## Collisional Excitation and N-Level Atoms.

## 1 Collisional Excitation \& Deexcitation

Consider an atom or ion with a lower energy level 1 and an upper level 2 . Collision of a free electron with kinetic energy greater than $E_{12}$ may excite the ion from 1 to 2 , while collisions with electrons of any energy may deexcite the ion from 2 to 1 . In such a collisional deexcitation, no radiation is emitted; rather the colliding electron carries away the deexcitation energy $E_{12}$.

It is convenient to introduce the dimensionless collision strength, $\Omega$, to describe such transitions. The collision strength is related to the collision cross section $\sigma$ (units of area) by

$$
\begin{equation*}
\sigma_{21}(E)=\left(\frac{h^{2}}{8 \pi m E}\right) \frac{\Omega_{21}(E)}{g_{2}}, \tag{1}
\end{equation*}
$$

where $m$ is the mass of the electron, $g_{2}$ is the statistical weight of the originating level and $E$ is the kinetic energy of the colliding electron. The rate of collisional deexcitations can then be written

$$
\begin{equation*}
R_{21}=N_{e} N_{2} \int_{0}^{\infty} \sigma_{21}(E) \mathrm{v}(E) f(E) d E=N_{e} N_{2} q_{21} \tag{2}
\end{equation*}
$$

Here, the velocity $\mathrm{v}(E)=\sqrt{2 E / m}$, and $f(E)$ is the Maxwellian distribution:

$$
\begin{equation*}
f(E)=\frac{2 E^{1 / 2}}{\pi^{1 / 2}(k T)^{3 / 2}} \mathrm{e}^{-E / k T} \tag{3}
\end{equation*}
$$

Combining the above, we see that the rate coefficient, $q_{21}$, is

$$
\begin{equation*}
q_{21}=\frac{h^{2}}{8 \pi m g_{2}} \sqrt{\frac{2}{m}} \frac{2}{\pi^{1 / 2}(k T)^{3 / 2}} \int_{0}^{\infty} \Omega_{21}(E) \mathrm{e}^{-E / k T} d E \tag{4}
\end{equation*}
$$

We thus define the Maxwellian averaged collision strength (or the effective collision strength) by the expression

$$
\begin{equation*}
\Upsilon_{21}(T)=\int_{0}^{\infty} \Omega_{21}(E) \mathrm{e}^{-E / k T} d\left(\frac{E}{k T}\right) \tag{5}
\end{equation*}
$$

and see that the rate coefficient can be written as

$$
\begin{equation*}
q_{21}=\frac{\beta}{\sqrt{T}} \frac{\Upsilon_{21}}{g_{2}} \quad \text { where } \quad \beta=\left(\frac{2 \pi \hbar^{4}}{k m^{3}}\right)^{1 / 2} \tag{6}
\end{equation*}
$$

Note that we introduced $\hbar=h / 2 \pi$ into the definition of the constant $\beta$. In cgs units, its numerical value is $\beta=8.629 \times 10^{-6}$.

Next consider the rate of collisional excitation. In this case the kinetic energy must be equal or greater than the energy separation of the levels. Thus

$$
\begin{equation*}
R_{12}=N_{e} N_{1} \int_{E_{12}}^{\infty} \sigma_{12}\left(E^{\prime}\right) \mathrm{v}\left(E^{\prime}\right) f\left(E^{\prime}\right) d E^{\prime}=N_{e} N_{1} q_{12} \tag{7}
\end{equation*}
$$

and

$$
\begin{equation*}
q_{12}=\frac{h^{2}}{8 \pi m g_{1}} \sqrt{\frac{2}{m}} \frac{2}{\pi^{1 / 2}(k T)^{3 / 2}} \int_{E_{12}}^{\infty} \Omega_{12}\left(E^{\prime}\right) \mathrm{e}^{-E^{\prime} / k T} d E^{\prime} \tag{8}
\end{equation*}
$$

If we change the variable of integration to $E=E^{\prime}-E_{12}$, we see that the upward collision rate can be written as

$$
\begin{equation*}
q_{12}=\frac{\beta}{\sqrt{T}} \frac{1}{g_{1}} \mathrm{e}^{-E_{12} / k T} \int_{0}^{\infty} \Omega_{12}\left(E+E_{12}\right) \mathrm{e}^{-E / k T} d\left(\frac{E}{k T}\right) \tag{9}
\end{equation*}
$$

For many ions, in the energy range of interest, the collision strength $\Omega$ is approximately constant. In that case, the integral in equation (5) is unity, $\Upsilon_{21}=\Omega_{21}$, and

$$
\begin{equation*}
q_{21}=\frac{\beta}{\sqrt{T}} \frac{\Omega_{21}}{g_{2}} \tag{10}
\end{equation*}
$$

