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Transient Quantum Mechanical Processes

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Abstract

Our principal objective has centered on the development of sophisticated computational techniques to solve the time-dependent Schrodinger equation that governs the evolution of quantum mechanical systems. We have perfected two complementary methods, discrete variable representation and real space product formula, that show great promise in solving these complicated temporal problems. We have applied these methods to the interaction of laser light with molecules with the intent of not only investigating the basic mechanisms but also devising schemes for actually controlling the outcome of microscopic processes. Lasers now exist that produce pulses of such short duration as to probe a molecular process many times within its characteristic period - allowing the actual observation of an evolving quantum mechanical system. We have studied the potassium dimer as an example and found agreement with experimental changes in the intermediate state populations as a function of laser frequency - a simple control prescription. We have also employed elaborate quantum chemistry programs to improve the accuracy of basic input such as bound-bound and bound-free coupling moments. These techniques have far-ranging applicability; for example, to trapped quantum systems at very low temperatures such as Bose-Einstein condensates.

Background and Research Objectives

Examining atomic interactions while in progress and controlling the products of such processes have long been dreams of atomic and molecular scientists, or as one practitioner[1] has succinctly stated "to observe and make molecules dance." Whether the step becomes a minuet, a tango, or something to a more modern beat depends both on the basic molecular properties and the nature of the probing or controlling device. With the advent of lasers with pulses of shorter duration than the molecular process, calling and watching the dance became realistic possibilities. The ephemeral nature of the pulse permits tracking the step-by-step temporal evolution of particle interactions. In addition, the characteristics of the pulse, such as its duration, shape, and intensity, allow the systematic selection of particular mechanisms by favoring one end-product over another. In fact, experiments[2] to control the excitation and ionization of heavy diatomic molecules have been performed at Los Alamos and other research facilities. Such a situation is ripe for a joint experimental-theoretical endeavor. For in the case of control, the usual situation of predicting the result from a set of initial conditions is inverted.

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We instead select the *final* outcome and then solve the problem "backwards" to determine the pulse characteristics that yield the desired result. This requires much closer involvement of both parties since the experimental parameters become an intricate part of the theoretical model. Paramount to any theoretical interpretation is the ability to generate quantum mechanical wavepackets, the solutions to the time-dependent(TD) Schrodinger equation. These packets provide detailed information on the temporal evolution of the system as well as a pedagogical visualization of the underlying molecular processes. The packets behave in an intuitive fashion more like actual particles. For example, they vibrate in a potential well; or they travel inward on such curves, collide with a wall, change character, and move outward. Therefore, such visualizations provide a natural means of extracting very intricate information about the basic process and the possible control parameters.

We have principally focused on the pump-probe mechanism for diatomic molecules as studied in many recent experiments[2] and, as an example, describe in Figure 1 the process for the dimer of potassium K_2. The procedure employs two different laser frequencies. The first laser or **pump** pulse(ν_1) excites the molecule from its ground state[X] to a bound excited state[A]:

$$h\nu_1 + K_2[X] \Rightarrow K_2^*[A] \quad .$$

The excited-state wavepacket forms and then begins to oscillate back and forth in the bound-state well. After a given time(τ), a second or **probe** laser of a different frequency(ν_2) fires and ionizes the molecule:

$$h\nu_2 + K_2^*[A] \Rightarrow K_2^+ + e^- \quad .$$

The measured free-electron(e^-) signal characterizes the motion of the excited-state packet at the time of impact. Since the probe pulse has a duration so much shorter than the characteristic vibrational period of the molecule, we actually obtain a snapshot of the wavepacket at a given point during its period. By varying the shape of the pulse, we can likewise change the form and nature of the exited-state packet and thus in a simple case, exert a form of control on a microscopic process. A proper representation of this process requires a multi-state treatment of the time-dependent evolution of the molecular system. A first glance at Figure 1 would seem to indicate that this pump-probe scheme consists of only three states. However, the ionized electron can emerge in a continuous energy band, the width dictated by conservation principles. We have a new "state" associated with the ion and each possible electron energy. The problem is particularly complicated due to the need to encompass this extensive band of continuum states. This necessitates large coupled-channel representations of the order of a hundred states, which taxes the most sophisticated of current time-dependent methods.

Our objective, then, centers on the theoretical study of transient quantum mechanical phenomena in several diverse areas such as quantum control of molecular collisions. Our goals range from the accurate modeling of these systems using sophisticated quantum mechanical techniques for the temporal propagation of multidimensional wavepackets and representation of reaction surfaces to the application of the methods to experiments.

