Nonadiabatic transition probabilities for quantum systems in time-dependent fields

Katharine L. C. Hunt
Department of Chemistry, Michigan State University
Institute for Advanced Studies, Department of Physics and Materials Science,
University of Luxembourg

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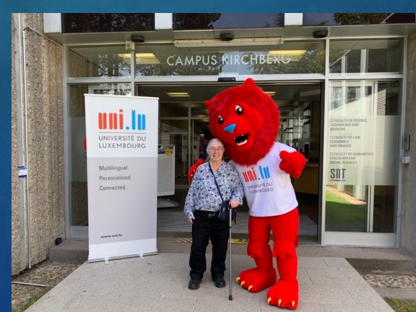


What is the probability of a transition when a quantum system is subject to a time-dependent applied field?

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

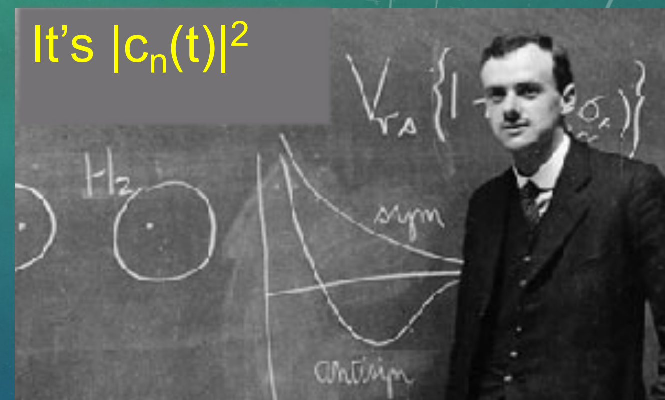
P. A. M. Dirac, CORBIS, *The Daily Telegraph*

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.

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

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

Then to find the transition probability . . .



P. A. M. Dirac

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

From the time-dependent Schrödinger equation, we find

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

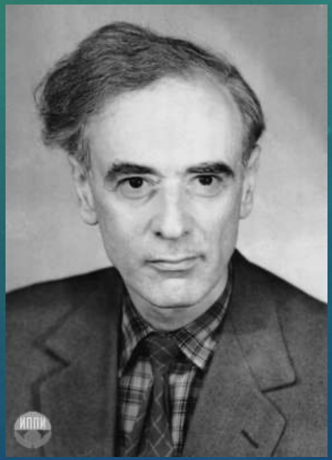
Coefficients $c_n(t)$ and $c_k(t)$ are related by

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

Suggestion of Landau and Lifshitz: Integrate by parts!

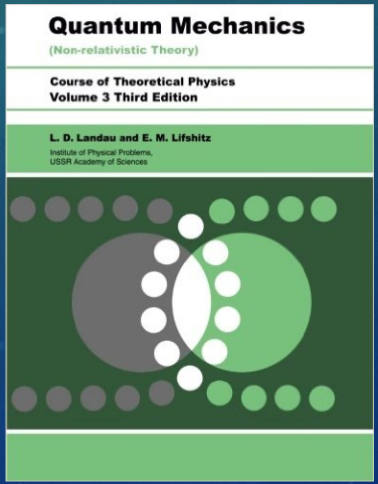
Start from the first-order excited state coefficients $c_n^{(1)}(t)$

