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# H<sup>-</sup> photodetachment and radiative attachment for astrophysical applications

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#### Abstract

We combine *R*-matrix calculations, asymptotic relations, and comparison to available experimental data to construct an H<sup>-</sup> photodetachment cross section reliable over a large range of photon energies and take into account the series of auto-detaching shape and Feshbach resonances between 10.92 and 14.35 eV. The accuracy of the cross section is controlled by ensuring that it satisfies all known oscillator strength sum rules, including contributions from the resonances and single-photon double-electron photodetachment. From the resulting recommended cross section, spontaneous and stimulated radiative attachment rate coefficients are obtained. Photodetachment rates are also computed for the standard interstellar radiation field, in diffuse and dense interstellar clouds, for blackbody radiation, and for high redshift distortion photons in the recombination epoch. Implications are investigated for these astrophysical radiation fields and epochs.

Supplementary material for this article is available online

Keywords: photodetachment, radiative attachment, stimulated radiative attachment, early Universe, interstellar medium, autoionisation

(Some figures may appear in colour only in the online journal)

#### 1. Introduction

The hydrogen negative ion,  $H^-$ , has played an important role in both atomic physics and astrophysics for more than eight decades [1]. In the 1930s it was proposed as a source of continuum opacity in the Sun before its atomic structure was fully understood. Being the lightest and simplest three-body, two-electron system, it has since been studied by nearly all possible experimental and theoretical approaches. While its importance in astrophysics cannot be overstated (see sections 4–6), it has yet to be spectroscopically detected outside the laboratory [2]. The only bound–bound transition



 $\mathrm{H}^-$  is primarily created through the (spontaneous) radiative attachment process,

$$\mathbf{H} + e^- \to \mathbf{H}^- + \nu, \tag{1}$$

while in environments with sufficient numbers of photons with energies greater than  $\sim 0.75 \text{ eV}$ , it may be destroyed via the reverse process of photodetachment,

$$\mathrm{H}^{-} + \nu \to \mathrm{H} + e^{-}, \tag{2}$$

whereby a single electron is ejected through the absorption of a single photon. Astrophysical models today typically adopt a fit to the cross section calculations of Wishart [3, 4] for the



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latter process, while radiative attachment rate coefficients are obtained by detailed balance using the photodetachment cross section [5].

It is interesting to note in a recent publication, Keating and co-workers [6] compared and contrasted production of the positron radiative attachment rate coefficient for antihydrogen with that by electrons on hydrogen. It was found in that work, that only above about 30 000 K were differences seen in the corresponding rate coefficients. Therefore, understanding the dynamics of the H<sup>-</sup> system has important implications for a variety of applications.

Due to the role of these processes in hydrogen chemistry at high redshift and in metal-poor environments, we have revisited H<sup>-</sup> photodetachment. In the present study we combined accurate cross section calculations, asymptotic relations, and comparison to available experimental data to construct an H<sup>-</sup> photodetachment cross section reliable over a large range of photon energies, and take account of the series of auto-detaching shape and Feshbach resonances between 10.92 and 14.35 eV for applications in astrophysics. Further, the accuracy of the cross sections are improved by extending the unique approach of Yan et al [7] to ensure that the cross sections satisfy essentially exact oscillator strength sum rules. The layout of this paper is as follows. In section 2 we indicate how we obtained our cross sections. In section 3 we derive the sum rules. In section 4 the photodetachment rates are presented, while the corresponding radiative attachment rates are given in section 5. In section 6 we discuss astrophysical applications. Finally, in section 7 conclusions are drawn from our work.

#### 2. Photodetachment cross section

#### 2.1. New single photodetachment calculations

Photodetachment cross section calculations were performed in LS–coupling on the two-electron H<sup>-</sup> ion using the *R*-matrix methodology [8–11]. In the present work, we adopted two approaches: (i) the eigenchannel *R*-matrix method (SRM) [12] and (ii) the *R*-matrix plus pseudostates (RMPS) method [13]. In the eigenchannel approach, separate calculations were performed near each auto-detaching threshold for principal quantum numbers n = 2, 3, and 4, as well as for the background cross section below the n = 2 resonance region down to threshold. Reaction box sizes, number of initial states, and final states consisted of (25 a<sub>0</sub>, 158, 250); (35 a<sub>0</sub>, 300, 514), and (65 a<sub>0</sub>, 372, 646), respectively. See the work of Sadeghpour and co-workers [12] for further details on the eigenchannel method.

In the RMPS method a pseudo-state basis was used to allow for correlation effects and coupling to the continuum. An appropriate number of hydrogenic target states (60 levels) were included. A basis set consisting of n = 4 spectroscopic and  $\overline{n\ell} = \overline{5\ell} \dots \overline{14\ell}$ , correlation/pseudo orbitals of hydrogen was used to represent the target wavefunctions. The orbital angular momentum for the pseudo orbitals was  $\ell = 0, 1, 2, 3$ , and 4, thereby allowing  $\overline{ns}$ ,  $\overline{np}$ ,  $\overline{nd}$ ,  $\overline{nf}$  and  $\overline{ng}$  correlation orbitals (5  $\leq n \leq$  14) to be included in the close-coupling expansion. All of these hydrogenic orbitals were determined using the AUTOSTRUCTURE program [14]. The Thomas-Fermi–Amaldi scaling parameters  $\lambda_{\overline{n\ell}}$  used for the correlation orbitals,  $\overline{5\ell} \dots \overline{14\ell}$  were  $\lambda_{\overline{ns}} = 1.01$ ,  $\lambda_{\overline{np}} = 1.03$ ,  $\lambda_{\overline{nd}} = 1.09$ ,  $\lambda_{\overline{nf}} = 1.16$  and  $\lambda_{\overline{ng}} = 0.97$ . Double-electron promotions from specific base configuration sets were used to describe the  $(H + e^{-})$  scattering wavefunction in the RMPS calculations. An energy mesh size of 13.6  $\mu$ eV was required to resolve all the fine resonances in the photodetachment cross sections. For the electron affinity of atomic hydrogen we obtained an estimate of 0.750 787 eV from our RMPS calculations. This is in close agreement with the highly accurate calculations of Drake [15] who obtained a value of 0.754 204 eV and the acceptable experimental value of  $0.754\,195\pm0.000\,02\,\text{eV}$ from the Lineberger group [16, 17] and  $0.7539 \pm 0.002 \,\text{eV}$ from Feldman [18]. This is within 3.417 meV and 3.408 meV respectively of the best theoretical value of Drake [15] and the experimental determinations of the Lineberger group [16]. Finally, we note that Scott and co-workers [19] have showed recently that the intermediate energy R-matrix (IERM) results for single-photon, single-and-double ionization and detachment are in excellent agreement with our RMPS calculations on  $H^{-}$  [20] giving enhanced confidence in our theoretical data for astrophysical applications.

