Ionization Cross Sections for Rydberg-Atom–Rydberg-Atom Collisions

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A classical-trajectory Monte Carlo method has been applied to collisions of two Rydberg atoms. Numerical calculations were made for velocities $v = 0.01v_e$ to $10v_e$, where the Rydberg electron's velocity $v_e(\text{a.u.}) = 1/n$ and n is the principal quantum number of the Rydberg atom. The total ionization cross sections scale as n^4 and show a $v^{-0.65}$ dependence at low v, a slight maximum around v_e, and a rapid decrease at high v. The cross sections are almost an order of magnitude larger than $\pi n^4 a_0^2$ at thermal energies.

Considerable experimental work has been performed recently on collisions between Rydberg atoms and ground-state atoms and molecules leading to excitation transfer,[1,2] ionization,[3] and negative-ion formation.[4] Correspondingly, theoretical work has been directed to "l-changing" collisions between Rydberg and ground-state atoms,[2,5-7] along with studies of ionization[8,9] and negative-ion formation.[10] An important class of collision processes that has not been investigated experimentally and has only been studied theoretically[11-13] at high velocities, $v \gtrsim v_e$, are Rydberg-atom–Rydberg-atom interactions. Cross sections for these interactions are extremely large and could limit the formation of high densities of Rydberg atoms requisite for some proposed ir laser applications[14] and could lead to spurious ion signals even at low Rydberg-atom densities. In this Letter, we employ a classical-trajectory Monte Carlo theoretical method to determine for the first time over a broad range the velocity dependence of the cross section for Rydberg-atom–Rydberg-atom collisions. The method is valid for collision energies ranging from thermal energies to tens of keV. The calculations also elucidate the different collision mechanisms responsible for ionization in the different velocity regimes and, in particular, indicate the importance at low velocities of electron-electron interactions lead to simultaneous electronic deexcitation of one atom and ionization of the other atom.

Interactions between two Rydberg atoms take place high in the continuum for autoionization where there are an almost infinite number of channels available for ionization and excitation transfer. This complexity makes it difficult to use a quantum-mechanical method to describe the scattering such as is used in Penning ionization problems,[15] but lends itself nicely to a classical analysis. Also, application of the first Born approximation at collision velocities $v \lesssim v_e$ [$v_e = 1/n$ a.u. $= 2.2 \times 10^8/n$ cm/sec] is not justified because it neglects the important electron exchange in the ionization process.

Because of the above constraints, we chose to apply a four-body classical-trajectory Monte Carlo method (CTMC) to the Rydberg-atom–Rydberg-atom scattering problem. Using this method, it is possible to follow trajectories that lead to elastic scattering and excitation transfer, autodetaching negative-ion states, and single- and double-electron-ionization collisions. In this Letter, we are specifically concerned with the collision processes that lead to positive-ion formation by any of the above-mentioned processes:

$$A^{**}(n) + A^{**}(n) \to A^{+} + \ldots, \tag{1}$$

when both Rydberg atoms are in the same principal quantum level n. We expect there to be only a slight dependence of the cross sections on the orbital angular momentum quantum number l when $l \ll n$.

Application of the three-dimensional, four-body CTMC requires for each trajectory the solution of a set of eighteen coupled first-order differential equations, which are Hamilton's equations of motion.[16] The CTMC method includes the Coulomb forces between all four bodies, the two electrons and two point charges for the nuclei, for which the angular scattering between two point charges is the same in both classical and quantum mechanical frameworks. A very important consideration is the classical description the electron distributions of the reactant Rydberg atoms. However, Abrines and Percival[17] have shown that it is possible to use Kepler's equation of planetary motion to represent hydrogenic atoms with a randomly determined set of initial conditions that are constrained to yield the binding energy of the atom. A microcanonical set of classical descriptions of the hydrogenic particle has been shown to yield the same momentum distribution for the electron as is found quantum mechanically.[17] Also, three-body CTMC calculations for charged-particle collisions with hydrogenic targets, where the target is represented in the same manner, have been found to yield very accurate cross sections.[18,19]

From the classical correspondence principle, we would expect the Rydberg-atom–Rydberg-atom ionization cross sections σ_{ion} to scale with the size of the atom $\pi n^4 a_0^2$ and the heavy-particle collision velocity v will scale with the orbital velocity of the Rydberg electron v_e. However, as a check, the calculations were performed for Rydberg atoms in $n=10$ and $n=20$ levels and also compared to the high-velocity H(1s) + H(1s) results presented previously.[11] Numerical stability and reproducibility were repeatly checked throughout the calculations. Extreme caution was necessitated by the large impact-parameter and collision ranges dictated by the large dimensions of the Rydberg atoms (for $n=20$ at $v=0.01v_e$, the maximum impact parameter was $2000a_0$ with integration required at $6000a_0$). An error in our previous calculations[11] was also detected which entailed the large difference between the positions of the center of mass of the Rydberg electron-nucleus system and that of the nucleus. The high-velocity $n=10$ and $n=20$ cross sections were recalculated and are a factor of 2 larger than given previously.

