Transition probabilities for quantum systems in time-dependent fields

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What is the probability of a transition when a quantum system is subject to a time-dependent applied field?

Standard answer: P. A. M. Dirac, 1926, 1927

Solve the Schrödinger equation for the system in a time-dependent perturbation $H'(t)$ by expanding the wave function as a series in the eigenstates of the unperturbed Hamiltonian H_0.

$$[H_0 + H'(t)] \,|\, \psi(t) \rangle = i \hbar \, \partial \,|\, \psi(t) \rangle / \partial t$$

Ansatz: $| \, \psi(t) \rangle = \Sigma_n \, c_n(t) \exp(-iE_n t/\hbar) \, | \, n_0 \rangle$

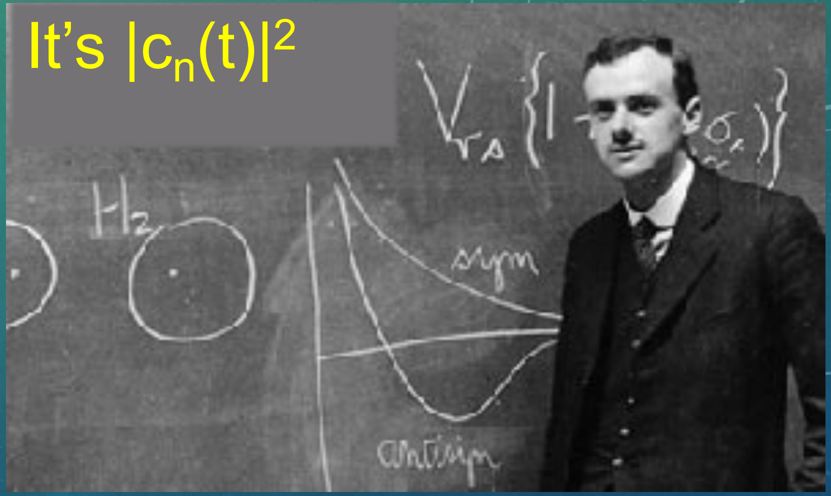
P. A. M. Dirac, CORBIS, *The Daily Telegraph*

Then to find the transition probability . . .

$| \psi(t) \rangle = \Sigma_n c_n(t) \exp(-iE_n t/\hbar) \, | n_0 \rangle$

From the time-dependent Schrödinger equation, we find

$$dc_n(t)/dt = -(i/\hbar) \Sigma_k \langle n_0 | H'(t) | k_0 \rangle \bullet c_k(t) \exp[-i (E_k - E_n) t/\hbar]$$



P. A. M. Dirac, AIP Emilio Sergé: Visual Archives

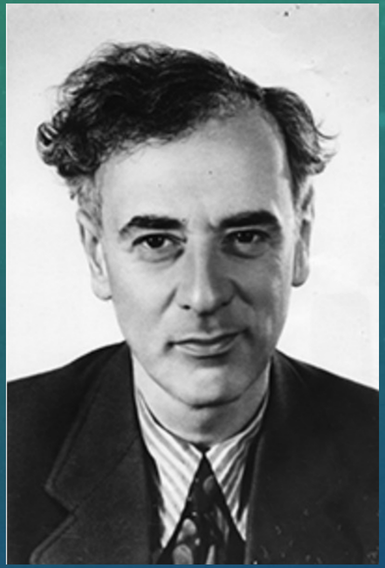
The coefficients $c_n(t)$ and $c_k(t)$ are related by

$$c_n(t) = c_n(-\infty) - (i/\hbar) \Sigma_k \int_{-\infty}^{t} dt' \langle n_0 | H'(t') | k_0 \rangle c_k(t') \exp[-i(E_k - E_n)t'/\hbar]$$

Suggestion of Landau and Lifshitz: Integrate by parts!

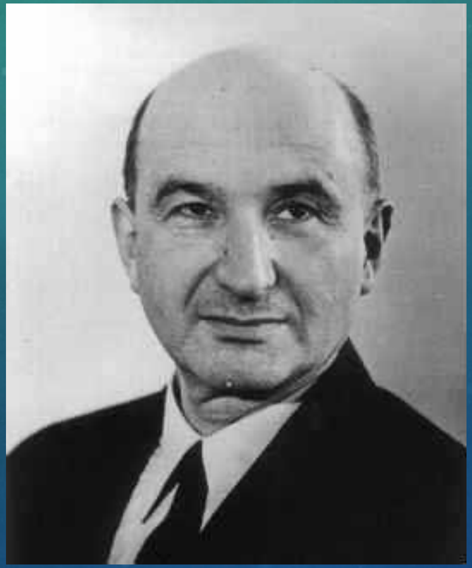
Start from the first-order excited state coefficients $c_n^{(1)}(t)$

$$c_n^{(1)}(t) = (-i/\hbar) \int_{-\infty}^{t} dt' \langle n_0 \mid H'(t') \mid 0_0 \rangle \exp[i(E_n - E_0)t'/\hbar]$$



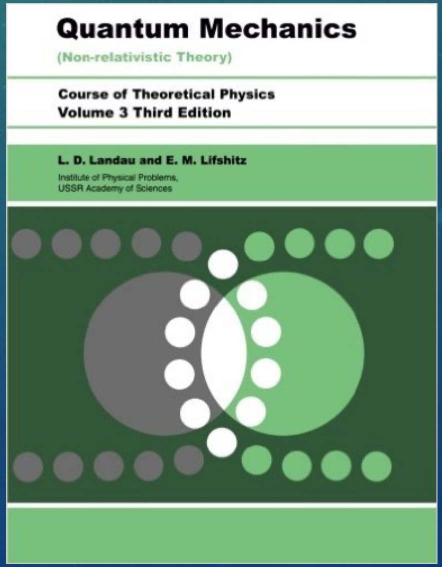
L. D. Landau

Niels Bohr Library and Archive, history.aip.org



E. M. Lifshitz

mathshistory.st-andrews.ac.uk



The first-order excited state coefficients $c_k^{(1)}(t)$ are

$$c_k^{(1)}(t) = (-i/\hbar) \int_{-\infty}^{t} dt' \langle k_0 \mid H'(t') \mid 0_0 \rangle \exp[i(E_k - E_0)t'/\hbar]$$

Integration by parts gives: $c_k^{(1)}(t) = a_k^{(1)}(t) + b_k^{(1)}(t)$

$$a_k^{(1)}(t) = \langle k_0 \mid H'(t) \mid 0_0 \rangle \exp[i(E_k - E_0)t/\hbar]\,(E_0 - E_k)^{-1}$$

$$b_k^{(1)}(t) = (E_k - E_0)^{-1} \int_{-\infty}^{t} dt' \langle k_0 \mid \partial H'(t')/\partial t' \mid 0_0 \rangle \exp[i(E_k - E_0)t'/\hbar]$$

$a_k^{(1)}(t)$: adiabatic coefficient

$b_k^{(1)}(t)$: nonadiabatic coefficient

Important observation: Up to a phase, $b_k(t) = \langle k'(t) \mid \Psi(t) \rangle$ where $\mid k'(t) \rangle$ is the instantaneous excited state, which differs from $\mid k_0 \rangle$

Two views of a transition

Dirac: For a system that started in the unperturbed ground state $| 0_0 \rangle$, a transition to an excited state $| k_0 \rangle$ has occurred if $| k_0 \rangle$ is present in the wave function.

Landau and Lifshitz: For a system that started in the unperturbed ground state, a transition to an excited state has occurred if the wave function contains states that are not adiabatically connected to the ground state $| 0_0 \rangle$, but that are connected instead to an excited state $| k_0 \rangle$ of the unperturbed system.

