MODELING MOLECULAR HYPERFINE LINE EMISSION

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ABSTRACT

In this paper, we discuss two approximate methods previously suggested for modeling hyperfine spectral line emission for molecules whose collisional transition rates between hyperfine levels are unknown. Hyperfine structure is seen in the rotational spectra of many commonly observed molecules such as HCN, HNC, NH₃, N₂H⁺, and C¹⁷O. The intensities of these spectral lines can be modeled by numerical techniques such as Λ-iteration that alternately solve the equations of statistical equilibrium and the equation of radiative transfer. However, these calculations require knowledge of both the radiative and collisional rates for all transitions. For most commonly observed radio frequency spectral lines, only the net collisional rates between rotational levels are known. For such cases, two approximate methods have been suggested. The first method, hyperfine statistical equilibrium, distributes the hyperfine level populations according to their statistical weight, but allows the population of the rotational states to depart from local thermal equilibrium (LTE). The second method, the proportional method, approximates the collision rates between the hyperfine levels as fractions of the net rotational rates apportioned according to the statistical degeneracy of the final hyperfine levels. The second method is able to model non-LTE hyperfine emission. We compare simulations of N₂H⁺ hyperfine lines made with approximate and more exact rates and find that satisfactory results are obtained.

Key words: ISM: molecules – radiative transfer

Online-only material: machine-readable table

1. INTRODUCTION

The rotational spectra of many commonly observed molecules such as HCN, HNC, NH₃, N₂H⁺, and C¹⁷O exhibit hyperfine structure from the splitting of the rotational energy levels by electric quadrupole and magnetic dipole interactions induced by the nuclear moments of atoms such as N or O with non-zero spin. Hyperfine lines reduce the effective optical depth of the rotational transition by spreading the emission out over a wider bandwidth. Because estimates of the density, temperature, and molecular abundance depend on the optical depth, the hyperfine structure should be taken into account in analyzing spectral line observations. Properly treated, the hyperfine structure is quite useful. The observed relative intensities of pairs of hyperfine lines constrain the optical depth independently of the molecular abundance and independently of the spatial coupling of the telescope beam with the cloud structure (beam filling factor). In contrast, optical depth determination from the brightness ratios of spectral lines of isotopologues such as ¹²CO and ¹³CO requires knowledge of the isotopic abundance ratios, and furthermore the lines may be at sufficiently different frequencies that the observing beam may be differently coupled to the structure of the cloud.

Numerical techniques such as Λ-iteration that alternately solve the equations of statistical equilibrium to determine the level populations and the equation of radiative transfer to determine the mean radiation field are able to predict line intensities over a broad range of conditions including varying temperature and density, and non-local thermal equilibrium (LTE) excitation. However, these calculations require knowledge of both the radiative and collisional rates for all transitions. This presents a problem in the case of the hyperfine lines. For most molecules, the radiative rates, Einstein Aᵦᵢᵢ, are known for all the transitions including hyperfine transitions, but the collisional rates are known only as the net rates between rotational levels. These net rates represent the weighted sum of the rates of all the individual hyperfine transitions between the rotational levels. Collisional rates between the individual hyperfine levels themselves have been calculated for only three molecules: HCN (Monteiro & Stutzki 1986), NH₃ (Chen et al. 1998), and N₂H⁺ (Daniel et al. 2005) and even then for only a limited number of hyperfine levels.

Two approximations have been suggested for modeling the emission from molecules with unknown hyperfine collisional rates. The first approximation, hyperfine statistical equilibrium (HSE), assumes that the hyperfine levels within each rotational level are populated in proportion to their statistical weights (Keto 1990; Keto et al. 2004). The second approximation, the proportional approximation, assumes that the collisional rates between the individual hyperfine levels are proportional to the total rate between their rotational levels and the statistical degeneracy of the final hyperfine level of the transition (Guilloteau & Baudry 1981; Daniel et al. 2006).

In this paper, we discuss and evaluate these two approximations and compute sample N₂H⁺ spectra from each method. Because the collisional rates for the hyperfine transitions of N₂H⁺ are known (Daniel et al. 2005), we can compare N₂H⁺ spectra produced using the approximate collisional rates of the proportional method against spectra produced using the "exact" rates determined from the numerical quantum mechanical calculations. We also show how the collisional rates for the elastic (ΔJ = 0) rotational transitions may be determined by extrapolation from the inelastic rates. These elastic rates are required in the proportional approximation in order to determine the collisional rates for hyperfine transitions within the same rotational state. However, the elastic rates are generally not included in compilations of calculated rate coefficients.

