## Katharine C. Hunt

## Quantum Theory


**University Distinguished Professor**

(b. 1953)

B.S., 1975, Michigan State Univ.;

Ph.D., 1978, Univ. of Cambridge;

NSF Postdoctoral Fellow, 1978-79, Massachusetts Institute of Technology.

517-353-1152


### Selected Publications


*The interaction-induced dipole of $H_2$-H: New ab initio results and spherical tensor analysis*, Hua-Kuang Lee, Xiaoping Li, Evangelos Miliordos, and Katharine L. C. Hunt, *J. Chem. Phys.* **2019**, *150*, 204307, *Featured Article*.

*Dependence of the multipole moments, static polarizabilities, and static hyperpolarizabilities of the hydrogen molecule on the H-H separation in the ground singlet state*, Evangelos Miliordos and Katharine L. C. Hunt, *J. Chem. Phys.* **2018**, *149*, 234103.

*Nonadiabatic transition probabilities in a time-dependent Gaussian pulse or plateau pulse: Toward experimental tests of the differences from Dirac's transition probabilities*, Anirban Mandal and Katharine L. C. Hunt, *J. Chem. Phys.* **2018**, *149*, 204110, *Editor's Pick*.

*Quantum transition probabilities during a perturbing pulse: Differences between the nonadiabatic results and Fermi's golden rule forms*, A. Mandal and K. L. C. Hunt, *J. Chem. Phys.* **2018**, *148*, 194107.

*Gauge-invariant expectation values of the energy of a molecule in an electromagnetic field*, Anirban Mandal and Katharine L. C. Hunt, *J. Chem. Phys.* **2016**, *144*, 044109.

*Non-adiabatic current densities, transitions, and power absorbed by a molecule in a time-dependent electromagnetic field*, Anirban Mandal and Katharine L. C. Hunt, *J. Chem. Phys.* **2015**, *143*, 034102.

*Quantum mechanical calculation of the collision-induced absorption spectra of $N_2$-$N_2$ with anisotropic interactions*, Tijs Karman, Evangelos Miliordos, Katharine L. C. Hunt, Gerrit C. Groenenboom, and Ad van der Avoird, *J. Chem. Phys.* **2015**, *142*, 084306.

*Ground and excited states of vanadium hydroxide isomers and their cations, $VOH^{0,+}$ and $HVO^{0,+}$*, Evangelos Miliordos, James F. Harrison, and Katharine L. C. Hunt, *J. Chem. Phys.* **2013**, *138*, 114305.

*Adiabatic and nonadiabatic contributions to the energy of a system subject to a time-dependent perturbation*, Anirban Mandal and Katharine L. C. Hunt, *J. Chem. Phys.* **2012**, *137*, 164109.


***Quantum systems in time-dependent fields —*** We have derived new theoretical results for transition probabilities in quantum systems in time-dependent electromagnetic fields. These results challenge Dirac's expression for the transition probability, which depends on the norm-square of the coefficient $c_k(t)$ for the excited state $|k_0\rangle$ of the original unperturbed Hamiltonian $H_0$, in the time-dependent wave function. By integrating by parts, Landau and Lifshitz separated $c_k(t)$ into an adiabatic term $a_k(t)$ that follows the adiabatic theorem of Born and Fock, and a nonadiabatic term $b_k(t)$ that depends on the time-derivative of the perturbation up to time t. The adiabatic term describes the adjustment of the initial state to the perturbation without actual transitions, while the transition probability is given by the norm-square of $b_k(t)$. Our work reinforces this statement and goes beyond the results of Landau and Lifshitz. We proved that the energy separates into adiabatic and nonadiabatic terms. The nonadiabatic term in the energy is given by the sum over excited states of $|b_k(t)|^2$ times the transition energy $(E_k - E_0)$, corrected for the perturbation. We proved that the power absorbed by a molecule from an electromagnetic field is equal to the time-derivative of the nonadiabatic term in the energy. Further, the vibrational wave packets associated with $a_k(t)$ and $b_k(t)$ evolve on *different* electronic potential energy surfaces. Our results for transition probabilities differ significantly from the results of Dirac's theory, during short perturbing pulses with frequencies that are off-resonant from the transition frequency. For a cosine wave of frequency $\omega$ in a Gaussian envelope, $|b_k(t)|^2$ is larger than $|c_k(t)|^2$ when $\omega > \omega_{k0}$, the transition frequency to state k; while the opposite is true when $\omega < \omega_{k0}$. These results are independent of the phase of the oscillating wave relative to the peak of the Gaussian envelope. The differences are also quite stark for a perturbing pulse that rises to a level plateau, and later falls off. While the perturbation is constant, the nonadiabatic transition probability is constant as required physically, since a static perturbation cannot induce transitions; in contrast Dirac's form of the transition probability continues to oscillate while the perturbation is constant, as shown in ***Figure 1***.