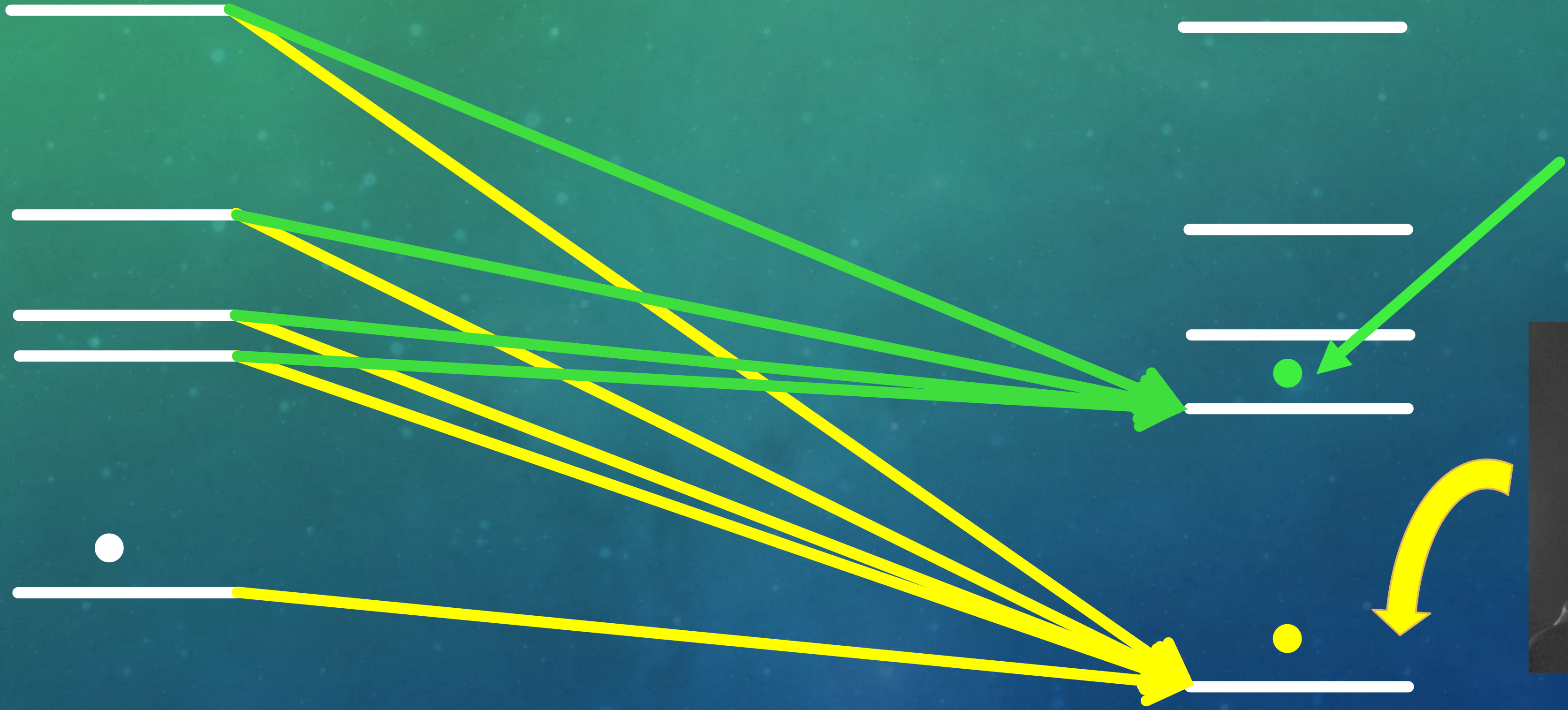
We have explored the suggestion by Landau and Lifshitz and its further implications.

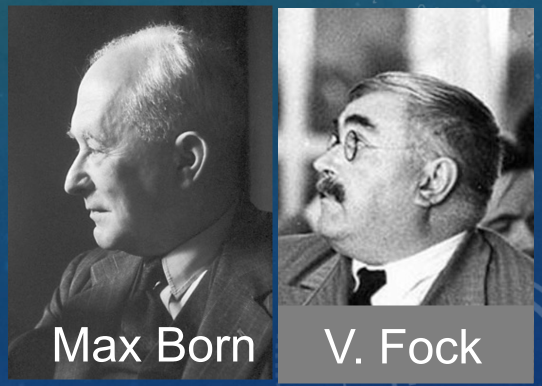
Adiabatic coefficients $a_k^{(1)}(t)$

Nonadiabatic coefficients $b_k^{(1)}(t)$

Transition probability:

$| b_k(t) |^2$





Unperturbed System

Perturbed System

Photo of Max Born from the Nobel Foundation Archive;
Photo of Vladimir Fock from Andrzej Trautman, in terpconnect.umd.edu/~yskim/

The energy also separates into adiabatic and nonadiabatic parts!

Adiabatic adjustment of the ground state

$$E^{(2)}(t) = \Sigma_{k\neq 0} \langle 0_0 \mid H'(t) \mid k_0 \rangle \langle k_0 \mid H'(t) \mid 0_0 \rangle/(E_0 - E_k)$$

$$+ \Sigma_{k\neq 0} \mid b_k^{(1)}(t)|^2 (E_k - E_0)$$

Transitions!

A. Mandal and K. L. C. Hunt, *J. Chem. Phys*. **137**, 164109 (2012).
Variance of the energy in terms of $| b_k(t)|^2$:
A. Mandal and K. L. C. Hunt, *J. Chem. Phys*. **152**, 104110 (2020).

Molecule in an electromagnetic field: Power absorbed from the field

Photo and concept credit: Richard Box, University of Bristol

Perturbation due to an external electromagnetic field

$$H'(t) = -c^{-1} \int d^3r \; \mathbf{j}(\mathbf{r}) \cdot \mathbf{A}(\mathbf{r}, t)$$

$$\mathbf{E}(\mathbf{r}, t) = -c^{-1} \, \partial \mathbf{A}(\mathbf{r}, t)/\partial t$$

[Coulomb gauge]

Adiabatic coefficient

$$a_k^{(1)}(t) = -c^{-1} \exp(iE_{k0}t/\hbar) \, (E_0 - E_k)^{-1} \int d^3r \; \langle k_0 \,|\, \mathbf{j}(\mathbf{r}) \,|\, 0_0 \rangle \cdot \mathbf{A}(\mathbf{r}, t)$$

Nonadiabatic coefficient

$$b_k^{(1)}(t) = (E_k - E_0)^{-1} \int d^3r \int_{-\infty}^{t} dt' \exp(iE_{k0}t'/\hbar) \, \langle k_0 \,|\, \mathbf{j}(\mathbf{r}) \,|\, 0_0 \rangle \cdot \mathbf{E}(\mathbf{r}, t')$$

Power $\mathcal{P}$ absorbed from the external field

$$\mathcal{P} = dw/dt = \int d^3r \, \langle \, j(r, t) \, \rangle \cdot E(r, t)$$

Adiabatic coefficients $a_k^{(1)}(t) \propto A(r, t)$

Nonadiabatic coefficients $b_k^{(1)}(t)$ depend on $E(r, t')$

Power absorption $\mathcal{P}$ is determined by $b_k^{(1)}(t)$!

$$\mathcal{P} = \partial E_b(t)/\partial t = \partial \, [\Sigma_{k\neq 0} \, | \, b_k^{(1)}(t) \, |^2 \, (E_k - E_0)]/\partial t$$

A. Mandal and K. L. C. Hunt, *J. Chem. Phys*. **143**, 134012 (2015).

GAUGE ISSUES

$$E_e(r, t) = -\nabla\varphi(r, t) - \partial A(r, t)/\partial t$$

$$B_e(r, t) = \nabla \times A(r, t)$$

Gauge transformation:

$$A(r, t) \rightarrow A_\Lambda(r, t) = A(r, t) + \nabla\Lambda(r, t)$$

$$\varphi(r, t) \rightarrow \varphi_\Lambda(r, t) = \varphi(r, t) - \partial\Lambda(r, t)/\partial t$$

Result: No change in $E(r, t)$ or $B(r, t)$

Effect of a gauge transformation on the molecular Hamiltonian

$$H = \sum_{\alpha} [p_\alpha - q_\alpha A(r_\alpha)]^2/(2m_\alpha)$$

$$+ V_C - \int d^3r \, \rho(r, t) \, \partial\Lambda(r, t)/\partial t$$

But $\Lambda(r, t)$ exists only *on paper*! How can it affect the energy?

