"Physics of Correlated Studies"

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Overview

During the three year period of this grant, a major initiative was started to develop theoretical methods to treat complex open-shell atoms in a manner permitting a simple interpretation of the dynamics. This project has been far more successful than originally hoped, with accurate ground state photoionization cross sections calculated for nine different open-shell atoms in the periodic table. This work culminated in our first application to multichannel autoionizing spectra of a transition metal atom, scandium. These methods were also extended and adapted to permit a description of nonresonant two-photon processes at the perturbative level, and some nonperturbative multiphoton processes. The angular distribution of photoelectrons ejected in resonant multiphoton ionization of magnesium was also successfully calculated. We made headway toward understanding aspects of the diamagnetic quasi-Landau problem, specifically interpreting the observed simplicity of the spectrum when plotted simultaneously versus energy and field. High two-electron excitations of H^- and Li^- were treated using R-matrix methods, combined with a time delay analysis to quantitatively test various propensity rules proposed in the literature. These calculations also gave the first accurate description of H^- experiments at Los Alamos, up to the $n = 6$ threshold. A new set of computer programs were developed to handle double-Rydberg "planetary" states of barium and strontium, incorporating long range multipole interactions explicitly. Finally, we studied triply-excited states of H^{--} in an attempt to clarify the question of whether such resonances exist. Each of these projects is described in greater detail below.

Spectra of Heavy Open-Shell Atoms

One of the primary goals for this project was to develop and extend present theoretical methods for describing photoabsorption and scattering properties of complex atoms. The main tools used in this study were the eigenchannel R-matrix approach in LS -coupling, and multichannel quantum defect methods combined with a frame transformation to handle the most conspicuous spin-orbit effects. Starting largely from scratch, but building on the ideas that have proven to be successful recently in describing spectra of the alkaline earth atoms, postdoctoral research associate Francis Robicheaux wrote a new set of computer programs capable of handling arbitrarily complicated (in principle) open-shell atomic configurations. The first application¹ was to photoabsorption spectra of the outermost np -subshell of all the nonradioactive halogen atoms, F, Cl, Br, and I, in the energy range near the lowest ionization thresholds $ns^2np^4\ ^3P^e$, $^1D^e$, and $^1S^e$. This is an energy range which

had been studied extensively in previous experimental work (mainly by the Samson and Berkowitz groups) and theoretical work. One of the most dramatic experimental findings was Berkowitz' discovery that the autoionizing spectra of all these atoms show striking regularities, with the exception of F which differs qualitatively from the heavier halogens. Much like the rare gas spectra, a series of broad "sawtooth-shaped" md resonances appear in the heavy halogen spectra, along with narrower ms resonances. The only previous calculation of these resonances was the LS -coupled calculation of Kelly's group, which reproduced much of the Cl spectrum, at least qualitatively.

Robicheaux's calculations¹ were able to reproduce most of the complicated autoionizing spectra of these atoms to virtually spectroscopic accuracy. Moreover, study of the wavefunctions showed in detail how the strong overlap of the np and nd orbitals in the heavy halogens is responsible for the similarity in their spectra, and in particular for the dominance of the $p \rightarrow d$ excitations over $p \rightarrow s$. In contrast, for F the $2p$ has very poor spatial overlap with the $3d$ orbital, as expected from independent particle considerations, and the s and d resonances both tend to be narrow. The entire set of calculations for one atom required less than 3 hours on a Decstation 5000/200 desktop workstation, which includes R-matrix calculations for seven different final state symmetries (2S , 2P , 2D , 2F , 4P , 4D , 4F), the largest of which had about 700 many-electron basis functions. After a $jj-LS$ recoupling transformation and a further "intermediate-coupling" transformation (needed because the ionic states are not purely LS -coupled), the 15-channel MQDT calculations were then performed with up to 20,000 energy mesh points to describe the narrowest spectral features.

Another set of calculations² of the ns -subshell photoionization spectra for Cl and Br at higher energies (up to about 24 eV photon energy) gave the best quantitative theoretical interpretation available to date for recent extensive synchrotron measurements (by van der Meulen, Krause, Caldwell, and coworkers). The calculation successfully reproduced much of the observed complexity in partial photoionization cross sections and photoelectron angular distributions across a complex array of mutually perturbing autoionizing states. Doubly-excited resonances omitted from the calculation apparently caused most of the residual discrepancies between theory and experiment.