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



L. D. Landau

E. M. Lifshitz



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

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

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

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

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

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

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

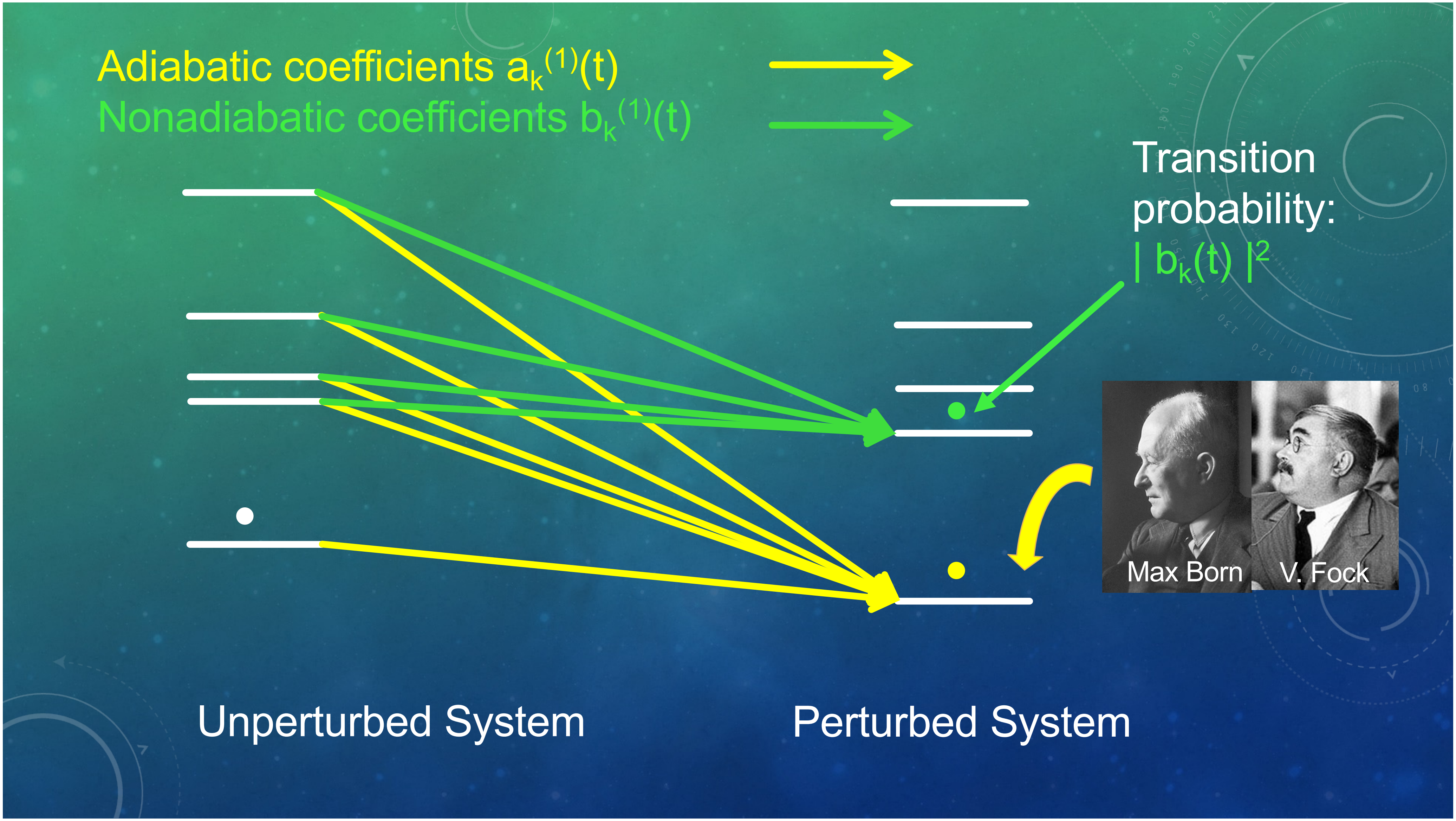
Important observation: Up to a phase, $b_k(t) = \langle k'(t) | \Psi(t) \rangle$
where $| k'(t) \rangle$ is the instantaneous excited state, which differs from $| k_0 \rangle$

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:
$|\ b_k(t)\ |^2$
Max Born
V. Fock
Unperturbed System
Perturbed System

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

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

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

[Coulomb gauge]

Adiabatic coefficient

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

Nonadiabatic coefficient

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

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).

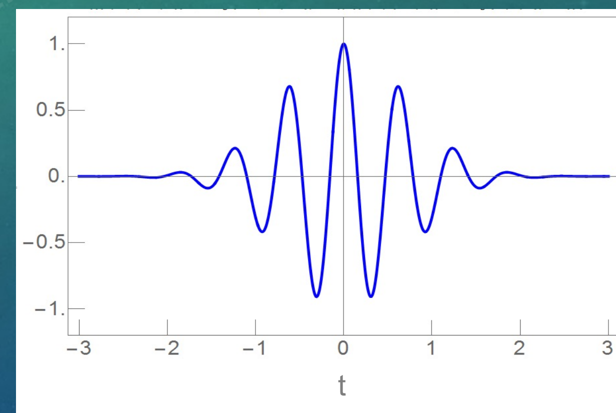
Response to a perturbing electromagnetic pulse