Likewise, if $\Omega_{12}$ is constant,

$$
\begin{equation*}
q_{12}=\frac{\beta}{\sqrt{T}} \frac{\Omega_{12}}{g_{1}} \mathrm{e}^{-E_{12} / k T} . \tag{11}
\end{equation*}
$$

Now consider the case of thermodynamic equilibrium, where detailed balance must apply. Then $R_{12}=R_{21}$, that is,

$$
\begin{equation*}
N_{e} N_{1} \frac{\beta}{\sqrt{T}} \frac{\Omega_{12}}{g_{1}} \mathrm{e}^{-E_{12} / k T}=N_{e} N_{2} \frac{\beta}{\sqrt{T}} \frac{\Omega_{21}}{g_{2}} . \tag{12}
\end{equation*}
$$

Canceling and rearranging, we have

$$
\begin{equation*}
\frac{N_{2}}{N_{1}}=\frac{\Omega_{12}}{\Omega_{21}} \frac{g_{2}}{g_{1}} \mathrm{e}^{-E_{12} / k T} \tag{13}
\end{equation*}
$$

But in thermodynamic equilibrium, the relative populations of the levels must be given by the Boltzmann distribution:

$$
\begin{equation*}
\frac{N_{2}}{N_{1}}=\frac{g_{2}}{g_{1}} \mathrm{e}^{-E_{12} / k T} . \tag{14}
\end{equation*}
$$

We thus see that the collision strengths are symmetric: $\Omega_{12}=\Omega_{21}$.
This result is more general than the case of constant $\Omega$. We see, in fact, that if $\Omega_{12}\left(E+E_{12}\right)=$ $\Omega_{21}(E)$, then equation (9) becomes

$$
\begin{equation*}
q_{12}=\frac{\beta}{\sqrt{T}} \frac{\Upsilon_{21}}{g_{1}} \mathrm{e}^{-E_{12} / k T} \tag{15}
\end{equation*}
$$

This symmetry of $\Omega$ also follows from the condition that the collision process be invariant under time reversal.

## 2 The Two Level Atom

Consider an atom or ion with two levels. Suppose that the only processes which are of importance are collisional excitation, collisional deexcitation and spontaneous radiative decays (no radiative excitations or stimulated emissions). We can then write down the equation of statistical equilibrium, which requires that upward transitions balance the downward transitions:

$$
\begin{equation*}
N_{e} N_{1} q_{12}=N_{e} N_{2} q_{21}+N_{2} A_{21} \tag{16}
\end{equation*}
$$

From this we see that

$$
\begin{equation*}
\frac{N_{2}}{N_{1}}=\frac{N_{e} q_{12}}{A_{21}+N_{e} q_{21}}=\frac{N_{e}}{A_{21}} \frac{\beta}{\sqrt{T}} \frac{\Upsilon_{21}}{g_{1}} \mathrm{e}^{-E_{12} / k T}\left[1+\frac{N_{e}}{A_{21}} \frac{\beta \Upsilon_{21}}{\sqrt{T} g_{2}}\right]^{-1} \tag{17}
\end{equation*}
$$

The first term is just the population ratio that would result if collisional deexcitation were neglected, while the term in brackets is the correction for this effect. We can see that in limit of low $N_{e}$, $[\ldots] \rightarrow 1$, while in the limit of high density, $N_{e} q_{21} / A_{21} \gg 1$ and we have

$$
\begin{equation*}
\frac{N_{2}}{N_{1}} \rightarrow \frac{N_{e}}{A_{21}} \frac{\beta}{\sqrt{T}} \frac{\Upsilon_{21}}{g_{1}} \mathrm{e}^{-E_{12} / k T}\left(\frac{A_{21}}{N_{e}} \frac{\sqrt{T}}{\beta} \frac{g_{2}}{\Upsilon_{21}}\right)=\frac{g_{2}}{g_{1}} \mathrm{e}^{-E_{12} / k T} \tag{18}
\end{equation*}
$$

just the Boltzmann ratio. A simple measure of the importance of collisional deexcitation is provided by the critical density, $N_{e}^{c r i t}$, which is defined as the electron density for which $N_{e} q_{21}=A_{21}$, i.e.

$$
\begin{equation*}
N_{e}^{c r i t}=\frac{A_{21} g_{2} \sqrt{T}}{\beta \Upsilon_{21}}=1.159 \times 10^{5} \sqrt{T} \frac{g_{2} A_{21}}{\Upsilon_{21}} \tag{19}
\end{equation*}
$$

(For multilevel atoms, we may define the critical density for a particular level by replacing $A_{21}$ and $q_{21}$ by the sums of all the downward $A$ 's and $q$ 's from that level.) We can use $N_{e}^{c r i t}$ to simplify the appearance of equation (17):

$$
\begin{equation*}
\frac{N_{2}}{N_{1}}=\frac{N_{e}}{N_{e}^{c r i t}} \frac{g_{2}}{g_{1}} \mathrm{e}^{-E_{12} / k T}\left[1+\frac{N_{e}}{N_{e}^{c r i t}}\right]^{-1} \tag{20}
\end{equation*}
$$