These computer programs were next used³ to calculate odd parity, $J = 0 - 3$ spectra of four atoms of the carbon group, namely C, Si, Ge, and Sn. These were chosen because there exist extensive experimental data from Ginter and coworkers which have not been previously treated by nearly *ab initio* calculations. The experimental spectra showed remarkable similarities in the dynamics of Ge, Sn, and Pb, but the degree of similarity with Si and C was difficult to ascertain. The new calculations, in addition to reproducing the photoabsorption spectra and bound level positions to generally good accuracy, showed the evolution of channel interactions from atom to atom. In particular, carbon has very small channel interactions, reflecting the inability of d-waves to penetrate the core. This was expected since all first row atoms have this same behavior. Silicon was somewhat surprising because the channel interactions are still generally small, although they are larger than in

carbon of course. (In contrast Cl, Br, and I all have very similar channel interactions.) Our calculations show that Ge and Sn have similarly strong s-d channel mixing, but the mixing is much weaker for Si. Part of the difference between Si and the heavier atoms of this group was traced to the different location in energy of the $nsnp^3$ perturbing levels for these atoms. One major result of this study was the discovery of an important limitation of the $LS - jj$ recoupling frame transformation for the heavier atoms. A fundamental ambiguity arises in how to apply the frame transformation in the presence of large ionic fine structure. For Ge this recoupling is adequate but for Sn it becomes quite inaccurate in some limited energy ranges. Accordingly no calculations were even attempted for Pb, as a better treatment of spin-orbit effects is clearly a prerequisite.

With numerous successful calculations now completed for open- p -subshell atoms, we have recently finished a set of calculations⁴⁻⁶ for a transition metal atom, scandium, having three electrons outside of closed subshells with a ground state configuration $4s^2 3d^2 D^e$. Nontrivial complications arise for scandium because the density of ionic thresholds is far greater than in any other atom we have studied to date. Fourteen relevant thresholds occur for the configurations $4s3d$, $3d^2$, and $4s^2$. Ground state photoabsorption near the lower ionic thresholds probes continuum states with p - and f -wave electrons attached to even parity ionic levels. The calculations were done for the short-range reaction matrices for 11 different LS -coupled symmetries, $2,4S^o$, $2,4P^o$, $2,4D^o$, $2,4F^o$, $2,4G^o$, $4H^o$. The calculation of all 11 LS -coupled reaction matrices at 200 energies required only 22 minutes on a Decstation 5000/200 workstation. After recoupling these LS -coupled matrices into jj -coupling, the quantum defect calculations of spectra were carried out on a fine mesh with roughly 10^5 points distributed over about $13,000 \text{ cm}^{-1}$ in energy. The calculated spectra show very substantial complexity, and they agree reasonably well with ground state photoabsorption plates measured by Garton and coworkers. Conspicuous discrepancies can occur near a perturbing level "attached" to a higher-lying threshold, even when the error in the calculated quantum defect of the perturber relative to that threshold is only 0.01 - 0.02. Such discrepancies are likely to plague any theoretical method in the immediate vicinity of such perturbers. Photoionization of the scandium excited state $(3d)^3 \text{ } ^2D_{3/2}$ was also predicted by the same calculations,⁶ and a subsequent measurement showed much better agreement with theoretical predictions than was observed for the ground state spectrum. This better agreement stems from the fact that this excited state spectrum predominantly probes final f -states, which are less susceptible to perturber interactions than the p -states for scandium. Another study⁷ has shown why the eigenchannel R-matrix method has advantageous convergence properties in comparison with conventional implementations of the Wigner-Eisenbud formulation of R-matrix theory.

