

Class 7 Notes: Ionisation and recombination I

In this class we will discuss the processes that ionise interstellar and intergalactic gas, and the processes that allow it to recombine. In the next class we will use this information to calculate the mean ionisation state of gas. Our goal at the end of this to be able to understand the ionisation state of the various phases of the ISM.

I. Ionisation balance in LTE

As a prelude to examining the individual processes that drive ionisation and recombination, it is useful to ask what we expect the ionisation states of atoms to be in gas that it is local thermodynamic equilibrium (LTE). The vast majority of the ISM will not in LTE, but the LTE case gives us a baseline that provides some intuition, and also provides a limit that we will use below to derive some useful results in analogy with the way we have deduced the relationship between forward and backward collision rates and between different Einstein coefficients by considering what must happen in LTE.

The basis for our LTE calculation is the Boltzmann distribution, which requires that if we have two energy states u and ℓ , the number densities of particles in those two states obeys

$$\frac{n_u}{n_\ell} = \frac{g_u}{g_\ell} e^{-E_{u\ell}/k_B T}. \quad (1)$$

If we now regard the lower state as an atom of some species X that has been ionised i times (so $i = 0$ corresponds to the atom being neutral), and the upper state as a member of the species that has been ionised $i + 1$ times, then we have

$$\frac{n_{i+1}}{n_i} = \frac{g_{i+1} g_e}{g_i} e^{-I/k_B T}, \quad (2)$$

where I is the ionisation potential for going from X^{i+} to $X^{(i+1)+}$.

Note an important subtlety here in the degeneracy factors: in the denominator we have g_i , the degeneracy of the lower ionisation state. In the numerator, however, we have to include the total possible number of states of the ionised system, and this includes not just the degeneracy g_{i+1} of the upper ionisation state, it includes the product of this and the number of possible states of the free electron g_e – after all, the electron is part of the “upper state”, so we need to include its statistical weight as well.

So what is the statistical weight of the free electron? The general answer to this is the partition function: the the sum of the Boltzmann factors for all available states. Since the electron is a free particle, we can compute the available states using the classic particle in a box problem: we say that each electron has a volume available to it $V_e = 1/n_e$, where n_e is the number density of free electrons, and a particle in a box of this volume has three quantum numbers (n_x, n_y, n_z) , with the energy of any particular

state given by

$$E = \frac{h^2}{8m_e l_e^2} (n_x^2 + n_y^2 + n_z^2), \quad (3)$$

where $l_e = V_e^{1/3} = n_e^{-1/3}$ is the length of the “box” the electron is confined to. Since the electron is a spin 1/2 particle, there are two distinct spin states for each combination of (n_x, n_y, n_z) . Thus the statistical weight of the electron is

$$g_e = 2 \sum_{n_x} \sum_{n_y} \sum_{n_z} e^{-E/k_B T} \quad (4)$$

$$= 2 \sum_{n_x} \sum_{n_y} \sum_{n_z} \exp \left[-\frac{h^2 n_e^{2/3}}{8m_e k_B T} (n_x^2 + n_y^2 + n_z^2) \right] \quad (5)$$

$$= 2 \left[\sum_n \exp \left(-\frac{h^2 n_e^{2/3} n^2}{8m_e k_B T} \right) \right]^3 \quad (6)$$

$$\approx 2 \left[\int_0^\infty \exp \left(-\frac{h^2 n_e^{2/3} n^2}{8m_e k_B T} \right) dn \right]^3 \quad (7)$$

$$= 2 \frac{(2\pi m_e k_B T)^{3/2}}{n_e h^3}. \quad (8)$$

In the second step we used the fact that the sums over n_x , n_y , and n_z are all the same to rewrite the expression as the cube of a single sum over n , and in the third step, we assumed that we are in the classical limit whereby n_e is small (to be precise, n_e is much less than the quantum concentration) and therefore we can approximate the infinite sum by an integral.

Plugging this in, we arrive at our expression for the ratio of ionisation states:

$$\frac{n_{i+1}}{n_i} = \frac{(2\pi m_e k_B T)^{3/2}}{n_e h^3} \frac{2g_{i+1}}{g_i} e^{-I/k_B T}. \quad (9)$$

This result is known as the Saha equation. The main thing to notice is that, as one might expect, the ratio is exponential in $I/k_B T$. However, there is also an additional $T^{3/2}$ scaling, which arises from the temperature dependence of the phase space volume available to the electron.

