Cl}) = 0.3072 \text{ cm}^{-1}$$

- (i) (4 points) What physical property is required for the rotational spectrum of HCl to be observable?

A permanent electric dipole moment is required for observation of a pure rotation (microwave) spectrum. [A dipole derivative, $\frac{d\mu}{dR}$, is required for observation of a vibrational spectrum.]

- (ii) (4 points) What is the B_e value for H^{37}Cl ?

The B_e value for H^{37}Cl is

$$\begin{aligned} B_e(\text{H}^{37}\text{Cl}) &= \frac{\mu(\text{H}^{35}\text{Cl})}{\mu(\text{H}^{37}\text{Cl})} B_e(\text{H}^{35}\text{Cl}) \\ &= \frac{0.97957}{0.98105} 10.593416 \\ &= 10.57743 \text{ cm}^{-1} \end{aligned}$$

- (iii) (7 points) What are the transition frequencies (in cm^{-1} units) of the $J = 1 \leftarrow J = 0$ transitions in H^{35}Cl and H^{37}Cl ?

The $J = 1 \leftarrow J = 0$ transitions are at $\sim 2B_e$

$$\text{H}^{35}\text{Cl} \quad 2(10.593416) = 21.186832 \text{ cm}^{-1}$$

$$\text{H}^{37}\text{Cl} \quad 2(10.57743) = 21.15486 \text{ cm}^{-1}$$

+2 extra credit if the calculation was for the $v = 0$ level where $2\alpha_e$ was subtracted from the values above.

+1 additional credit if concern was expressed for the difference between α_e for H^{35}Cl vs. H^{37}Cl .

- (iv) (5 points) What is the difference (in cm^{-1} units) between the $J = 1 \leftarrow J = 0$ transition frequencies in H^{35}Cl for $v = 0$ and $v = 1$? The rotational constants depend on v , as specified by the equation

$$B(v) = B_e - \alpha_e(v + 1/2).$$

For H^{35}Cl the $J = 1 - 0$ transitions are

$$\text{for } v = 0 \quad 2 \left[10.593416 - \frac{1}{2}(0.3072) \right] \text{ cm}^{-1}$$

$$v = 1 \quad 2 \left[10.593416 - \frac{3}{2}(0.3072) \right] \text{ cm}^{-1}$$

Full credit given for

$$\nu_{v=0} - \nu_{v=1} = 2(0.3072) = 0.6144 \text{ cm}^{-1}.$$

B. (12points) Harmonic Oscillator Plus Barrier or Well

$$\hat{H}^{(0)} = -\frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} + \frac{1}{2} kx^2$$

$$\hat{H}^{(1)} = V_0 \quad -x_0 \leq x \leq x_0, \quad V_0 = 0 \quad |x| > x_0$$

$$E^{(0)}(v) = \hbar\omega(v + 1/2)$$

- (i) (6 points) Does the second-order perturbation theory correction term, $E_v^{(2)}$, depend on the sign of V_0 ?

The value of $E_v^{(2)}$ does *not* depend on the sign of V_0 because $E_v^{(2)} \propto V_0^2$.

- (ii) (6 points) Does perturbation theory predict that the energy levels of a harmonic oscillator plus a barrier ($V_0 > 0$) are different from those of a harmonic oscillator plus a well ($V_0 < 0$)? Explain your answer.

YES perturbation theory does predict a very substantial difference between the energy levels for $V_0 > 0$ vs. $V_0 < 0$ because

$$E_v^{(1)} = \int_{-x_0}^{x_0} d\tau \psi_v^* V_0 \psi_v \propto 2x_0 V_0.$$

C. (8 points) Rigid Rotor

For a freely-evolving rigid rotor (\hat{H} is time-independent).

- (i) (4 points) You find $\langle \hat{J}^2 \rangle_{t=0} = \hbar^2 3.000$. What does this imply about $\Psi(\theta, \phi, t = 0)$?