Multiphoton Ionization Processes in Real Atoms

In a collaboration with Bo Gao, Robicheaux completed a novel and substantial adaptation of eigenchannel R-matrix and quantum defect methods to treat two-photon ionization of many-electron atoms. An initial report⁸ describing the basic approach treated atomic

aluminum over a wide frequency range. In a more detailed description of the method,⁹ additional new applications to magnesium and calcium were presented. The calcium spectrum shows how autoionizing states can enhance the two-photon ionization rate, in much the same way as bound states are known to behave. These calculations predict rich and complex resonance structures which have not yet been tested by experiment. Robicheaux and Gao have shown how these techniques can be extended to treat absorption of more than two photons, and also how to calculate "smooth" short range parameters which are suitable for applying a frame transformation. This should ultimately permit realistic calculations even for atoms as heavy as barium.

More recently, Robicheaux has predicted¹⁰ how an atomic spectrum excited by a weak probe laser near an ionic threshold can be affected nonperturbatively when that ionization rate is strongly coupled by an intense (preferably cw-) laser driving a transition to another ionic level. Qualitatively, the two ionic levels coupled by the strong laser can undergo Rabi oscillations. When these oscillations become comparable to the Rydberg electron period, the spectra become multichannel in nature, with Rydberg levels attached to the dressed-ionic states. The usual isolated-core approximation scheme can be successfully applied to give a nearly exact description of this nonperturbative photon-atom interaction. Detailed predictions were given for the spectrum of atomic magnesium, in the presence of a strong cw laser at the frequency of either the $3s - 3p_{1/2}$ or else the $3s - 3p_{3/2}$ ionic line. These predictions have not yet been confirmed by experiment, but such an experiment appears to be feasible.

Angular Distribution of Photoelectrons Ejected from Aligned Two-Electron Atoms

Since the early 1980's, a number of groups have explored the complicated photoelectron angular distributions which result from multistep photoabsorption up to an excited bound state in the alkaline earth atoms, followed by one-photon ionization of the excited state. Because more than one electric dipole photon is absorbed, the angular distribution involves spherical harmonics of rank higher than $P_2(\cos \theta)$. The early experiments were done in the groups of S. Smith, R. S. Berry, and others, and were restricted to primarily qualitative interpretations of the resulting differential cross sections. With the advent of successful eigenchannel R-matrix and quantum defect calculations of other alkaline earth atomic spectra, it is natural to investigate this more sensitive test to see if such calculations can describe such complicated angular distributions.

In collaboration with the experimental group of Tom Gallagher, we have performed such a study¹¹ for atomic magnesium, with the Virginia group carrying out all the experimental work. The experiments used two linearly-polarized laser excitation steps to reach a high-lying $3snd\ ^1D^e$ state of Mg, which was then photoionized by a third linearly-polarized laser whose frequency was scanned. All linear polarization axes were chosen to be parallel in this investigation, which simplifies the theoretical analysis since it leads to an angular

distribution of the form.

$$\frac{d\sigma}{d\Omega} = N \left(1 + \beta P_2(\cos \theta) + \gamma P_4(\cos \theta) + \epsilon P_6(\cos \theta) \right).$$

Here θ is the angle between the electron ejection axis and the common linear polarization axis, and N is a constant proportional to the total photoionization cross section of the excited $3snd$ state. Analysis of the differential cross sections determines the anisotropy parameters β, γ, ϵ which can in turn be computed using R-matrix and quantum defect methods as in previous work by the Gallagher group. The final results of this study¹¹ can be summarized as follows: (i) experiment and theory are in generally excellent agreement, although the agreement is somewhat poorer than for the total cross section (as expected since the angular distribution is sensitive to additional coherences and interferences); (ii) both experiment and theory have confirmed a "propensity rule", whereby one expects the photoelectrons to be ejected along the polarization vector since this is the direction of the force applied to the electron cloud. The propensity rule is followed for the most part, although at some energies the interferences conspire to eject the photoelectron sideways from the direction of the applied force, which is somewhat counterintuitive and in any case comparatively rare.

Few-Electron Correlations

A collaboration with H. Sadeghpour and M. Cavagnero extended R-matrix and quantum defect calculations to handle the true two-electron systems He and H^- . These are complicated by the accidental degeneracy of the hydrogenic thresholds, which can be treated using the methods of Gailitis and Damburg coupled with generalized quantum defect theory. The first results of this work were accurate calculations of H^- photodetachment spectra up to the $n = 4$ threshold.¹² More recently, He spectra have been calculated. This work confirmed propensity rules for excitation and decay of two-electron resonance states, which had emerged from qualitative considerations in hyperspherical and molecular coordinates and from group theoretical classifications. Specifically, they were found to be correct to about the 10% or 20% level.