2. FIRST APPROXIMATION: HYPERFINE STATISTICAL EQUILIBRIUM

Within a non-LTE model of radiative transfer such as the Approximate (or Accelerated) Lambda Iteration (ALI) or Monte Carlo methods, we can approximate the splitting of hyperfine
emission in a simple way even if we only know the net collisional rates for the rotational transitions. The approximation is based on the difference in the magnitude of the energies of the hyperfine and rotational transitions. The hyperfine levels of molecules that emit in the millimeter radio spectrum are typically separated by energies in the milli-Kelvin range whereas the separations between rotational levels are several tens to hundreds of Kelvin. Therefore, the hyperfine levels may sometimes be populated approximately in statistical equilibrium even if the rotational levels are not. For example, observations of N$_2$H$^+$ often show brightness ratios between hyperfine lines that depart from LTE at only 10% of the line brightness (Tafalla et al. 2004). In such cases, for some observational purposes, the assumption of HSE may be adequate. If not, the HSE method is not appropriate.

This HSE approximation has several advantages. It automatically takes into account overlapping emission from the hyperfine lines. Therefore, it may be implemented with a simple alteration of the standard ALI algorithm (Rybicki & Hummer 1991) rather than the more complex ALI algorithm for overlapping lines (Rybicki & Hummer 1992). Another advantage is that only the rotational lines require radiative transfer modeling. There are always fewer rotational lines than hyperfine lines. Of course, a rotational transition split by hyperfine structure requires a larger bandwidth, but even so, the computational time is much faster than modeling all the individual hyperfine lines.

We implement this method in ALI starting the same way as for molecules without hyperfine splitting. We solve the equations of statistical equilibrium to determine the populations in the rotational levels and an estimate of the mean radiation field from the previous iteration (RH91, Equation (2.27)):

$$\sum_{J} n_J A_{JJ'} (1 - \tilde{A}_{JJ'}) - (n_J B_{JJ'} - n_J B_{JJ'}) \tilde{J}_{JJ'}^{\text{ef}} + \sum_{J} n_J A_{JJ'} (1 - \tilde{A}_{JJ'}) - (n_J B_{JJ'} - n_J B_{JJ'}) \tilde{J}_{JJ'}^{\text{ef}} + \sum_{J} (n_J C_{JJ'} - n_J C_{JJ'}) = 0,$$

where the effective mean radiation field, $\tilde{J}_{JJ'}^{\text{ef}}$, is defined in ALI as

$$\tilde{J}_{JJ'}^{\text{ef}} = \tilde{J}_{JJ'} - \tilde{A}_{JJ'} S_{JJ'}.$$

Here, the initial and final rotational levels are denoted by subscripts $J$ and $J'$, the Einstein $A$ and $B$ rate coefficients by $A$ and $B$, the collisional rate coefficients by $C_{JJ'}$, the mean intensity by $\tilde{J}_{JJ'}$, and the level populations by $n_J$. The ALI operator is $\tilde{A}_{JJ'}$, where the overbar indicates the average over frequency. (In RH91, this operator is denoted by $\tilde{A}_{JJ'}^{\text{ef}}$.) The source function, $S_{JJ'}$, is the usual source function between rotational levels,

$$S_{JJ'} = \frac{j_{JJ'}}{\alpha_{JJ'}},$$

where $j_{JJ'}$ and $\alpha_{JJ'}$ are the emissivity and opacity as defined below.

To determine the approximate hyperfine line emission, we assume that the population of each rotational level is divided among its hyperfine states according to their statistical weights,

$$n_{JH} = g_{JH} n_J,$$

where $g$ is the statistical weight and $H$ denotes a hyperfine level.

We do not need to actually compute or store the populations of the hyperfine levels. The assumption of HSE is equivalent to the assumption that the spectral line profile function of the rotational transition including the hyperfine structure is the sum of the spectra of the individual hyperfine lines with the same relative intensities as in optically thin emission. Because these relative intensities depend only on the dipole matrix elements of the hyperfine radiative transitions, we compute the composite profile function once and then replace the simple line profile function of the rotational transition with the composite profile function everywhere in the calculation.