#### 2.2. Survey of previous single photodetachment calculations

The resonance structure of two-electron systems is an excellent testing ground for different computational methods [21, 22]. In 'Other Men's Flowers,' Bates [23] reviewed the history of H<sup>-</sup> photodetachment calculations using various approaches applied to this system up to 1978, from the early calculations to more modern methods [24] that accounted for resonance effects, using the J-matrix approach. Among the older and classical works we mention the truncated diagonalisation method [25] and the algebraic close-coupling approach [26]. The work of Wishart [3, 4] used a 1s, 2s, 2pclose-coupling approach with the addition of an extended  $\overline{2p}$ Hylleraas pseudo-orbital to calculate the background photodetachment cross section. We note the cross section data of Wishart [3] has been used in astrophysical applications, but unlike [4], lacks resonance features. Hylleraas type-functions for H<sup>-</sup> with an exchange approximation for the photoelectron in the final continuum states was also considered in the photodetachment cross section study by Bhatia and coworkers [27–29]. Recent textbooks [30] and reviews [31, 32] give extended accounts of the various theoretical methods that have been applied to this system which the reader should consult [27, 28, 33–37]. We point out that in recent years very accurate results have been obtained by a number of different theoretical approaches. Extensive *R*-matrix studies [33, 38] were performed using the standard SRM [11] and the IERM [11, 19] for the energies and widths of resonances for the  ${}^{1}S$ ,  ${}^{1}P^{o}$ ,  ${}^{1}D$ ,  ${}^{3}S$ ,  ${}^{3}P^{o}$  and  ${}^{3}D$  symmetries. The eigenchannel SRM was also used by Sadeghpour et al [12] and the hyperspherical close-coupling approach by Shimamura and coworkers [39] to obtain the photodetachment cross section.

The effect of Coulomb interaction screening on the photodetachment cross section below the n = 2 threshold using the *R*-matrix approach, but with a rather limited basis set (n = 1, n)2, ..., 5, physical states excluding the 5g and  $\overline{n} = 6$  pseudostates), has been investigated by Zhang and co-workers [40]. A non-variational configuration interaction procedure [36] has also been used to obtain the detachment cross section. While Brage and co-workers [41, 42] used the extended multi-configuration Hartee-Fock method [42-45] to treat autoionisation [46] with configuration interaction in a continuum approach [47, 48]. Exterior scaling complexcoordinate methods have also been applied to the problem [49-52]. Furthermore, a discretisation of the continuum method was used by Macias and co-workers [53, 54], the complex rotation method applied to Z-dependent perturbation theory [55] and B-splines [56] have also been used. Finally, a review by Rost and co-workers [57] on the theory of twoelectron atoms may also be consulted. In summary a variety of different theoretical methods have been used to obtain the photodetachment cross section.

Many of these calculations have focused on the autodetaching resonances near n = 2 and higher. A full discussion and comparison of resonance positions and widths is beyond the scope of this work. These have been tabulated in numerous publications including [4, 12, 24, 39, 58–61].

### 2.3. Survey of experimental single photodetachment cross section

Experiments at ASTRID by Balling and co-workers [62] measured photodetachment cross sections at extremely high resolution (40  $\mu$ eV) where they investigated the negative hydrogen ion by a spectroscopic approach in the region near the n = 2 threshold of the neutral hydrogen atom. The technique is based on Doppler-tuned spectroscopy using an H<sup>-</sup> beam in a ion storage ring collinearly overlapped with a fixedfrequency narrow-bandwidth vacuum ultraviolet (UV) laser beam (118 nm). The position of the Feshbach resonance was measured to be 10.9243(3) eV which is in good agreement with various elaborate theoretical predictions [12, 24, 50, 59-61] but deviates from the 10.9264(6) eV value previously reported in earlier experiments [63]. Resonances have previously been observed by Bryant and co-workers [63–67] in a series of experiments performed at LAMPF using an 800 MeV H<sup>-</sup> beam overlapped, over a variable angle, by a visible or UV laser beam. The experiments of Byrant and coworkers [63–67] have covered an impressive range of photon energies from below threshold to above the limit for twoelectron ejection (10.9-11.1, 13.4-14.6 eV). Further studies at ASTRID on the two lowest-lying members of the  ${}^{1}P^{o}$  dipole series of autodetaching resonances in H<sup>-</sup> located just below the H(n = 2) threshold were characterized utilizing Dopplertuned collinear laser spectroscopy by Anderson and coworkers [68]. Detailed comparisons were made with experiment in the calculations of Lindroth [61], where relativistic effects were found to be necessary. The resonance positions were determined for both H<sup>-</sup> and D<sup>-</sup>, allowing the first critical test of predicted isotope effects. Other measurements



**Figure 1.** Current H<sup>-</sup> photodetachment cross section (solid line, merged and scaled result) compared to a fit of the cross section of Wishart [3, 4] (dashed line). Inset: auto-detaching resonance region with  $H(n) + e^-$  series as indicated (current merged and scaled result).

include [69-72] where the latter provides detailed comparison to all prior theory and calculations from threshold to 2.4 eV.

