Theoretical studies of interactions of atoms, molecules and surfaces

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In this abstract we report progress and future plans in the theoretical developments in three areas: (1) Interactions of intense laser fields with atoms and molecules. (2) Hyperspherical approach for ion-atom collisions at low energies. (3) Classification of intershell triply excited states of atoms. Computations carried out in conjunction with new ion-atom collision experiments are also summarized.

1. Interaction of intense laser fields with atoms and molecules

Background.

In conjunction with the new experimental initiative in the JR Macdonald Laboratory we have also started a theoretical program studying the interaction of atoms and molecules with intense lasers. After surveying the literature, we decided to take on the theory of ionization of molecules by an intense laser . There are a number of puzzling experimental observations where even a simple qualitative interpretation is not available.

The ionization of atoms, especially of rare gas atoms, by femtosecond Ti:Sapphire lasers has been well studied experimentally and the ionization yield has been found to be well-described by the tunneling ionization model, or the so-called ADK model. In this model the ionization by an intense laser field is calculated from the ionization rate of a static electric field which can be approximately expressed in analytic form. The ADK model has been widely used by experimentalists for the ionization of atoms.

When comparing the ionization of molecules vs. atoms with similar ionization potentials, it was found that there were irregularities. For N_2 vs. Ar, where the potentials are nearly the same, their ionization rates were found to be about the same too. On the other hand, O_2 and Xe also have nearly identical ionization potentials, but the ionization rates for O_2 are significantly smaller than Xe. Thus O_2 ionization is suppressed.

The origin of ionization suppression of O_2 has been controversial. It has been "explained" in terms of many-electron effect [Guo, PRL85,2276,(2000)] , or in terms of interference from the two atomic centers [Muth-Bohm et al PRL, 85, 2280(2000)].

Progress in the last year

We have succeeded in extending the ADK model to describe tunneling ionization of molecules. The basic idea is rather simple. Since the ADK model was derived for the one-center atoms, to apply it to molecules, one needs to extract the one-center parameters from the two-center (for diatomic molecules) molecular wavefunctions. By fitting the asymptotic electronic wavefunction of a molecule in proper form, we derived the parameters needed for the ADK model for molecules. With these parameters the tunneling ionization rates for each molecule can be calculated for any pulse shape, laser intensity and pulse duration, in analytical form. Our theory also accounts for the dependence on the alignment of molecules.

We have completed two manuscripts on molecular tunneling ionization so far. The theoretical paper [#A1] which detailed the theory has been submitted for publication. In this paper we also calculated the ratio of the ionization yield of the molecule with its companion atom, as a function of the peak laser intensity. The molecular tunneling model results are compared to the experimental data from Bob Jones' group in Virginia. We found generally good agreement with their data.

The molecular tunneling model predicts that most molecules would show ionization suppression if its valence electron is a π orbital. This is the case for O_2. Since ionization suppression means a higher saturation intensity to ionize the molecule, this implies that the cutoff for the harmonic generation would be greater for the molecule than for its companion atom. This has been shown to be true by Z. H. Chang's group in their first experiment at the J. R. Macdonald Laboratory. Indeed the cutoff for O_2 was found to be much higher than for Xe, but N_2 and Ar have an essentially identical cutoff. A combined experimental and theoretical paper on this work has been submitted for publication [see #A2].

Future Plans

Our molecular tunneling ionization model also predicts the dependence of ionization rates on the alignment of molecules. In the coming year we will calculate the ionization yields for molecules that are aligned. It is well known that molecules exposed to a short pulse laser will be found partially aligned at each "revival" time. We will calculate the ionization rates of molecules in the short interval near the revival period which can be tested experimentally. We expect the dependence for O_2 and N_2 to be quite different.

Our tunneling model has been applied to molecules near the equilibrium internuclear distance so far. To understand the dissociation of molecules we need to obtain the ionization rates of molecules and molecular ions at all internuclear distances. We hope to extend the present tunneling model to all internuclear distances, to account for the so-called charge resonance enhancement effect in the tunneling model as well.

2. Hyperspherical approach to ion-atom collisions at low energies

Background

Ion-atom collisions at low energies are usually carried out using the close-coupling expansion with molecular orbitals. This is the so-called Perturbed Stationary State (pss) approximation. While the pss model is widely used, this "standard" approach has serious fundamental difficulties since the theory is not Galilean invariant. In the past few decades translational factors were introduced in an ad hoc manner to account for such a deficiency. The validity of such an approach is difficult to assess. It is well-known that the problems associated with the pss model can be avoided if the collision theory is formulated using hyperspherical coordinates. However, the hyperspherical approach has not been used for ion-atom collisions so far since one has to sum over thousands of partial waves to obtain a converged scattering cross section. However, in previous studies, we have shown that simplified calculations are possible.