If $\langle J^2 \rangle_{t=0} = \hbar^2 3.000$ the system cannot be in an eigenstate of \hat{J}^2 . The eigenvalues are

J	$\int d\tau \psi^* \hat{J}^2 \psi$
0	$0\hbar^2$
1	$2\hbar^2$
2	$6\hbar^2$

One way to achieve $\langle J^2 \rangle_{t=0} = \hbar^2 3.00$ is for

$$\psi(\theta, \phi) = \left(\frac{3}{4}\right)^{1/2} \psi_{2,M} + \left(\frac{1}{4}\right)^{1/2} \psi_{3,M}$$

because

$$\left(\frac{3}{4}\right) 2 + \left(\frac{1}{4}\right) 6 = 3.$$

There are many other ways to arrive at this value of $\langle J^2 \rangle$.

- (ii) (4 points) Will $\langle \hat{J}^2 \rangle_t$ be time-dependent? Explain your answer.

The $J = 2$ and $J = 3$ eigenstates of \hat{J}^2 have different energies, so the minimum criterion for time-dependence of an expectation value is met. However the selection rule for \hat{J}^2 is $\Delta J = 0$. Thus there is no contribution to $\langle \hat{J}^2 \rangle_t$ from a cross term between $\psi_{2,M}$ and $\psi_{3,M'}$ regardless of the values of M and M' .

II. The Two-Level Problem: Bright and Dark States**(40 Points)**

Consider the 2-level problem where

$$\begin{aligned}
 E_1^{(0)} &= A + \Delta/2 & (\Delta > 0) \\
 E_2^{(0)} &= A - \Delta/2 \\
 H_{12}^{(1)} &= V & (|V| \ll \Delta) \\
 H_{11}^{(1)} &= H_{22}^{(1)} = 0.
 \end{aligned}$$

The eigen-energies and eigen-functions are

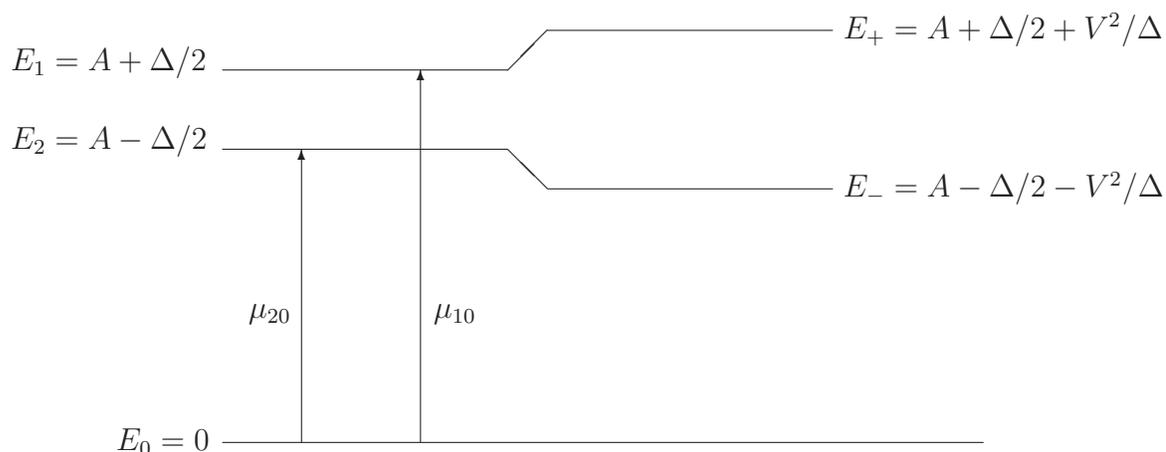
$$\begin{aligned}
 E_{\pm} &= A \pm (\Delta/2 + V^2/\Delta) \\
 \star \quad \psi_+ &= [1 - (V/\Delta)^2]^{1/2} \psi_1 + (V/\Delta) \psi_2 \\
 \star \quad \psi_- &= -(V/\Delta) \psi_1 + [1 - (V/\Delta)^2]^{1/2} \psi_2 \\
 &\psi_1 \text{ and } \psi_2 \text{ are normalized and orthogonal.}
 \end{aligned}$$