II. Ionisation processes

Now that we have understood how things should behave in the LTE limit, we are in a position to examine the individual mechanisms that govern ionisation and recombination, so we can see when and where we will get to LTE, and how the non-LTE results differ from the LTE ones. The first step in that is to discuss processes that ionise atoms. We will again consider an atom of species X that has been ionised i times, X^{i+} , and discuss the ways it can change its ionisation state to $X^{(i+1)+}$. Broadly speaking, we can break ionisation processes into two categories: those that involve interaction with a photon, and those that involve interaction with a fermion, usually but not always an electron. We refer to the former as photoionisation and to the latter as collisional ionisation.

A. Photoionisation

1. Primary photoionisation

Photoionisation consists of an interaction between species X and a photon:

$$X^{i+} + h\nu \rightarrow X^{(i+1)+} + e^{-}. \quad (10)$$

The rate at which photoionisations happen depends on a cross-section, which is a function of the frequency of the radiation and the properties of the atom. The simplest case, ionisation of a single-electron atom in the $1s^1$ electronic state (the ground state), is solvable analytically. This is useful, since this case includes the most important interstellar element, hydrogen. For a single-electron atom in its ground state, the ionisation rate for photons of frequency $\nu > Z^2 I_H/h$ is

$$\sigma_{\text{pi}}(\nu) = \sigma_0 \left(\frac{Z^2 I_H}{h\nu} \right)^4 \frac{e^{4-(4 \tan^{-1} x)/x}}{1 - e^{-2\pi/x}}, \quad (11)$$

where

$$x = \sqrt{\frac{h\nu}{Z^2 I_H} - 1} \quad (12)$$

$$\sigma_0 = \frac{2^9 \pi}{3e^4} Z^{-2} \alpha \pi a_0^2 = 6.304 \times 10^{-18} Z^{-2} \text{ cm}^2 \quad (13)$$

Z is the charge of the nucleus, $I_H = 13.6 \text{ eV}$ is the ionisation potential of hydrogen, and $\alpha = e^2/\hbar c$ is the fine structure constant. The quantity σ_0 is known as the ionisation potential at threshold. Note that the ionisation potential varies with charge as Z^2 , not as Z . This is because the potential increases linearly with Z , but the expectation value of the separation for a given quantum state of the electron also scales inversely with Z , so the net scaling of the ionisation potential with charge is as Z^2 .

A variety of simple analytic approximations to this formula are given in *Draine*. The important thing to note is that this function reaches a maximum at $h\nu = Z^2 I_H$, and declines at higher frequencies as roughly ν^{-3} to $\nu^{-3.5}$.

In principle we could also calculate ionisation cross section for atoms in other electronic states $n\ell$; the threshold energy and the cross section are obviously different if the electron is in an excited state rather than the ground state. In practice, however, this is generally unimportant. This is because the Einstein A 's for transitions from excited electronic states to lower states are generally very large – these are allowed transitions, so typical values are $\sim 10^9 \text{ s}^{-1}$. This means that excited states have lifetimes measured in nanoseconds. By contrast, the mean time between encounters between an atom and an ionising photon is vastly larger than this in any realistic interstellar environment. The implication is that, under conditions where we are interested in photoionisation, we can safely assume that the vast majority of atoms are in the ground

state. We will, however, worry about distinguishing between the different states when it comes to recombination, below.

For multi-electron atoms there is generally no simple expression for the ionisation cross section, and the frequency-dependence can be complex. In particular, one common feature for many multiple-electron atoms is that they show a jump in the ionisation cross section at the frequency that corresponds to the energy required to remove an electron from the $1s$ shell. This is called an absorption edge.¹

Given the cross section, one can compute the total photoionisation rate by integrating over the rate at which ionising photons pass an atom:

$$\zeta_{\text{pi}} = \int_{\nu_0}^{\infty} \sigma_{\text{pi}}(\nu) 4\pi \frac{J_{\nu}}{h\nu} d\nu. \quad (14)$$

Here $4\pi J_{\nu}$ is the radiation intensity averaged over all 4π sr. The factor of $h\nu$ in the denominator is to convert the intensity, which is in units of energy, to number of photons.

