Quantum systems in time-dependent fields – We are deriving new results for quantum systems that are perturbed by time-dependent electromagnetic fields, in cases where the adiabatic theorem does not hold. In their text Quantum Mechanics, Landau and Lifshitz showed that the excited-state coefficients in the wave function can be separated into adiabatic and non-adiabatic terms. Ordinarily, one would expect to find cross-terms between the adiabatic and non-adiabatic coefficients, when the expectation value of the Hamiltonian is computed. However, Anirban Mandal and I proved that the cross-terms vanish identically. The energy separates completely into adiabatic and non-adiabatic terms. The adiabatic term accounts for the adjustment of the ground state to the perturbation—without transitions—while the non-adiabatic term gives the energy change due to transitions to excited states. Subsequently, we proved that the power absorbed by a molecule from an applied field is equal to the time-derivative of the non-adiabatic term in the energy.

The standard Hamiltonian for a molecule in an electromagnetic field includes an arbitrary gauge potential, which arises when the vector and scalar potentials of the applied field are altered by a gauge transformation, leaving the electric and magnetic fields themselves unchanged. Physically meaningful quantities must be gauge-invariant, so the expectation value of the standard molecular Hamiltonian cannot be interpreted as the energy of a molecule in an applied field—a problem recognized in the mid-1950’s by Kramers. Anirban Mandal and I analyzed the full Hamiltonian for the molecule and the electromagnetic field, and showed that the standard Hamiltonian for the field contains a gauge-dependent term that exactly cancels with the gauge-dependent term in the molecular Hamiltonian. This opens a route to determine the energy of a molecule in a field, in a gauge-invariant way.

Currently, we are investigating the differences between our results for the probability of transitions to excited states for systems in laser fields vs. transition probabilities obtained from Fermi’s “golden rule.” We are looking at donor/acceptor complexes and three-state model systems, where there is rapid decay from the initially excited state.

Collision-induced spectroscopic processes – Spectroscopic processes that are forbidden for single molecules may be observed in dense gases and liquids, due to electronic charge redistribution that occurs during molecular collisions. Our recent work has focused on collision-induced absorption of infrared radiation by samples containing $\text{H}_2$ or $\text{H}_2$/He mixtures in stellar atmospheres, and on collision-induced absorption by oxygen and nitrogen in Earth’s atmosphere. We evaluate the total dipole moments as functions of the bond lengths, intermolecular distances, and orientation angles, and then express the results in the spherical-tensor form needed for spectroscopic line shape calculations. Line-shape calculations based on our results have been carried out by our collaborators, Lothar Frommhold and Martin Abel (University of Texas, Austin) and Tijs Karman, Gerrit Groenenboom, and Ad van der Avoird (Radboud University, Nijmegen, Netherlands).

Manipulation of labeled biomolecules with light – We are also working on a theoretical analysis of the dynamics of fluorescently labeled protein molecules in laser fields. The theory of optical manipulation of molecules is well established for small molecules where the induced dipole forces predominate, and for very large molecules where the net forces associated with Mie scattering predominate. Fluorescently labeled proteins fall into an intermediate size range, where neither of the limiting cases applies and new theory is needed. This project involves collaboration with members of Bob Bukir’s research group, who provide expertise in molecular dynamics simulations. Our current work focuses on leucine zipper proteins interacting with fluorescently labeled DNA strands.

Selected Publications


Infrared absorption by collisional $\text{H}_2$/He complexes at temperatures up to 9,000 K, and frequencies from 0 to 20,000 cm$^{-1}$, Martin Abel, Lothar Frommhold, Xiaoping Li, and Katharine L. C. Hunt, J. Chem. Phys. 2012, 136, 044319.