The zero-order wave functions, expressed in terms of the eigenfunctions are

$$\begin{aligned}
 \star \star \quad \psi_1^{(0)} &= [1 - (V/\Delta)^2]^{1/2} \psi_+ - (V/\Delta) \psi_- \\
 \star \star \quad \psi_2^{(0)} &= (V/\Delta) \psi_+ + [1 - (V/\Delta)^2]^{1/2} \psi_-
 \end{aligned}$$

A. (10 points) Show that ψ_+ and ψ_- in the \star equations are normalized and orthogonal.

$$\begin{aligned}
 \int d\tau \psi_+^* \psi_+ &= [1 - (V/\Delta)^2] + (-V/\Delta)^2 = 1 \\
 \int d\tau \psi_-^* \psi_- &= (V/\Delta)^2 + [1 - (V/\Delta)^2] = 1 \\
 \int d\tau \psi_-^* \psi_+ &= (V/\Delta)[1 - (V/\Delta)^2]^{1/2} - (V/\Delta)[1 - (V/\Delta)^2]^{1/2} = 0.
 \end{aligned}$$

B. (10 points) Suppose that a laser is used to excite molecules from level 0 (at $E_0 = 0$) to the two-level system

where $\mu_{10} \neq 0$ and $\mu_{20} = 0$.

Consider an experiment in which the total fluorescence intensity is recorded as the frequency of a long-pulse excitation laser is scanned through the frequency region that includes the $\frac{E_+ - E_0}{h}$ and $\frac{E_- - E_0}{h}$ eigenstate to eigenstate transition frequencies. This is called a “fluorescence excitation spectrum”. The fluorescence intensity from the E_+ level is proportional to

$$I_{+0} \propto |\mu_{+0}|^2 \equiv \left| \int dx \psi_+^* \hat{\mu} \psi_0 \right|^2.$$

Sketch the observed fluorescence excitation spectrum and specify the relative intensities of the transitions in the spectrum.

I was trying to trick you by labeling the frequency axis for both actual and zero-order frequencies. The transitions occur between the actual energy levels

$$\frac{E_- - E_0}{h} \quad \text{and} \quad \frac{E_+ - E_0}{h}.$$

The intensities of transitions into the + and - eigenstates are proportional to the fractional character of the bright state in each eigenstate. The bright state is ψ_1 because $\mu_{10} \neq 0$ and $\mu_{20} = 0$.

In ψ_+ fractional character of ψ_1 is $[1 - (V/\Delta)^2]$.

In ψ_- fractional character of ψ_1 is $(\frac{V}{\Delta})^2$.

A basic assumption of perturbation theory is $|V| \ll |\Delta|$.



Any answer that shows

$$\frac{I_{E_- - E_0}}{h} < \frac{I_{E_+ - E_0}}{h}$$

gets full credit.

C. (20 points) Now consider short-pulse excitation of the two-level system from level E_0 .

- (i) (3 points) Which zero-order level (level 1 or level 2) is “bright” and which is “dark”?

Level 1 is bright because $\mu_{10} \neq 0$.
Level 2 is dark because $\mu_{20} = 0$.

- (ii) (3 points) Based on your answer to part (i), what is $\Psi(x, t = 0)$?

$\Psi(x, t = 0) = \psi_1^{(0)}(x) = [1 - (V/\Delta)^2]^{1/2}\psi_+ - (V/\Delta)\psi_-$

- (iii) (4 points) Write an expression for $\Psi(x, t)$, following the prescription that the bright state produced at $t = 0$ must be expressed as a linear combination of the eigenstates, each with a phase factor $e^{-iE_{\pm}t/\hbar}$.

$\Psi(x, t) = [1 - (V/\Delta)^2]^{1/2}e^{-iE_+t/\hbar}\psi_+ - (V/\Delta)e^{-iE_-t/\hbar}\psi_-$

- (iv) (10 points) The observed fluorescence intensity will exhibit quantum beats where

$$I(t) \propto \left| \int dx \Psi^*(x, t) \hat{\mu} \psi_0 \right|^2.$$

Describe the features of this quantum beating signal.

One prepares a coherent superposition of ψ_+ and ψ_- at $t = 0$, as shown in (iii) above because one prepares the bright zero-order state.