2. Auger ionisation

If photoionisation ejects an electron from an inner rather than an outer shell, it provides the atom with more energy than is required to remove the least bound electron, and so the resulting ion is left in an excited state. It can decay out of this excited state radiatively, but it is more likely to do so via a two-electron process in which one electron drops down into the vacated slot, and another electron is promoted into a more excited state. If there is sufficient energy available, this more excited state may be unbound, leading to a second ionisation. This is referred to as the Auger effect. Formally we can write the process as

$$\text{X}^{i+} + h\nu \rightarrow \text{X}^{(i+1)+(*)} + e^{-} \rightarrow \text{X}^{(i+2)+} + 2e^{-}. \quad (15)$$

For neutral C, N, O, and Ne, ionisations of electrons from the $1s$ level are generally followed by ejection of a second electron via the Auger effect. For more complex atoms multiple Auger electrons may be emitted if the photon that causes the initial ionisation is sufficiently energetic. This is an important effect for ionisation by X-rays.

3. Secondary ionisation

In addition to the Auger effect, another way of getting more than one ionisation out of a single photon is for the ejected electron to produce more

¹You will sometimes see the $1s$ shell referred to as the K shell, and the ionisation edge associated with it as the K shell edge, particularly in the X-ray literature. This notation comes from the experimental X-ray literature from the first decades of the 20th century before quantum mechanics was fully worked out. Spectroscopists at the time noticed the X-rays emitted by light elements fell into distinct energy groupings, which they labeled alphabetically as K, L, M, N, etc.

ionisation. If the primary photon has much more energy than the minimum required to eject the electron, the bulk of the remaining photon energy goes into the kinetic energy of the ejected electron. For an X-ray, this excess energy can easily be hundreds or thousands of eV, so that the electron then carries more than enough energy to cause a second ionisation, or possibly even more.

Calculating the number of secondary ionisations is a complex problem that depends not just on the energy of the ejected electron, but also on the state of the gas. In a mostly ionised gas the ejected electron will rapidly lose energy via Coulomb interactions with other electrons, so it may not find a neutral atom before thermalizing and losing the ability to ionise again. In a neutral gas, the electron may lose energy via interactions that excite but do not ionise the particles with which it collides. In general the problem must be solved numerically, though analytic fitting formulae are given in *Draine* and elsewhere.

B. Collisional ionisation

1. Thermal electrons

The second main ionisation process in the ISM is collisional ionisation, usually due to a collision with a free electron. Electrons usually dominate because their masses are so small compared to other particles, which maximizes their speed and leads to a stronger perturbation to the wavefunctions of bound electrons than would a slower interaction with a more massive particle.

As with other collisional processes, we describe the rate at which collisional ionisation happens in terms of a cross section and a rate coefficient, using our standard formula for collisional processes:

$$k_{\text{ci}} = \int_I^\infty \sigma_{\text{ci}}(E) v f_E dE = \left(\frac{8k_B T}{\pi m_e} \right)^{1/2} \int_{I/k_B T}^\infty \sigma_{\text{ci}}(x) x e^{-x} dx, \quad (16)$$

where I is the ionisation potential for the atom in question and $x = E/k_B T$. Note that this implicitly assumes that the electrons have a Maxwellian velocity distribution, which is generally a safe assumption, but fails in some circumstances – we’ll get to those in a bit. The total number of collisional ionisations per unit volume per unit time is then

$$\zeta_{\text{ci}} = k_{\text{ci}} n_e n_I, \quad (17)$$

where n_I is the number density of particles being ionised.

Unlike photoionisation, where the cross section is at maximum at the threshold and declines at higher energies, for collisional ionisation the cross section is zero at threshold and rises smoothly as the energy increases, before falling off at even higher energies.

The behavior at low energies can be understood as follows. If an electron arrives with energy E , then after ionisation the two free electrons must have total energy $E - I$. The volume in phase space that is allowed therefore depends on $E - I$, and as $E \rightarrow I$ it shrinks to zero. Since the transition probability is proportional to the volume in phase space the electrons are allowed to occupy after ionisation, it must go to zero as this volume goes to zero. This is different than photoionisation, because after photoionisation there is only one electron, and the number of states accessible to it is non-zero even at very low energies.

