

Katharine Clarke Hunt
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Katharine Clarke Hunt completed her bachelor's degree in Chemistry in 1975 at Michigan State University, where she held an Alumni Distinguished Scholarship and a National Merit Scholarship. As an undergraduate, she took five graduate-level lecture courses in chemistry (two by special arrangement, since they were reserved for Ph.D. students) and four graduate-level lecture-courses in physics. Katharine wrote her undergraduate thesis on Rayleigh-Thompson light scattering by a fluid in a temperature gradient, with Professor Robert I. Cukier as her research adviser. She was elected to the scholastic honorary society Phi Beta Kappa and received her degree with the highest honors that Michigan State University offers.

For her graduate work, Katharine was awarded a Marshall Scholarship from the government of the United Kingdom, a National Science Foundation Pre-Doctoral Fellowship, and a Danforth Fellowship. She accepted the Marshall Scholarship to conduct research with Professor A. David Buckingham CBE FRS FAA in the Department of Organic, Inorganic, and Theoretical Chemistry at the University of Cambridge. Her thesis research focused on the effects of intermolecular interactions on polarizabilities, based on *ab initio* calculations at the full configuration-interaction level, perturbation theory including anti-symmetrization effects, and quantum mechanical models, all including van der Waals dispersion effects. Her development of nonlocal electromagnetic response theory started at that time. Professor Paul Madden FRS FRSE, former Provost of Queen's College, Oxford collaborated with Katharine and David. While at Cambridge, she also served as a Tutor in mathematics for physics undergraduates in King's College of the University of Cambridge. She was especially pleased that two of the six students she taught in 1977 placed in the top ten in the University on the end of year examination in Mathematics for Physicists. Katharine completed her Ph.D. in September 1978. Professor John Murrell FRS served as the external examiner for her thesis.

For post-doctoral research, Katharine returned to the United States, where she received a National Science Foundation National Needs Postdoctoral Fellowship, to conduct research with Professor John Ross, then at the Massachusetts Institute of Technology, beginning in October 1978. With John, she worked on topics in nonequilibrium statistical mechanics, in particular on the solution of stochastic differential equations (Langevin and Fokker-Planck equations) for non-linear irreversible processes, using functional path integral methods. Earlier, it had been suggested in the literature that the Lagrangian appearing in the path integral, and more significantly the Euler-Lagrange equations derived from it, could not have physical meaning, because they appeared to differ in the Itô stochastic calculus from their version in the Stratonovich stochastic calculus. Katharine recognized that in Itô's analysis, the Fundamental Theorem of the Calculus differs from its Newtonian form. After taking that difference into account, she obtained a single version of the Euler-Lagrange equation, which characterizes the most heavily weighted path for the evolution of the nonequilibrium system. She also showed that the conditional propagator could be separated into kinetic and thermodynamic factors. In subsequent work with Professor John Ross and her spouse Professor Paul Hunt, she proved that it is possible to find the conditional propagator analytically for selected nonequilibrium problems, where the nonlinearity is confined to the thermodynamic factor.

After five months of post-doctoral research, Katharine and her spouse Paul were each offered tenure-track faculty appointments in the Department of Chemistry at Michigan State University (MSU). They completed a year of post-doctoral research (Paul with Professor Roy Gordon at Harvard) and then started their faculty positions at MSU in September 1979. Katharine expanded her research on the interaction effects on molecular properties. She developed a simple

quantitative model for interaction induced dipoles, quadrupoles, and hyperpolarizabilities, and applied her theory of nonlocal polarizability densities to van der Waals dispersion interactions between extended molecular structures as well as interaction induced electrostatic properties.

Katharine received tenure as an Associate Professor in 1984, promotion to Full Professor in 1989, and designation as a University Distinguished Professor in 1992. She was the first woman in her Department to be appointed to each of these positions. Katharine and Paul traveled to Stanford University to continue research collaborations with Professor John Ross for sabbaticals during 1985-86 and 1993-94. From 1998-2002, she served as the Chair of the Department of Chemistry.