For example, if the line profile function of an unsplit rotational transition would be described by a particular function, $\phi(v)$—for example a Gaussian—the line profile function with hyperfine splitting would be the sum of copies of the same Gaussian, one for each of the individual hyperfine transitions from $JH$ to $J'H'$, each weighted by the individual relative line intensity, $R_{IJHH'}$, and shifted in frequency according to the energy difference, $\nu_{JHH'}$, of the hyperfine splitting:

$$\phi_{JJJ'}(v) = \sum_{HH'} \phi_{JJHH'}(v) \nu_{JHH'} R_{IJHH'}.$$

Here, $JHJ'H'$ means $JH \rightarrow J'H'$. If the relative intensities, $R_{IJHH'}$, are normalized, then so is the composite profile function:

$$\int \phi_{JJJJ'}(v)dv = 1.$$

The relative intensities of the hyperfines and their frequency shifts are very simply calculated for molecules with only one atom with an interacting nuclear moment. This case requires only the angular momentum quantum numbers of the initial and final states using the same formulae for the relative intensities and frequencies of atomic fine structure lines (Equations (6-6a) and (6-6b) in Townes & Schawlow 1975). This follows from the analogy between a transition that changes the angular momentum of a molecule without altering its nuclear spin and a transition that changes the orbital angular momentum of the electrons in an atom without changing the electron spins. The hyperfine relative intensities and frequencies in molecules with two mutually interacting atoms such as N$_2$H$^+$ may be determined with a perturbation technique (Townes & Schawlow 1975) but generally numerical techniques (Pickett 1991) are required for high precision.

Using the composite profile function, the line emissivity and opacity including the hyperfine lines can now be calculated from the level populations, $n_{JH}$, of the rotational states. The line emissivity is

$$j_{JJ'} = \frac{h \nu}{4\pi} n_{JH} A_{JJ'} \phi_{JJ'}(v),$$

and the line opacity is

$$\alpha_{JJ'} = \frac{h \nu}{4\pi} (n_{JH} B_{JJ'} - n_{JH} B_{JJ'}) \phi_{JJ'}(v).$$

The mean radiation field is also computed with the composite line profile function:

$$\tilde{J}_{JJ'} = \int \phi_{JJJJ'}(v) \nu_{JHH'} R_{IJHH'} dv.$$
Similarly, the ALI operator is
\[ \tilde{\Lambda}_{JJ'} = \int_{\Omega} d\Omega \int d\nu (1 - \exp(-\tau_{JJ'}(\nu)))r_{JJ'}C_{JJ'} \phi_{JJ'} \] (11)
if we use just the diagonal term. Here, the optical depth, \( \tau_{JJ'} \), is defined as the line opacity (Equation (9)) plus the continuum opacity times the pathlength, \( L \),
\[ \tau_{JJ'} = (\alpha_{JJ'}(\nu) + \alpha_C)L. \] (12)
The factor, \( r_{JJ'} \), is defined as in RH91, Equation (2.91),
\[ r_{JJ'} = \frac{\alpha_{JJ'}(\nu)}{\alpha_{JJ'}(\nu) + \alpha_C}, \] (13)
and \( \alpha_C \) is the opacity of the continuum. If there is no continuum, then \( \alpha_C = 0 \) and \( r_{JJ'} = 1 \).
We can now calculate the radiation along a ray in the usual way by dividing the ray into cells, \( i \), with constant excitation temperature and density:
\[ I_{JJ'}^{i+1}(\nu) = I_{JJ'}^{i}(\nu) \exp(-\tau_{JJ'}(\nu)) + S_{JJ'}(1 - \exp(-\tau_{JJ'}(\nu))), \] (14)
where the source function including the continuum is defined as
\[ S_{JJ'}(\nu) = \frac{1}{2k} \frac{\lambda_{JJ'}(\nu)}{\alpha_{JJ'}(\nu) + \alpha_C}. \] (15)
Equation (14) shows that the relative intensities of the individual hyperfine lines in the spectrum \( I_{JJ'}(\nu) \) are appropriately modified by partial saturation at higher optical depths even though the relative intensities of the line profile function are identical to the optically thin case.

From Equations (14) and (10), we can estimate the mean radiation field, \( J \), for use in the statistical equilibrium equations (Equation (1)). This completes the \( \Lambda \)-iteration.

In summary, the HSE approximation is easily implemented in a standard ALI or Monte Carlo code that models molecular rotational lines simply by changing the line profile function. We do not need to compute or store the hyperfine level populations. We do not need to model the radiative transfer of each hyperfine line individually since the hyperfine lines are included in the composite line profile function of the rotational transition. Because the optical depth of the rotational lines is split among their hyperfine components, the line trapping in the rotational lines is approximately correct.

