Mg-H collision rates for non-LTE determination of stellar atmospheric parameters

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Abstract. Non-LTE (Local Thermodynamical Equilibrium) modeling implies competition between radiative and collisional processes. The influence of inelastic hydrogen atoms collisions, dominant in cold atmospheres has been and remains to be a significant source of uncertainty for stellar abundance analysis. In the particular case of Mg atoms, a large number of electronic states of the MgH molecule as well as the associated couplings that mix the states during the collision were calculated by high level quantum chemical methods and then used in full quantum scattering calculations. This allows to treat the excitation processes between the seven lowest atomic states of magnesium in collision with hydrogen atoms, as well as the ion-pair production and the mutual neutralization processes. The detailed mechanisms involved during the collision process have been analysed in detail. Our calculations show that the usual approximate Drawin formula leads to errors by factors up to $10^5$. As was already found in Li+H and Na+H collisions, excitation processes were found to be less important than charge transfer processes. However, unlike Li and Na, Mg has different spin terms, singlet and triplet, leading both to doublet molecular MgH electronic states. Collisional rates between spin-allowed and optically spin-forbidden atomic states are found to be of the same order of magnitude although optically spin-forbidden states are only collisionally coupled. Thus we may expect consequences on non-LTE calculations.

1. Context

Non-LTE modeling implies a competition between radiative and collisional processes. The radiative data are well known thanks to the Opacity and the Iron projects. The influence of inelastic hydrogen atom collisions dominant in cold atmospheres on non-LTE spectral line formation has been, and remains to be, a significant source of uncertainty for stellar abundance analyses, due to the difficulty in obtaining accurate data for such low-energy collisions, either experimentally or theoretically. For lack of a better alternative, the classical so-called Drawin formula is often used. Recent results on Li [1, 2] and Na [3, 4] in collisions with H atoms show that the Drawin formula may overestimate the cross sections by factors of one to five orders of magnitude. This implies new calculations of accurate cross sections and rates. We present
in the following results for Mg-H collisions. Mg is of particular interest as giving some of the strongest absorption lines in stellar spectra which are easily detected.

2. MgH interaction potentials, related couplings and cross sections

In the standard adiabatic approach, the theoretical treatment of atomic collisions requires two steps: (i) calculations of fixed-nuclei potential energies and non adiabatic radial and rotational couplings, (ii) an appropriate treatment of the nuclear motion based on the previous calculated molecular data leading to the wave function for the nuclear motion. This leads in the Jacobi coordinates system to the usual close-coupled equations. But, most of the non-adiabatic couplings are nonzero when the internuclear distance goes to infinity. This corresponds to the fact that the Jacobi system is not appropriate for the description of the collisions partners long before and after the collision. To remove this difficulty, Belyaev et al. [5] proposed a way to connect the R-matrix calculated at some $R_0$ internuclear distance from close coupled equations in the Jacobi coordinates system to the asymptotic S-matrix allowing the calculation of cross sections.

The first step concerns quantum chemistry and the main challenge is to build large basis sets adapted to the study of highly excited states. All the electronic states arising from Mg+H for energies up to Mg 3s3d $^1D$ (see figure 1, levels identified in blue) and later to Mg 3s3d $^3D$, Mg 3s4p $^1P$ and Mg 3s4p $^3P$ states (see figure 1, levels identified in red) were considered using large active spaces and basis sets [6, 9]. The energies and related couplings of $9 2^2\Sigma^+$, $5 2\Pi$, $2 2\Delta$, $2 4^2\Sigma^+$, $1 4\Pi$ were calculated using the version 2009.1 of the MOLPRO code [7]. The potential energy functions (PEFs) are represented on figure 2 as function of the internuclear distance. The more striking feature of these potentials is the presence of a series of avoided crossings among the $2^2\Sigma^+$ states due to a strong mixing with the Mg$^+$-H$^-$ ionic state. Those pseudo-crossings occur at larger and larger distances for the highest molecular states (see details in figure 3). This leads to possible ionisation of Mg atoms by collisions with H, ion pair production and to the reverse reaction, mutual neutralisation.

This perturbation due to the Mg$^+$-H$^-$ ionic configuration leads to large non-adiabatic radial coupling terms among consecutive states (see figure 4). Strong radial couplings occur at short internuclear distances as well as rotational coupling terms [6]. It was shown in Ref. [8] that radial couplings between the lowest-lying MgH($^2\Sigma^+$) states dominate over rotational couplings involving states of other symmetries, in particular the $^2\Pi$ states. States of the same symmetry are coupled via non-adiabatic radial couplings. The ionic Mg$^+$-H$^-$ configuration has $^2\Sigma^+$ symmetry.
Figure 2. Potential energy functions of the lowest doublet electronic states of the MgH molecule. Black curves: $^2\Sigma^+$, blue curves: $^c$ and red curves: $^2\Delta$.

leading to large non-adiabatic radial couplings among consecutive states (see figure 4) which represent the most important mechanism for transitions among low-lying states. We present in the following calculations involving eight $^2\Sigma^+$ states up to and including the ionic channel.

