COMPREHENSIVE RATE COEFFICIENTS FOR ELECTRON-COLLISION-INDUCED TRANSITIONS IN HYDROGEN

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Received 2013 September 13; accepted 2013 October 17; published 2013 December 6

ABSTRACT

Energy-changing electron–hydrogen atom collisions are crucial to regulating the energy balance in astrophysical and laboratory plasmas and are relevant to the formation of stellar atmospheres, recombination in H I clouds, primordial recombination, three-body recombination, and heating in ultracold and fusion plasmas. Computational modeling of electron–hydrogen collision has been attempted through quantum mechanical scattering state-to-state calculations of transitions involving low-lying energy levels in hydrogen (with principal quantum number \( n < 7 \)) and at large principal quantum numbers using classical trajectory techniques. Analytical expressions are proposed that interpolate the current quantum mechanical and classical trajectory results for electron–hydrogen scattering in the entire range of energy levels for nearly the entire temperature range of interest in astrophysical environments. An asymptotic expression for the Born cross section is interpolated with a modified expression previously derived for electron–hydrogen scattering in the Rydberg regime using classical trajectory Monte Carlo simulations. The derived formula is compared to existing numerical data for transitions involving low principal quantum numbers, and the dependence of the deviations on temperature is discussed.

Key words: atomic processes – early universe – radio lines: general – stars: atmospheres

Online-only material: color figure

1. INTRODUCTION

Energy-changing electron–hydrogen atom collisions are relevant in several areas, for example, the formation of stellar atmospheres (Mashonkina 1996), radio emission in the recombination processes of H I clouds, the primordial cosmological recombination of hydrogen (Chluba et al. 2010), and plasma fusion physics (Janev & Reiter 2003). Although elastic scattering and excitation of low-lying atomic states in collisions of electrons with ground state hydrogen atoms have been extensively studied theoretically and experimentally (Janev & Reiter 2003), the literature for transitions among high-lying Rydberg states is scarce. Little direct experimental data is available for \( e^{-\rightarrow}H(n) \) collisional excitation and transition into Rydberg states (Roljes et al. 1993; Nagesha & MacAdam 2003). Therefore, for these processes one must rely mainly on theory and, due to the various approximation schemes, accuracy among the results within a factor of two is considered to be excellent (Przybilla & Butler 2004).

For electron-impact transitions of low Rydberg states \((n < 7)\), quantum mechanical methods, such as the \( R \)-matrix method (Anderson et al. 2002) and convergent close coupling (CCC; Bray et al. 1991), can be relied upon to produce reasonably accurate cross sections and rate coefficients. At the other end of the spectrum, for highly excited states near the ionization threshold, the Bohr correspondence principle allows statistical classical trajectory techniques (Mansbach & Keck 1969) to obtain precise rate constants for such collisions. However, in the intermediate \( n \) range, satisfactory models do not exist. Quantum mechanical calculations become exceedingly difficult as the size of the basis sets grows exponentially, and classical techniques obviously fail because they do not take into account quantum effects.

It is the aim of this work to provide expressions for the collision-induced rate coefficients that properly bridge this intermediate gap. To this end, we employ expressions for the rate coefficients from Pohl et al. (2008), developed for small-energy transfer (small Δ\( n \) transitions), low-temperature processes in ultracold laboratory plasmas, and analytically extend these expressions for application to high-temperature conditions, in agreement with quantum mechanical data for \( e^{-\rightarrow}H(n) \) energy-changing collisions. The new recommended expressions are globally accurate for electron impact transitions in hydrogen atoms, and for both small-energy and large-energy transfers.