We are often interested in the amount of energy radiated by the downward radiative transitions. This rate of energy loss is given by the number of transitions $\mathrm{cm}^{-3}$ times the energy of the transition:

$$
\begin{equation*}
L_{12}=N_{2} A_{21} E_{12}=N_{1} A_{21} E_{12}\left(\frac{N_{2}}{N_{1}}\right) \tag{21}
\end{equation*}
$$

The total number density of our two level ions is $N=N_{1}+N_{2}$. If the densities are high, $N_{1} \simeq N$ may not be a good approximation. Since $N_{1}=N /\left(1+N_{2} / N_{1}\right)$, we can show from equation (17) that

$$
\begin{equation*}
N_{1}=\left[\frac{A_{21}+N_{e} q_{21}}{A_{21}+N_{e}\left(q_{21}+q_{12}\right)}\right] N \tag{22}
\end{equation*}
$$

and thus the energy loss is

$$
\begin{equation*}
L_{12}=N A_{21} E_{12}\left[\frac{A_{21}+N_{e} q_{21}}{A_{21}+N_{e}\left(q_{21}+q_{12}\right)}\right]\left[\frac{N_{e} q_{12}}{A_{21}+N_{e} q_{21}}\right] \tag{23}
\end{equation*}
$$

Putting in the explicit expressions for the $q$ 's, we thus obtain

$$
\begin{equation*}
L_{12}=N_{e} N E_{12} \frac{\beta}{\sqrt{T}} \frac{\Upsilon_{21}}{g_{1}} \mathrm{e}^{-E_{12} / k T}\left[1+\frac{N_{e}}{A_{21}} \frac{\beta \Upsilon_{21}}{\sqrt{T}}\left(\frac{1}{g_{2}}+\frac{1}{g_{1}} \mathrm{e}^{-E_{12} / k T}\right)\right]^{-1} \tag{24}
\end{equation*}
$$

Or, in terms of the critical density,

$$
\begin{equation*}
L_{12}=N_{e} N E_{12} \frac{\beta}{\sqrt{T}} \frac{\Upsilon_{21}}{g_{1}} \mathrm{e}^{-E_{12} / k T}\left[1+\frac{N_{e}}{N_{e}^{c r i t}}\left(1+\frac{g_{2}}{g_{1}} \mathrm{e}^{-E_{12} / k T}\right)\right]^{-1} \tag{25}
\end{equation*}
$$

We see that at low densities, ( $\left.N_{e} \ll N_{e}^{c r i t}\right)$, the emission rate is

$$
\begin{equation*}
L_{12}=N_{e} N E_{12} \frac{\beta}{\sqrt{T}} \frac{\Upsilon_{21}}{g_{1}} \mathrm{e}^{-E_{12} / k T} \propto N_{e} N \tag{26}
\end{equation*}
$$

while at high densities $\left(N_{e} \gg N_{e}^{c r i t}\right)$, the rate becomes

$$
\begin{equation*}
L_{12}=N A_{21} E_{12}\left(1+\frac{g_{1}}{g_{2}} \mathrm{e}^{+E_{12} / k T}\right)^{-1} \propto N A_{21} \tag{27}
\end{equation*}
$$

As an example, consider the $\mathrm{C}^{+}$(C II) ion. It has a ${ }^{2} \mathrm{P}^{o}$ ground state split into lower ${ }^{2} \mathrm{P}_{1 / 2}^{o}$ and upper ${ }^{2} \mathrm{P}_{3 / 2}^{o}$ levels. These levels are 0.00786 eV apart, and the transition between them gives rise to the far infrared line at $158 \mu \mathrm{~m}$. The line is highly forbidden, with $A_{21}=2.29 \times 10^{-6} \mathrm{sec}^{-1}$. The collision strength varies a bit with temperature: at $10,000 \mathrm{~K}, \Upsilon_{21}=2.15$, while at 1000 K , $\Upsilon_{21}=1.58$. Then, from equation (19), we find $N_{e}^{c r i t}=49$ and $21 \mathrm{~cm}^{-3}$, respectively. We see that in all but the lowest density regions, collisional deexcitation will be important for this line.

For more examples, see Dopita \& Sutherland, Table 3.3.