Progress in the last year

In the last two years, we have developed the computer codes needed to perform close-coupling calculations for ion-atom collisions in hyperspherical coordinates. We formulated the theory in the body-frame of the quasi-molecule. To avoid calculating the nonadiabatic coupling terms directly we adopted the slow discretized variable approach. From the S-matrix the differential as well as total inelastic scattering cross sections can be extracted.

In the last months, we finally have all the programs developed and a first calculation has been carried out. We calculated the charge transfer cross sections for He^{++} on H from 500 eV down to about 10 eV in the center-of-mass frame. In this energy region, the cross section drops by a factor of about 10^6. We have found that our results differ significantly from calculations based on the molecular orbitals with translational factors. At higher energies the discrepancy becomes smaller. There are no experimental data available for comparison but our results at low energies agree with another calculation that uses expansion of the wavefunction in two sets of Jacobi coordinates. It is difficult to generalize the latter method to other systems.

Future plans

Our goal for this project is to provide benchmark results for simple ion-atom collision systems. We intend to explore the energy region from subdegree Kelvins up to about a few keV's where the semiclassical approach can be used. We expect to study basic systems such as H^++H for the excitation and charge transfer at low energies, electron capture of H by multiply charged ions where some experiments are available from the merged-beam experiments at ORNL. By treating atoms or ions using model potentials we expect to be able to study their collisions at low energies as well.

In the future, we can also extend the newly developed hyperspherical code for collisions involving atom and diatom, to test how well this package compares to other reactive scattering codes.

3. Classification of Intershell triply excited states of atoms

Background

In the previous years we have succeeded in classifying the $2l2l'2l''$ and $3l3l'3l''$ intrashell triply excited states of atoms. The states are classified in terms of the bending vibrational normal modes of an XY_3 molecule with X being the nucleus and Y the electron. These normal modes have been abbreviated as A, B and C and they are to distinguish the different modes of angular correlations.

Progress in the last year

In the last year we made an effort to classify the intershell triply excited states. Specifically our goal was to classify the 49 *2l2l'3l"* triply excited states. There are eight *2l2l'2l"* intrashell states, and thus only eight of the 49 states can be classified as radially excited from the *2l2l'2l"* intrashell states. The other 41 of them have to be classified separately.

For the *2l2l'3l"* intershell states, the first two electrons have the same principal quantum number so that the radial motion of these two electrons corresponds to "+", since the two-electron states would belong to intrashell doubly excited states. A new radial quantum number has to be added to describe the "+" or "-" of the radial motion of the third electron with respect to the first two. To incorporate such radial correlations, the states that have intrashell states as the first member of the Rydberg series are designated as A^{++}, B^{++} and C^{++}. For the others we would have A^{+-}, B^{+-} and C_s^{+-} and C_h^{+-}. Such states have been identified. There are only a few other states that are not easily classified. They belong to the high-energy states and are probably difficult to treat as similar to the rovibrational motion of a rigid body.

Future plans

Once we have classified the intershell triply excited states, we are not planning to pursue the more complicated higher states in view of the lack of any experimental work. Instead we plan to start looking into quadruply excited states. The calculations and the understanding of such a 4-electron system will be complicated and slow. On the other hand, there are intriguing questions to address. Since a 4-electron system can have two possible equilibrium configurations –a square with all the four electrons and the nucleus on a plane, or a tetrahedron where the four electrons occupy the corners with the nucleus at the center. What would happen to the other normal modes? For such an investigation we need to build up all the necessary programs so we can do some preliminary calculations. Exploratory calculations in the limited subspace are underway.

4. Ion-atom collisions

Progress in the last year

We undertook two projects involving ion-atom collisions last year. We have performed careful studies of the differential and integral charge transfer cross sections for Na^+ on the ground and the excited states of Rb. The experiment was carried out in ***Brett DePaola's*** group. We have been able to reproduce their experimental results quite well, except that the predicted oscillatory structures in the differential cross sections were not reproduced by the experiment due to the limited angular resolution. At the lowest energy point where the cross section is rather small, we noticed some discrepancies between the calculation and the experiment. We will use the hyperspherical quantum calculation (see #2) to look at the low-energy region in the future.

In the last year we also revisited the shakeoff theory. The motivation of this study is from an experiment carried out at Stockholm. In that experiment, they measured the ratio of a transfer ionization cross section to single electron capture cross section of He as a function of the proton collision energy. By determining the momentum of the recoil ion, they were able to show that for the so-called kinematic transfer ionization (KTI) process, this ratio is very similar to the ratio of double ionization to single ionization by high energy photons in He. Intuitively the similarity points out that both processes could be understood in terms of the shakeoff theory where the first electron is ejected with a different mechanism but the ejection of the second electron is the result of shakeoff. The shakeoff theory in the literature assumes that the first electron escapes with an infinite velocity, thus the inability to predict the energy dependence of the ratios mentioned. We have performed the correct shakeoff calculations using correlated He wavefunctions and confirmed that the experimental results are in good semiquantitative agreement with the shakeoff theory.

Publications including preprints (2000-2002)

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