#### 2.4. Initial merged single photodetachment cross section

In an effort to establish a highly accurate single photodetachment cross section, we have merged our two R-matrix cross sections with the existing computations in the literature [24, 73, 74], and the available experimental data. The resulting merged cross section is displayed in figure 1 for photon energies  $E_{\rm ph}$  up to the Lyman limit (13.6 eV), while figures 2, 3, and 4, cover from threshold to 3 eV, 9-20 eV, and 10-10 000 eV, respectively. In figure 1, comparison is made to a fit of the Wishart [3] cross section. As pointed out in our previous study on this system [5, 20], the simple fit to the calculations of Wishart [3] cannot reproduce the behavior of the cross section in the region of the auto-detaching resonances beyond  $\sim 8 \text{ eV}$ , though the actual cross sections in [4] do obtain the n = 2 resonances. Figures 2 and 3 show excellent agreement between the two current R-matrix calculations up to about 10 eV. In addition, the actual calculations of Wishart [3], not shown, would be indistinguishable from the current *R*-matrix calculations on the scale of figure 2. We note also in figure 2 the excellent consistency of all previous calculations and measurements, except the Kheifets and Bray [74] result at 2.8 eV and the recent measurement of Vandevraye *et al* [71] appear to be anomalies.

Figure 3 focusses on the auto-detaching resonance region. The two current *R*-matrix calculations show discrepancies above 10 eV, while the sparser results from Kheifets and Bray [74] are in excellent agreement with the RMPS calculations. The inset shows the n = 3-7 resonance



**Figure 2.**  $H^-$  photodetachment cross section comparison of some available experimental and theoretical results as indicated. The current *R*-matrix calculations (RMPS and eigenchannel) are shown to be in excellent agreement over this photon energy range. The adopted merged and scaled cross section is only slightly smaller.



**Figure 3.** Same as figure 2, but for photon energies 9–20 eV. Symbols are as indicated in figure 2. Inset: the auto-detaching resonance region for n = 3-7 with comparison to Tang and Shimamura [39] as indicated.

regions where we find good agreement with the calculations of Tang and Shimamura [39]. For  $E_{\rm ph} > 20 \,\text{eV}$ , figure 4 shows there is excellent agreement among all four sets of theoretical cross sections which merge smoothly with the high-energy limit obtained by Qiu and co-workers [73].

In summary, our merged cross section is based on the RMPS results for photon energies from 0.7678 to 50 eV and the calculations of Qiu *et al* [73] from 1000 to 100 000 eV. This is supplemented by a fit to the Wigner threshold law,  $460.8 \times (E_{\rm ph} - E_0)^{1.5}$  Mb below 0.7678 eV to the adopted threshold of  $E_0 = 0.754$  204 eV [15] guided by the *R*-matrix eigenchannel results and a fit from 50 to 1000 eV of the form 723 23  $\times E_{\rm ph}^{-3.307}$  Mb guided by the Broad and Reinhardt and



**Figure 4.** High energy H<sup>-</sup> photodetachment cross section for single-photon, single-electron and double-electron detachment. Single electron detachment: solid line (current *R*-matrix RMPS results), x [24], + [74], dotted line [73], and dashed line (current interpolation). Double-electron detachment: dot–dashed line, based on [74].

Kheifets and Bray calculations. Beyond 100 000 eV, the cross section is extended by a fit to the form  $E_{\rm ph}^{-7/2}$ .

#### 2.5. The double photodetachment cross section

Since  $H^-$  has two electrons, there is a significant probability that both can be ejected with the absorption of a single photon. This single-photon double-electron detachment process

$$H^- + \nu \to H^+ + e^- + e^-,$$
 (3)

has a threshold of 14.359 89 eV. While early calculations of the H<sup>-</sup> single-photon double-electron detachment cross section were performed by Broad and Reinhardt [24], we adopt the convergent close-coupling results of Kheifets and Bray [74] illustrated in figure 4, from 14.5 to 500.75 eV. Similar to the single-electron detachment cross section, the other portions of the double-electron detachment cross section are built from a fit to the Wannier relation from threshold to 14.5 eV, a fit through the Kheifits and Bray results from 600 to 1000 eV to the form  $E_{\rm ph}^{-7/2}$ , the results of Qiu *et al* [73] from 1000 to 100 000 eV, followed by a high-energy fit to the form  $E_{\rm ph}^{-7/2}$ . At all photon energies, it gives a cross section at least an order of magnitude smaller then single-electron photodetachment.

#### 3. Sum rules and cross section optimization

The accuracy of the photodetachment cross sections can be assessed and improved by comparing the continuum oscillator-strength moments, or sum rules S(k), to sum-rule values obtained explicitly from initial-state property calculations. Table 1 lists sum rules available in the literature and those adopted in the current work.

The sum rule in terms of continuum oscillator-strength moments is given by

$$S(k) = \int \frac{\mathrm{d}f}{\mathrm{d}E} (E_0 + E)^k \mathrm{d}E,\tag{4}$$

<i>S</i> (2)	<i>S</i> (1)	<i>S</i> (0)	S(-1)	S(-2)	S(-3)	Source	
1.378 75	1.01	2	$15\pm0.2$	$212\pm8$	$4000\pm320$	А	
1.378 554 924	0.747 507 731	2	14.968 515 61			В	
		1.999 95		206.165		С	
				206.147 618	3773.398 65	D	
1.378 554 924	0.747 507 731	2	14.968 515 61	206.147 618	3773.398 65	Adopted	

**Table 1.** Sum rules for  $H^-$  from initial state properties.

(A) Dalgarno and Ewart [75], and references therein.

(B) Drake formulae and data [15].

(C) Pipkin and Bishop [76].

(D) Bhatia and Drachman [27].

Table 2. Computed single photodetachment sum rules for H<sup>-</sup> in different photon energy bins from the current merged cross section.

Sum	$E_{ m ph}$ bin						
Rule	0.755–10 eV	10–15 eV	15–100 eV	0.1–10 keV	10–100 keV	0.1–10 MeV	Total
S(2)	0.035 652	0.066 043	0.454 418	0.561 024	0.079 136	0.033 475	1.229 749
<i>S</i> (1)	0.183 196	0.145 000	0.360 739	0.045 251	0.000 101	0.000 003	0.734 290
<i>S</i> (0)	1.307 583	0.322 251	0.364 904	0.006 951	0.000 000	$0.000\ 000$	2.001 689
S(-1)	13.845 728	0.724 814	0.437 720	0.001 319	0.000 000	0.000 000	15.009 581
S(-2)	204.946 70	1.649 380	0.584 627	0.000 276	0.000 000	0.000 000	207.180 98
S(-3)	3794.089 53	3.795 531	0.835 309	0.000 061	0.000 000	0.000 000	3798.720 43

Table 3. Computed sum-rule moments for H<sup>-</sup>.