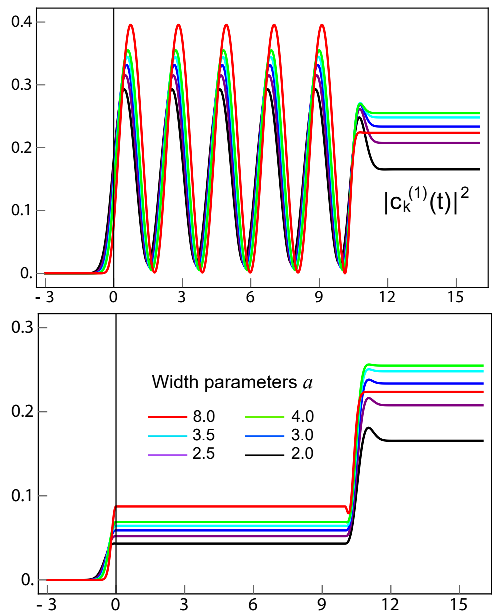


***Figure 1. Dirac's transition probability (top) and nonadiabatic transition probability (bottom), for a quantum system in a pulse with a plateau lasting 10 units of time. Different colors correspond to different rates of turning on the perturbation. A. Mandal and K. L. C. Hunt,*** **J. Chem. Phys.** ***2018, 149, 204110.***

***Collision-induced spectroscopic processes —*** Spectroscopic processes that are forbidden for single molecules are observed in dense gases and liquids, because the electronic charge distorts during molecular collisions. Our work has focused on collision-induced absorption in the IR by $H_2$ gas, $H_2$/H and $H_2$/He mixtures, $N_2$ gas and $O_2$ gas, with applications in astrophysics and in atmospheric profiling. Interaction-induced absorption affects the radiative profiles of gases in star-forming nebulae; very old, very cool white dwarf stars; the outer planets and exoplanets that are termed "hot Jupiters" and "warm Neptunes," and the atmospheres of satellites of the outer planets. My research group calculates the total dipole moments *ab initio* and then expresses the results in spherical-tensor form for subsequent line-shape calculations. Dipole surfaces for $H_2$-H are shown in ***Figure 2***. This research area involves collaborations with Lothar Frommhold and Martin Abel (University of Texas, Austin), Magnus Gustafsson (Luleå, Sweden), Tijs Karman, Gerrit Groenenboom, and Ad van der Avoird (Nijmegen, the Netherlands), and Richard Dawes (Missouri University of Science and Technology).

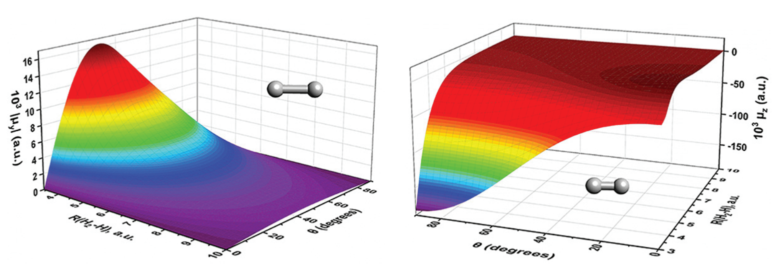

***Figure 2. Cartesian components of the dipole of $H_2$-H, figures from AIP Scilight 2019, 220002-1 by Adam Liebendorfer, a report of work by H.-K. Lee, X. Li, E. Miliordos, and K. L. C. Hunt,*** **J. Chem. Phys.** ***2019, 150, 204307.***