Figure 3. Zoom on the highest calculated potential energy functions

The cross sections for the excitation and ion-pair production processes (see figure 5) show large variations in amplitude for different transitions, from as large as 120 to as small as $10^{-6}$ A$^2$. We point out that cross sections for transitions between spin-allowed and spin-forbidden atomic states are of the same order of magnitude owing to relevant molecular mechanisms. The largest cross section is for ion-pair production from the Mg(3s4s $^1$S) state. The physics for the inelastic processes in the treated collisions was carefully studied and several mechanisms were found [9]. It is shown that some of the mechanisms are determined by interactions between adjacent molecular states due to interactions between ionic and covalent configurations. However, mechanisms at
short distances, not restricted to adjacent states, are found to be important. These mechanisms explain the relatively large cross sections for excitation of highly excited states.

3. Mg+H rate coefficients

3.1. Full quantum results

From the cross sections, one can obtain the corresponding thermal rate coefficients at temperature T by an average over a Maxwellian velocity distribution. Rate coefficients at 4000 K for excitation and de-excitation processes:

\[
\text{Mg}(3s \, n \ell \, 2S+1L) + \text{H}(1s) \rightleftharpoons \text{Mg}(3s \, n' \ell' \, 2S'+1L') + \text{H}(1s)
\]

and for the charge transfer processes, ion-pair production and mutual neutralisation:

\[
\text{Mg}(3s \, n \ell \, 2S+1L) + \text{H}(1s) \rightleftharpoons \text{Mg}^+ (3s \, 2S) + \text{H}^-
\]

are displayed in table 1. As expected, the rate coefficients follow the same trends as cross sections, i.e. large rate coefficients for ion-pair production/mutual neutralisation and large rates even for optically spin-forbidden transitions.

3.2. Comparison with Drawin approximate formula

The quantum rate coefficients for Mg+H are plotted (see figure 6) vs transition energy \( \Delta E \) and data obtained from the Drawin formula are displayed in figure 7. The Drawin formula is an extension of the classical formula for ionisation of atoms by electron impact [11]. This formula has only two parameters, \( \Delta E \) and the \( f \)-value of the atomic transition. The most remarkable aspect of the Drawin formula [4] results is that among the 21 excitation transitions considered, only 5 transitions are optically allowed and can be calculated with the Drawin formula. For the optically allowed transitions, the Drawin results are generally larger than the quantum results.
Table 1. Mg+H rate coefficients at 4000 K.

| Initial/Final states | 3s 1S | 3p 3P₀ | 3p 1P₀ | 4s 3S | 4s 1S | 3d 1D | ionic |
|----------------------|-------|--------|--------|-------|-------|-------|-------|
| 3s 1S | —     | 1.67 e-17 | 9.32 e-20 | 5.37 e-20 | 2.14 e-20 | 6.31 e-21 | 5.05 e-22 |
| 3p 3P₀ | 4.87 e-15 | —     | 2.76 e-13 | 7.95 e-14 | 2.07 e-14 | 4.35 e-15 | 1.47 e-16 |
| 3p 1P₀ | 1.05 e-14 | 1.07 e-10 | —     | 5.21 e-11 | 7.88 e-12 | 9.96 e-13 | 1.84 e-13 |
| 4s 3S | 5.26 e-14 | 2.67 e-10 | 4.52 e-10 | —     | 1.38 e-10 | 1.18 e-11 | 9.14 e-12 |
| 4s 1S | 1.46 e-13 | 4.83 e-10 | 4.75 e-10 | 9.56 e-10 | —     | 1.42 e-09 | 8.64 e-10 |
| 3d 1D | 2.23 e-14 | 5.28 e-11 | 3.12 e-11 | 4.28 e-11 | 7.41 e-10 | —     | 1.73 e-10 |
| ionic | 2.42 e-13 | 2.42 e-10 | 7.84 e-10 | 4.48 e-09 | 6.10 e-08 | 2.35 e-09 | —     |

by a few orders of magnitude [10]. The same trend was already found for Li [2] and Na [4] atoms in collision with H.

Figure 6. Rate coefficients at 6000 K in Mg+H collisions for excitation and ion-pair production processes plotted vs the transition energy ΔE: full quantum results.

Figure 7. rate coefficients at 6000 K in Mg+H collisions for excitation and ion-pair production, processes plotted vs the transition energy ΔE: Results from Drawin formula.

4. Concluding remarks
As found previously in calculations for Li and Na, collisional excitation rate coefficients are smaller than rate coefficients for charge transfer. A comparison with the results found for Li and Na show that Mg-rate coefficients for excitation from the ground to the first excited states are roughly an order of magnitude larger [10]. Moreover, contrarily to Li and Na atoms, Mg has two spin symmetries and large collisional rates are found between singlet and triplet states which are only weakly radiatively coupled. This fact, together with the high rates lead one to expect that H-collisional processes could be important for non-LTE modeling. However, other factors, in particular the physical conditions of the stellar atmosphere (effective temperature, gravity, metallicity), contribute to the modeling. So, presently, any conclusion must await for detailed non-LTE calculations.

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