The calculated $n=10$ and $n=20$ ionization cross sections scaled by $\pi n^4 a_0^2$ versus scaled velocity v/v_e are presented in Fig. 1. At low velocities the cross sections behave as $\sim v^{-0.65}$ and for thermal energies extrapolate to approximately an order of magnitude larger than what is sometimes referred to as the geometric cross section ($\pi n^4 a_0^2$). A slight maximum in the cross sections is reached at $v \approx v_e$ with a magnitude of $\pi n^4 a_0^2$, while at high velocities, the cross sections decrease as $\sim v^{-1}$.

Analysis of the trajectories leading to positive-ion formation indicates that at high velocities, $v > v_e$, the mechanism is predominately impact ionization (i.e., close collisions of the electrons and nuclei) with double ionization (both electrons ejected) an important component at the highest velocities. At intermediate velocities, $v \approx v_e$, the impact ionization component is still important, but classical exchange or capture to form a transient negative ion must also be taken into account. The classical exchange maximizes when the collision velocity is comparable to the orbital velocities of the electrons, $v \approx v_e$, and gives rise to the slight maximum on the cross section. At low velocities, $v \ll v_e$, which reach into the thermal-energy regime, another collision mechanism dominates. This mechanism is electronic

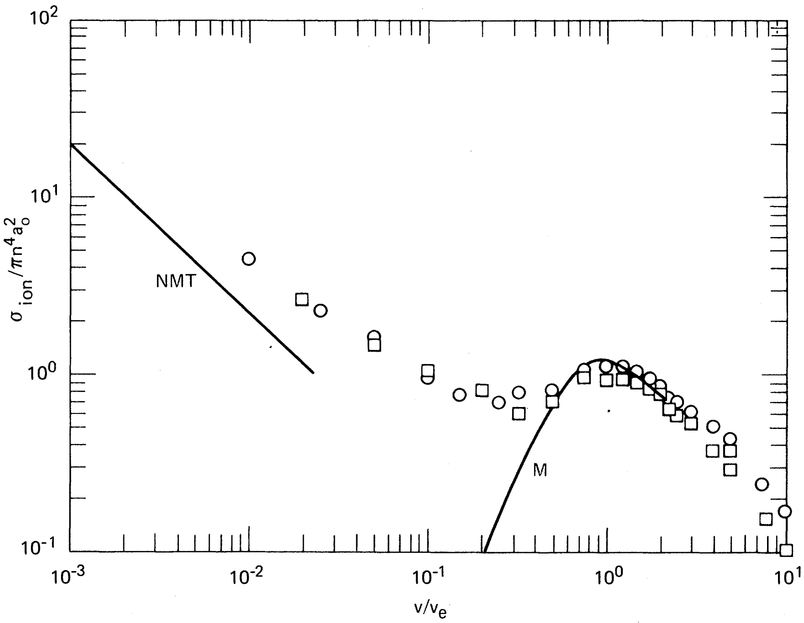

FIG. 1. Classical-trajectory Monte Carlo Rydberg-atom–Rydberg-atom ionization cross sections for $n=10$ (squares) and $n=20$ (circles) scaled as $\sigma_{\text{ion}}/\pi n^4 a_0^2$ and v/v_e. The H(1s) + H(1s) high-velocity measurements of the McClure (Ref. 20) and the He* ($n=2$) + He* ($n=2$) of Neynaber, Magnuson, and Tang (Ref. 21) are depicted by the lines.

deexcitation of one Rydberg atom with simultaneous transfer of the electronic energy to the ionization of the electron on the second Rydberg atom. In essence, the heavy nuclei are spectators to the ionization process. This long-range electron-electron interaction does not change the momenta of the heavy nuclei and results in "n-changing" cross sections for changing n to $n' \leqslant n/\sqrt{2}$ being very nearly equal to the ionization cross section. The low-velocity classical cross sections presented are, of course, expected to be valid only when there is almost a continuum of electronic states available in the $n/\sqrt{2}$ region. We should also note here that analysis of the total "n-changing" cross sections (for hydrogenic atoms) indicates these are approximately an order of magnitude larger than the ionization cross section since the transition $\Delta n = \pm 1$ and ± 2 are most easily realized.

It is possible to compare the CTMC cross sections to experimentally derived values. At high velocities we show in Fig. 1 the $H(1s) + H(1s)$ ionization cross sections of McClure.[20] Good agreement for $v \gtrsim 0.5\ v_e$ is obtained since the ionization mechanisms (impact and exchange) are well described by a classical model. However, at lower velocities the CTMC method greatly overestimates the cross section. The reason for the difference is that the $H(1s) + H(1s)$ system is extremely nonclassical and the electron-electron simultaneous deexcitation and ionization mechanism predicted by the classical model is not allowed because both electrons are already in their quantum ground states.