Somewhat unexpectedly, molecular hyperpolarization affects the dispersion contribution to dipole moments and polarizabilities, because the response may be independent in an externally applied field, or linear in that field, while being nonlinear in the local field. This phenomenon had been identified early on by David Buckingham. Katharine discovered that there is an additional dispersion effect on properties, because the applied field modifies the spontaneous, purely quantum mechanical fluctuations in the charge density and their correlation. She accounted for this in publications with her Ph.D. student J. E Bohr. Throughout her career, Katharine has continued to conduct research on transient, collision-induced changes in molecular properties, and their spectroscopic consequences. She has collaborated on parts of this work with Professors David Bishop (Ottawa), Patrick Fowler (Exeter, Sheffield), Andrzej Sadlej (Nicolaus Copernicus University), and Robert Harris (Berkeley). She was recruited into a collaboration with Professor Lothar Frommhold in the Physics Department of the University of Texas at Austin and Professor Magnus Gustafsson now at the Luleå University of Technology in Sweden, to work on highly accurate *ab initio* calculations of the dipoles due to interactions between H atoms, He atoms, and H₂ molecules for astrophysical applications. The theoretical spectra based on this work have been incorporated into the HITRAN data base of the Harvard Smithsonian Center for Astrophysics. They also collaborated to calculate the rototranslational Raman spectra of hydrogen gas. Katharine's work with her own group members on the dipole of H₂...H was selected as a Featured Article and Editor's Choice in the *Journal of Chemical Physics*; it was the subject of an American Institute of Physics Scilight as well.

With Professors John Ross and Paul Hunt, Katharine conducted research in nonequilibrium thermodynamics, aimed at clarifying the relative stability of different nonequilibrium steady states and modeling the time-evolution of systems far from equilibrium, including those that show kinetic limit cycles. Part of this work involved the determination of the conditional propagator for the master equation in species-number space. They identified a work function that governs the time-evolution of nonequilibrium systems, and with Dr. Marcel Vlad proposed a means of finding thermodynamic and stochastic potentials from macroscopic measurements.

Research by Professors Paulo Lazzeretti and Riccardo Zanasi had established a somewhat counter-intuitive relationship between the derivative of the dipole moment with respect to a nuclear coordinate and the Sternheimer electric field shielding tensor (the electric field analog of the chemical shift). Katharine realized that the relationship could be explained by use of the nonlocal polarizability density. This insight led to her proof of a set of intertwining relationships between the permanent charge moments, the polarizability, and the hyperpolarizability. The derivatives of each depend on the susceptibility density of the next higher order.

In 1939, Richard Feynman had suggested that the long-range van der Waals dispersion forces between atoms in S states are attributable to dipolar distortions of the charge distribution on each center, with the nuclei being attracted to their "own" electronic charge cloud. He based this suggestion on the observed that both the dispersion dipole and the dispersion force vary as R^{-7} in the separation R between the nuclei. This suggestion was termed Feynman's "conjecture" by Professors Joseph Hirschfelder (Wisconsin) and Morton Eliason (Augustana), who succeeded in

1967 in demonstrating that the statement holds numerically, to four figures for two H atoms in S states. The conjecture eluded study for larger systems, however. In 1990, Katharine applied her nonlocal polarizability density theory and her connections between the hyperpolarizability and the derivative of the polarizability with respect to nuclear coordinates to prove Feynman's conjecture analytically within the polarization approximation, which holds when exchange effects are negligible. She noted that Feynman's rationale breaks down if either or both of the interacting molecules are non-centrosymmetric. In that case, the dispersion force still varies as R^{-7} , but the dispersion dipole varies as R^{-6} . Katharine proved a generalization of the Thomas-Reiche-Kuhn sum rule, which permitted her to establish that Feynman's conjecture about dispersion forces also holds for molecules of arbitrary symmetry.

More recently, Katharine has continued to work on high accuracy *ab initio* calculations of the dipoles and polarizabilities due to molecular interactions. She has developed a rigorous quantum mechanical analysis that shows how dielectric theory can be extended to the intramolecular scale, thus describing electronic screening within a molecule and screening in a medium. She has also worked with a group of students on topics in quantum computing, including studies of violations of the Bell and Clauser-Horne-Shimony-Holt inequalities on quantum computers, and calculations of the von Neumann and Shannon entropies of multi-qubit Schrödinger's cat states.

With her Ph.D. student and later post-doctoral research associate Dr. Anirban Mandal, Katharine has explored the consequences of a suggestion by Lev Landau and Evgeny Lifshitz that the excited-state coefficients in P. A. M. Dirac's theory of transitions in time-dependent fields should be separated into adiabatic and nonadiabatic terms. They stated that the norm-square of the nonadiabatic coefficient determines the probability of a transition to a state that is not connected adiabatically to the original ground state, but rather to an excited state. Katharine and Anirban developed the theory well beyond the original suggestion by Landau and Lifshitz (which occupies just three pages in their text on quantum mechanics), by first showing that the energy of the molecule in the field also separates into adiabatic and nonadiabatic terms with simple physical interpretations. Katharine and Anirban then proved that the power absorbed from an applied field is equal to the time-derivative of the nonadiabatic term in the energy. Because questions about gauge dependence naturally arise, when considering the energy of a molecule in a time-dependent field, Katharine and Anirban examined the Hamiltonian for the full system, consisting of the molecule and the field. They found that the expectation value of the gauge-dependent term that is usually assigned to the molecular Hamiltonian exactly cancels with the expectation value of a gauge-dependent term assigned to the field Hamiltonian, after applying Gauss's law. Currently, they are analyzing the effects of coupling to a thermal bath, within Redfield theory in the secular approximation. Katharine's work has been supported by twenty grants, including eleven grants from the National Science Foundation; the most recent runs from 2022 to 2025. She has given invited talks at Stanford, Berkeley, Caltech, Yale, and many international conferences.