Sum	Exact		Original				Adjusted	
Rule		Total	$\%\Delta^{a}$	Single	Double	Total	$\%\Delta^{a}$	
S(2)	1.378 554 924	1.281	-7.10	1.223	0.051	1.348	-2.26	
S(1)	0.747 507 731	0.762	1.89	0.734	0.027	0.778	4.09	
<i>S</i> (0)	2.0	2.027	1.34	2.002	0.025	2.044	2.19	
S(-1)	14.968 515 61	15.037	0.46	15.010	0.028	15.014	0.30	
S(-2)	206.157(16)	207.22	0.51	207.181	0.035	205.87	-0.14	
S(-3)	3773.398 65	3798.77	0.67	3798.720	0.046	3765.31	-0.21	

<sup>a</sup>  $\%\Delta$  is the percentage difference between the exact and the total.

where

$$\frac{\mathrm{d}f}{\mathrm{d}E} = \frac{m_e}{2\pi^2 e^2 \hbar} \sigma \tag{5}$$

is the differential oscillator strength for absorption into the continuum,  $\sigma$  the photodetachment cross section, E the ejected electron energy, and  $E_0$  the electron affinity of H<sup>-</sup> with  $E_{\rm ph} = E + E_0$ . The calculation of S(k) is simplified by the absence of discrete (i.e., bound-bound) transitions, but equation (4) does include contributions from the single-photon double-electron photodetachment process and autodetaching resonances.

Using equation (4) and the merged single photodetachment cross section described above, we computed the sum rules as given in table 2 where contributions from various photon energy bins are shown. For k < 0, the dominant contribution to S(k) is due to the single detachment cross section with  $E_{\rm ph} < 10$  eV. As k increases, the higher energy region of the single photodetachment cross section becomes more important, but except for S(2), contributions for  $E_{\rm ph} > 10 \text{ keV}$  are negligible. The resonance region (10–15 eV) is seen to be primarily important for S(1)followed by S(0), S(2), and then S(-1), but practically unimportant for S(-2) and S(-3).

In table 3, sum rule results are given for the total singlephoton single-electron detachment, double-electron detachment, and their summation (total). The single-photon double-electron detachment sum rules were obtained using the merged cross section described above, mostly based on [73, 74], and is seen to give the maximum contribution to S(2) at about 4% of the total. The total sum rule values from the merged cross section are compared to the exact values adopted from table 1. The maximum deviation of 7% occurs for S(2). The original merged cross section is then scaled to improve the agreement with the exact moments. Here we adopt the very pragmatic approach of



**Figure 5.** (a)  $H^-$  blackbody photodetachment rate as a function of radiation temperature  $T_r$  obtained with current merged and scaled cross section. (b) Current  $H^-$  rate compared to that of Galli and Palla [77].

multiplying the single-electron photodetachment cross section by a simple tilt function

$$\sigma_{\text{scaled}}(E_{\text{ph}}) = \sigma_{\text{original}}(E_{\text{ph}}) \times (E_{\text{ph}}/a)^b.$$
(6)

Taking  $a = 2.484 \times 10^{-4}$  and b = 0.012 reduces the maximum deviation to less than 4.1%, but more importantly the sum rules for k < 0, which are dominated by the low photon energy portion of the cross section and therefore of relevance to astrophysical applications, are significantly improved. The largest discrepancy occurs for those sum rules, S(1) and S(0), dominated by the resonance region. The final merged and scaled recommended single-electron photodetachment cross section is provided as supplementary data available online at stacks.iop.org/JPB/50/114001/mmedia, can be obtained from the authors' database website<sup>6</sup>, and is adopted below in calculations of astrophysically-relevant rates and rate coefficients.

#### 4. Photodetachment rates

Due to its small electron affinity,  $H^-$  is easily destroyed in environments with a significant radiative flux with photon energies larger than 0.75 eV. In our previous study on this complex [20], the merged  $H^-$  single-photon single-electron detachment cross section was used to study photodetachment rates, and the effect of the auto-detaching resonances, in cosmological environments focusing on radiative feedback effects. Here we compute photodetachment rates for a variety of environments. The photodetachment rate (in s<sup>-1</sup>) is given in terms of the photon energy  $E_{\rm ph}$  by

$$k = \int_{E_0}^{\infty} \frac{4\pi J(E_{\rm ph})}{E_{\rm ph}} \sigma(E_{\rm ph}) dE_{\rm ph},\tag{7}$$

where  $J(E_{\rm ph})$  is the mean radiation intensity.



**Figure 6.** H<sup>-</sup> blackbody (CBR) and distortion photodetechment rates in the recombination era of the early Universe as a function of redshift *z*. The distortion rate dominates the rate due to the CBR near the redshift that H<sub>2</sub> begins to form via H + H<sup>-</sup> associative detachment suppressing the H<sub>2</sub> abundance (see figure 10).

For a blackbody with radiation temperature  $T_r$ ,  $J(E_{ph}) = B(T_r, E_{ph})$ , where

$$B(T_{\rm r}, E_{\rm ph}) = \frac{2E_{\rm ph}^2}{h^2 c^2} \frac{1}{\exp(E_{\rm ph}/kT_{\rm r}) - 1}.$$
 (8)

The H<sup>-</sup> blackbody photodetachment rate using the single-photon single-electron merged cross section with equations (7) and (8) is displayed in figure 5(a) for ~400 <  $T_{\rm r}$  < 10<sup>8</sup> K. Figure 5(b) compares the current rate to the fit given by Galli and Palla [77]. The Galli and Palla [77] fit is based on the single-photon single-electron detachment cross section calculated by Wishart [3, 4] and is limited to the temperature range,  $700 < T_{\rm r} < 2 \times 10^4$  K. While there is good agreement between the two calculations, the behavior of the fit diverges from the current result above 10<sup>4</sup> K. In [20] we demonstrated that the auto-detaching resonances enhanced the photodetachment rate by at most 20% for  $T_{\rm r} > 100\ 000$  K, while below 25 000 K, the differences between the rates based on the merged cross section and those based on the fit to Wishart [3] was less than 10%.