Very highly excited double-Rydberg states of He, H^- , and of the alkaline earth atoms continue to pose stringent difficulties for theoretical descriptions. One of the new directions that has blossomed in the past year has been an extension of our R-matrix and quantum defect methodologies to handle such spectra for which much experimental information is available. In fact, one of the biggest limitations of the eigenchannel R-matrix calculations carried out in recent years has been the neglect of long-range multipole coupling terms beyond the R-matrix box radius. These are known to be important in many cases and have been incorporated in the calculations carried out by other groups. Accordingly we have eliminated this limitation within the past year in two independent approaches.

For neutral atoms, graduate student R. Wood and the PI have developed programs to directly solve the close-coupling equations without exchange in the external region, out

to distances sufficiently large that quantum defect theory can be used. These calculations now appear to give the first quantitative description¹³ of Sr doubly-excited levels up to the $\text{Sr}^+(6h)$ ionization threshold, measured by W. Sandner and coworkers. Similar calculations have accounted for Ba spectra near the $\text{Ba}^+ 8s$ and $5f$ ionization thresholds measured by the Orsay group of P. Camus. These new programs give far more power and should permit a description of a greatly enlarged class of problems.

For negative ions, a collaboration with A. Starace and Cheng Pan has demonstrated a need to improve upon the use of generalized quantum defect theory in the range beyond the R-matrix reaction volume. A new computer program directly solves the coupled equations inward from infinity to the reaction surface, where a matching procedure gives the physical observables. New calculations of Li^- and H^- photodetachment have been carried out up to the $n = 6$ thresholds, giving the first quantitative reproduction of Los Alamos experiments in that energy range.⁸ No experiments have yet been conducted in Li^- at the higher end of this energy range, but the calculations predict a remarkable qualitative similarity between Li^- and H^- from the $n = 4$ to $n = 6$ thresholds (and probably higher). In the coming months these exploratory calculations will be continued, a paper will be prepared¹⁴ on the initial findings, and extensions will be made to treat electron scattering from alkali atoms at high energies.

Finally, the techniques used to search for resonances of H^{--} continue to be refined. We expect that our preliminary findings will be reported in a publication within the year as part of the Ph.D. thesis work of R. Wood.

Atomic Hydrogen in a Strong Magnetic Field

A graduate student working on this project, Qiaoling Wang, successfully defended her Ph.D. thesis in August of 1991. Her work made substantial progress in understanding quantitatively the nature of the absorption spectrum at superstrong magnetic field strengths, not yet realizable in the laboratory ($B \geq 10^3$ Tesla). A first paper¹⁵ formulated the general features to be expected whenever the thresholds in a multichannel Rydberg spectrum vary as functions of a tunable parameter such as the magnetic field strength. This paper showed how many of the features observed by the Li diamagnetism experiments of Kleppner and coworkers must generally be present in such a parameter-dependent Rydberg spectrum. A second study¹⁶ presented detailed R-matrix calculations of photoionization spectra for hydrogen in fields ranging from 10^3T to 10^4T . These calculations showed how the spectrum becomes increasingly complicated as the magnetic field strength is decreased, leading to the formation of quasi-Landau-type resonances which can be viewed as "short-range" perturbations (i.e. short-range in their extent parallel to the field). A novel prediction of this work, which should be applicable even at laboratory-strength fields, is that the branching ratio for photoionization into the different available Landau channels should behave completely differently for final states with $m = 0$ and $m = 1$. In particular, if a low-lying s -state of a one-electron atom is photoionized with circularly polarized light along the field axis, the highest accessible Landau channels tend to be excited. Instead.

light polarized linearly along the field tends to excite the lowest available Landau channels. The cylindrical coordinate R-matrix treatment developed in this work becomes increasingly unstable at lower field strengths, and it is therefore not too promising for treating the 6T region. But independent work by O'Mahony and Watanabe has shown the usefulness of R-matrix and quantum defect methods applied to this problem, when combined with a frame transformation from spherical to cylindrical coordinates.

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