Cosine wave in a Gaussian envelope

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

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

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



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

Comparisons off resonance

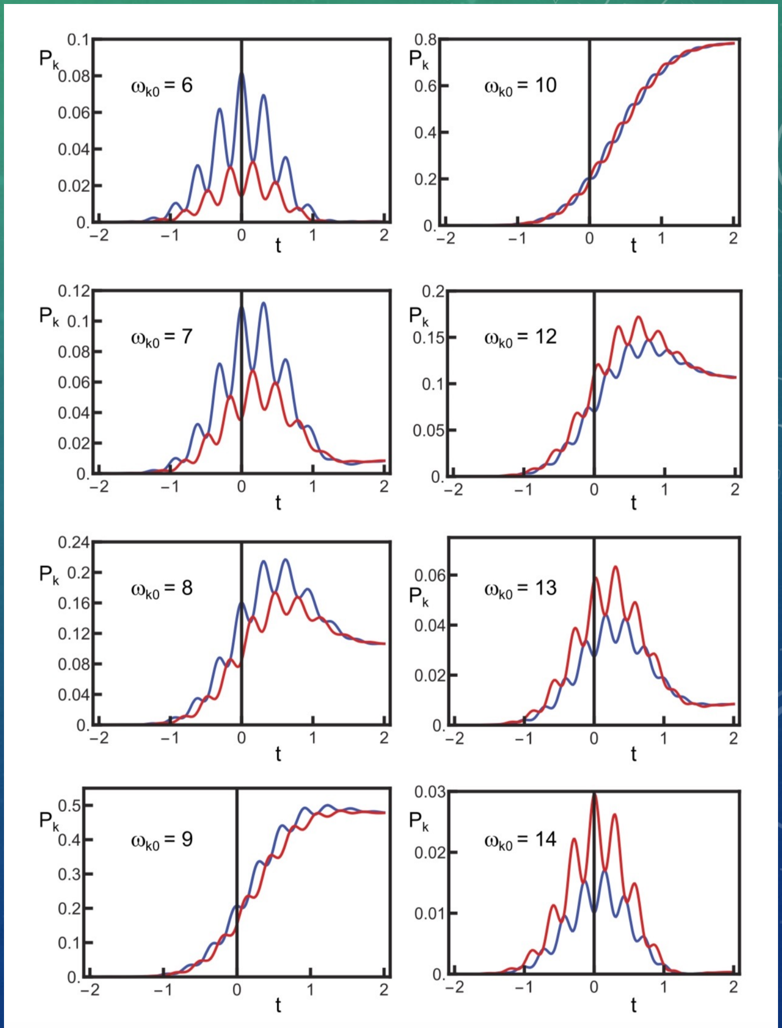
Scaled transition probabilities P_k vs. time

Resonant frequency $\omega = 10$

Blue: Nonadiabatic transition probability

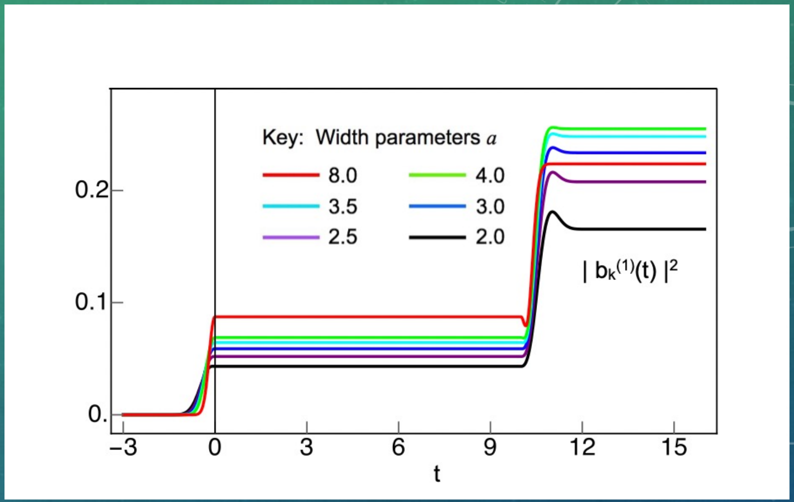
Red: Dirac's form, $c_k(t)$

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.

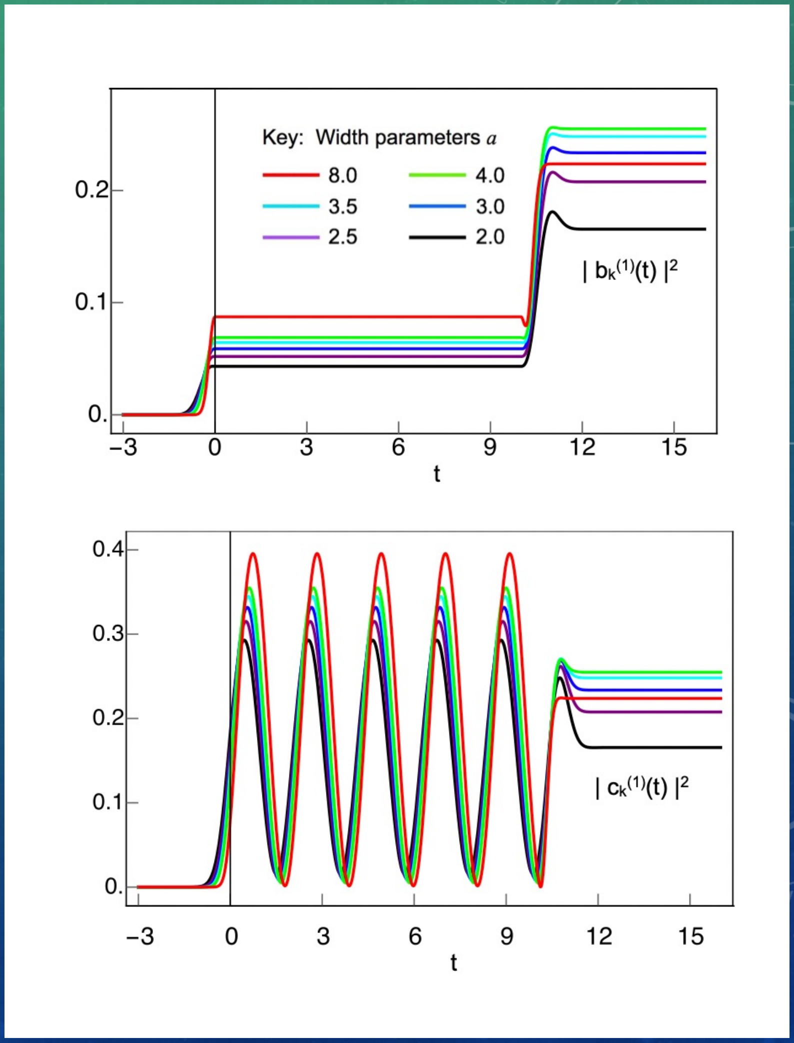
A. Mandal and K. L. C. Hunt, *J. Chem. Phys*. **149**, 204110 (2018).