At low energies, $E \lesssim 3I$, this behavior can be approximated by a cross section

$$\sigma_{\text{ci}}(E) = C\pi a_0^2 \left(1 - \frac{I}{E}\right), \quad (18)$$

where C is a constant of order unity. For hydrogen, $C = 1.07$. Plugging this into the integral gives

$$k_{\text{ci}} \approx C\pi a_0^2 \left(\frac{8k_B T}{\pi m_e}\right)^{1/2} e^{-I/k_B T} \quad (19)$$

At higher but still non-relativistic electron energies, the collisional ionisation cross section falls off as $1/E$. This is because, as we showed toward the beginning of class, the momentum transfer due to a Coulomb interaction scales as $\Delta p_{\perp} \propto 1/bv \propto 1/bE^{1/2}$, where p is the impact parameter. Thus to transfer a fixed amount of momentum and energy and ionise the electron, the impact parameter must vary as $E^{-1/2}$, and the cross section as $\sigma \propto b^2 \propto 1/E$. However, by the time thermal electrons are moving fast enough to be in the $1/E$ regime, ionisation is generally near complete anyway.

2. Cosmic rays

Most electrons and ions in the ISM have a Maxwellian velocity distribution, but there is a population of much faster, relativistic particles known as cosmic rays as well. There are particularly important in environments such as the interiors of dense clouds, where other ionisation processes are ineffective – the gas is too cold for collisional ionisations, and there is too much extinction to photoionising photons to penetrate. Cosmic rays, on the other hand, can have very long mean free paths, even through dense gas.

The cosmic ray ionisation rate is given by the usual collision integral, generalised to include a non-Maxwellian velocity distribution:

$$\zeta_{\text{CR}} = 4\pi \int_{E_{\text{min}}}^{\infty} \sigma_{\text{ci}}(E) E \frac{dF}{dE} \cdot \frac{dE}{E}. \quad (20)$$

Here dF/dE is the flux per unit solid angle of cosmic rays with energies from E to $E + dE$. The cross section for photoionisations by extremely relativistic

particles of charge Ze and velocity βc is approximately

$$\sigma_{\text{ci}} = 0.285 \frac{2\pi e^4 Z^2}{m_e c^2 I_H \beta^2} \left\{ \ln \left[\frac{2m_e c^2 \beta^2}{I_H (1 - \beta^2)} \right] + 3.04 - \beta^2 \right\}. \quad (21)$$

Of course this is only good to the extent that we know dF/dE , which is set by complicated processes of cosmic ray injection, transport, energy loss, and escape from the galaxy. In practice this means that we are generally trying to evaluate this using empirically-determined cosmic ray spectra.

As with photoionisation, cosmic ray ionisations often yield fast electrons that can induce secondary ionisation. The mean energy of the secondary photoelectrons produced in this process is nearly independent of the energy of the primary cosmic ray, and is typically around 35 eV, although there is a tail to much higher energies so that the mean is close to 70 eV. In neutral gas this yields ~ 0.67 secondary ionisations per primary ionisation, with the number decreasing with the ionisation fraction of the ambient gas for the reasons we discussed earlier. *Draine* gives an approximation formula for this decline.

III. Recombination processes

Now we turn to recombination processes, which are those that change a charge state from $X^{(i+1)+}$ to X^{i+} .

A. Radiative recombination

Radiative recombinations take the form

$$X^{(i+1)+} + e^- \rightarrow X^{i+} + h\nu, \quad (22)$$

with the electron being captured into an electronic state $n\ell$ that was formerly unoccupied.

1. The Milne Relation and recombination rates

The recombination rate via this process can be written in terms of a cross-section, and we can relate this cross section to the ionisation cross section using the same approach we have been using throughout the class to derive rates of inverse processes. The resulting relation is known as the Milne Relation. Consider an atom of species X^{i+} in state ℓ , and it can absorb a photon, transitioning to species $X^{(i+1)+}$ in state u and emitting an electron. The reaction is

$$X_\ell^{i+} + h\nu \leftrightarrow X_u^{(i+1)+} + e^-. \quad (23)$$

The difference in energy between the ionised and unionised states is $I_{X,u\ell}$.