It gets worse . . .

Gauge transformations from zero external vector and scalar potentials to non-zero potentials, with the applied E and B fields held at zero, produces essentially arbitrary energy differences between the 1s and 2s states of the H atom!

H atom, 1s: $\langle \psi_{1s} \mid \varphi_{\Lambda}(r, t) \mid \psi_{1s} \rangle = C_{\omega}\, f_{1s}(k) \exp(-i\omega t)$

H atom, 2s: $\langle \psi_{2s} \mid \varphi_{\Lambda}(r, t) \mid \psi_{2s} \rangle = C_{\omega}\, f_{2s}(k) \exp(-i\omega t)$

k	$f_{1s}(k)$	$f_{2s}(k)$
1	16/25	0
2	1/4	21/625
3	16/169	17/1250
4	1/25	465/83521
5	16/841	147/57122

A. Mandal and K. L. C. Hunt, *J. Chem. Phys*. **144**, 044109 (2016).

"How can we know the dancer from the dance?"

W. B. Yeats

Photo from catzenspace.com/2013/08/

$$H = \sum_{\alpha} [p_\alpha - q_\alpha A(r_\alpha)]^2/(2m_\alpha) + V_C$$

$$- \int d^3r\ \hat{\rho}(r, t)\ \partial\Lambda(r, t)/\partial t$$

$$+ (\varepsilon_0/2) \int d^3r\ [E_\perp^{\,2}(r, t) + c^2\, B^2(r, t)]$$

$$+ \varepsilon_0 \int d^3r\ [\nabla\cdot E(r, t)]\ \partial\Lambda(r, t)/\partial t$$

Now apply Gauss's law to the expectation values. The expectation values of the gauge-dependent term in the molecular Hamiltonian and the gauge-dependent term in the field Hamiltonian cancel!

A. Mandal and K. L. C. Hunt, *J. Chem. Phys.* **144**, 044109 (2016).

$$H = \sum_{\alpha} [p_\alpha - q_\alpha A(r_\alpha)]^2/(2m_\alpha) + V_C$$

$$+ (\varepsilon_0/2) \int d^3r \, [E_\perp^2(r, t) + c^2 B^2(r, t)]$$

We have split H into an energy operator for the molecule + an energy operator for the field, *both* with gauge-independent expectation values.

Molecular Hamiltonian: Coulomb gauge
Field Hamiltonian: Transverse fields

A. Mandal and K. L. C. Hunt, *J. Chem. Phys.* **144**, 044109 (2016).

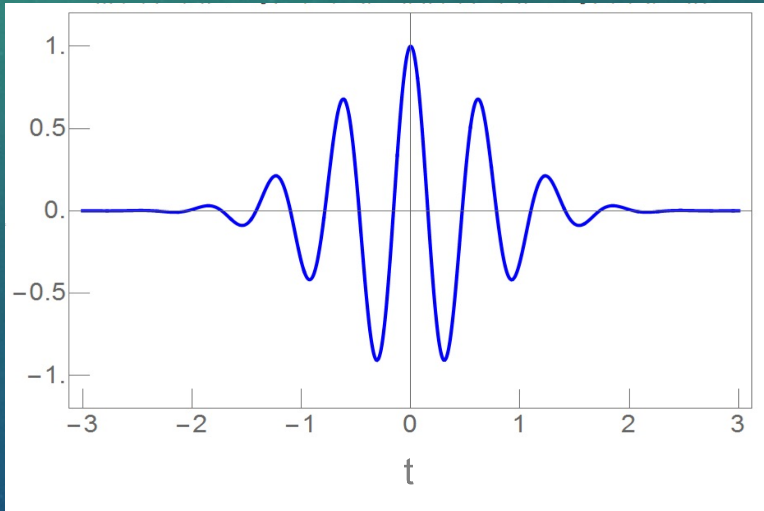
Response to a perturbing electromagnetic pulse

Cosine wave in a Gaussian envelope

$$c_k^{(1)}(t) = (-i/\hbar) \int_{-\infty}^{t} \langle k \mid H'(t') \mid 0 \rangle \exp(i\omega_{k0}t')\, dt'$$

$$a_k^{(1)}(t) = \langle k \mid H'(t) \mid 0 \rangle \exp(i\omega_{k0}t)/(E_0 - E_k)$$

$$b_k^{(1)}(t) = (\hbar\omega_{k0})^{-1} \int_{-\infty}^{t} \langle k \mid \partial H'(t')/\partial t' \mid 0 \rangle \exp(i\omega_{k0}t')\, dt'$$



$$b_k^{(1)}(t) = 1/(4\omega_{k0})\lambda \langle k|\, V\, |0\rangle \exp[-t^2 - i\omega t - (\omega + \omega_{k0})^2/4]\{2[\exp[(i\omega_{k0}t + (\omega + \omega_{k0})^2/4] + \exp[(\omega + \omega_{k0})^2/4 + it(2\omega + \omega_{k0})]$$
$$- i\pi^{1/2}\omega_{k0} \exp[t(t + i\omega)] - i\pi^{1/2}\omega_{k0} \exp(t^2 + i\omega t + \omega\, \omega_{k0})] + i\pi^{1/2}\omega_{k0} \exp[t(t + i\omega)]\, [\exp(\omega\, \omega_{k0})\, \mathrm{erfc}[t + i(\omega - \omega_{k0})/2]$$
$$+ \mathrm{erfc}[t - i(\omega + \omega_{k0})/2]]\},$$