In the recombination era of the early Universe, the cosmic background radiation (CBR) field is a perfect blackbody. However, an additional source of photons results from the radiative recombination to form H and He [78-81]. This socalled distortion field adds an additional component to the total radiation intensity. At relatively low redshifts z, the radiation intensity at high photon energies can exceed that of the CBR field. As a consequence, the distortion field can also contribute to the photo-destruction of primordial atoms and molecules. Adopting the distortion field radiation intensity from the H and He recombination models of Wong et al [78], we computed the photodetachment rate of H<sup>-</sup> due to the distortion field as shown in figure 6. For z < 100, the distortion-field photodetachment rate is seen to exceed that due to the CBR. Since  $T_r = 2.7(1 + z)$  K in the recombination era, the resonance enhancement to the blackbody rate is not visible on the scale of figure 6, as discussed above.

<sup>&</sup>lt;sup>6</sup> www.physast.uga.edu/amdbs

	Unatten. <sup>A</sup> $k_{pd}^{o}$ (s <sup>-1</sup> )	Dense cloud <sup>B</sup>		Diffuse Cloud <sup>B</sup>			
		$a(s^{-1})$	b	$a(s^{-1})$	b	с	
UMIST <sup>C</sup>	2.4(-7)	2.4(-7)	0.5	—	—	_	
Heays <sup>B</sup> Heays <sup>E</sup>	1.5(-7) 2.718(-8)	1.5(-7) 1.241(-8)	1.24 0.768	1.982(-8)	0.951	1.052	
Current	2.724(-8)	1.243(-8)	0.768	1.985(-8)	0.953	1.05	

**Table 4.** H<sup>-</sup> photodetachment rates in the ISM.

<sup>A</sup> ISRF of Draine [82].

<sup>B</sup> Assumes grain model of Draine and Lee [84], total-to-selective-extinction  $R_v = 3.1$ , and total visual extinction  $A_v^{\text{total}} = 1$  (diffuse cloud) and  $A_v^{\text{total}} = 20$  (dense cloud).

<sup>C</sup> [<mark>87</mark>].

<sup>D</sup> [86].

<sup>E</sup> Recomputed with the cross section from [85, 86].

In the interstellar medium (ISM) of the Galaxy, an intense UV field permeates the gas and dominates the destruction of atoms, ions, and molecules in diffuse gas. An average radiation field across the Galaxy has been constructed by a number of authors and here we adopt that of Draine [82]. This average interstellar radiation field (ISRF) falls off rapidly as the photon energy increases toward the Lyman limit and is taken to be zero for energies larger than the Lyman limit. This latter property is a result of efficient removal of ISRF photons via atomic hydrogen photoionization. For photon energies less than about 11 eV, the intensity of the ISRF is fairly uniform. Using the radiative transfer code of Roberge et al [83], we computed the so-called unattenuated  $H^-$  photodetachment rate for the ISRF as given in table 4. We also obtained attenuated rates into typical diffuse and dense interstellar clouds with total visual extinction of  $A_{\rm V}^{\rm total} = 1$ and  $A_{\rm v}^{\rm total} = 20$ , respectively. These were obtained with the Roberge et al [83] radiative transfer code assuming a planeparallel semi-infinite geometry and the grain model of Draine and Lee [84]. The attenuated rates are fit to the form

$$k_{\rm ISM} = a \exp(-bA_{\rm V} + cA_{\rm V}^2),\tag{9}$$

with the fit coefficients given in table 4 and the current photodetachment rate shown in figure 7. We find significant discrepancies with other calculations as shown in table 4, even when we adopt the  $H^-$  cross section from the tabulation of [85, 86].

#### 5. Radiative attachment rate coefficients

Using our single-photon single-electron detachment cross section, the rate coefficient for the reverse process, radiative attachment to form H<sup>-</sup>, reaction (1) can be readily obtained by detailed balance. The radiative attachment rate coefficient as a function of collision temperature  $T_c$  has been estimated previously by numerous authors [5, 28, 88–90]. In figure 8 we compare our current results with a representative sample from these previous studies. Excellent agreement is seen with the early calculations of Dalgarno and Kingston [88] and the recent work of Bhatia [90]. In the  $T_c \rightarrow 0$  limit, the rate coefficient is proportional to  $T_c$ , while as  $T_c \rightarrow \infty$ , the rate



**Figure 7.** H<sup>-</sup> ISRF photodetachment rate as a function of visual extinction  $A_V$  for a diffuse cloud ( $A_V^{\text{total}} = 1$ ).



**Figure 8.** H<sup>-</sup> radiative attachment rate coefficients as a function of collision temperature  $T_c$ . The current results shown are compared with previous values from Dalgarno and Kingston [88], Stancil and Dalgarno [5], the KIDA database [91] and Bhatia [90].



**Figure 9.** H<sup>-</sup> stimulated radiative attachment rate coefficients as a function of collision temperature  $T_c$ , for various radiation temperatures  $T_r$  over the range 0–100 000 K.

coefficient falls off as  $T_c^{-3/2}$ . The current results are also in excellent agreement with the radiative attachment rate coefficient computed by Stancil and Dalgarno [5] and adopted in the 2012 release of the UMIST database [87]. These rate coefficients were based on an earlier version of the *R*-matrix eigenchannel cross sections. Unfortunately, the Kinetic Database for Astrochemistry [91] still lists an inaccurate rate coefficient fit.