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

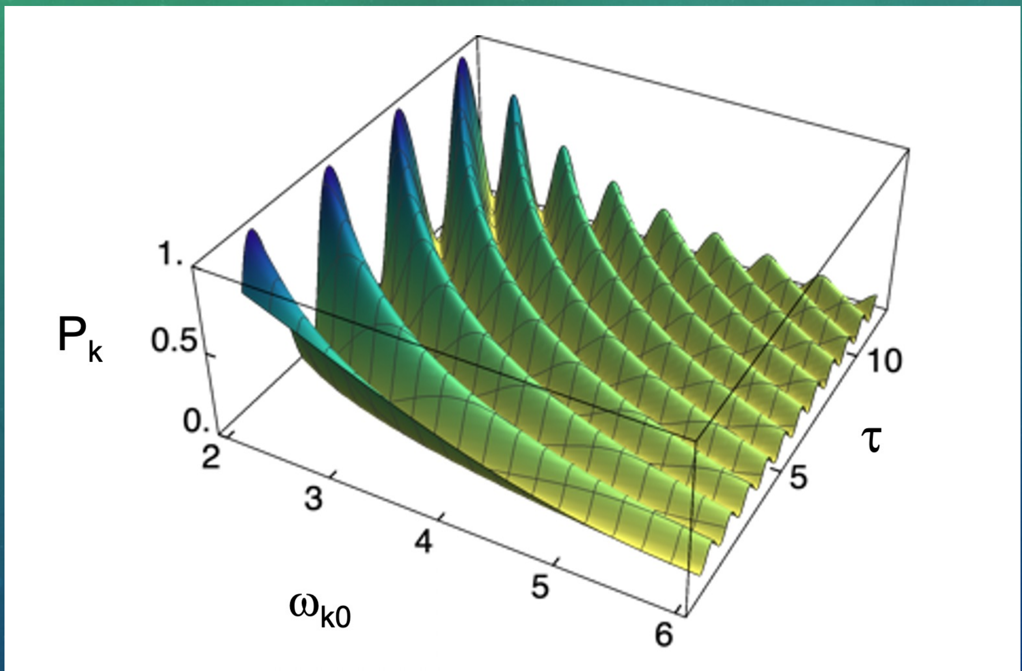
Nonadiabatic transition probability, $| b_k(t) |^2$

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

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:

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

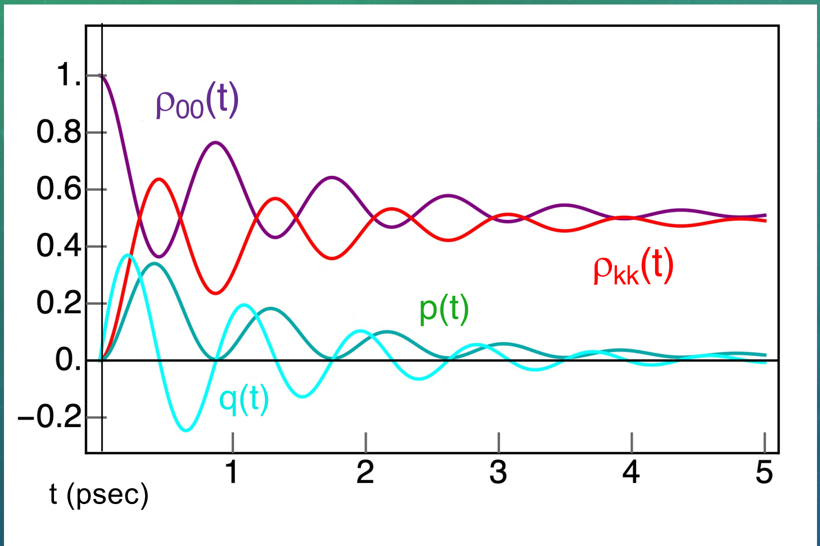
$$\partial\rho_{kk}(t)/\partial t = -\,2\, h_{0k}\, q(t) - \xi_0\, R\, \rho_{kk}(t) + R\, \rho_{00}(t)$$