Let $\sigma_{\text{pi}}(E)$ be the photoionisation cross section to a photon of energy E , and $\sigma_{\text{rr}}(E)$ be the radiative recombination cross section for an atom encountering an electron with relative energy E . In LTE, the rate per unit volume with

which photons with energies in the range $(E, E + dE)$ are absorbed by atoms must be equal to the rate at which they are created by radiative recombinations. As we have already written down, the total photoionisation rate is

$$\zeta_{\text{pi}} = \int_{\nu_0}^{\infty} \sigma_{\text{pi}}(\nu) 4\pi \frac{B_{\nu}}{h\nu} d\nu, \quad (24)$$

where we have taken $B_{\nu} = J_{\nu}$ since we are in LTE. The rate per unit volume is simply $\zeta_{\text{pi}} n_{X_{\ell}}$, i.e. the photoionisation rate multiplied by the density of target particles. To figure out the rate at which photoionisation creates electrons in a given energy range, we simply have to differentiate this with respect to energy, obtaining

$$\text{absorptions cm}^{-3} \text{ erg}^{-1} = 4\pi n_{X_{\ell}} \frac{B_{\nu}}{h\nu} \sigma_{\text{pi}}(h\nu) d(h\nu). \quad (25)$$

The radiative recombination rate is slightly more complicated, because we must figure out what electron energy will give rise to a photon of frequency ν . Conservation of energy requires that the electron energy E be related to the photon energy $h\nu$ by

$$E = h\nu - I_{X,ul}. \quad (26)$$

Thus an electron of 0 energy produces a photon of frequency $I_{X,ul}/h$. The recombination rate therefore is

$$\text{recombinations cm}^{-3} \text{ erg}^{-1} = n_{X_u^+} n_e v f_E(h\nu - I_{X,ul}) \sigma_{\text{rr}}(h\nu - I_{X,ul}) (1 + n_{\gamma}) h d\nu. \quad (27)$$

Here $f_E(h\nu - I_{X,ul})$ is the value of the Maxwellian distribution of electron energies evaluated at energy $E = h\nu - I_{X,ul}$. The $1 + n_{\gamma}$ term is the correction for stimulated recombination; in LTE, the photon occupation number is

$$n_{\gamma} = \frac{1}{e^{h\nu/k_B T} - 1}. \quad (28)$$

Now we can set absorptions equal to recombinations. Doing so and solving for σ_{rr} gives

$$\sigma_{\text{rr}}(h\nu - I_{X,ul}) = \frac{4\pi B_{\nu}}{h\nu} \frac{1}{v f_E(h\nu - I_{X,ul}) (1 + n_{\gamma}) h} \left(\frac{n_{X_{\ell}}}{n_{X_u^+} n_e} \right) \sigma_{\text{pi}}(h\nu). \quad (29)$$

In LTE the quantity in parentheses can be computed from the Saha equation, giving

$$\frac{n_{X_u^+} n_e}{n_{X_{\ell}}} = \left[\frac{(2\pi m_e k_B T)^{3/2}}{h^3} \right] \frac{g_u}{g_{\ell}} e^{-I_{X,ul}/k_B T}. \quad (30)$$

If the states are not ground states, a more general form of this equation can be derived by analogous means. Plugging this in, along with the Maxwellian velocity distribution

$$v f_E = \left(\frac{8}{\pi \mu k_B T} \right)^{1/2} \frac{E}{k_B T} e^{-E/k_B T}, \quad (31)$$

and solving, we arrive at the Milne relation:

$$\sigma_{\text{rr}}(E) = \frac{g_{\ell}}{g_u} \frac{(I_{X,u\ell} + E)^2}{Em_e c^2} \sigma_{\text{pi}}(h\nu = I_{X,u\ell} + E). \quad (32)$$

Thus, given the photoionisation cross-section, we can directly calculate the radiative recombination rate cross section.

Once we know the recombination cross section, we can solve for the recombination rate using the usual method of integrating over the velocity distribution to obtain a rate coefficient. We normally write rate coefficients for radiative recombination with the letter α :

$$\alpha_{n\ell}(T) = \left(\frac{8k_B T}{\pi m_e} \right)^{1/2} \int_0^\infty \sigma_{\text{rr},n\ell}(E) x e^{-x} dx, \quad (33)$$

where $x = E/k_B T$, and the subscripts $n\ell$ are to remind us that this is the rate for recombination to a given $n\ell$ electronic level. Values of $\alpha_{n\ell}(T)$ for hydrogen are given in *Draine*.