Previously, Stancil and Dalgarno [5] considered the enhancement of radiative formation processes due to stimulated emission in a blackbody radiation field. The rate coefficients for stimulated radiative attachment are plotted in figure 9 and are given in terms of the photodetachment cross section by

$$\alpha(T_{\rm c}, T_{\rm r}) = \frac{g_{-}}{g_{0}} \left(\frac{2}{c^{4}\pi}\right)^{1/2} \left(\frac{1}{m_{e}kT_{\rm c}}\right)^{3/2} \times \exp(E_{0} / kT_{\rm c}) \\ \times \int_{E_{0}}^{\infty} \frac{E_{\rm ph}^{2}\sigma(E_{\rm ph})\exp(-E_{\rm ph}/kT_{\rm c})}{1 - \exp(-E_{\rm ph}/kT_{\rm r})} dE_{\rm ph}.$$
 (10)

The radiative attachment rate coefficient is only significantly enhanced for radiation temperatures  $T_{\rm r} > 5000$  K when  $T_{\rm c} \lesssim 3 \times 10^5$  K. However, for such radiation temperatures, the photodetachment rate as shown in figure 5 is large.

#### 6. Astrophysical implications

#### 6.1. Solar and stellar opacity

The photodetachment of H<sup>-</sup> is well-known to be an important opacity source in a variety of cool stellar atmospheres including the Sun, hydrogen-rich white dwarfs, and M dwarfs [92–94]. Its peak over the  $\sim$ 1–2 eV (1.2  $\mu$ m to  $\sim$ 620 nm)



**Figure 10.** H<sup>-</sup>, H<sub>2</sub>, and HD abundances  $(n(x)/n_{\rm H})$  in the recombination era of the early Universe with modern cosmological parameters as given in [101]. Destruction of H<sup>-</sup> by the CBR field only (solid lines) and including distortion photon effects (dashed lines). Note the H<sub>2</sub> abundance has been divided by 10<sup>3</sup> to fit on the plot.

photon energy range is in a region relatively devoid of other continuum opacity sources, such as atoms, positive atomic ions, and molecules. Their continuum opacities occur generally in the near to far UV and are generally smooth functions of wavelength [95]. On the other hand, the  $H^- n = 2$  Feshbach (113.49 and 113.21 nm) and shape (112.99 nm) resonances, as well as the high *n* autodetaching resonances may give observable sharp absorption features, though they have not been included in stellar opacity calculations. However, the UV is crowded with atomic bound-bound absorption features, such as the 113.50 nm N I line, which may limit the UV absorption contribution of  $H^-$ .

#### 6.2. The early Universe

The role of  $H^-$  in the recombination era of the early Universe has been appreciated since the early study of Peebles and Dicke [96]. Once  $H^-$  is abundant, it participates in the formation of  $H_2$  via the associative detachment process,

$$\mathbf{H}^- + \mathbf{H} \to \mathbf{H}_2 + e^-. \tag{11}$$

The abundance of H<sup>-</sup> is primarily regulated by its radiative attachment and photodetachment processes studied here. The abundances of  $H^-$  and  $H_2$  are presented in figure 10 assuming the standard CBR field and photodetachment rates given in figure 5. The H<sup>-</sup> abundance rises dramatically for z < 200due to the drop in the CBR temperature, decreasing the effectiveness of the photodetachment of H<sup>-</sup>. This in turn enhances H<sub>2</sub> until it freezes out at a fractional abundance of  $\sim 10^{-6}$  at lower redshfits. As the radiation temperature is less than 1000 K, the effects of differences in the H<sup>-</sup> photodetachment rates based on the current cross sections and those of Wishart [3, 4], with or without the inclusion of resonances, are not discernible on the scale of the plot in figure 10. However, the inclusion of distortion photons due to H and He recombination (see figure 6) enhances H<sup>-</sup> photodetachment from  $z \sim 150$  to  $z \sim 40$ , which suppresses the H<sub>2</sub> abundance

by a factor of about two. As HD is primarily formed by the rearrangement reaction

$$D^+ + H_2 \rightarrow HD + H^+, \tag{12}$$

it tracks the  $H_2$  abundance and is also depressed due to  $H^-$  photodetachment due to distortion photons. While the  $D^-$  abundance tracts that of  $H^-$ ,  $D^-$  photodetachment due to distortion photons has a negligible effect on the HD abundance.

While the abundance of H<sup>-</sup> may be increased due to stimulated radiative attachment (see figure 9), the required radiation temperature ( $T_r$ ) is too large to be important in the early Universe. Nevertheless, both the incorporation of accurate H<sup>-</sup> cross sections and an accurate local radiation field are necessary for reliable early Universe chemistry simulations.

Glover [97] has recently studied how rate coefficient uncertainties effect simulations of the formation of massive seed black holes in the early Universe. He found that for collision temperatures above ~2000 K that there are significant variations in adopted radiative attachment rate coefficients which leads to 20%–30% uncertainty in predicted critical UV radiation field for suppressing H<sub>2</sub> formation. He also tested the effect of the auto-detaching resonances on the photodetachment rate, as discussed in Miyake *et al* [20]. Inclusion of the resonances results in about a 20% variation in the detachment rate, consistent with our findings in [20], though this is small compared to the large uncertainty in the UV spectrum of high redshift protogalaxies.

#### 6.3. ISM

In the general ISM, H<sup>-</sup> is expected to be present in environments where both atomic hydrogen and electrons are abundant, such as in planetary nebulae, circumstellar shells, and the surfaces of protoplanetary disks, all typically referred to as photodissociation regions (PDRs). In a PDR, an intense UV radiation source shines on a molecular cloud creating a highly ionized zone near the source, a so-called HII region. High-energy UV photons are removed from the radiation field by H photoionization as one moves away from the source and eventually, neutral H becomes abundant as the H recombination rate exceeds that of the H photoionization rate, though a residual electron fraction remains. This is referred to as an HI region. As one moves even further into the cloud, photons in the H<sub>2</sub> Lyman and Werner bands ( $\sim$ 11–13.6 eV) are removed so that molecular hydrogen becomes abundant, also reducing the fraction of atomic H. Yet further away from the source, photons which can destroy other less bound molecules are removed allowing for a rich chemistry known as the molecular region. The PDR resides between the HII and molecular regions [98]. H, H<sub>2</sub>, H<sup>+</sup>, and  $e^-$  are all expected to be relatively abundant in the PDR and once the radiation intensity below 11 eV becomes weak, H<sup>-</sup> should also be abundant. In early studies of planetary nebulae, Black [99] estimated the H<sup>-</sup> fractional abundance to be  $\sim 10^{-7}$ - $10^{-8}$ . This has motivated many searches [2], but to date H<sup>-</sup> has not been spectroscopically detected outside of the laboratory.