- ★ Does the fluorescence intensity at $t = 0$, $I(t = 0)$, correspond to a maximum or minimum?

The fluorescence intensity is maximum at $t = 0$.

- ★ Are the oscillations observed at frequency

$$\frac{E_1 - E_2}{h} \quad \text{or} \quad \frac{E_+ - E_-}{h}$$

or both?

The oscillations occur at frequency $\frac{E_+ - E_-}{\hbar}$. Full credit for $\frac{E_+ - E_-}{\hbar}$ but that is angular frequency, ω , rather than the ordinary frequency, ν .

- ★ What is the ratio of the intensity at the first minimum of $I(t)$ to that at the first maximum, I_{\min}/I_{\max} ?

This can be algebraically complicated without a trick. The QB intensities are maximum at

$$2\pi n = \frac{E_+ - E_-}{\hbar} t_{\max}$$

$$t_{\max} = n \frac{2\pi\hbar}{E_+ - E_-}$$

For the minima, we require

$$t_{\min} = \left(2n + \frac{1}{2}\right) \frac{h}{E_+ - E_-} \quad \text{so for the earliest minimum}$$

$$t_{\min} = \frac{1}{2} \frac{2\pi\hbar}{E_+ - E_-}$$

$$\Psi(x, t_{\min}) = e^{-iE_+ t_{\min}/\hbar} \left[[1 - (V/\Delta)^2]^{1/2} \psi_+ - (V/\Delta) e^{i(E_+ - E_-)t_{\min}/\hbar} \psi_- \right]$$

$$e^{i(E_+ - E_-)t_{\min}/\hbar} = e^{i\pi} = -1$$

$$\Psi(x, t_{\min}) = e^{-iE_+ t_{\min}/\hbar} \left[[1 - (V/\Delta)^2]^{1/2} \psi_+ + (V/\Delta) \psi_- \right]$$

term in [] = $[1 - (V/\Delta)^2]^{1/2} [1 - (V/\Delta)^2]^{1/2} \psi_1$

$$+ [1 - (V/\Delta)^2]^{1/2} V/\Delta \psi_2$$

$$- (V/\Delta)^2 \psi_1 + (V/\Delta) [1 - (V/\Delta)^2]^{1/2} \psi_2$$

$$= \underbrace{[1 - 2(V/\Delta)] \psi_1}_{\text{bright}} + \underbrace{2(V/\Delta) [1 - (V/\Delta)^2]^{1/2} \psi_2}_{\text{dark}}$$

So intensity at t_{\min} is $[1 - 2(V/\Delta)^2]^2 \mu_{10}^2$ and at t_{\max} it is μ_{10}^2 .

III. VIBRATIONAL TRANSITION INTENSITIES (20 Points) AND ANHARMONIC INTERACTIONS

The intensities of vibrational absorption transitions are proportional to

$$I_{v',v''} \propto \left| \int dQ \psi_{v'}(Q) \hat{\mu}(\hat{Q}) \psi_{v''}(Q) \right|^2$$

where

$$\hat{\mu}(\hat{Q}) = \mu_0 + \frac{d\mu}{dQ} \hat{Q} + \frac{1}{2} \frac{d^2\mu}{dQ^2} \hat{Q}^2$$

where, for a harmonic oscillator, the displacement from equilibrium (called \hat{x} in the lecture notes)

$$\hat{Q} = \left(\frac{\hbar}{2\mu\omega} \right)^{1/2} [\hat{\mathbf{a}} + \hat{\mathbf{a}}^\dagger]$$

and, for a harmonic oscillator

$$\int dQ \psi_{v-1} \hat{\mathbf{a}} \psi_v = v^{1/2}$$

$$\int dQ \psi_{v+1} \hat{\mathbf{a}}^\dagger \psi_v = (v+1)^{1/2}.$$

- A. (5 points) What is the ratio of transition probabilities for the $v' = 1 \leftarrow v'' = 0$ fundamental transition to that for the $v' = 2 \leftarrow v'' = 1$ hot band?