Theoretical models based on classical mechanics have the advantage that the resulting collision cross sections and rates obey simple scaling laws. Therefore, based on the correspondence principle, their validity is expected to hold for states with a large principal quantum number, described by classical orbits that satisfy Bohr’s quantization condition. Early simple Thomson models with a frozen target were followed by applications of classical perturbation theory (Gryzinski 1959), impulse approximation (Gerjuoy 1966), and binary encounter (Flannery 1970). Statistical methods follow an ensemble of trajectories to provide exact classical results. Classical trajectory Monte Carlo (CTMC) simulations were introduced (Percival 1973) and applied to transition state theory (Mansbach & Keck 1969), and extensive results were obtained in Vrinceanu (2005) and Pohl et al. (2008). However, the classical approach is not expected to provide reliable results at low energies, close to the reaction threshold for excitation (although surprisingly good results can be obtained, as demonstrated in Wannier 1953), and it fails to reproduce the characteristic high-energy log\((E)/E\) behavior of the cross section, predicting instead a \(1/E\) behavior (Beigman & Lebedev 1995).

A rigorous quantum mechanical approach must include the Born approximation as a limiting case (Bethe 1930). Expressions can be derived for transitions between any Rydberg states by involving the atom inelastic form factor, which satisfactorily describes the impulsive part of the interaction.
Figure 1. Electron–hydrogen collision rate coefficients vs. temperature for low level transitions \( n_i \rightarrow n_f \) up to \( n_i = 5 \) and \( n_f = 7 \) as computed via Equation (7) are represented with the solid lines, by using the semi-empirical formulae proposed by Johnson (1972) are represented with the dashed lines, and by Beigman & Lebedev (1995) are represented with dash-dotted lines. Semi-classical results (Mansbach & Keck 1969) are represented by the dotted lines and the \( R \)-matrix calculations of Przybilla & Butler (2004) are marked by the disks.

(A color version of this figure is available in the online journal.)

of the electron projectile with the Rydberg atom. For the case of dipole (optically allowed) transitions, this approach correctly predicts the logarithmic asymptotic cross section at large energy. A Born approximation in the impact parameter representation (Seaton 1962) accurately describes the long range part of the interaction, but has issues preserving unitarity.
Table 1
Electron–Hydrogen Collision Rate Coefficients for Specified Transitions in cm$^3$ s$^{-1}$ at Temperatures up to 30,000 K, Calculated by the Present Formula (Upper Value) and by the $R$-matrix Method (Przybilla & Butler 2004; Lower Value)

| Transition | 0.25 | 0.5 | 0.75 | 1 | 1.5 | 2 | 2.5 | 3 |
|------------|------|-----|------|---|-----|---|-----|---|
| $1 \rightarrow 2$ | 3.14E-30 | 1.45E-19 | 6.37E-16 | 4.61E-14 | 3.73E-12 | 3.60E-11 | 1.45E-10 | 3.75E-10 |
| $1 \rightarrow 3$ | 1.75E-34 | 6.52E-22 | 1.23E-17 | 1.86E-15 | 3.14E-13 | 4.38E-12 | 2.20E-11 | 6.58E-11 |
| $1 \rightarrow 4$ | 4.26E-36 | 7.36E-23 | 2.33E-18 | 4.54E-16 | 9.90E-14 | 1.57E-12 | 8.53E-12 | 2.68E-11 |
| $1 \rightarrow 5$ | 6.59E-37 | 2.31E-23 | 9.29E-19 | 3.03E-16 | 5.01E-14 | 8.43E-13 | 4.74E-12 | 1.52E-11 |
| $1 \rightarrow 6$ | 2.19E-37 | 1.13E-23 | 5.17E-19 | 1.21E-15 | 2.51E-13 | 3.16E-12 | 1.03E-11 | 2.61E-11 |
| $1 \rightarrow 7$ | 1.48E-28 | 2.20E-18 | 9.04E-15 | 1.76E-13 | 3.57E-12 | 9.17E-11 | 4.08E-11 |

$T$ (10^4 K)
according to the formula

\[ R_{i\rightarrow f} = N_e \langle v \rangle \int_{\Delta E/kT}^{\infty} x e^{-x} Q_{i\rightarrow f}(x) \, dx, \]  