At low velocities, we have compared the calculations to the $He^*(n=2) + He^*(n=2)$ results of Neynaber, Magnuson, and Tang.[21] Although this system is not in a high Rydberg state, it does possess some of their characteristics; that is, there is a lower quantum level available for the electron-electron ionization mechanism. In order to plot the He* data on Fig. 1, we have used a hydrogenic model and have scaled the He* ionization energy to obtain an effective quantum number $n = (2I)^{-1/2} = 1.71$, where the ionization potential I chosen for the He* system corresponds to the 87% $He(2^3S)$ and 13% $He(2^1S)$ beam composition reported in Ref. 21. The experimental data are depicted by a line and display almost the same velocity dependence as predicted by the classical model. As expected, the magnitude of the experimental cross sections is less than the CTMC results since there is not a true continuum of product electronic levels available for the electron-electron ionization mechanisms.

An interesting comparison, moreover, is in the apparent agreement between theory and experiment in the low velocity $\sim v^{-0.65}$ dependence of the cross sections. Naively, we would expect the classical cross sections to be proportional to the time of the collision and behave as v^{-1}. However, a velocity dependence less than this is calculated which most probably indicates the particles avoid the strong electron-electron interactions necessary for ionization by inducing almost adiabtic changes at large internuclear separations during each collision event. This latter process, of course, gives rise to large "n-changing" cross sections for small changes in n, and we predict there will also be extremely large "l-changing" cross sections.

It is also of interest to note that according to the Langevin criterion,[22] a van der Waals interaction will yield a $E^{-1/3}$ or $v^{-2/3}$ cross section dependence for thermal energy collisions, almost identical to what is obtained in the exact classical calculations which assume only Coulomb interactions.

In conclusion, we have made an initial step toward understanding Rydberg-atom–Rydberg-atom interactions and have presented ionization cross sections over almost six orders of magnitude in collision energy. The four-body CTMC method appears to be especially well adapted to this problem, gives a physical insight into the collision processes, and should yield cross sections that are accurate to better than a factor of 2. Further investigations are planned which include mixed-n-value Rydberg collisions systems and the determination of "n-changing" and "l-changing" cross sections.

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Dielectronic Satellite Spectrum of Heliumlike Iron (Fe XXV)

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Dielectronic satellite spectra of Fe XXV near 1.8500 Å have been observed from PLT (Princeton Large Torus) tokamak plasma discharges for electron temperatures in the range from 1.5 to 3 keV and an electron density of 2×10^{13} cm^{-3}. The electron temperature was independently determined from the electron cyclotron radiation emitted by the plasma. The quality of the spectra allows a detailed comparison with theoretical predictions, which is of importance in view of diagnostic applications.

The spectra of heliumlike ions, which can be observed in stellar and laboratory plasmas, show, in addition to the characteristic helium lines, a series of satellites due to transitions of the type $1s^2nl$-$1s2pnl$ with $n \geqslant 2$. These lithiumlike configurations are almost entirely formed by dielectronic recombination, the inverse process of autoionization. Exceptions are the $1s^22s$-$1s2p2s$ satellites, which can also be produced by collisional inner-shell excitation.[1,2]

In addition to providing information on fundamental aspects of atomic physics, the spectra of heliumlike ions have important diagnostic applications. These include measurement of the electron temperature (T_e) and determination of the departure from ionization equilibrium with use of the intensity of appropriate satellites relative to the intensity of the heliumlike resonance line. In a recent experiment[3] the resonance line of Fe XXV has also been used for Doppler-broadening measurements to determine the ion temperature (T_i) in the hot central core of PLT (Princeton Large Torus) tokamak plasma discharges.

A theory of the satellite spectrum of heliumlike ions has been given by Gabriel[1] and Bhalla, Gabriel, and Presnyakov[2] who performed wavelength and intensity calculations for the well-resolved $n = 2$ satellites. In preparation for the Solar Maximum Mission orbiting flare study during 1979/1980, the theory of the satellite spectrum of Fe XXV has recently been improved to include dielectronic satellites with $n = 3-11$.[4] Most of these satellites fall into the narrow wavelength range of 1.8500 ± 0.0010 Å and cannot be resolved from the heliumlike resonance line. This leads to an apparent intensity increase of the resonance line, which must be taken into account for a correct evaluation of intensity ratios.

Experimental data on highly ionized high-atomic-number (Z) ions are rare because of the experimental difficulties of producing suitable high-temperature plasma sources. Spectra of the high-charge states of iron have been obtained from experiments on high-current sparks[5,6] and earlier observations of solar flares[7] from the Intercosmos IV satellite. The quality of these spectra is, however, insufficient for a detailed comparison with theory.