$$\int dQ \psi_{v+1}^* \hat{Q} \frac{d\mu}{dQ} \psi_v \propto (v+1)^{1/2}$$

Transition intensity is $\propto v$ of higher state

$$\frac{I_{2-1}}{I_{1-0}} = \frac{2}{1}.$$

- B. (15 points) In OCS there are 3 normal modes and $\frac{\partial\mu}{\partial Q_i} \neq 0$ for normal modes numbered $i = 1, 2$, and 3. This means that there are allowed fundamental transitions $(1, 0, 0) \leftarrow (0, 0, 0)$, $(0, 1, 0) \leftarrow (0, 0, 0)$, and $(0, 0, 1) \leftarrow (0, 0, 0)$ where each zero-order vibrational level is denoted by (v_1, v_2, v_3) . Suppose that there is an important anharmonic resonance, $k_{122} \hat{Q}_1 \hat{Q}_2^2$.

- (i) (3 points) What are the selection rules for anharmonic interactions caused by

$$k_{122} \hat{Q}_1 \hat{Q}_2^2?$$

$$\Delta v_1 = \boxed{\pm 1}$$

$$\Delta v_2 = \boxed{\pm 2, 0}$$

$$\Delta v_3 = \boxed{0}$$

$$\hat{Q}_1 \text{ selection rule is } \Delta v_1 = \pm 1$$

$$\hat{Q}_2^2 \text{ selection rule is } \Delta v_2 = 0, \pm 2$$

$$\hat{Q}_3^0 \text{ selection rule is } \Delta v_3 = 0$$

- (ii) (3 points) Consider the anharmonic interaction between the $\psi_{(1,0,0)}^{(0)}$ and $\psi_{(0,2,0)}^{(0)}$ zero-order states:

$$\begin{aligned}
 V &\equiv \int dQ_1 dQ_2 dQ_3 \psi_{(1,0,0)}^{(0)} \widehat{Q}_1 \widehat{Q}_2^2 \psi_{(0,2,0)}^{(0)} \\
 \Delta &\equiv E_{(0,2,0)}^{(0)} - E_{(1,0,0)}^{(0)} \\
 E_+ - E_- &= \Delta + 2V^2/\Delta \\
 \psi_{(1,0,0)}^{(0)} &= [1 - (V/\Delta)^2]^{1/2} \psi_+ - (V/\Delta) \psi_- \\
 \psi_{(0,2,0)}^{(0)} &= (V/\Delta) \psi_+ + [1 - (V/\Delta)^2]^{1/2} \psi_- \\
 \psi_+ &= [1 - (V/\Delta)^2]^{1/2} \psi_{(1,0,0)}^{(0)} + (V/\Delta) \psi_{(0,2,0)}^{(0)} \\
 \psi_- &= -(V/\Delta) \psi_{(1,0,0)}^{(0)} + [1 - (V/\Delta)^2]^{1/2} \psi_{(0,2,0)}^{(0)}
 \end{aligned}$$

A short infrared pulse excites a coherent superposition of ψ_+ and ψ_- . What is $\Psi(Q_1, Q_2, Q_3, t = 0)$?

This is a vibrational transition. The $\psi_{(1,0,0)}^{(0)}$ state is bright (vibrational fundamental) and the $\psi_{(0,2,0)}^{(0)}$ state is dark (vibrational overtone).

$$\Psi(Q_1, Q_2, Q_3, t = 0) = \psi_{(1,0,0)}^{(0)}$$

- (iii) (5 points) The number operator $\widehat{N}_i = \widehat{\mathbf{a}}_i^\dagger \widehat{\mathbf{a}}_i$ tells us the number of quanta in the i -th zero-order normal mode. What are the expectation values of \widehat{N}_1 and \widehat{N}_2 at $t = 0$?

at $t = 0$

$$\langle \widehat{N}_1 \rangle_{t=0} = 1, \quad \langle \widehat{N}_2 \rangle_{t=0} = 0.$$

- (iv) (4 points) Describe what you expect for the time evolution of $\langle \hat{N}_1 \rangle$ and $\langle \hat{N}_2 \rangle$ for the coherent superposition state excited by the short infrared pulse. Your description can be in words, pictures, or equations.