Importance to LANL's Science and Technology Base and National R&D Needs

While in its infancy, the field holds great promise. Some of this promise has already been realized in experiments and theoretical endeavors that have demonstrated the basic validity of the underlying principles. However, the effectiveness of the technique must rely on more complex mechanisms. Certainly, quantum control offers a unique opportunity to analyze the intricacies of basic atomic and molecular processes. These experiments glean not only dynamical information but also extremely accurate determinations of static properties such as the potential energy surfaces along the reaction trajectory. Therefore, they challenge existing theoretical models, which must address instantaneous rather than averaged properties. Even if no practical applications emerge, the benefit to basic Atomic, Molecular, and Optical (AMO) theory remains immense. However, the techniques may, at least on a small scale, lead to design procedures for specific molecules that cannot be assembled by standard chemical procedures and as such may have interest to certain industries. The broader claims of industrial level production must await far more extensive testing and research before validated.

Scientific Approach and Accomplishments

We emphasize the fundamental point embodied in all our theoretical efforts: the same time-dependent quantum mechanical wavepacket propagation techniques apply to a diversity of physical processes that at first may appear totally unrelated. The same package of programs that predict transmission efficiency in artificial atoms also addresses the intricacies of quantum control or the nature of a Bose-Einstein condensate.

We have developed two promising techniques for solving the time-dependent Schrodinger equation: 1) the discrete variable representation (DVR) and 2) the Real Space Product Formula (RSPF). Since detailed expositions appear elsewhere [3], we give only a brief description here. Both procedures place the spatial part of the Schrodinger equation on a finite grid of points. This use of a discrete spatial representation converts the problem to a first-order ordinary differential equation (FODE) in time, in which the effect of the spatial operators on the wave function occurs through matrix operations. In turn, the solution of the temporal FODE is given by a matrix function evaluated through a split-operator procedure.

Having two complementary approaches provides excellent cross-checking capabilities, essential when pushing studies into unexplored areas. In addition, the methods have particular strengths and weaknesses in different, though overlapping, regimes. Their combination allows for probing a much wider variety of quantum control problems. Both techniques yield highly efficient, state-of-the-art computational algorithms.

We have already extensively tested these techniques for one, two, and three spatial dimensions. In 1-D, we have accurately modeled such diverse processes as atoms in intense oscillatory electrical fields, electron transmission in barrier-well potentials that crudely resemble the GaAs layers of quantum dots, laser-assisted electron scattering, photoionization, and recombination. In addition, the method has been extended to two spatial dimensions in order to follow the collinear collision of H with H_2. The 3D application, just initiated, has centered on atoms in traps at very low temperatures. As indicated above, our principal development has centered on solutions of a multi-state representation of the TD Schrodinger equation for studying pump-probe laser interactions with molecules. The representation of the electron continuum complicates the solution. We have developed very powerful methods for determining an accurate, discrete form for the free-electron states. This maintains the total number a states treated to a manageable number.

While the solution of the TD Schrodinger equation captures center stage for the modeling, other quantities must be provided. These include the potential surfaces upon which the molecules move. Two types of curves are important to the control experiments: bound and auto-ionizing. We have the capability of determining very accurate bound state curves from the Quantum Chemistry packages in the Theoretical Chemistry and Molecular Physics Group. In addition, we have developed electron-molecule programs that calculate the necessary auto-ionizing lifetimes and positions as a function of internuclear separation. In particular, we have at our call a wide diversity of highly developed sophisticated AMO programs that can treat all levels of these processes.

We have concentrated on pump-probe mechanisms in the potassium dimmer K_2 since considerable experimental results are available. Our general findings agree well with experiment . Since the details appear in Ref. [3], we present a short summary here. First, a very clear correlation exists between the number of ionized electrons observed and the nature of the wave packet in the bound excited state of the molecule. A Fourier transform of the temporal electron signal yields two distinct peaks in frequency space. The first and more prominent corresponds to the basic vibrational frequency of the excited K_2 while the second reflects the tendency of the wave packet to spend a larger proportion of its time near the classical turning points of the potential energy well. A closer examination of a representative free-electron signal in Figure2 shows repetitive structure within the electron signal which

relates to actual positions of the wave packet within the well. Therefore, we can use the ionization mechanism to actually follow the motion of a temporally evolving quantum mechanical system. Second, as also demonstrated in Figure 2, we find a distinct dependence of the ionized electron signal on the frequency of the laser. This indicates tuning the laser can actually affect the result of a quantum mechanical event. This arises from the probing of different parts of the excited-state potential energy curve. Third, we find considerable sensitivity in the basic molecular quantities employed, indicating that accurate comparisons with experiments require very high quality calculations of potential energy curves and coupling matrix elements. Fourth, we also found that large continuum bases were required to give a well-converged electron signal profile. Earlier studies, using only a few free-particle states, produced spurious oscillations in the signal.