(1)

where \( N_e \) is the number density of electron gas with temperature \( T \) and average velocity \( \langle v \rangle = \sqrt{8 k_B T / \pi m} \). \( \Delta E \) is the difference in energy between the states \( j \) and \( f \), \( x = E/(k_B T) \) is the scaled energy of the electron projectile, and \( Q_{i\rightarrow f} \) is the scattering cross section. The last two factors in Equation (1) constitute the rate coefficient \( k_{ij} \), such that the rate is written simply as \( R_{i\rightarrow f} = N_e k_{ij} \). In the case of excitation, the cross section \( Q_{i\rightarrow f} \) is finite at the threshold because of dipole coupling between the degenerate states. For a high-energy projectile, the cross section is dominated by a logarithmic term that has the slowest decrease in the following asymptotic expansion (Bethe 1930; Przybilla \\& Butler 2004; Lower Value):

\[ Q_{i\rightarrow f}(E) = \frac{A}{E} \log \frac{E}{\Delta E} + \frac{B}{E} + \frac{C}{E^2} + \cdots. \]  

(2)

The origin of the slow logarithmic term is the optically allowed transition between states \( i \) and \( f \). When no optical transition
is allowed between states $i$ and $f$, then the cross section has the inverse energy $1/E$ decrease. Asymptotically, at high energies, the Born cross section (Equation (2)) is exact, and the coefficients $A$, $B$, and $C$ depend on the initial and final states.

Substituting the Born cross section (Equation (2)) into Equation (1), one obtains the Born rate coefficient that is dominated by the “quantum factor” $\Gamma(0, z)$, where $z = \Delta E/kT$, which may be expressed in terms of the incomplete gamma function

$$\Gamma(0, z) = \int_z^\infty \frac{e^{-x}}{x} \, dx.$$  

There are several other forms encountered in the literature for this integral, relating to the exponential integral functions $E_n(z)$ and $\text{Ei}(z)$. For small arguments, i.e., high temperatures, $T \to \infty$, the incomplete gamma has the expansion

$$\Gamma(0, z) = -\gamma - \log(z) + z + O(z^2),$$

where $\gamma$ is Euler’s constant. For large arguments $z$, the incomplete gamma can instead be approximated as

$$\Gamma(0, z) = \frac{e^{-z}}{z} + O(1/z^2).$$

CTMC calculations (Pohl et al. 2008) demonstrated that while previous rate coefficients obtained by Mansbach & Keck (1969) are correct for large-energy transfers, significant corrections, singular in $1/\Delta E$, have to be introduced for the proper description of collisions at small-energy transfer. For excitation collisions, the proposed formula is

$$k_{if} = k_0 \epsilon_f^{3/2} \left[ \frac{22}{(\epsilon_i + 0.9)^{7/3}} + \frac{9/2}{\epsilon_i^{5/2} \Delta \epsilon^{4/3}} \right] e^{\Delta \epsilon / \epsilon_i},$$

where $k_0 = e^4/(k_B T \sqrt{m R})$, and $\epsilon_i = R/(n_i^2 k_B T)$, $\epsilon_f = R/(n_f^2 k_B T)$, with $R$ the Rydberg constant, and $\Delta \epsilon = \epsilon_f - \epsilon_i = (E_f - E_i)/(k_B T)$.