3. THE PROPORTIONAL APPROXIMATION

The HSE approximation is adequate if the hyperfine levels are approximately in LTE even if the rotational levels are not. However, observations sometimes find that the relative intensities of the hyperfine lines do not correspond to those predicted by statistical equilibrium, even for two lines with the same predicted intensities (Guilloteau & Beaudry 1981; Caselli et al. 1995; Tafalla et al. 2002). In this case, we can model the non-LTE excitation of the individual hyperfine lines by approximating the collisional rate coefficients for the hyperfine transitions rather than approximating the populations for the hyperfine levels. The proportional approximation assumes that the unknown rate for each collisional transition between hyperfine levels is proportional to the known net rate between the rotational levels and the statistical degeneracy of the final hyperfine level (Guilloteau & Beaudry 1981; Daniel et al. 2006). The proportional approximation is computationally more demanding than the HSE approximation for two reasons. First, the number of levels in the statistical equilibrium equations now includes the hyperfine levels. Second, the mean radiation field and approximate Lambda operators must be determined for each hyperfine line individually. The proportional approximation generally results in greater accuracy, particularly for non-LTE hyperfine emission.

The approximate collision rates for the hyperfine transitions are simply
\[ C_{JJ'} = \sum_{HH} \frac{g(JH)}{g(J)} C_{JJ'}. \] (16)
This definition guarantees two requirements. First, the average net collisional rate \( C_{JJ'} \) between rotational levels \( J \) and \( J' \) is equal to the weighted sum of the rates between the hyperfine levels,
\[ C_{JJ'} = \sum_{HH} \frac{g(JH)}{g(J)} C_{JJ'}. \] (17)
Second, the LTE populations, indicated by an asterisk, and collision rates between any two levels satisfy statistical equilibrium,
\[ \frac{n_{JH}^*}{n_{J'H'}^*} = \frac{\tilde{c}_{J'H'}^*}{\tilde{c}_{JH}^*} = \frac{g_{JH}}{g_{J'H'}} \exp(h\nu/kT), \] (18)
where \( h\nu = \Delta E \) is the energy difference between the levels.

With the approximate collision rates for all the transitions, we can solve the statistical equilibrium equations for the populations of the hyperfine levels,
\[ \sum_{J>J'} n_{JH} A_{JJ'HH} (1 - \tilde{\Lambda}_{JJ'HH}) - n_{JH} B_{JJ'HH} + \sum_{J'>J} n_{J'H} A_{J'H'H'H} (1 - \tilde{\Lambda}_{J'H'H'H}) - \sum_{J'>J} n_{J'H} B_{J'H'H} \tilde{J}^{eff}_{J'H'H'} S_{J'H'H'} = 0. \] (19)
The effective mean radiation field is
\[ \tilde{J}^{eff}_{J'H'H'} = \tilde{J}_{J'H'H'} - \tilde{\Lambda}_{J'H'H'} S_{J'H'H'}, \] (20)
and the source function is
\[ S_{J'H'H'} = \frac{\tilde{J}_{J'H'H'}}{\tilde{\alpha}_{J'H'H'}}, \] (21)
where the emissivity and opacity are
\[ j_{JJ'}(\nu) = \sum_{HH} j_{JJ'HH} \phi_{JJ'HH}(\nu) \] (22)
and
\[ \alpha_{JJ'}(\nu) = \sum_{HH} \alpha_{JJ'HH} \phi_{JJ'HH}(\nu), \] (23)
with \( \phi_{JJ'HH}(\nu) \) defined as in Equation (6). These equations are essentially identical apart from notation to Equations (1), (3), (8), and (9). However, with this emissivity and opacity, the source function, even without the continuum, is no longer independent of frequency.

The radiation field and the ALI operator are computed slightly differently in the proportional approximation than in the HSE
Figure 1. Extrapolation to $\Delta J = 0$ by empirical fit of the known inelastic collisional rates. The upper six panels show the collisional rates $C_{JJ'}$ for six different $\Delta J$ written as $K_{JJ'} = \log_{10}(\frac{C_{JJ'}}{g_J g_{J'}} \times 10^{10})$ vs. $(\Delta E/kT)^{1/2}$. Equation (28) is linear in this choice of coordinate axes and is plotted for the six different $a(\Delta J)$ and $b(\Delta J)$ in each of the six panels. The lower two panels show these six lines for $\Delta J = 1–6$ and the extrapolation to $\Delta J = 0$.