## 3 The Three Level Atom

Next, consider an atom or ion with three levels. We can write down the equation for the third level by equating the transitions into that level with the transitions out of it:

$$
\begin{equation*}
N_{1} C_{13}+N_{2} C_{23}=N_{3}\left(A_{32}+C_{32}+A_{31}+C_{31}\right) \tag{28}
\end{equation*}
$$

where we are using the notation $C_{i j}=N_{e} q_{i j}$ for the collisional transitions. Likewise, equating transitions into and out of level 2 , we have

$$
\begin{equation*}
N_{1} C_{12}+N_{3}\left(A_{32}+C_{32}\right)=N_{2}\left(A_{21}+C_{21}+C_{23}\right) \tag{29}
\end{equation*}
$$

With $N=N_{1}+N_{2}+N_{3}$ as the third equation, we can easily find explicit expressions for the relative populations, $N_{1}, N_{2}$, and $N_{3}$, but they are complex and not very illuminating. Since we are interested in the $N_{3} / N_{2}$ ratio, we can isolate the $N_{1}$ terms of the above two equations and take their ratio:

$$
\begin{equation*}
\frac{N_{1} C_{13}}{N_{1} C_{12}}=\frac{N_{3}\left(A_{32}+C_{32}+A_{31}+C_{31}\right)-N_{2} C_{23}}{N_{2}\left(A_{21}+C_{21}+C_{23}\right)-N_{3}\left(A_{32}+C_{32}\right)} . \tag{30}
\end{equation*}
$$

Canceling $N_{1}$ and solving for the population ratio yields

$$
\begin{equation*}
\frac{N_{3}}{N_{2}}=\frac{C_{13}\left(A_{21}+C_{21}+C_{23}\right)+C_{12} C_{23}}{C_{12}\left(A_{31}+C_{31}+A_{32}+C_{32}\right)+C_{13}\left(A_{32}+C_{32}\right)} . \tag{31}
\end{equation*}
$$

### 3.1 Temperature Sensitive Line Ratios

There are a number of important ions with $2 s^{2} 2 p^{2}$ or $3 s^{2} 3 p^{2}$ electron configurations which can be treated as 3-level atoms. The prime example is $\mathrm{O}^{2+}$ (O III); others are $\mathrm{N}^{+}(\mathrm{N} \mathrm{II}), \mathrm{Ne}^{4+}(\mathrm{Ne} \mathrm{V})$ and $\mathrm{S}^{2+}$ (S III). These ions have a ${ }^{3} \mathrm{P}_{0,1,2}$ ground term which we will treat as a single level. The first excited level is ${ }^{1} \mathrm{D}_{2}$; well above that is the ${ }^{1} \mathrm{~S}_{0}$ level. Transitions between these levels are forbidden, but under typical nebular conditions the electron density $N_{e}$ is well below their critical densities. Thus the $C$ 's are small compared to the $A$ 's, and equation (31) becomes

$$
\begin{equation*}
\frac{N_{3}}{N_{2}}=\frac{C_{13} A_{21}}{C_{12}\left(A_{31}+A_{32}\right)+C_{13} A_{32}} \simeq \frac{C_{13}}{C_{12}} \frac{A_{21}}{\left(A_{31}+A_{32}\right)} \tag{32}
\end{equation*}
$$

where the last expression is a good approximation if $C_{13} \ll C_{12}$. This will be the case if $E_{23} / k T \gg 1$, as is true for these ions at the temperatures of interest. We can now write down the ratio of the intensity of the $3 \rightarrow 2$ line to the $2 \rightarrow 1$ line:

$$
\begin{equation*}
\frac{F_{32}}{F_{21}}=\frac{E_{23} N_{3} A_{32}}{E_{12} N_{2} A_{21}}=\frac{E_{23}}{E_{12}}\left(\frac{C_{13}}{C_{12}}\right) \frac{A_{32}}{\left(A_{31}+A_{32}\right)} . \tag{33}
\end{equation*}
$$

The ratio of the energies is just the inverse of the ratio of the wavelengths of the transitions, $\lambda_{21} / \lambda_{32}$. Further, $C_{13} / C_{12}=q_{13} / q_{12}$, and using equation (15), we find

$$
\begin{equation*}
\frac{F_{32}}{F_{21}}=\frac{\lambda_{21}}{\lambda_{32}} \frac{\Upsilon_{31}}{\Upsilon_{21}} \frac{A_{32}}{\left(A_{31}+A_{32}\right)} \mathrm{e}^{-E_{23} / k T} . \tag{34}
\end{equation*}
$$

The quantity $A_{32} /\left(A_{31}+A_{32}\right)$ is the branching ratio; it gives the fraction of radiative decays from level 3 which take the $3 \rightarrow 2$ route.