As Chair of the Department of Chemistry at MSU, Katharine was responsible for five new faculty set-ups, including three senior hires, eight tenure decisions (all positive), and five promotions to full professor. During her term as Chair, MSU Chemistry rose twenty ranks in the ranking of federal funding for research, and more than doubled funding from the National Institutes of Health in a single year. She undertook major efforts to improve safety in the Department of Chemistry, including the installation of the first eyewashes in the teaching laboratories, the first flame-proof chemical storage cabinets, the first smoke-detection system, and upgrades in the ventilation system for the lecture wing of the building, and a major HVAC renovation to permit the addition of 75 hoods for chemical synthesis, as well as other safety-related improvements.

Katharine and her spouse Paul have one daughter, Laurel, who is a published poet.

References: Selected Publications

Sara D. Jovanovski, Anirban Mandal, and Katharine L. C. Hunt, Nonadiabatic transition probabilities for quantum systems in electromagnetic fields: Dephasing and population relaxation due to contact with a bath, *J. Chem. Phys.* **158**, 164107 (2023).

N. D. Jansen, M. Loucks, S. Gilbert, C. Fleming-Dittenber, J. Egbert, and K. L. C. Hunt, Shannon and von Neumann entropies of multi-qubit Schrödinger's cat states, *Phys. Chem. Chem. Phys.* **24**, 7666-7681 (2022).

D. Z. Wang, A. Q. Gauthier, A. E. Siegmund, and K. L. C. Hunt, Bell inequalities for entangled qubits, *Phys. Chem. Chem. Phys.* **23**, 6370-6387 (2021); inside cover article.

A. Mandal and K. L. C. Hunt, Quantum transition probabilities due to overlapping electromagnetic pulses, *J. Chem. Phys.* **154**, 024116 (2021).

H.-K. Lee, X. Li, E. Miliordos, and K. L. C. Hunt, The interaction-induced dipole of H₂...H: New *ab initio* results and spherical tensor analysis, *J. Chem. Phys.* **150**, 204307 (2019).

A. Mandal and K. L. C. Hunt, Nonadiabatic transition probabilities in a time-dependent Gaussian pulse or plateau pulse, *J. Chem. Phys.* **149**, 204110 (2018); Editor's Pick.

A. Mandal and K. L. C. Hunt, Quantum transition probabilities during a perturbing pulse, *J. Chem. Phys.* **148**, 194107 (2018).

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

A. Mandal and K. L. C. Hunt, Non-adiabatic current densities, transitions and power absorbed by a molecule in a time-dependent electromagnetic field, *J. Chem. Phys.* **143**, 034012 (2015).

T. Karman, E. Miliordos, K. L. C. Hunt, G. C. Groenenboom, and A. van der Avoird, Quantum mechanical calculation of the collision-induced absorption spectra of N₂-N₂ with anisotropic interaction, *J. Chem. Phys.* **142**, 084306 (2015).

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

M. Abel, L. Frommhold, X. P. Li, and K. L. C. Hunt, Collision-induced absorption by H₂ pairs: From hundreds to thousands of Kelvin, *J. Phys. Chem. A* **115**, 6805 (2011).

K. L. C. Hunt, The energy as a functional of the charge density and the charge-density susceptibility, *J. Chem. Phys.* **116**, 5440-47 (2002).

J. Ross, K. L. C. Hunt, and P. M. Hunt, Thermodynamic and stochastic theory for non-equilibrium systems with multiple reactive intermediates, *J. Chem. Phys.* **96**, 618-29 (1992).

K. L. C. Hunt, Dispersion dipoles and dispersion forces, *J. Chem. Phys.* **92**, 1180-1187 (1990).

K. L. C. Hunt, Relationships between electric field shielding tensors and infrared or Raman intensities, *J. Chem. Phys.* **90**, 4909-15 (1989).

K. L. C. Hunt and J. E. Bohr, Effects of van der Waals interactions on molecular dipole moments: The role of field-induced fluctuation correlations, *J. Chem. Phys.* **83**, 5198-202 (1985).

K. L. C. Hunt and J. Ross, Path integral solutions of stochastic equations for non-linear irreversible processes, *J. Chem. Phys.* **75**, 976-984 (1981).

K. L. C. Hunt, Long-range dipoles, quadrupoles, and hyperpolarizabilities of interacting inert gas atoms, *Chem. Phys. Lett.* **70**, 336-342 (1980).