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

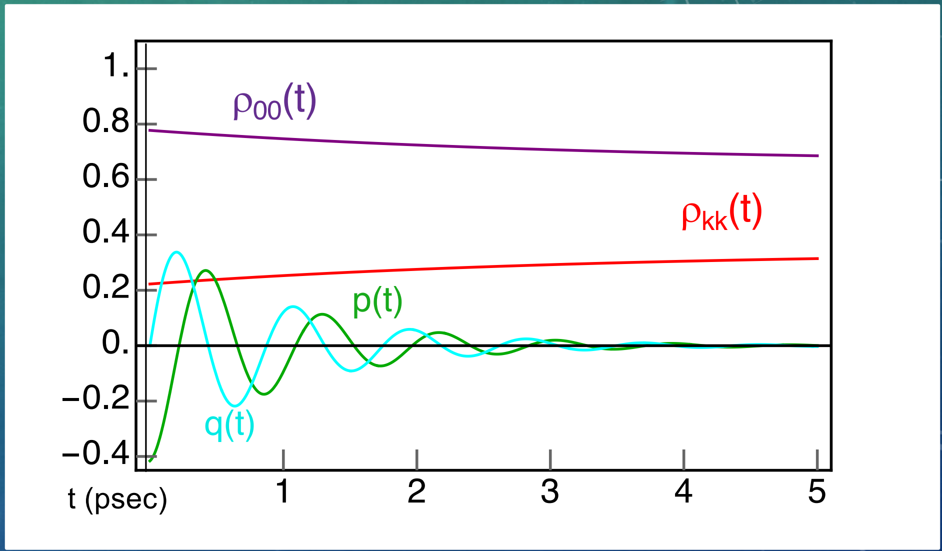
$$\partial q(t)/\partial t = -\,\omega_{k0}\, p(t) + h_{0k}\,[\rho_{kk}(t) - \rho_{00}(t)] - (1/T_2)\, q(t)$$

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:

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

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

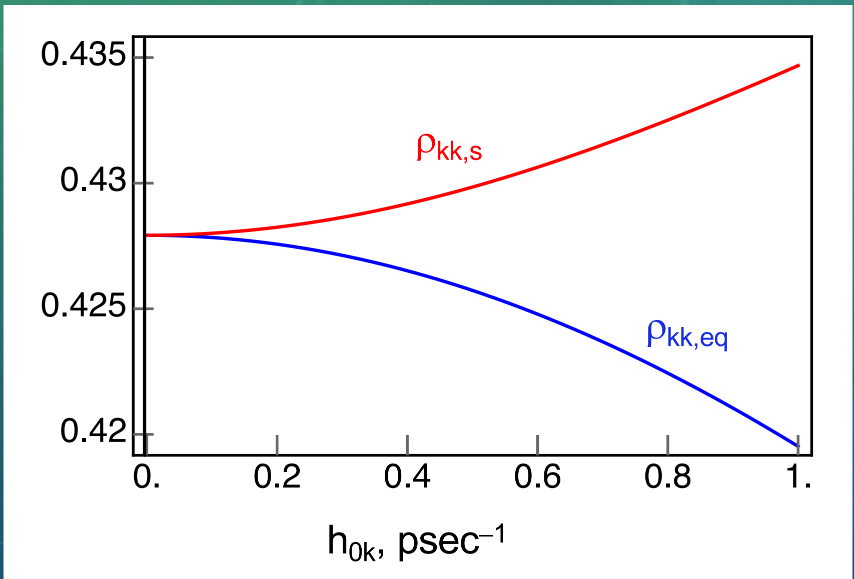
$$p_s = [h_{0k} R\, (1 - \xi_0)\, \omega_{k0}]/\beta$$