As with our other applications of the law of mass action, note that, although we derive this result in LTE, the value of $\sigma_{\text{rr}}(E)$ is a purely quantum mechanical constant that does not depend on anything but internal properties of the ion in question. Thus the result is general. For $\alpha_{n\ell}$, we have assumed that the electrons have a Maxwellian velocity distribution, but that is the only assumption.

2. Case A and case B recombination

If we want to know the total recombination rate, we can simply sum the $\alpha_{n\ell}$ values over all possible levels of the newly-bound atom. However, there is a complication, which comes from radiative transfer. Suppose that we have a hydrogen recombination that goes directly to the ground state, $1s$. The resulting photon will have an energy of at least 13.6 eV. The cross section of neutral hydrogen atoms to photons of this energy is very high: $6.3 \times 10^{-18} \text{ cm}^2$ at threshold. This means that even if a region is mostly ionised, even a small fraction of neutral hydrogen is likely to render it optically thick to photons with energies above 13.6 eV. This means that every such photon that is emitted will be re-absorbed by a neutral hydrogen atom nearby, ionising it and resulting in no net recombinations.

If the region in question is sufficiently hot, low density, or small, then it will have so little neutral gas as to be optically thin even to ionising photons. We refer to this as case A. The opposite limit is when the gas is assumed to be optically thick to ionising photons, and we refer to this as case B. Generally speaking, coronal and IGM gas with temperatures $\gtrsim 10^6 \text{ K}$ are case A, and H II regions around O and B stars are case B.

In case A, the total recombination rate is exactly what one would naively

have guessed, a sum of recombinations to all levels of the bound atom:

$$\alpha_A(T) = \sum_{n=1}^{\infty} \sum_{\ell=0}^{n-1} \alpha_{n\ell}(T). \quad (34)$$

A typical number to keep in mind for case A is $\alpha_A \approx 4.1 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ for hydrogen at 10^4 K . More accurate approximation formulae are given in *Draine*.

In case B, on the other hand, only recombinations to excited states “count” for producing recombinations, since the photons emitted in this case are now too low energy to cause further ionisations. For case B, the net recombination rate is simply the case A rate, but omitting $n = 1$:

$$\alpha_B(T) = \sum_{n=2}^{\infty} \sum_{\ell=0}^{n-1} \alpha_{n\ell}(T) = \alpha_A(T) - \alpha_{1s}(T) \quad (35)$$

For hydrogen at 10^4 K , $\alpha_B \approx 2.5 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$.

B. Radiative recombination of heavier elements

Thus far we have only discussed hydrogen, but radiative recombination occurs for other elements as well. The method of calculating the recombination rates and the emitted spectrum is similar, with one exception: helium is the only element for which we ever have to worry about case B. No other element is abundant enough for ionised regions to become optically thick to recombination radiation. The case of helium is treated in the book, but we will not discuss it in class.

C. Other recombination mechanisms

Several other recombination processes can be important in special circumstances or for particular elements, particularly in very cool regions. We will not discuss these in detail, just go over them briefly so that you know they exist.

In multiple-electron atoms, one such mechanism is dielectronic recombination. The idea is that a recombination requires that energy be lost by the free electron to render it bound. In radiative recombination it goes into a photon. In a multi-electron atom, it could also go into one of the bound electrons in the ion, pumping that electron into an excited state, leaving the atom with two electrons in excited states. Dielectronic recombination is most important in high temperature plasmas, where there are many electrons with enough energy to produce atoms with two electrons both in excited states. However, in some atoms there are accessible excited states even for plasmas as cold as $\sim 10^4 \text{ K}$.

One important recombination mechanism in predominantly molecular regions is dissociative recombination. This happens when a molecular ion, for example OH^+ or H_3^+ , captures a free electron. The excess energy can be dumped into vibrational excitations of the molecule, and it is usually enough to leave the resulting molecule in an unbound state.

A final recombination mechanism is charge exchange, in which an ion collides with a neutral particle or a dust grain, and grabs an electron from it. This can happen if the ionisation potential of the species grabbing the electron is greater than that of the species losing it.