For the particular case of $\mathrm{O}^{2+}$, the $3 \rightarrow 2$ transition is the [O III] $\lambda 4363$ line, while the $2 \rightarrow 1$ transition produces two lines: [O III] $\lambda 5007\left({ }^{1} \mathrm{D}_{2} \rightarrow{ }^{3} \mathrm{P}_{2}\right)$ and [O III] $\lambda 4959\left({ }^{1} \mathrm{D}_{2} \rightarrow{ }^{3} \mathrm{P}_{1}\right)$. Let us define $\mathcal{R}$ as the ratio of the intensity of the $2 \rightarrow 1$ transition to the $3 \rightarrow 2$ transition: $\mathcal{R}=I(\lambda 5007+\lambda 4959) / I(\lambda 4363)$. Then equation (34) becomes

$$
\begin{equation*}
\mathcal{R}^{-1}=\frac{5000}{4363} \frac{\Upsilon_{31}}{\Upsilon_{21}} \frac{A_{32}}{\left(A_{31}+A_{32}\right)} \mathrm{e}^{-11605 \epsilon_{23} / T} \tag{35}
\end{equation*}
$$

where " 5000 " is a mean wavelength for the $\lambda \lambda 4959$, 5007 pair, and $\epsilon_{23}=2.84$, the energy separation in eV. Now for O III we find that the branching ratio is 0.888 and the collisions strengths are $\Upsilon_{21}=2.29$ and $\Upsilon_{31}=0.293$ (at $T=10,000 \mathrm{~K}$, ignoring the mild temperature dependence of the $\Upsilon$ 's). Inserting these numerical values we have

$$
\begin{equation*}
\mathrm{e}^{32960 / T}=1.145 \times 0.128 \times 0.888 \times \mathcal{R} \tag{36}
\end{equation*}
$$

and solving for the temperature, we finally obtain

$$
\begin{equation*}
T=\frac{32,960 \mathrm{~K}}{\ln (0.130 \mathcal{R})} \tag{37}
\end{equation*}
$$

The [O III] $\lambda 5007$ line is about three times stronger than $\lambda 4959$; the ratio is a constant, determined by the Einstein A-values. Thus, if we define $\mathcal{R}^{\prime} \equiv I(\lambda 5007) / I(\lambda 4363)$, then $\mathcal{R}^{\prime}=0.744 \mathcal{R}$ and we have

$$
\begin{equation*}
T=\frac{32,960 \mathrm{~K}}{\ln \left(0.175 \mathcal{R}^{\prime}\right)} \tag{38}
\end{equation*}
$$

For example, if $\lambda 5007$ is 150 times the intensity of $\lambda 4363$, then $\mathcal{R}^{\prime}=150$ and $T=10,087$ K . Because this line ratio is such an important temperature diagnostic for strongly ionized gases, observers make an effort to measure the relatively faint $\lambda 4363$ line. We see that as $T$ ranges from $20,000 \mathrm{~K}$ to $8,000 \mathrm{~K}, \mathcal{R}^{\prime}$ increases from 30 to 350 - below $8,000 \mathrm{~K}$ it becomes difficult to measure $\lambda 4363$.

Other ions with similar temperature-sensitive line ratios include [N II] $\lambda 6584 / \lambda 5755$, [S III] $\lambda 9533 / \lambda 6310$, [Ne V] $\lambda 3425 / \lambda 2974$, [C I] $\lambda 9849 / \lambda 8727$, etc. The [N II] ratio is especially important, since many $\mathrm{H}^{+}$regions may be photoionized by stars too cool to produce many $\mathrm{O}^{2+}$ ions the ionization potential of $\mathrm{O}^{+}$is 35 eV - but will still have plenty of $\mathrm{N}^{+}$. The analogous relation to equation (38) for [ $\mathrm{N} \mathrm{II]}$ is

$$
\begin{equation*}
T=\frac{25,000 \mathrm{~K}}{\ln \left(0.164 \mathcal{R}^{\prime}\right)} \quad \text { where } \quad \mathcal{R}^{\prime}=\frac{I(\lambda 6584)}{I(\lambda 5755)} . \tag{39}
\end{equation*}
$$

The problem we may encounter here is that the critical density of the upper level of the $\lambda 6584$ line is only $N_{e}^{\text {crit }}=1.76 \times 10^{4} \mathrm{~cm}^{-3}$. As a result, the assumptions we have made in deriving equation (34) may break down, and the [N II] line ratio may also depend upon density. The temperatures that result from applying equation (39) under such circumstances will be too high, since the $2 \rightarrow 1$ transition is more strongly affected by collisional deexcitation that the $3 \rightarrow 2$ transition.

### 3.2 Density Sensitive Line Ratios

Another important class of line ratios arises from ions with $2 s^{2} 2 p^{3}$ or $3 s^{2} 3 p^{3}$ electron configurations, such as [O II] or [S II]. These ions have a single ${ }^{4} \mathrm{~S}_{3 / 2}$ ground level, with the first excited levels being ${ }^{2} \mathrm{D}_{5 / 2}$ and ${ }^{2} \mathrm{D}_{3 / 2}$, which are only a few thousandths of an eV apart. The critical densities of these levels are $\sim 10^{3}-10^{4} \mathrm{~cm}^{-3}$, so collisional deexcitation will play a role at typical nebular densities. As a result, the ratio of the $3 \rightarrow 1$ to the $2 \rightarrow 1$ transition $-\mathrm{I}(\lambda 3726) / \mathrm{I}(\lambda 3729)$ in [O II] - is sensitive to density but not to temperature. Let us write down the expression for the ratio of the fluxes in these lines:

$$
\begin{equation*}
\frac{F_{31}}{F_{21}}=\frac{E_{13} N_{3} A_{31}}{E_{12} N_{2} A_{21}}=\frac{N_{3} A_{31}}{N_{2} A_{21}} \tag{40}
\end{equation*}
$$

since $E_{13} \simeq E_{12}$ for these lines. We can insert our expression for $N_{3} / N_{2}$ from equation (31). Now we see from the definition of the $q$ 's - equation (15) - that for $E_{13} \simeq E_{12}, C_{13} / C_{12}=\Upsilon_{31} / \Upsilon_{21}$. Thus we have

$$
\begin{equation*}
\frac{F_{31}}{F_{21}}=\frac{A_{31}}{A_{21}} \frac{\Upsilon_{31}\left(A_{21}+C_{21}+C_{23}\right)+\Upsilon_{21} C_{23}}{\Upsilon_{21}\left(A_{31}+C_{31}+A_{32}+C_{32}\right)+\Upsilon_{31}\left(A_{32}+C_{32}\right)} . \tag{41}
\end{equation*}
$$

Now, the ${ }^{2} \mathrm{D}_{3 / 2}$ to ${ }^{2} \mathrm{D}_{5 / 2}$ transition is very unlikely, i.e., $A_{32} \ll A_{31}$ for these lines, so we can simplify the expression further:

$$
\begin{equation*}
\frac{F_{31}}{F_{21}}=\frac{A_{31}}{A_{21}} \frac{\Upsilon_{31}\left(A_{21}+C_{21}+C_{23}\right)+\Upsilon_{21} C_{23}}{\Upsilon_{21}\left(A_{31}+C_{31}+C_{32}\right)+\Upsilon_{31} C_{32}} \tag{42}
\end{equation*}
$$

We immediately see that in the limit of low densities, where $A \gg C$, this becomes

$$
\begin{equation*}
\frac{F_{31}}{F_{21}}=\frac{A_{31}}{A_{21}} \frac{\Upsilon_{31}}{\Upsilon_{21}} \frac{A_{21}}{A_{31}}=\frac{\Upsilon_{31}}{\Upsilon_{21}} \tag{43}
\end{equation*}
$$

Now when we have a collisional transition between a term with a single level (like ${ }^{4} \mathrm{~S}_{3 / 2}$ ) and a term with fine structure splitting (like ${ }^{2} \mathrm{D}_{5 / 2},{ }^{2} \mathrm{D}_{3 / 2}$ ), the collision strengths are in proportion to the statistical weights of the $J$ levels of the multiplet. (Strictly speaking, this is an approximation that breaks down for heavier ions, where relativistic effects become important.) Thus we have $\Upsilon_{31} / \Upsilon_{21}=g_{3} / g_{2}$, and

$$
\begin{equation*}
\frac{F_{31}}{F_{21}}=\frac{g_{3}}{g_{2}} \tag{44}
\end{equation*}
$$

In the case of O II (and similar ions), the second level is ${ }^{2} \mathrm{D}_{5 / 2}$, so $J=5 / 2$ and $g_{2}=2 J+1=6$. Likewise, the third level is ${ }^{2} \mathrm{D}_{3 / 2}$, so $g_{3}=4$. As a result, we have

$$
\begin{equation*}
\lim _{N_{e} \rightarrow 0}\left\{\frac{I(\lambda 3726)}{I(\lambda 3729)}\right\}=\frac{2}{3} . \tag{45}
\end{equation*}
$$

On the other hand, in the limit of high density, collisions will set up a Boltzmann distribution [equation (14)], and since $E_{23} / k T \ll 1$, this is just $N_{3} / N_{2}=g_{3} / g_{2}$. Thus from equation (40) we find

$$
\begin{equation*}
\frac{F_{31}}{F_{21}}=\frac{g_{3}}{g_{2}} \frac{A_{31}}{A_{21}} . \tag{46}
\end{equation*}
$$

Now for the case of [O II], $A_{31}=A\left({ }^{2} D_{3 / 2} \rightarrow{ }^{4} S_{3 / 2}\right)=1.79 \times 10^{-4}$ and $A_{21}=A\left({ }^{2} D_{5 / 2} \rightarrow{ }^{4} S_{3 / 2}\right)=$ $3.50 \times 10^{-5}$. Thus

$$
\begin{equation*}
\lim _{N_{e} \rightarrow \infty}\left\{\frac{I(\lambda 3726)}{I(\lambda 3729)}\right\}=\frac{4\left(1.79 \times 10^{-4}\right)}{6\left(3.50 \times 10^{-5}\right)}=3.41 . \tag{47}
\end{equation*}
$$

So we see that as $N_{e}$ ranges from low to high values, the $\lambda 3726 / \lambda 3729$ ratio ranges from 0.667 to 3.41 . The measurement of this ratio can therefore be used to determine $N_{e}$. To do this, we must tabulate the line ratio as a function of $N_{e}$, using equation (42) - or preferably the full N -level equations, including higher levels. Graphs of this line ratio can be found in Osterbrock, AGN ${ }^{2}$, p 134 (note that he plots $\lambda 3729 / \lambda 3726$ ). The other frequently used line ratio of this type is that of [S II] $\lambda 6731 / \lambda 6716$. Dopita and Sutherland plot this ratio on p 51. Note that for S II, the ${ }^{2} D_{5 / 2}$ level lies above ${ }^{2} D_{3 / 2}$.