Comparisons off resonance

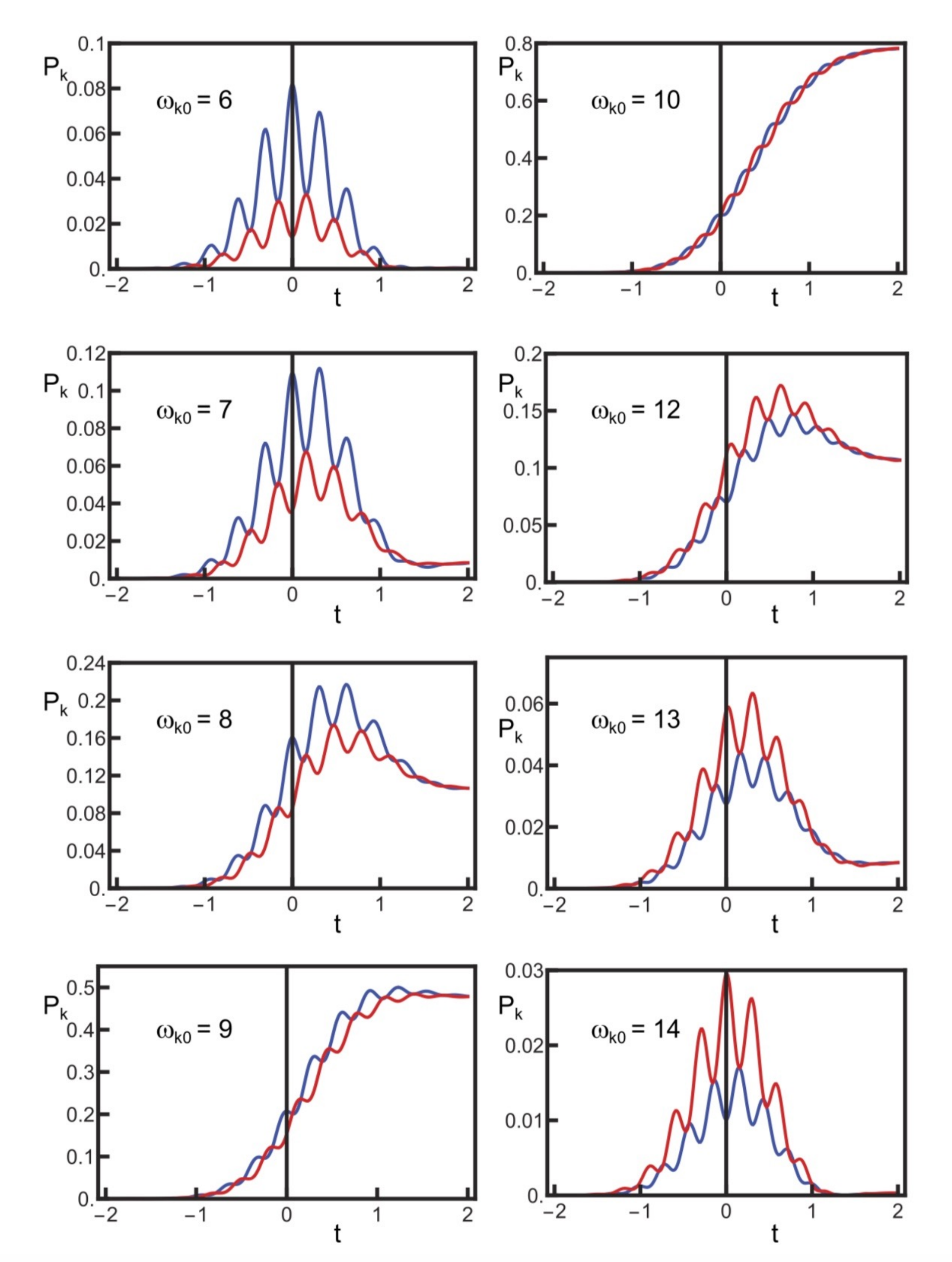
Scaled transition probabilities P_k vs. time

Applied frequency ω = 10
Resonant frequency ω = 10

Blue: Nonadiabatic transition probability

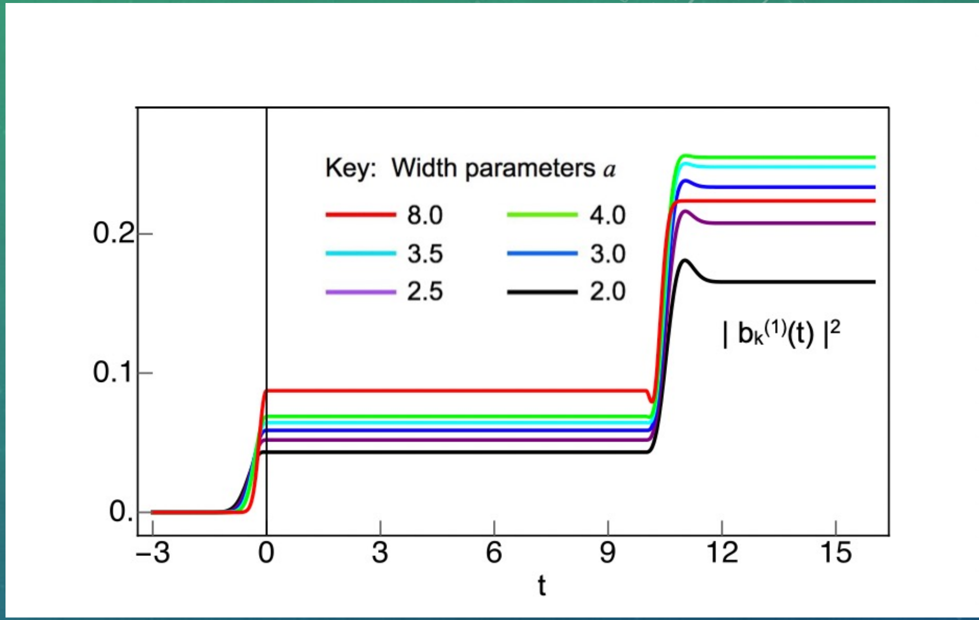
Red: Dirac's form, $c_k(t)$

A. Mandal and K. L. C. Hunt, *J. Chem. Phys*., **148**, 194107 (2018).



Effect of a perturbing “plateau pulse” with an interval in which the field is constant

Nonadiabatic transition probability, $| b_k(t) |^2$



No transitions occur while the perturbation is constant.

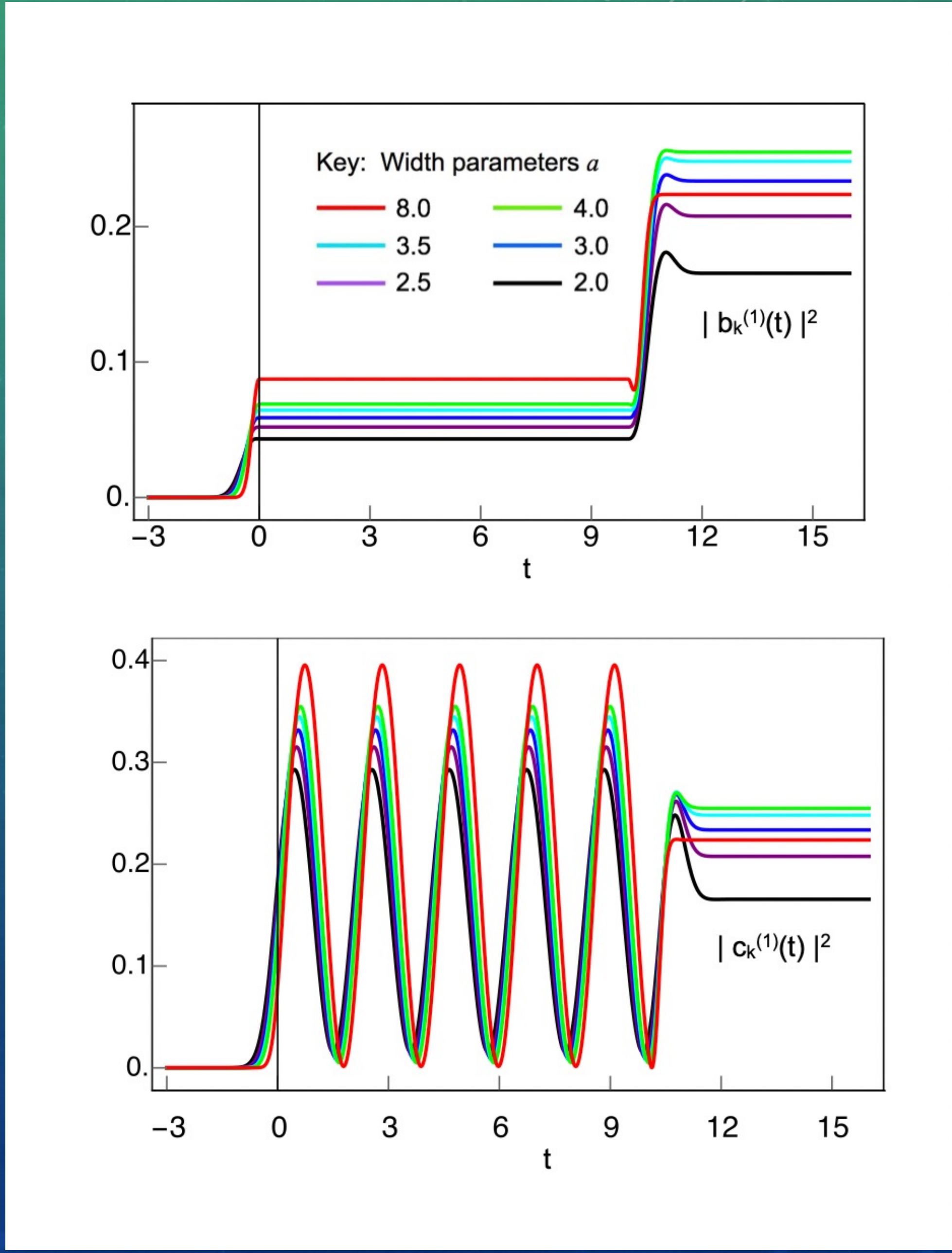
A. Mandal and K. L. C. Hunt, *J. Chem. Phys.* **149**, 204110 (2018).