The mean radiation field is defined for each individual hyperfine line so that Equation (10) is replaced by

$$\bar{J}_{JJHH} = \int_v I_{JJ}(v)\phi_{JJHH}(v)dv.$$ (24)

The ALI operator is almost the same as Equation (11), but averaged separately over each individual hyperfine line profile (Equation (6)) instead of over the summed profile (Equation (5)):

$$\bar{\Lambda}_{JJHH} = \int_v (1 - \exp(-\tau_{JJ'C}(v)))r_{JJHH'C} \phi_{JJHH}dv$$ (25)

and

$$r_{JJHH'C} = \frac{\alpha_{JJHH'C}(v)}{\alpha_{JJ'C}(v) + \alpha_C}$$ (26)

replace Equation (13), with $\alpha_{JJ'}$ defined as in Equation (9). The radiative transfer solution is defined the same way as in the HSE approximation by Equations (14), (15), and (12).

4. EXTRAPOLATION TO ELASTIC RATES

Compilations of collisional rate coefficients for rotational transitions generally do not include the elastic rates for transitions between the same rotational level, $\Delta J = 0$, because the forward and reverse rates are the same and therefore cancel out in the equations of statistical equilibrium. However, hyperfine levels within a rotational state can have different energies, and the forward and reverse hyperfine collisional rates do not necessarily cancel even for transitions with $\Delta J = 0$. In order to estimate these hyperfine collisional rates from Equation (16), we need to know the net rate for $\Delta J = 0$.

de Jong et al. (1975) suggested that collisional rates between rotational levels could be parameterized by an equation of the form

$$K_{JJ'} = a(\Delta J)\frac{g_J' g_J}{g_J} \left(1 + \frac{\Delta E_{JJ'} kT}{kT}\right) \times \exp\left[-b(\Delta J)\left(\frac{\Delta E_{JJ'}}{kT}\right)^{1/2}\right].$$ (27)

where $a(\Delta J)$ and $b(\Delta J)$ are parameters to be determined. This approximation is based on the assumption that all transitions with the same $\Delta J$ are related because transitions which change the angular momentum by $\Delta J$ are induced by the same term, $P_{\lambda}$, in the Legendre expansion of the interaction potential,

$$V(R, \Theta) = \sum_{\lambda} \psi_{\lambda}(R) P_{\lambda}(\cos \Theta),$$ (28)

where $R$ and $\Theta$ are the separation and orientation of the collision partners (Green & Chapman 1978).

If we know a few rate coefficients, for example, at a set of temperatures, we can determine the two parameters, $a(\Delta J)$ and $b(\Delta J)$, by a least-squares fit. Equation (28) can then be used to interpolate or extrapolate the rate coefficients as a function of temperature. It turns out that the two parameters, $a(\Delta J)$ and $b(\Delta J)$, vary smoothly as a function of $\Delta J$. Therefore, we can also use this equation to extrapolate to transitions with different $\Delta J$, in particular to $\Delta J = 0$. Figure 1 illustrates this. The symbols in the upper six panels show collision rates for transitions with six different $\Delta J$'s. Here, we use the collisional rates for HCO$^+$
Figure 2. Observed $\text{N}_2\text{H}^+(1\rightarrow0)$ spectrum of L1544 modeled with the HSE approximation. The dots show the observational data from Caselli et al. (1995). The line shows a model spectrum computed for a theoretical dark cloud (Keto & Caselli 2008) using our three-dimensional radiative transfer code, MOLLIE, and the HSE approximation. In this approximation, the three hyperfine lines, 101–012, 121–011, and 111–010, necessarily have equal relative intensities. The velocity labeling includes the velocity of the L1544 cloud with respect to the Sun.

Figure 3. Observed $\text{N}_2\text{H}^+(1\rightarrow0)$ spectrum of L1544 modeled with the proportional approximation. The same as Figure 2 except that the model spectrum is computed with the proportional approximation, again using our radiative transfer code, MOLLIE. Non-LTE excitation results in unequal relative intensities for the three lines, 101–012, 121–011, and 111–010 and a better match to the data.

Figure 4. Convergence of the $\Lambda$-iteration with and without acceleration. The lines show the source function (Equation (21)) of the main (123–012) hyperfine line at the location of the center of the model cloud. The brightness of the spectrum in Figure 3 is lower than the source function because of averaging lower brightness regions around the cloud center within the observing beam. This figure shows that in this calculation, the acceleration halves the required number of iterations.