Since the collisional terms vary as $N_{e} / \sqrt{T}$, it is traditional to introduce a variable $x=0.01 N_{e} / \sqrt{T}$ (at $\mathrm{T}=10,000 \mathrm{~K}$ and $N_{e}=10^{4}, \mathrm{x}=1$ ). Going back to equation (42), and with a lot of manipulation, making use of $\Upsilon_{31} / \Upsilon_{21}=g_{3} / g_{2}, g_{2} C_{23}=g_{3} C_{32}, C_{21}=C_{31}$, etc., we can reduce this expression to

$$
\begin{equation*}
\frac{F_{31}}{F_{21}}=\frac{A_{31}}{A_{21}} \frac{g_{3}}{g_{2}}\left\{\frac{A_{21}+\mathcal{Z} x}{A_{31}+\mathcal{Z} x}\right\} \tag{48}
\end{equation*}
$$

where

$$
\begin{equation*}
\mathcal{Z}=8.629 \times 10^{-4}\left\{\frac{\Upsilon_{21}}{g_{2}}+\frac{\Upsilon_{32}}{g_{2}}+\frac{\Upsilon_{32}}{g_{3}}\right\} \tag{49}
\end{equation*}
$$

Now, for [O II] at $10,000 \mathrm{~K}, \Upsilon_{21}=0.801$ and $\Upsilon_{32}=1.17$, so $\mathcal{Z}=5.36 \times 10^{-4}$. Thus the [O II] line ratio, as a function of the parameter $x$ is given by

$$
\begin{equation*}
\frac{I(\lambda 3726)}{I(\lambda 3729)}=3.41\left\{\frac{0.0653+x}{0.334+x}\right\} \tag{50}
\end{equation*}
$$

The next page shows a plot of this expression (the solid line), along with a plot obtained by solving the first five levels of $\mathrm{O}^{+}$exactly (the dashed line) - they are nearly coincident. Finally, if we let $\mathcal{R}=I(\lambda 3726) / I(\lambda 3729)$, the explicit solution is $x=(0.334 \mathcal{R}-0.223) /(3.41-\mathcal{R})$.

Note that if we observe a line ratio, we can use this curve to determine $x$, not $N_{e}$. To obtain $N_{e}$, we at least need an estimate of the temperature $T$. And strictly speaking, since the $\Upsilon$ 's are functions of $T$, we need an approximate value of $T$ to evaluate $\mathcal{Z}$. This temperature dependence is, however, a second order effect.

## 4 The N-Level Atom

Let us consider the problem of an atom or ion with $N$ energy levels. Assume that the only processes of importance are spontaneous radiative decays and collisional excitations and deexcitations. Assume that we know the temperature of the gas and the electron density. Statistically speaking, what are the relative populations of the levels?

Consider a particular level - call it $i$. The rate of transitions out of this level will be proportional to the population of that level, $N_{i}$. Atoms in level $i$ can leave by collisional excitation upward at rate $N_{i} N_{e} q_{i k}$, where $k>i$, or by collision or radiative decay downward at rate $N_{i}\left(N_{e} q_{i k}+A_{i k}\right)$, where $k<i$. In equilibrium, these transitions out of level $i$ must equal the sum of transitions into level $i$ from all other levels. This yields an equation of the following form:

$$
\begin{gathered}
\left(N_{e} q_{1 i}\right) N_{1}+\cdots+\left(N_{e} q_{i-1, i}\right) N_{i-1}-\left[N_{e} \sum_{k=i+1}^{N} q_{i k}+N_{e} \sum_{k=1}^{i-1} q_{i k}+\sum_{k=1}^{i-1} A_{i k}\right] N_{i} \\
+\left(N_{e} q_{i+1, i}+A_{i+1, i}\right) N_{i+1}+\cdots+\left(N_{e} q_{N, i}+A_{N, i}\right) N_{N}=0
\end{gathered}
$$

We thus have N equations in the N unknowns $N_{1} \cdots N_{N}$ of the form:

$$
\begin{gathered}
a_{11} N_{1}+a_{12} N_{2}+\cdots+a_{1 N} N_{N}=0 \\
a_{21} N_{1}+a_{22} N_{2}+\cdots+a_{2 N} N_{N}=0 \\
\cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \\
a_{N 1} N_{1}+a_{N 2} N_{2}+\cdots+a_{N N} N_{N}=0
\end{gathered}
$$