It is clear that Equation (6) does not correctly describe the collision rates in the limit of high temperature, because it has a power-like $T^{-2}$ decay as opposed to the much slower decrease $\log(T)$ suggested by Equation (4). The Born-inspired “quantum factor” (Equation (3)) has to be incorporated into the classical formula (Equation (6)) in order to obtain a better representation for the collision rates over the whole range of temperatures. A simple way to accomplish this is to use Equation (5) to obtain the classical limit of the “quantum factor” (Equation (3)) as

$$(\epsilon_i - \epsilon_f) \Gamma(0, \epsilon_i - \epsilon_f) \to \exp(\epsilon_f - \epsilon_i).$$

This suggests that by replacing the exponential factor $\exp(\epsilon_f - \epsilon_i)$ in formula (6) with the “quantum factor” $\Delta \epsilon \Gamma(0, \Delta \epsilon)$, one obtains a formula that has the correct behavior at both low and high temperatures, and large quantum numbers $n$. The last stage is to extend the corrected formula to low quantum numbers. To this end, a simple fitting factor, which is in the range of unity uniformly across all of the parameters, can be found by direct comparison with the accurate $R$-matrix results obtained by Przybilla & Butler (2004) for transitions between low quantum numbers.

The resulting comprehensive expression can now be applied for small and large quantum numbers and over a wide range of temperatures:

$$k_{if} = k_0 \left( \frac{\epsilon_f}{\epsilon_i} \right)^{3/2} \left[ \frac{22}{(\epsilon_i + 0.9)^{7/3}} + \frac{9/2}{\epsilon_i^{5/2} \Delta \epsilon^{4/3}} \right] \times \left( \frac{3.5 + 0.18 \epsilon_f^{5/2}}{1 + 1/\epsilon_i^{5/2}} \right) \Delta \epsilon \Gamma(0, \Delta \epsilon).$$

The plots in Figure 1 and Tables 1 and 2 show the comparison of the proposed formula with the $R$-matrix calculation, allowing for a direct comparison with the tables present in Przybilla & Butler (2004). In the same graphs of Figure 1 are also shown Johnson’s fitting formula (Johnson 1972), together with the semi-empirical rates recommended by Beigman & Lebedev (1995), and the original rates by Mansbach & Keck (1969). Both the plots and tables show a progressive agreement with the $R$-matrix calculation of Przybilla & Butler (2004) at increasing $\Delta \epsilon$, which is already visible for $\Delta \epsilon = 2$. In the Rydberg limit of large $n_i, n_f$, the correction term to Equation (6), $(3.5 + 0.18 n_f^2)/[\epsilon_i^{7/2}(1 + 1/\epsilon_i^{5/2})]$ in Equation (7), becomes $\approx 0.18(n_f/n_i)^2 R/(k_B T)$, which, for lowest energy Rydberg transitions with $n_f \approx n_i$, becomes of the order of unity at temperatures $T \approx 0.18 R/k_B \approx 3 \times 10^4 \text{ K}$, i.e., in the middle of the temperature range of interest.

3. CONCLUSIONS

We have introduced a formula for electron–hydrogen collision rate coefficients that interpolates between ab-initio quantum mechanical results at low principal quantum numbers and classical Monte Carlo simulations in the Rydberg regime, and compared it with results available in the literature in the range of temperatures in which rate coefficients are believed to be accurate. Among the possible applications, stellar astrophysics and the precision study of cosmic background radiation in the Planck era are two areas that can benefit most from this discussion. The use of ab-initio data is of great relevance in stellar astrophysics because, unlike former attempts (Mihalas et al. 1975), it is possible to reproduce stellar spectra in both the optical and infrared range for a broad variety of temperatures. Also, in observational cosmology, the accuracy of collisional rates limits the precision of predicting the recombination spectrum at frequencies smaller than 1 GHz (Chluba et al. 2010), especially due to the rearrangement of the populations in each energy manifold due to angular-momentum-changing collisions (Pengelly & Seaton 1964; Vrinceanu et al. 2012).

D.V. is grateful to Texas Southern University High Performance Computing Center for making available the necessary computational resources, and to the National Science Foundation for the support received through a grant for the Center for Research on Complex Network at Texas Southern University (HRD-1137732). This work was also partially supported by the National Science Foundation through a grant for the Institute for Theoretical Atomic, Molecular, and Optical Physics at Harvard University, and the Smithsonian Astrophysical Laboratory.

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