$\langle \hat{N}_1 \rangle_t$ oscillates at

$$\omega_{+-} = \frac{E_+ - E_-}{\hbar} = \frac{\Delta + 2V^2/\Delta}{\hbar}$$

It is at its maximum value of 1.00 at $t = 0$.

It is at its minimum value of $1.00 - \delta$ at

$$t_{\min} = \frac{1}{2} \frac{h}{E_+ - E_-}.$$

$$\begin{aligned} \langle \hat{N}_2 \rangle_t &= 0 & \text{at} & \quad t = 0 \\ &= 2\delta & \text{at} & \quad t_{\min} = \frac{1}{2} \frac{h}{E_+ - E_-}. \end{aligned}$$

δ is small, so it could be calculated as in problem **II.C (iv)**.

$$d = 4(V/\Delta)^2[(V/\Delta)^2 - 1]$$

POSSIBLY USEFUL INFORMATION

The classical mechanical relationship between x and p is

$$p(x) = [2m(E - V(x))]^{1/2}.$$

For a harmonic oscillator with $V(x) = \frac{1}{2}kx^2$, when $x = 0$ and $E_v = \hbar\omega(v + 1/2)$

$$p_v(0) = [2\mu\hbar\omega(v + 1/2)]^{1/2}.$$

$$\widehat{L}^2\psi_{L,M_L} = \hbar^2 L(L + 1)\psi_{L,M_L}$$

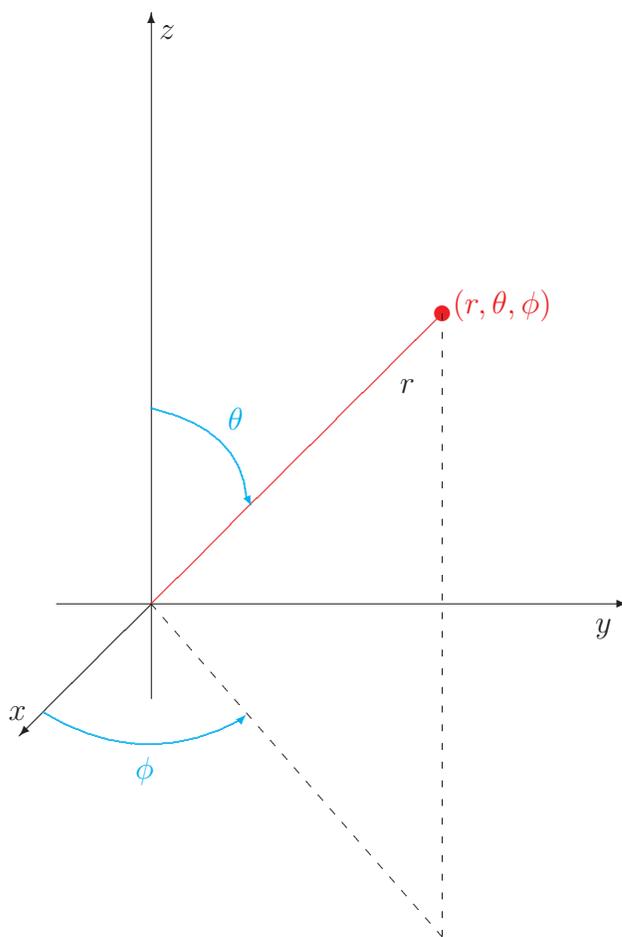
$$\widehat{L}_z\psi_{L,M_L} = \hbar M_L\psi_{L,M_L}$$

$$\widehat{L}_{\pm}\psi_{L,M_L} = \hbar[L(L + 1) - M_L(M_L \pm 1)]^{1/2}\psi_{L,M_L \pm 1}$$

$$E_{nl} = \frac{-\hbar c R}{n^2}$$

$$\widehat{H}^{\text{Zeeman}} = -\frac{\mu_B}{\hbar} B_z [\widehat{L}_z + 2\widehat{S}_z] \quad (\mu_B \text{ is the "Bohr magneton" and } B_z \text{ is the magnetic field along the } z\text{-axis})$$

$$\Psi_n(x, t) = e^{-iE_n t/\hbar} \psi_n(x)$$



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