We have therefore developed state-of-the –art computational methods for solving the time-dependent Schrodinger equation. The application to the pump-probe scheme in diatomic molecules has yielded considerable insight into the basic physics as well as the intricacies of the experimental findings as well as demonstrating a simple control mechanism.

Publications

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[3] Collins, L., Kress, J., and Walker, R., "Excitation and Ionization of Molecules by a Single-Mode Laser Field Using a Time-Dependent Approach," Comp. Phys. Comm. **114**, 15(1998).

Figure 1: Pump-Probe experiment. A pump laser pulse excites the molecule from its ground $K_2[X]$ to an excited state $K_2[A]$. The wave packet in the A state begins to move. At a delay time τ, a probe laser excites the packet to the state of the molecular ion $K_2^+[X]$ with the release of an electron.

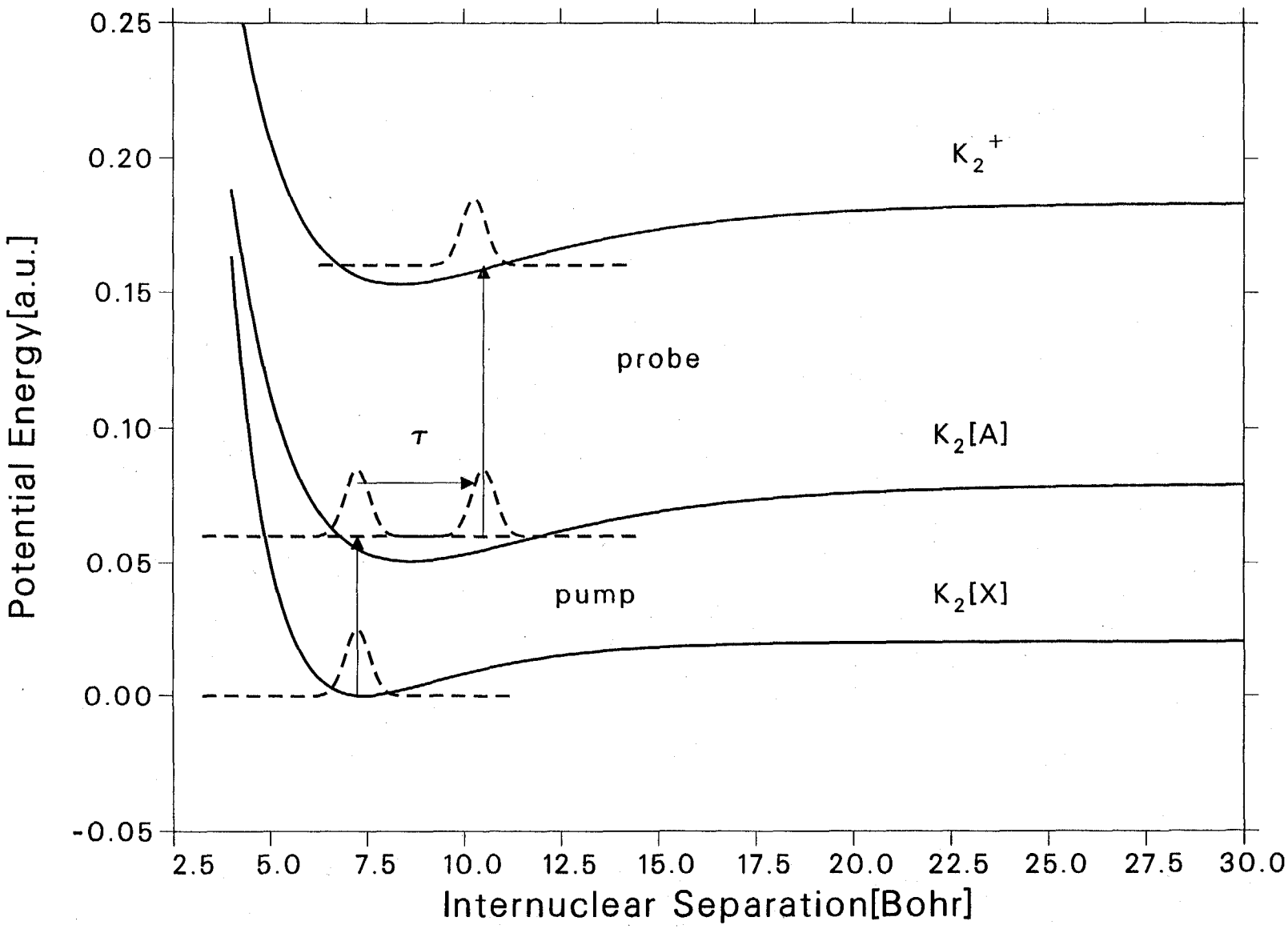
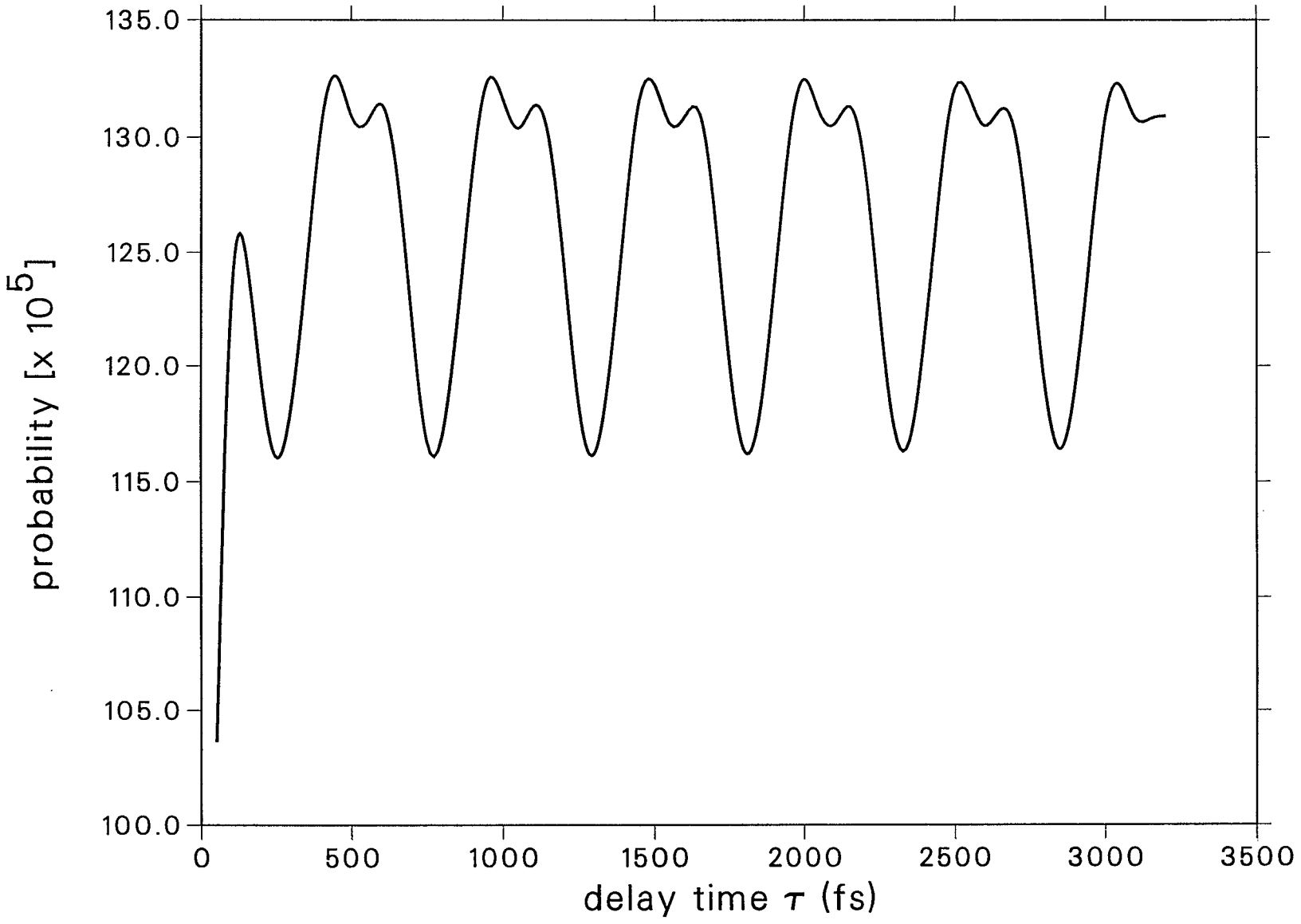
Figure 2: Representative electron signals $P_3(t)$ as a function of time resulting from the ionization of the excited molecular state by the probe pulse. Two probe pulses at different frequencies(wavelengths) are shown.