5. ANALYSIS OF MODELING

5.1. Comparison of HSE and Proportional Approximations with Observations

Figures 2 and 3 compare $\text{N}_2\text{H}^+(1\rightarrow0)$ spectra of the same model cloud computed using the HSE and proportional approximations against the observed spectrum of L1544 (Caselli et al. 1999). The model is taken from Keto & Caselli (2008) and represents a slowly contracting gas cloud in radiative equilibrium with external starlight. L1544 is thought to be an example of this type of cloud. These spectra were made with our three-dimensional radiative transfer code, MOLLIE (Keto 1990; Keto et al. 2004; Keto & Caselli 2008). The HSE approximation includes eight rotational levels from $J = 0$–7 and models the seven $\Delta J = 1$ rotational lines. The hyperfine splitting is included through the composite line profile function (Equation (5)). The proportional approximation includes 64 hyperfine levels in the rotational levels $J = 0$–7 and all 280 hyperfine lines between those hyperfine levels. The two approximations result in different relative intensities for the hyperfine lines. The most evident are the different intensities of the three lines $J^\text{FF} F_1^\text{FF} J_1^F F_1^F = 101–012$, 121–011, and 111–010. In the LTE case, these three lines necessarily have the same intensity whereas with non-LTE excitation, the 121–011 hyperfine is noticeably weaker and the 111–010 hyperfine is slightly brighter. The proportional approximation represents a better match to the data, yet for some purposes the HSE approximation may be good enough.

Figure 4 compares the convergence of the $\Lambda$-iteration in the proportional approximation with the acceleration term (Equation (25)) and without ($\Lambda_{J^\text{FF} J^F F} = 0$). In this example, the optical depth is less than 10 and the $\Lambda$-iteration converges quickly in both cases. However, convergence with the acceleration requires half the number of iterations. At higher optical depths, the acceleration would be considerably more significant.

5.2. Comparison of “Exact” with “Approximate” Collision Rates

Because the collisional rates for the hyperfine transitions of $\text{N}_2\text{H}^+$ have recently been calculated (Daniel et al. 2006), we can compare the spectra computed with these rates and with the approximate collision rates of the proportional approximation.
In this comparison, we again use the same model for both calculations, changing only the collisional rate coefficients. In this example, we consider a uniform plane-parallel model of a molecular cloud with a size of $4.11 \times 10^{17}$ cm, density of $10^5$ cm$^{-3}$, temperature of 8.9 K, abundance of $N_2H^+$ relative to $H_2$ of $3 \times 10^{-10}$, microturbulent line broadening of 0.06 km s$^{-1}$, and a constant and zero velocity field. The exterior boundary condition assumes radiation at the 2.728 K background. These parameters were chosen to reproduce the $N_2H^+(1–0)$ hyperfine line ratios in the observations of L1512 (Caselli et al. 1995). This calculation includes 37 hyperfine levels in the rotational levels $J = 0–4$ and all 145 hyperfine lines between those hyperfine levels. The fit to the data is shown in Figure 5. The data for L1512 show the same pattern of non-LTE hyperfine line ratios as for L1544 with the 121–011 hyperfine noticeably lower than the 101–012 and 111–010 lines.

Figure 6 compares the spectra computed from the approximate and “exact” collision rates. Spectra for the three lowest

| Line Label | Frequency (MHz) | Line Strength | Components | Component Strength |
|------------|----------------|--------------|------------|-------------------|
| $110-011$  | 93171.6086     | 0.33334      | $110 \rightarrow 011$ | 0.33334          |
| $112-012$  | 93171.9054     | 1.66667      | $112 \rightarrow 012$ | 1.40832          |
| $111-010$  | 93172.0403     | 1.00000      | $111 \rightarrow 010$ | 0.50797          |
| $122-011$  | 93173.4675     | 1.66667      | $122 \rightarrow 011$ | 1.40830          |
| $123-012$  | 93173.7643     | 2.33333      | $123 \rightarrow 012$ | 2.33333          |
| $121-011$  | 93173.9546     | 1.00000      | $121 \rightarrow 011$ | 0.64660          |
| $101-012$  | 93176.2527     | 1.00000      | $101 \rightarrow 010$ | 0.31402          |

Notes.

a Calculations by Luca Dore (1999, private communication) using the code of Pickett et al. (1991).
b Each line is labeled by its strongest component.
c Unit is $d^2$, where $d = 4.3 \times 10^{-18}$ esu cm is the permanent dipole moment of $N_2H^+$. 
rotational transitions of N$_2$H$^+$, (1–0), (2–1), and (3–2) are shown along with the difference between the two. The difference is less than 1% of the line strength. For most observations of radio frequency molecular lines from dark clouds, this difference would be below the typical signal-to-noise ratio. Based on this example, the proportional approximation is adequate for N$_2$H$^+$ and could be useful for other molecules with unknown hyperfine collision rates.