Effect of a perturbing "plateau pulse" with an interval in which the field is constant

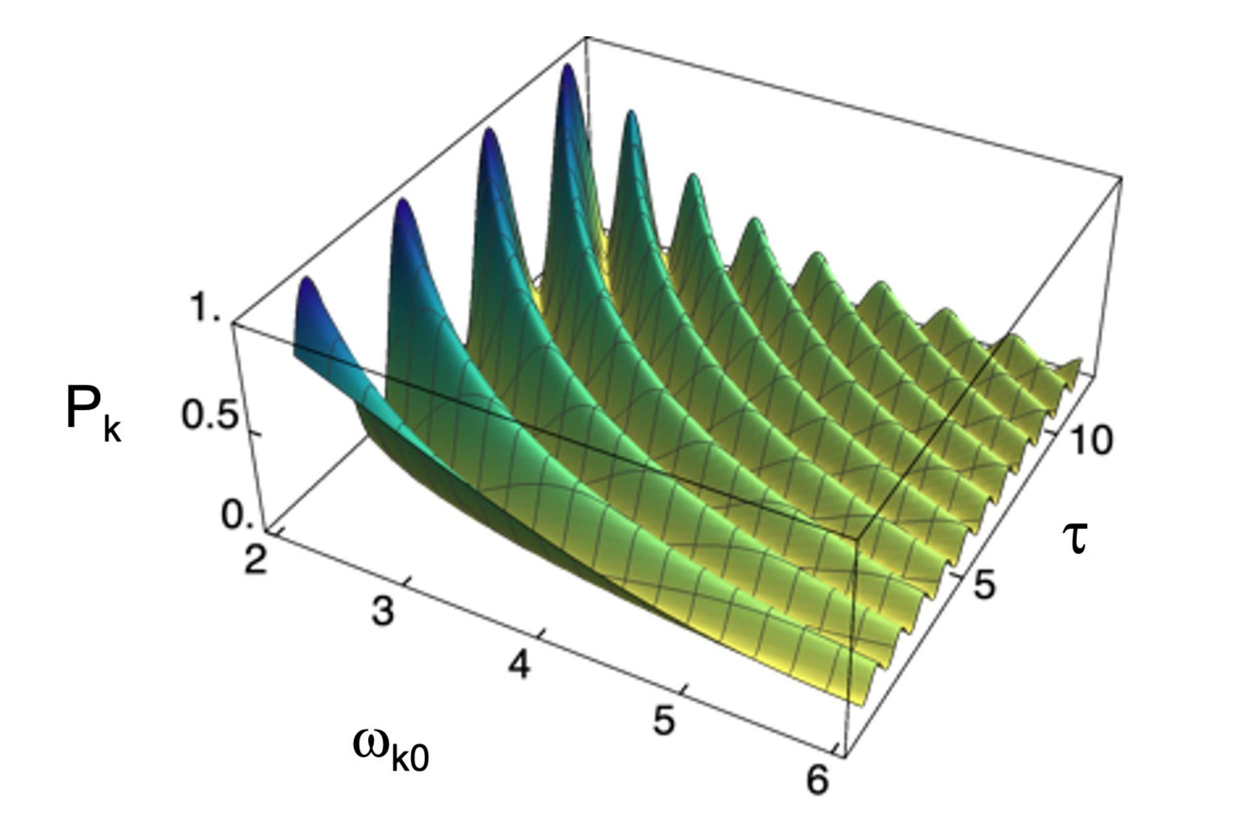
Nonadiabatic transition probability, $| b_k(t) |^2$

Dirac's transition probability $| c_k(t) |^2$

A. Mandal and K. L. C. Hunt, *J. Chem. Phys.* **149**, 204110 (2018).



Oscillatory pattern of transition probabilities found when a constant perturbation is imposed suddenly and turned off suddenly



The literature often represents these as Rabi oscillations. But are Rabi oscillations necessary to explain the pattern?

Dirac picture: Oscillations occur while the field is constant

Nonadiabatic picture: Oscillations occur due to jumps when the field starts and stops

S. D. Jovanovski, A. Mandal, and K. L. C. Hunt, J. Chem. Phys. *J. Chem. Phys*. **158**, 164107 (2023).

Analytical Strategy

Initial density matrices for a two-level model system

Unperturbed basis

$$\begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}$$

Perturbed basis

$$\begin{pmatrix} |b_k|^2 & b_k^* \\ b_k & 1 - |b_k|^2 \end{pmatrix}$$

Time evolve & allow for dephasing and population relaxation

$\rho_u(t)$

$\rho_p(t)$

$\rho_u(t)'$

$\rho_p(t)'$

Make all comparisons in the same basis!

Time Evolution Equations for the Density Matrix

Redfield theory for the density matrix in the secular approximation

$$\partial\rho_{cd}(t)/\partial t = -(i/\hbar)\,[H(t), \rho(t)]_{cd} - \Sigma_{ef}\, R_{cd,ef}\, \rho_{ef}(t)$$

Coupling to a bath!