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

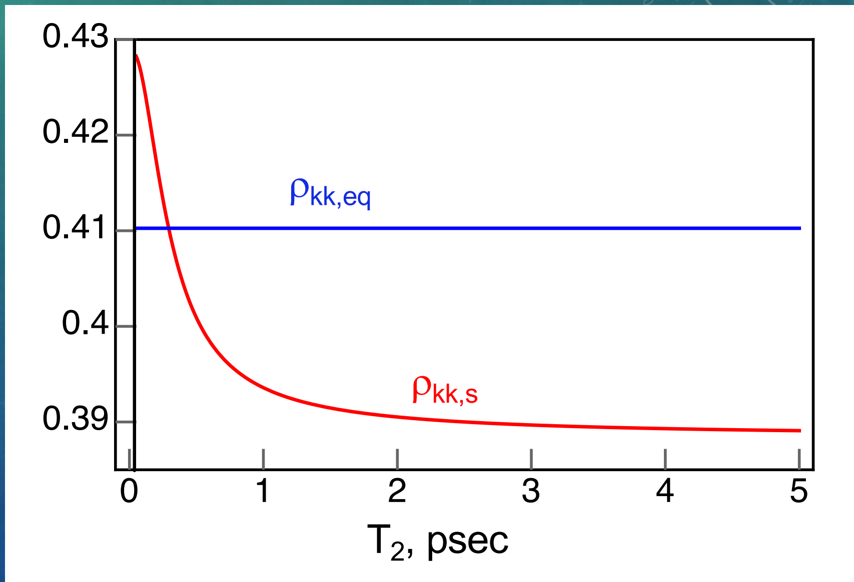
$$\beta = 4\, h_{0k}{}^2\, (1/T_2) + R\, (1 + \xi)\, [\omega_{k0}{}^2 + (1/T_2)^2]$$

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

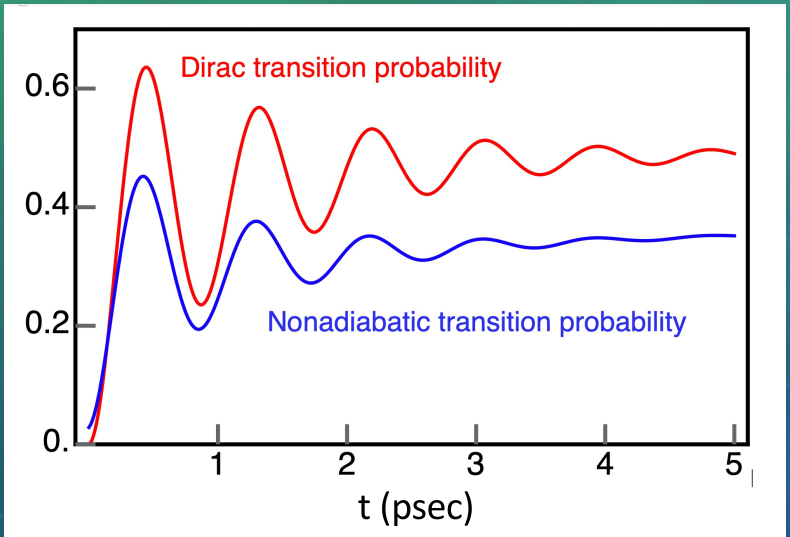


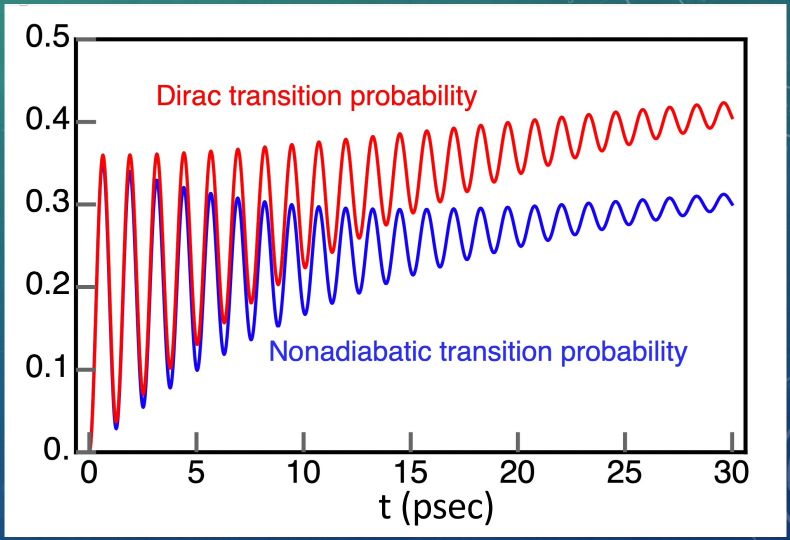
Excited-state population as a function of the dephasing time T_2