6. CONCLUSIONS

The modeling of molecular spectra with hyperfine splitting by ALI or Monte Carlo methods has been hampered by the lack of collisional rate coefficients for the hyperfine transitions. Two approximations previously suggested, the approximation of HSE and the proportional approximation, both provide satisfactory results in tests modeling N$_2$H$^+$ spectra. The HSE approximation, based on a modified line profile function, is simpler to implement, faster to compute, and models the non-LTE distribution in the rotational levels but cannot model non-LTE distributions of the hyperfine levels themselves. The proportional approximation uses easily computed approximate hyperfine collision rates and is able to model non-LTE hyperfine emission with an accuracy comparable to calculations using the exact hyperfine collision rates. These results suggest that these two methods could also be useful for other molecules with hyperfine splitting.

APPENDIX A

STATISTICAL WEIGHTS FOR N$_2$H$^+$

The hyperfine levels of N$_2$H$^+$ are described by three angular momentum quantum numbers, $J$, $F_1$, and $F$. The first of these, $J$, refers to the molecular rotation, which is coupled to the spins of the outer and inner nitrogen nuclei $I_1 = 1$ and $I_2 = 1$, respectively. The coupling proceeds in two steps, first \( \tilde{F}_1 = \tilde{J} + \tilde{I}_1 \), and then \( \tilde{F} = \tilde{F}_1 + \tilde{I}_2 \), which provide the remaining two quantum numbers $F_1$ and $F$. The statistical weight of a hyperfine level $F_1 F$ is given by $2F_1 + 1$, while the total statistical weight of rotational level $J$ is $g_J = (2J_1 + 1)(2J_2 + 1)(2J + 1) = 9(2J + 1)$.

In LTE, the population in hyperfine state $H = F_1 F$ relative to the total population in rotational level $J$ is

\[
n_{JJ} = n_J \left( \frac{2F_1 + 1}{9(2J + 1)} \right). \tag{A1}
\]

The statistical degeneracies of the hyperfine states belonging to each $J$ level sum to the total statistical degeneracy of the $J$ level.

\[
\sum_F (2F + 1) = 9(2J + 1). \tag{A2}
\]

APPENDIX B

EINSTEIN A FOR N$_2$H$^+$

The Einstein A of a transition between rotational levels $JJ'$ is a weighted sum of all the Einstein A's between the individual hyperfine states of each $J$ and $J'$ level. If the level populations are in LTE, indicated by an asterisk,

\[
n^*_J A_{JJ'} = \sum_{HH'} n^*_J A_{JJ'HH'} R_{JJ'HH'}. \tag{B1}
\]
If the relative intensities \( R_{\text{HH}}^J \) are normalized so that
\[
\sum_{\text{HH}} R_{\text{HH}}^J = 1 \quad \text{(B2)}
\]
then
\[
A_{\text{HH}}^J = \frac{9(2J + 1)}{2F + 1} A_{J'} R_{\text{HH}}^J. \quad \text{(B3)}
\]
For any rotational transition,
\[
A_{J'} = \frac{64\pi^2 v^3}{3\hbar c^3} |\mu_{ij}|^2. \quad \text{(B4)}
\]

The average dipole moment, \(|\mu_{ij}|^2\), for a rotational transition of a linear molecule is (Townes & Schawlow 1975, Equation (1–76), p. 23)
\[
|\mu_{ij}|^2 = \mu^2 \frac{J}{2J + 1}. \quad \text{(B5)}
\]

If \( J \) is the initial state and the upper state. In this case, \( J \rightarrow J - 1 \).

As in Townes & Schawlow (1975), \(|\mu_{ij}|^2\) can also be defined in “absorption,” \( J \rightarrow J + 1 \), with \( J \) as the initial and lower state, or in “emission,” \( J + 1 \rightarrow J \), with \( J \) as the final and lower state. In these two alternate definitions, \(|\mu_{ij}|^2 = \mu^2(J+1)/(2J+1)\) and \(|\mu_{ij}|^2 = \mu^2(J+1)/(2J+3)\), respectively.