In the basis of the perturbed eigenfunctions:

$$\partial\rho_{k'k'}(t)/\partial t = -\,\xi\, R\, \rho_{k'k'} + R\, \rho_{0'0'}$$

$$\partial\rho_{0'0'}(t)/\partial t = \xi\, R\, \rho_{k'k'} - R\, \rho_{0'0'}$$

$$\partial\rho_{k'0'}(t)/\partial t = -(i/\hbar)\,(E_{k'} - E_{0'})\,\rho_{k'0'}(t) - (1/T_2)\,\rho_{k'0'}(t)$$

In the basis of the original, unperturbed eigenfunctions:

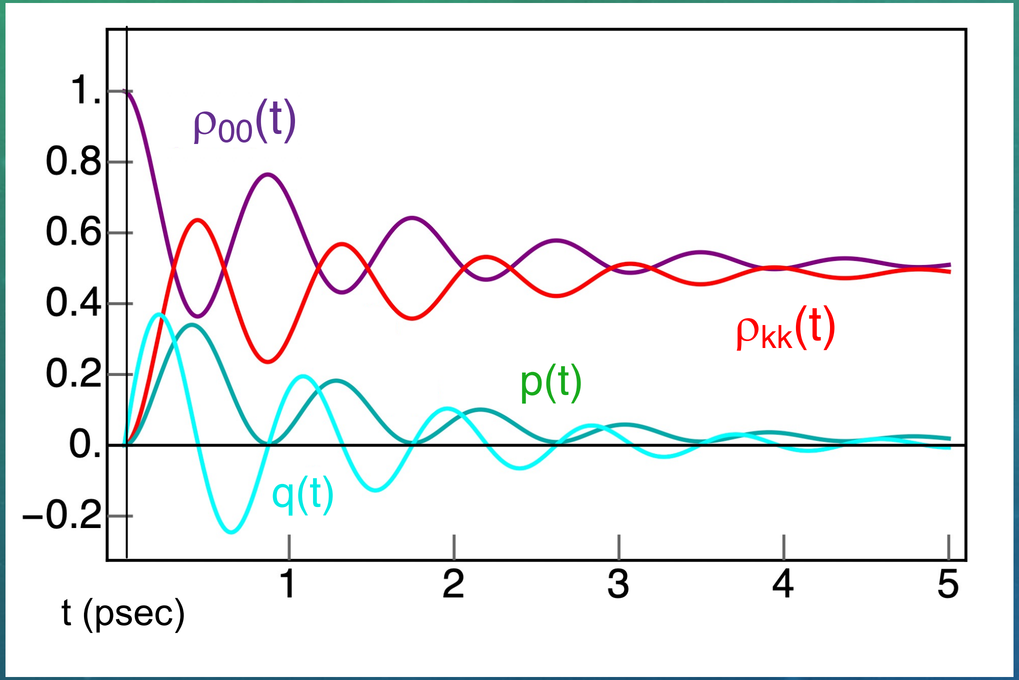
$$\partial\rho_{00}(t)/\partial t = 2\, h_{0k}\, q(t) - R\, \rho_{00}(t) + \xi_0\, R\, \rho_{kk}(t)$$

$$\partial\rho_{kk}(t)/\partial t = -\,2\, h_{0k}\, q(t) - \xi_0\, R\, \rho_{kk}(t) + R\, \rho_{00}(t)$$

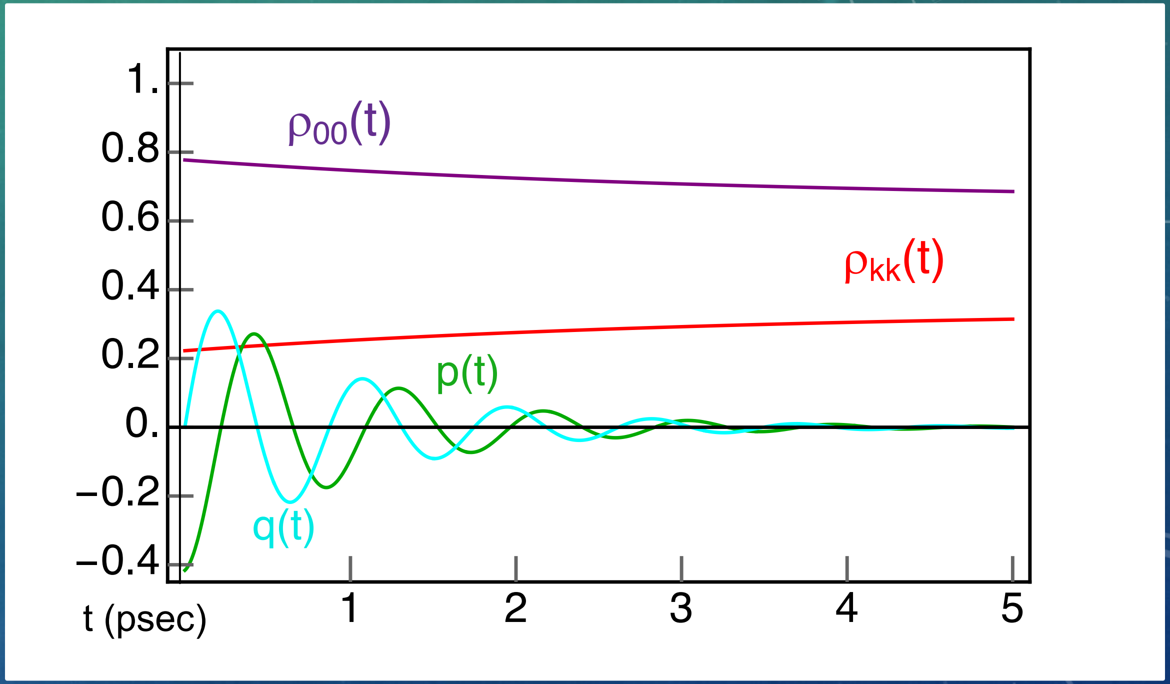
$$\partial p(t)/\partial t = \omega_{k0}\, q(t) - (1/T_2)\, p(t)$$

$$\partial q(t)/\partial t = -\,\omega_{k0}\, p(t) + h_{0k}\,[\rho_{kk}(t) - \rho_{00}(t)] - (1/T_2)\, q(t)$$

Results for HCl, starting in rotational ground state
Allow for dephasing and population relaxation—no longer a pure quantum state



Results in unperturbed basis



Results in perturbed basis

These results remain different when expressed in the same basis set!

In the perturbed basis, the populations relax to equilibrium:

$$\rho_{0'0'}(t) = \{\xi + [1 - |b_k(0)|^2 (1 + \xi)] \exp[-(1 + \xi) R t]\}/(1 + \xi)$$

$$\rho_{k'k'}(t) = \{1 - [1 - |b_k(0)|^2 (1 + \xi)] \exp[-(1 + \xi) R t]\}/(1 + \xi)$$

This does not happen in the unperturbed basis:

$$\rho_{00,s} = \{2 h_{0k}^2/T_2 + \xi_0 R [(1/T_2)^2 + \omega_{k0}^2]\}/\beta$$

$$\rho_{kk,s} = \{2 h_{0k}^2/T_2 + R [(1/T_2)^2 + \omega_{k0}^2]\}/\beta$$

$$p_s = [h_{0k} R (1 - \xi_0) \omega_{k0}]/\beta$$

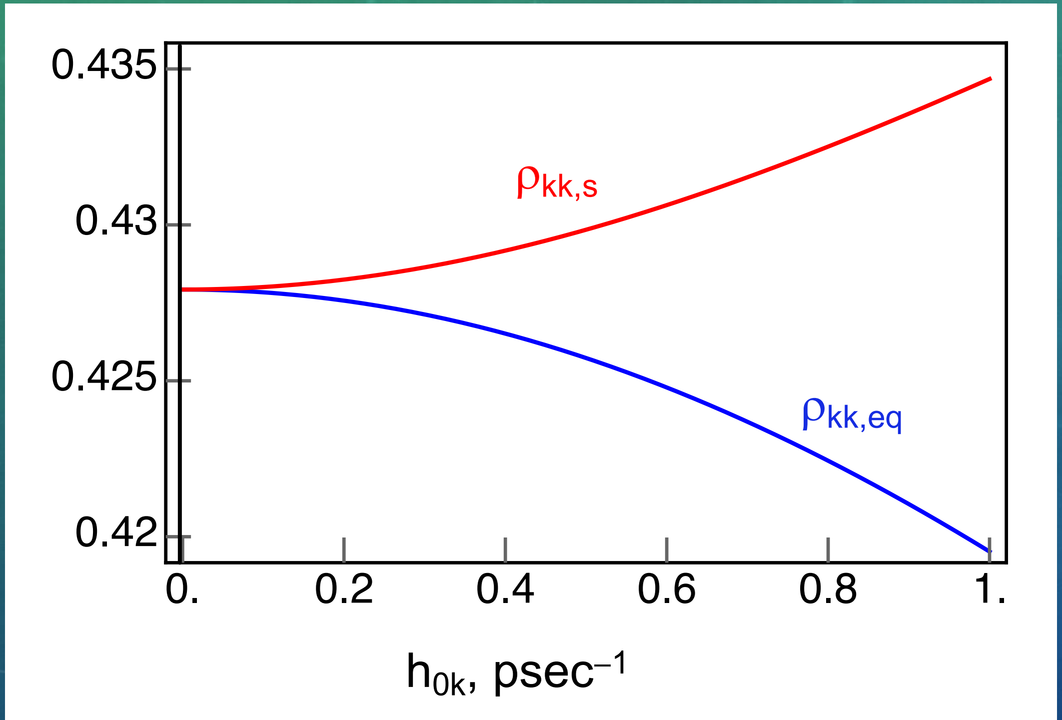
$$q_s = [h_{0k} R (1 - \xi_0)/T_2)]/\beta$$

$$\beta = 4 h_{0k}^2 (1/T_2) + R (1 + \xi) [\omega_{k0}^2 + (1/T_2)^2]$$

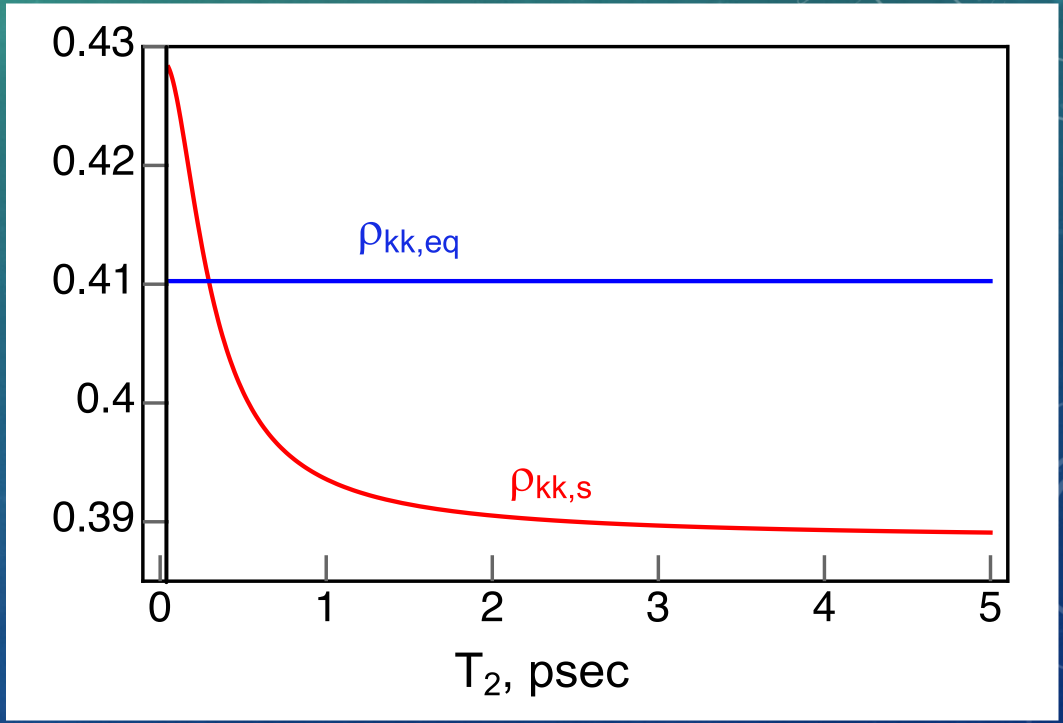
S. D. Jovanovski, A. Mandal, and K. L. C. Hunt, *J. Chem. Phys*. **158**, 164107 (2023).

What happens in the long-time limit, with coupling to a bath?

The results are not equivalent when expressed in the *same* basis set by direct calculation or by change of basis.



Excited-state population as a function of the off-diagonal element of the Hamiltonian



Excited-state population as a function of the dephasing time T_2

Why are these patterns observed?

In the perturbed basis,

$\rho_{k'k'}(t \to \infty) = 1/(1 + \xi)$ where $\xi = \exp(\Delta E_{k'0'}/kT)$
and the off-diagonal elements of the density matrix vanish as $t \to \infty$

Taking the stationary solution of the Redfield equations in the unperturbed basis, and then transforming to the perturbed basis,

$$\rho_{k'k',s} = h_{0k}^2 (\gamma^2/2 + \omega_{k0}\gamma/2)^{-1} \{ 2 h_{0k}^2/T_2 + \xi_0 R [(1/T_2)^2 + \omega_{k0}^2] \}/\beta$$
$$+ h_{0k}^2 R (1 - \xi_0) (\omega_{k0} + \gamma) (\gamma^2/2 + \omega_{k0}\gamma/2)^{-1}/\beta$$
$$+ (1/4) (\omega_{k0} + \gamma)^2 (\gamma^2/2 + \omega_{k0}\gamma/2)^{-1} \{ 2 h_{0k}^2/T_2$$
$$+ R [(1/T_2)^2 + \omega_{k0}^2] \}/\beta$$

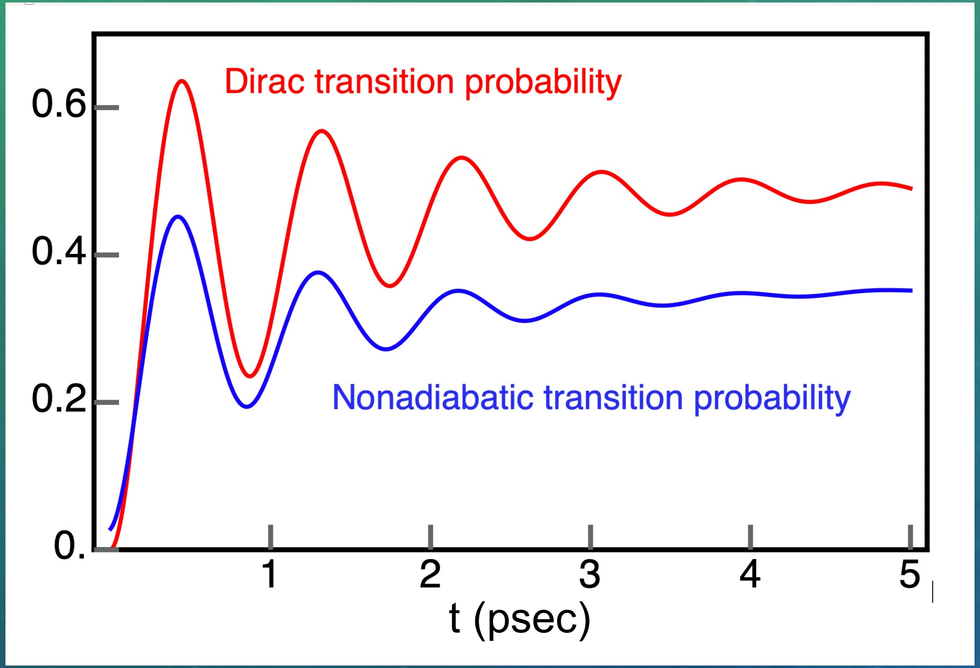
where $\gamma = (\omega_{k0}^2 + 4 h_{0k}^2)^{1/2}$ and