In typical ISM environments,  $H_2$  is formed by reactive processes on dust grains as opposed to reaction (11).

Nevertheless, Glover [100] has shown under conditions of low metallicity or high gas temperature,  $H^-$  gas-phase processes can be competitive or even dominate over gas-grain reactions.

#### 7. Conclusions

Using *R*-matrix calculations, asymptotic relations, and comparison to experimental data, an accurate photodetachment cross section was constructed by ensuring agreement between cross section moments and related oscillator strength sum rules. The resulting cross section was used to compute rate coefficients for radiative and stimulated attachment and photodetachment rates in a variety of astrophysical radiation fields. The accuracy of the new rate coefficients, and their underlying cross sections, will allow for reliable predictions of the abundance of H<sup>-</sup>, removing it as a possible source of error in astrochemical models. This is of particular importance given the high sensitivity, resolution, and angular resolving power of modern ground and space-based telescopes.

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#### References

[1] Stancil P C, Miyake S, Sadeghpour H R, McLaughlin B M and Forrey R C 2010 H<sup>-</sup> photodetachment in atomic physics and astrophysics *Proc. Dalgarno Celebratory Symp.* ed J F Babb *et al* (London: Imperial College Press) pp 102–16

- [2] Ross T, Baker E J, Snow T P, Destree J D, Rachford B L, Drosback M M and Jensen A G 2008 Astrophys. J. 684 358
- [3] Wishart A W 1979 Mon. Not. R. Astron. Soc. 187 59
- [4] Wishart A W 1979 J. Phys. B: At Mol. Phys. 12 3511
- [5] Stancil P C and Dalgarno A 1998 Faraday Discuss. 109 61
  [6] Keating C M, Pak K Y and Straton J C 2016 J. Phys. B: At.
- *Mol. Opt. Phys.* **49** 074002 [7] Yan M, Sadeghpour H R and Dalgarno A 1998 *Astrophys. J.* **496** 1044
- [8] Burke P G and Berrington K A 1993 Atomic and Molecular Processes: An R-matrix Approach (Bristol: IOP Publishing)
- [9] Berrington K A, Eissner W and Norrington P H 1995 Comput. Phys. Commun. 92 290
- [10] Robicheaux F, Gorczyca T W, Griffin D C, Pindzola M S and Badnell N R 1995 Phys. Rev. A 52 1319
- [11] Burke P G 2011 *R-Matrix Theory of Atomic Collisions: Application to Atomic, Molecular and Optical Processes* (New York: Springer)
- [12] Sadeghpour H R, Greene C H and Cavagnero M 1992 *Phys. Rev.* A 45 1587
- [13] Mitnik D M, Pindzola M S, Griffin D C and Badnell N R 1999 J. Phys. B: At. Mol. Opt. Phys. 32 L479
- [14] Badnell N R 1986 J. Phys. B: At Mol. Phys. 19 1541
- [15] Drake G W F 1995 High precision calculations for helium Handbook of Atomic Molecular and Optical Physics ed G W F Drake (Heidelberg: Springer) pp 199–219
- [16] Lykke K R, Murray K K and Lineberger W C 1991 Phys. Rev. A 43 6104
- [17] Andersen T, Haugen H K and Hotop H 1999 J. Phys. Chem. Ref. Data 28 1511
- [18] Feldman D 1975 Phys. Lett. A 53 82
- [19] Scott M P, Kinnen A J and McIntrye M W 2012 Phys. Rev. A 86 032707
- [20] Miyake S, Stancil P C, Sadeghpour H R, Dalgarno A, McLaughlin B M and Forrey R C 2010 Astrophys. J. Lett. 709 L168
- [21] Scully S W J et al 2006 J. Phys. B: At. Mol. Opt. Phys. 39 3957
- [22] McLaughlin B M 2013 J. Phys. B: At. Mol. Opt. Phys. 46 075204
- [23] Bates D R 1978 Phys. Rep. 35 305
- [24] Broad J T and Reinhardt W P 1976 Phys. Rev. A 14 2159
- [25] Lipsky L and Conneely M J 1976 Phys. Rev. A 14 2193
- [26] Seiler G J, Obemi R S and Callaway J 1971 Phys. Rev. A 3 2006
- [27] Bhatia A K and Drachman R J 1994 J. Phys. B: At. Mol. Opt. Phys. 27 1299
- [28] Bhatia A K 2006 Phys. Rev. A 73 012705
- [29] Bhatia A K and Drachman R J 2015 Phys. Rev. A 91 012702
- [30] Fano U and Rau A R P 1986 *Atomic Collision Spectra* (London: Academic)
- [31] Starace A F 1993 *Handbuch der Physik* ed S Flugge and W Mehlhorn vol 13 (New York: Springer)
- [32] Greene C H 1988 Variational calculation of channel interaction parameters *Fundamental Processes of Atomic Dynamics* ed J S Briggs *et al* (New York: Plenum) pp 105–28
- [33] Pathak A, Kingston A E and Berrington K A 1988 J. Phys B: At. Mol. Opt. Phys. 21 2939
- [34] Hamacher P and Hinze J 1989 J. Phys B: At. Mol. Opt. Phys. 22 3397
- [35] Froese Fischer C and Idrees M 1990 J. Phys. B: At. Mol. Opt. Phys. 23 619
- [36] Chang T N and Tang X 1991 Phys. Rev. A 44 232
- [37] van der Hart H and Hansen J E 1992 J. Phys. B: At. Mol. Opt. Phys. 25 41
  [38] Scholz T, Scott P and Burke P G 1988 J. Phys. B: At. Mol.
- Opt. Phys. 21 L139
- [39] Tang J and Shimamura I 1995 Phys. Rev. A 51 R1738