With our definitions for \( J \) and \( R \), the Einstein A for a hyperfine transition is
\[
A_{\text{HH}}^J = \frac{9(2J + 1)}{2F + 1} \left[ \frac{64\pi^2 v^3}{3\hbar c^3} \right] \mu^2 \frac{J}{2J + 1} R_{\text{HH}}^J. \quad \text{(B6)}
\]

The Einstein A's for the individual hyperfine transitions sum to
\[
\sum_{\text{HH}} \frac{2F + 1}{9(2J + 1)} A_{\text{HH}}^J = A_{J'}. \quad \text{(B7)}
\]

### B.1. Collision Rates for \( \text{N}_2\text{H}^+ \)

For \( \text{N}_2\text{H}^+ \) the approximate collisional rate coefficients in the \textit{proportional} approximation are
\[
\tilde{C}_{J'F'JF} = \frac{2F' + 1}{g(J')} C_{J'F'JF}. \quad \text{(B8)}
\]

### B.2. Frequencies and Relative Intensities of \( \text{N}_2\text{H}^+ \) Hyperfine Lines

The frequencies and relative intensities of the hyperfine lines of \( \text{N}_2\text{H}^+ \) are most accurately calculated by numerical methods (Pickett 1991). Dr. Luca Dore at the University of Bologna kindly supplied these data. Table 1 shows the results for \( J' = 1–0 \) rotational transition. This line is split into 16 hyperfine transitions at 7 different frequencies to produce 7 hyperfine lines. Tables 2 and 3 contain additional information on all the hyperfine states and transitions for \( J \) levels 1–7. Data on the frequencies and relative intensities of the hyperfine transitions of \( \text{N}_2\text{D}^+ \) are available in Gerin et al. (2001) and Dore et al. (2004).

### REFERENCES

Caselli, P., Myers, P., & Thaddeus, P. 1995, ApJ, 455, L77
Caselli, P., Walmsley, C., Tafalla, M., Dore, L., & Myers, P. 1999, ApJ, 523, L165
Chen, J., Zhang, Y.-H., & Zhou, T.-C. 1998, Chin. Astron. Astrophys., 22, 113
Daniel, F., Cernicharo, J., & Dubernet, M.-L. 2006, ApJ, 648, 461
Daniel, F., Dubernet, M.-L., Meuwly, M., Cernicharo, J., & Pagani, L. 2005, MNras, 363, 1083
de Jong, T., Dalgarono, A., & Chu, S.-J. 1975, ApJ, 199, 69
Dore, L., Caselli, P., Benniari, S., Bourke, T., Myers, P. C., & Cazzoli, G. 2004, A&A, 413, 1177
Dower, F. 1999, MNRAS, 305, 651
Gerin, M., Pearson, J. C., Roueff, E., Falgarone, E., & Phillips, T. G. 2001, ApJ, 551, L193
Green, S., & Chapman, S. 1985, ApJS, 57, 169
Guilloteau, S., & Baudry, A. 1981, A&A, 97, 213
Keto, E. 1990, ApJ, 355, 190
Keto, E., & Caselli, P. 2008, ApJ, 683, 238
Keto, E., Rybicki, G. B., Bergin, E. A., & Plume, R. 2004, ApJ, 613, 355
Monteiro, T. S., & Stutzki, J. 1986, MNRAS, 221, 33
Pickett, H. 1991, J. Mol. Spectrosc., 148, 371
Pickett, H. M., Poynter, I. R. L., Cohen, E. A., Delitsky, M.-L., Pearson, J. C., & Muller, H. S. P. 1998, J. Quant. Spectrosc. Radiat. Transfer, 60, 883
Rybicki, G. B., & Hummer, D. 1991, A&A, 245, 171 (RH91)
Rybicki, G. B., & Hummer, D. 1992, A&A, 262, 209
Tafalla, M., Myers, P., Caselli, P., & Walmsley, M. 2004, A&A, 416, 191
Tafalla, M., Myers, P. C., Caselli, P., Walmsley, C. M., & Comito, C. 2002, ApJ, 569, 815

Townes, C. H., & Schawlow, A. L. 1975, Microwave Spectroscopy (2nd ed.; New York: Dover)