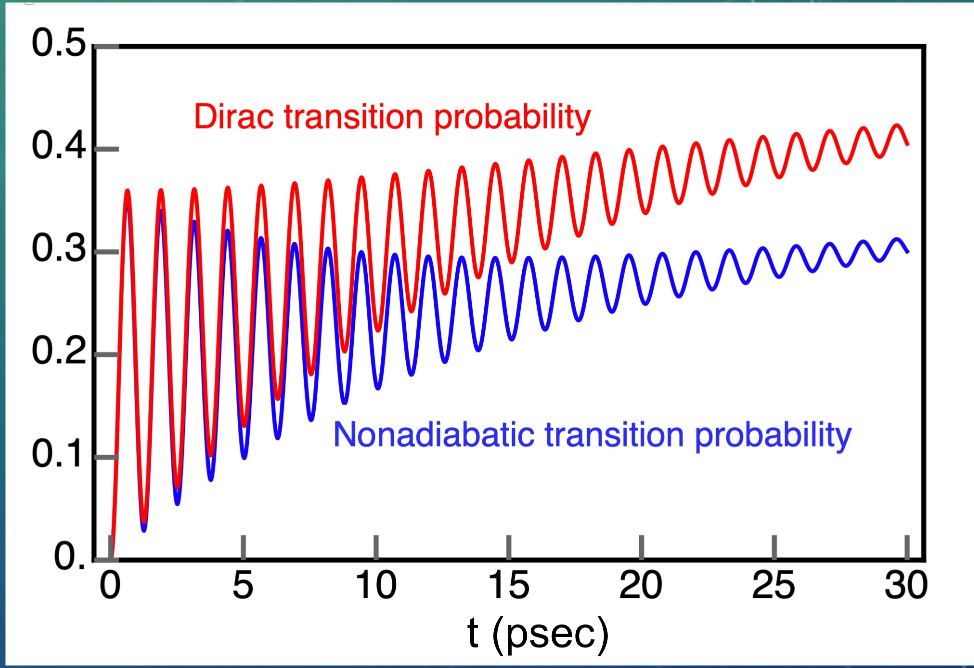
$\beta = 4 h_{0k}^2 (1/T_2) + R (1 + \xi_0) [\omega_{k0}^2 + (1/T_2)^2]$

Differences between $\rho_u(t)$ and $\rho_u(t)'$

Varied T_2 for HCl in argon at 105 K, starting in rotational ground state

Allow for dephasing, population relaxation—no longer a pure quantum state

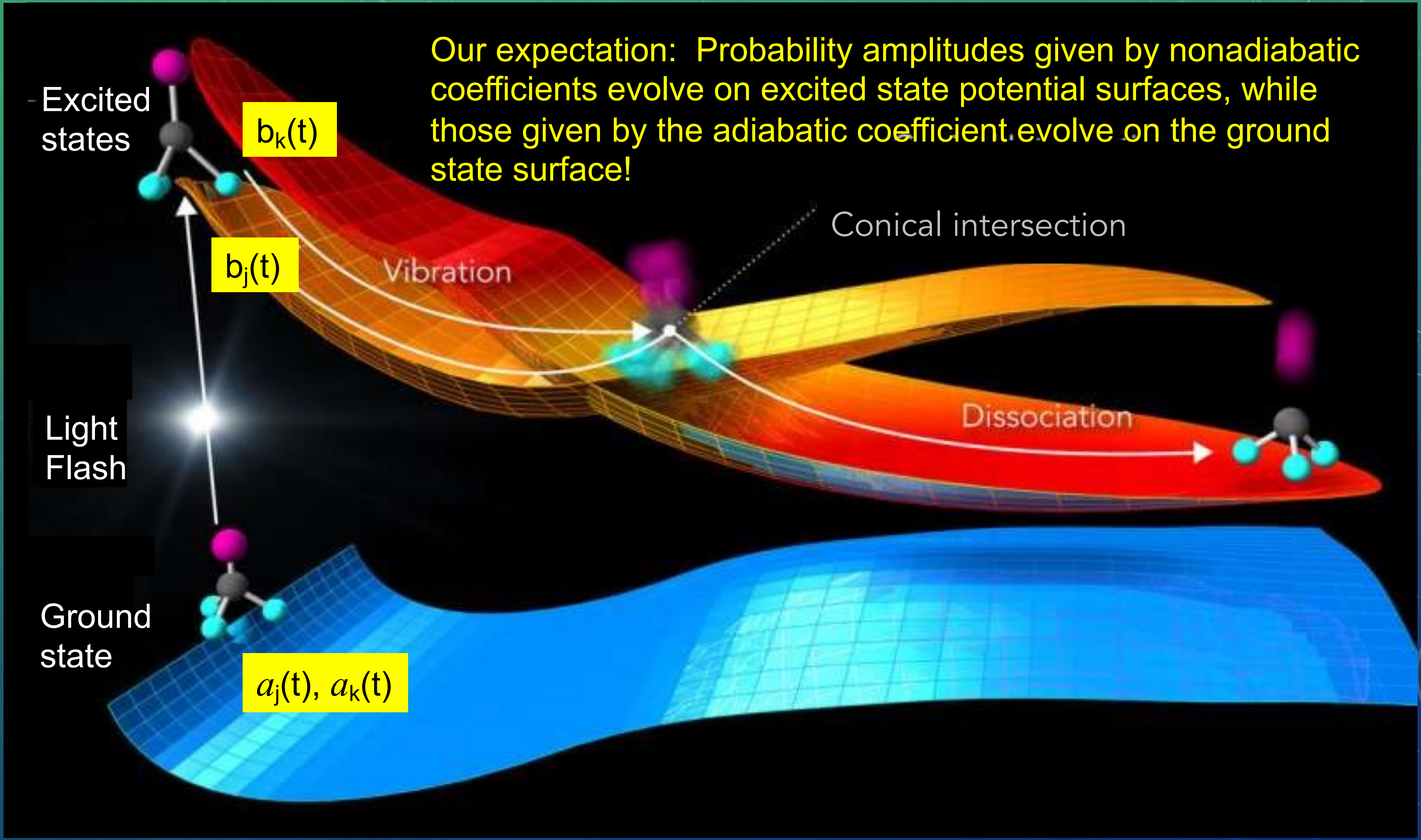




These results are compared in the *same* basis set, the unperturbed basis.

S. D. Jovanovski, A. Mandal, and K. L. C. Hunt, *J. Chem. Phys*. **158**, 164107 (2023).

Implications for electronic transitions due to very fast perturbing pulses



Greg Stewart/SLAC National Accelerator Laboratory, physics.org
https://phys.org/news/2018-07-ultra-high-speed-electron-camera-molecules-crossroads.html

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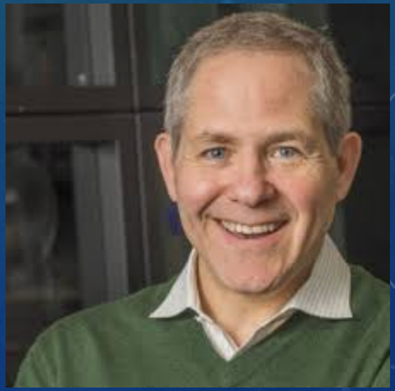

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