- [40] Zang S B, Wang J G, Janev R K, Qu Y Z and Chen X J 2010 *Phys. Rev.* A 81 065402
- [41] Brage T, Froescher Fischer C and Miecznk G 1992 J. Phys. B: At. Mol. Opt. Phys. 25 5289
- [42] Brage T, Froescher Fischer C and Vaeck N 1993 J. Phys. B: At. Mol. Opt. Phys. 26 621
- [43] Froese Fischer C 1977 The Hartree–Fock Method for Atoms: A Numerical Approach (New York: Wiley)
- [44] Froese Fischer C 1991 Comput. Phys. Commun. 64 369
- [45] Froese Fischer C 1992 Non-variational multiconfiguration Hartree–Fock calculations for continuum wave functions Many-Body Theory of Atomic Structure and Photoionization ed T N Chang (Singapore: World Scientific) pp 143–74
- [46] Froese Fischer C and Brage T 1993 Comput. Phys. Commun. 74 381
- [47] Fano U 1961 Phys. Rev. 124 1866
- [48] Nicolaides C A 1972 Phys. Rev. A 6 2078
- [49] Ho Y K 1981 Phys. Rev. A 25 2137
- [50] Ho Y K 1991 Chin. J. Phys. 29 327
- [51] Kuan W H, Jiang T F and Chung K T 1999 Phys. Rev. A 60 364
- [52] Sabyasachi K and Ho Y K 2009 J. Phys. B: At. Mol. Opt. Phys. 42 185005
- [53] Macias A and Riera A 1986 Phys. Rev. Lett. 119 28
- [54] Macias A, Martin F, Riera A and Yanez M 1987 Phys. Rev. A 36 4187
- [55] Manning L W and Sanders F C 1991 Phys. Rev. A 44 7206
- [56] Venuti M and Decleva P 1997 J. Phys. B: At. Mol. Opt. Phys. 30 4839
- [57] Tanner G, Richter K and Rost J M 2000 Rev. Mod. Phys. 72 497
- [58] Ajmera M P and Ching K T 1975 Phys. Rev. A 12 475
- [59] Tang J et al 1994 Phys. Rev. A 49 1021
- [60] Lindroth E 1995 Phys. Rev. A 57 2737
- [61] Lindroth E, Bürgers A and Brandefelt N 1998 Phys. Rev. A 52 R685
- [62] Balling P, Kristensen P, Andersen H H, Pedersen U V, Petrunin V V, Prastegaard L, Haugen H K and Andersen T 1996 Phys. Rev. Lett. 77 2906
- [63] MacArthur D W et al 1985 Phys. Rev. A 32 1921
- [64] Bryant H C et al 1977 Phys. Rev. Lett. 38 228
- [65] Bryant H C et al 1983 Phys. Rev. Lett. 27 2889
- [66] Harris P G et al 1990 Phys. Rev. A 42 6443
- [67] Halka M et al 1991 Phys. Rev. A 44 6127
- [68] Andersen H H, Balling P, Kristensen P, Pedersen U V, Aseyev S A, Petrunin V V and Andersen T 1997 *Phys. Rev. Lett.* **79** 4770
- [69] Smith S J and Burch D S 1959 Phys. Rev. 116 1125
- [70] Popp H-P and Kruse S 1976 J. Quant. Spectrosc. Radiat. Transfer 16 683
- [71] Vandevraye M, Babilottee P, Drag C and Blondel C 2014 Phys. Rev. A 90 013411
- [72] Génévriez M and Urbain X 2015 Phys. Rev. A 91 033403
- [73] Qiu Y, Tang J, Burgdörfer J and Wang J 1997 J. Phys. B: At. Mol. Opt. Phys. 30 L689
- [74] Kheifets A S and Bray I 1998 Phys. Rev. A 58 4501
- [75] Dalgarno A and Ewart R W 1962 Proc. Phys. Soc. 80 616
- [76] Pipin J and Bishop D M 1992 J. Phys. B: At. Mol. Opt. Phys. 25 17
- [77] Galli D and Palla F 1998 Astron. Astrophys. 335 403
- [78] Wong W Y, Seager S and Scott D 2006 Mon. Not. R. Astron. Soc. 367 1666
- [79] Chluba J and Sunyaev R A 2006 Astron. Astrophys. 458 L29
- [80] Rubiño-Martín J A, Chluba J and Sunyaev R A 2006 Mon. Not. R. Astron. Soc. 371 1939
- [81] Rubiño-Martín J A, Chluba J and Sunyaev R A 2008 Astron. Astrophys. 485 377
- [82] Draine B T 1978 Astrophys. J. Suppl. 36 595

- [83] Roberge W G, Jones D, Lepp S and Dalgarno A 1991 Astrophys. J. Suppl. 77 287
- [84] Draine B T and Lee H M 1984 Astrophys. J. 285 89
- [85] van Dishoeck E F 1988 *Rate Coefficients in Astrochemistry* (Dordrecht: Kluwer)
- [86] Heays A N, Bosman A D and van Dishoeck E F 2017 Astron. Astrophys. accepted (https://doi.org/10.1051/0004-6361/ 201628742)
- [87] McElroy D, Walsh C, Markwich A J, Cordiner M A, Smith K and Millar T J 2013 Astron. Astrophys. 550 A36
- [88] Dalgarno A and Kingston A E 1963 *Observatory* 83 39[89] Le Teuff Y H, Millar T J and Markwick A J 2000 *Astron.*
- Astrophys. Suppl. Ser. **146** 157
- [90] Bhatia A K 2013 Phys. Rev. A 87 042705

- [91] Wakelam V et al 2012 Astrophys. J. Suppl. 199 21
- [92] Wildt R 1939 Astrophys. J. 90 611
- [93] Stancil P C 1994 Astrophys. J. **430** 360
- [94] Del la Luz V 2016 Astrophys. J. 825 138
- [95] Fontenla J M, Stancil P C and Landi E 2015 Astrophys. J. 809 157
- [96] Peebles P J E and Dicke R H 1968 Astrophys. J. 154 891
- [97] Glover S C O 2015 Mon. Not. R. Astron. Soc. 453 2901
- [98] Hollenbach D J and Tielens A G G M 1999 Rev. Mod. Phys. 71 173
- [99] Black J H 1978 Astrophys. J. 222 125
- [100] Glover S C O 2007 Mon. Not. R. Astron. Soc. 379 1352
- [101] Gay C D, Stancil P C, Lepp S and Dalgarno A 2011 Astrophys. J. 735 44