If we specify a temperature and an electron density, and if we know the various atomic constants, we can evaluate all the $a_{i j}$ - they then just become constant coefficients for a set of linear equations for the unknown populations $N_{i}$. But it can be shown that this system is degenerate, i.e., any one of the equations can be constructed as a linear combination of the other $(N-1)$. (To see this in the simplest way, write down the two equations for a two level system: they are the same.) We thus introduce another equation, which is the equation of normalization: $\sum_{i=1}^{N} N_{i}=1$. This plus any $(N-1)$ of the others may then be solved for the relative populations $N_{i}$ :

$$
\begin{array}{r}
a_{11} N_{1}+a_{12} N_{2}+\cdots+a_{1 N} N_{N}=0 \\
a_{21} N_{1}+a_{22} N_{2}+\cdots+a_{2 N} N_{N}=0 \\
\cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \\
a_{N-1,1} N_{1}+a_{N-1,2} N_{2}+\cdots+a_{N-1, N} N_{N}=0 \\
1 \cdot N_{1}+1 \cdot N_{2}+\cdots+1 \cdot N_{N}=1
\end{array}
$$

This set of equations can usually be solved by standard techniques. However, if we try to use this set of equations under all conditions, we may run into problems at low densities and temperatures. Then the populations of the upper levels become so low that wildly wrong - even negative populations can satisfy the $\sum_{i=1}^{N} N_{i}=1$ constraint to the limit of precision of the computer. (For example, at $N_{e}=100$ and $T=8000 \mathrm{~K}$, the levels of the C IV ion that give rise to resonance $\lambda 1550$ doublet have a population of $\sim 10^{-18}$ relative to the ground state!) I have found that we can deal
with such situations by solving the equations by iteration. First, divide each row by the diagonal element of that row to obtain new coefficients $a^{\prime}{ }_{i j}$ :

$$
\begin{equation*}
a_{i j}^{\prime}=-\sum_{j=1}^{N}\left(\frac{a_{i j}}{a_{i i}}\right) \tag{51}
\end{equation*}
$$

We then see that the equations take the form:

$$
\begin{gathered}
0 \cdot N_{1}+a^{\prime}{ }_{12} N_{2}+\cdots+a^{\prime}{ }_{1 N} N_{N}=N_{1} \\
a^{\prime}{ }_{21} N_{1}+0 \cdot N_{2}+\cdots+a^{\prime}{ }_{2 N} N_{N}=N_{2} \\
\cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \\
a^{\prime}{ }_{N 1} N_{1}+a^{\prime}{ }_{N 2} N_{2}+\cdots+0 \cdot N_{N}=N_{N}
\end{gathered}
$$

Thus the matrix $a^{\prime}$ times the true populations - the column vector $\vec{N}$ - will just return $\vec{N}$. But if we start with arbitrary populations and multiply by $a^{\prime}$ we will get an improved $\vec{N}$. Since this set of equations does not contain the normalization condition, we should then renormalize the result by dividing each component by $\sum_{i=1}^{N} N_{i}$. Further, to prevent oscillations, I've found it necessary to operate with $a^{\prime}$ on not the last $\vec{N}$, but on an average of the last two $\vec{N}$ 's:

$$
\begin{gather*}
\vec{U}^{k+1}=a^{\prime} \times\left(\frac{\vec{N}^{k}+\vec{N}^{k-1}}{2}\right)  \tag{52}\\
\vec{N}^{k+1}=\frac{\vec{U}^{k+1}}{\sum_{i=1}^{N} U_{i}^{k+1}} \tag{53}
\end{gather*}
$$

As the first guess $\vec{N}^{0}$, we can use the Boltzmann distribution, since the populations of the excited levels will seldom exceed the thermodynamic equilibrium values:

$$
\begin{equation*}
U_{i}^{0}=g_{i} \exp \left(-E_{i} / k T\right), \quad N_{i}^{0}=U_{i}^{0} / \sum_{i=1}^{N} U_{i}^{0} \tag{54}
\end{equation*}
$$

This scheme seems to converge to correct populations under most any conditions. Once we have the populations, we can compute the energy lost in any transition of the ion from

$$
\begin{equation*}
L_{i j}=E_{j i} N_{i} A_{i j} \quad \text { where } \quad E_{j i}=h \nu_{i j}=h c / \lambda_{i j} \tag{55}
\end{equation*}
$$

Finally, the total energy radiated by that ion will be given by

$$
\begin{equation*}
\Lambda=\sum_{i=2}^{N} \sum_{j=1}^{i-1} L_{i j}=\sum_{i=2}^{N} \sum_{j=1}^{i-1} E_{j i} N_{i} A_{i j} \tag{56}
\end{equation*}
$$

(This is the loss per ion, since the $N_{i}$ are normalized to unity.)

