Quantum systems in time-dependent fields - derived new theoretical results for transition probabilities in quantum systems in time-dependent electromagnetic fields. Beginning with Dirac's work, the probability that a time-dependent perturbation induces a transition to an excited state has been expressed in terms of the norm-square of the coefficient $c_k(t)$ for the excited state $|k\rangle$ of the original unperturbed Hamiltonian $H_0$. 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 $t$; they stated that the transition probability is given by the norm-square of $b_k(t)$. Our work reinforces the claim of Landau and Lifshitz and goes beyond their results. We proved that the energy separates into 1) the energy of the adiabatically perturbed initial state and 2) the sum over excited states of $|b_k(t)|^2$ times the transition energy $(E_k - E_0)$, corrected for the perturbation. This is due to the orthogonality of the eigenfunctions of the perturbed Hamiltonian $H_0 + H(t)$; but since we have $b_k(t)$, we can give accurate numerical results for the transition probabilities and the nonadiabatic term in the energy. In our more general analysis, a perturbative framework is not needed. 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; and we note that 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 dramatically 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 $\omega > \omega_{\text{zero}}$, the transition frequency to state $k$; while the opposite is true when $\omega < \omega_{\text{zero}}$. These results are independent of the phase of the oscillating wave relative to the peak of the Gaussian envelope. For a perturbing pulse that rises to a level plateau, $|b_k(t)|^2$ is constant while the perturbation is constant, but $|c_k(t)|^2$ continues to oscillate.

The standard Hamiltonian for a molecule in an electromagnetic field includes an arbitrary gauge potential that is introduced when the vector and scalar potentials of an applied field are altered by a gauge transformation, which leaves the electric and magnetic fields themselves unchanged. The gauge-dependence of the standard molecular Hamiltonian has made it difficult to determine the energy of a molecule in an applied electric field. By analyzing the full Hamiltonian for the molecule and the field, we have found a gauge-dependent term that is normally assigned to the field Hamiltonian, but that exactly cancels the gauge-dependent term in the molecular Hamiltonian. This resolves the quandary and provides a firm footing for future research where accurate energies are needed for molecules in applied fields.

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 $H_2$, $H_2$/$He$ mixtures, $N_2$ gas, and $O_2$ gas, with applications in atmospheric profiling, including atmospheres of cool white dwarf stars. We calculate the total dipole moments $ab initio$ and then express them in spherical-tensor form for subsequent line-shape calculations. This work has been carried out in collaboration with Lothar Frommhold and Martin Abel (University of Texas, Austin), Magnus Gustafsson (Luleå, Sweden), and Tijs Karman, Gerrit Groenenboom, and Ad van der Avoird (Nijmegen, the Netherlands).

Manipulation of biomolecules with light - We are also studying the dynamics of fluorescently labeled DNA strands or protein/DNA complexes in laser fields. Fluorescently labeled DNA strands and proteins fall into a size range where a new approach is needed to calculate the laser-induced forces. This project has involved collaboration with Bob Cukier’s research group, benefiting from their expertise in molecular dynamics simulations. Our current work focuses on DNA strands labeled with an oxazole yellow dye; we plan work on dye-labeled small interfering RNA segments.