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

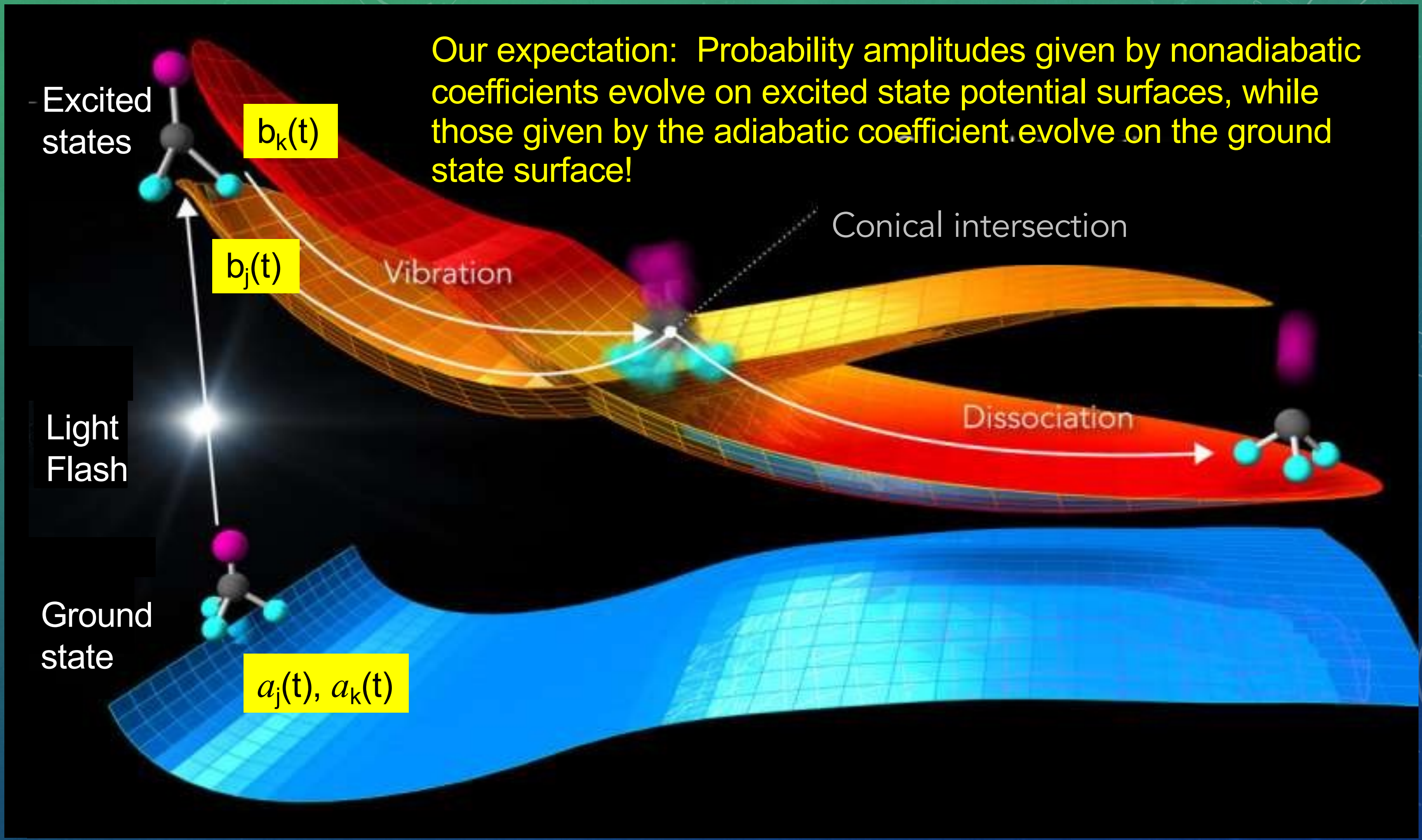




These results are compared in the *same* basis set;
in this case it is the unperturbed basis.

Implications for electronic transitions due to very fast perturbing pulses

Our expectation: Probability amplitudes given by nonadiabatic coefficients evolve on excited state potential surfaces, while those given by the adiabatic coefficient evolve on the ground state surface!



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

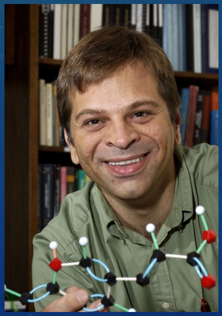
Connection to next speaker:

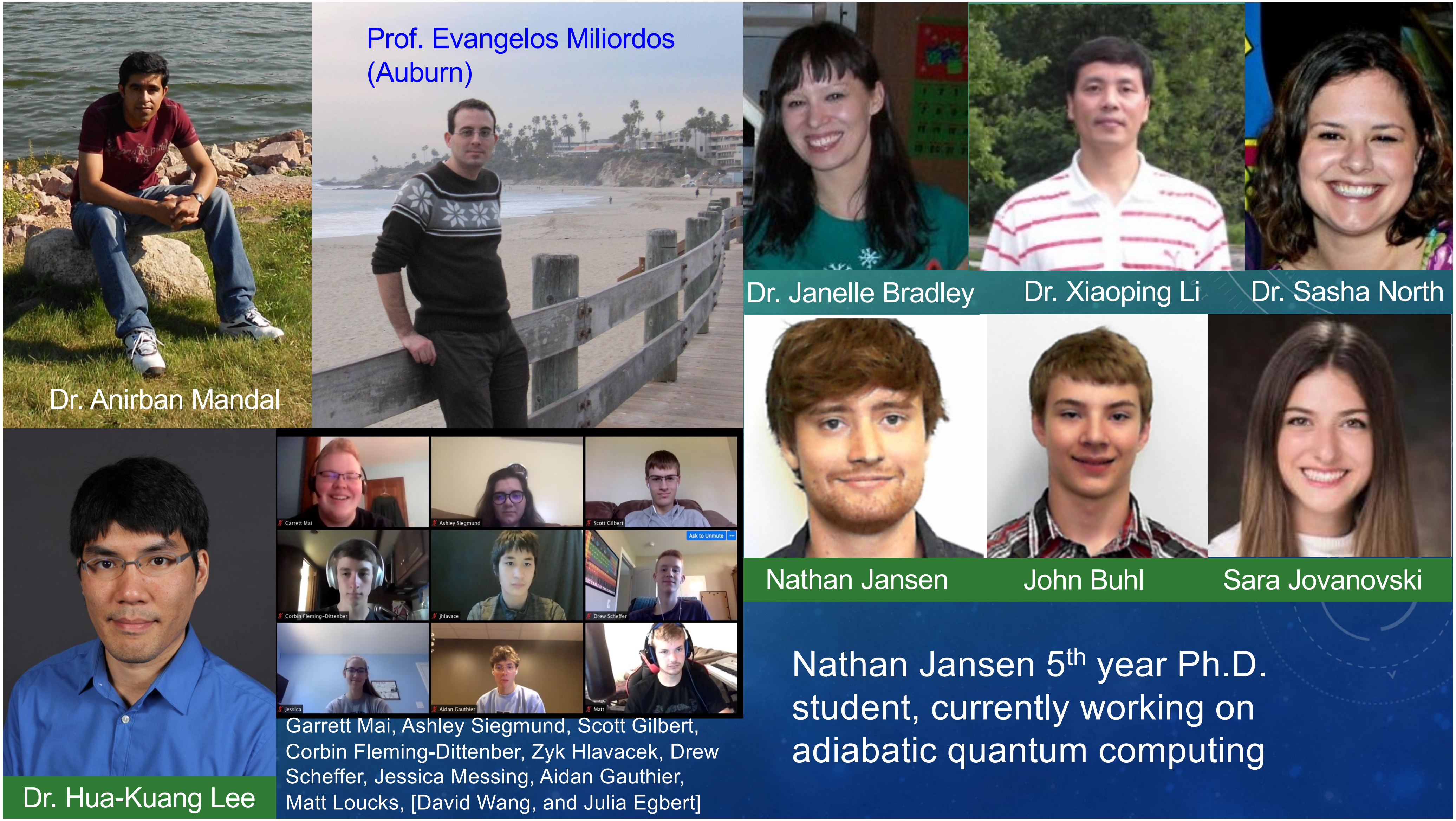
Diptarka Hait, Martínez Group, Department of Chemistry, Stanford University

Among Diptarka's research interests: Nonadiabatic dynamics, electronic excited states, computational spectroscopy

Also relevant: B. Mignolet, B. F. E. Curchod, and T. J. Martínez, XFAIMS: eXternal Field Ab Initio Multiple Spawning for electronic nuclear dynamics triggered by short laser pulses, *J. Chem. Phys*. **145**, 191104 (2016). Vibrational wave packets shift during a pulse

An incidental connection: Excited state relaxation pathways of organic radical ions, for applications in photocatalysis




Dr. Anirban Mandal
Prof. Evangelos Miliordos (Auburn)
Dr. Janelle Bradley
Dr. Xiaoping Li
Dr. Sasha North
Nathan Jansen
John Buhl
Sara Jovanovski
Dr. Hua-Kuang Lee
Garrett Mai, Ashley Siegmund, Scott Gilbert, Corbin Fleming-Dittenber, Zyk Hlavacek, Drew Scheffer, Jessica Messing, Aidan Gauthier, Matt Loucks, [David Wang, and Julia Egbert]
Nathan Jansen 5th year Ph.D. student, currently working on adiabatic quantum computing

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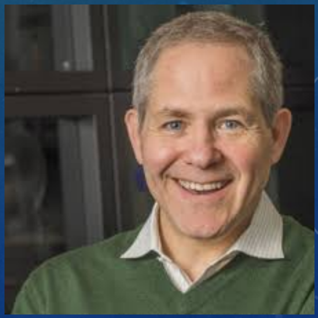
MSU

Prof. Warren Beck
MSU



Prof. Marcos Dantus
MSU

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 . . .

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 can 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).