Non-LTE and radiative transfer

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Abstract: In this part, we describe the radiative transfer modeling for LTE and non-LTE situations. The necessary extensions for consideration of vibrational and rotational non-LTE are discussed in detail. Finally, some aspects concerning the technical implementation are described.

1 Introduction

The calculation of radiative transfer within KOPRA is performed exclusively in the module radtra_m. Since also the main part of the simulation of non-LTE effects is done in this part of the code in the following we describe first the general LTE-radiative transfer and then the extensions for non-LTE. At the end we will make some remarks about the technical implementation, especially about the interpolation on the wavenumber axis.

2 The radiative transfer in LTE

In contrast to the analytic formulation of radiative transfer in Part II: 'Analytical expressions for radiative transfer modeling of instrumental effects in KOPRA' the discrete formula reads

$$S = B(T_{back}) \prod_{l=1}^{L} \tau_l + \sum_{l=1}^{L} \tilde{J}_l (1 - \tau_l) \prod_{l'=l+1}^{L} \tau_{l'} \tag{1}$$

where l is the index for the layers with layer 1 the farthest and layer L the nearest with respect to the observer. Mind that in this formulation only mean (Curtis-Godson) values of each layer along the ray-path are used. The index on wavenumber is omitted for clarity. T_{back} is the temperature of the background. $\tilde{J}_l$ is the source function for layer l and τ_l the single layer transmission:

$$\tau_l = \exp\left[-\delta_l\right] \tag{2}$$

δ_l is the optical depth for layer l:

$$\delta_l = \delta_{e,Aerosol,l} + \sum_g \sigma_{a,gl} m_{gl} \tag{3}$$

where $\delta_{e,Aerosol,l}$ is the optical depth of aerosol extinction, $\sigma_{a,gl}$ the absorption coefficient, and m_{gl} the partial column density of gas g in layer l.
For the most simple case

$$\tilde{J}_l = B(T_{kin,l}) = \frac{2hc^2\nu^3}{\exp\left(\frac{hc\nu}{k_B T_{kin,l}}\right) - 1}, \tag{4}$$

i.e. the Planck function for the Curtis-Godson temperature of air for layer l (with c: velocity of light, h: Planck's constant, k_B: Boltzmann's constant). The rigorous formulation (to be used for largely different Curtis-Godson temperatures for each gas, for different aerosol absorption and emission coefficients or in the case of non-LTE (see below)) reads

$$\tilde{J}_l = \frac{\hat{J}_l}{\delta_l} = \frac{B(T_{kin,l})\delta_{a,Aerosol,l} + \sum_g \left[J_{gl}\sigma_{a,gl}\right] m_{gl}}{\delta_l}, \tag{5}$$

where $\delta_{a,Aerosol,l}$ is the optical depth of aerosol absorption, $J_{gl} = B(T_{kin,gl})$ the Planck function for the Curtis-Godson temperature of gas g for layer l. Note that in this formulation the aerosol emission is determined by the absorption coefficient of aerosol. This means that only the emission of light by aerosols and not scattering of light into the light path is described in the source term. The scattering of photons out of the light path is considered in the optical depth δ_l by use of the aerosol extinction. For $\delta_{a,Aerosol} = \delta_{e,Aerosol}$ no scattering is described. While Eq. 1 at first glance seems to erroneously neglect the distinction between absorption and extinction the weighting by δ in Eq. 5 compensates for this.

3 Non-LTE

3.1 Introduction

Under conditions of local thermodynamic equilibrium (LTE) the relative populations of the lower and upper state of a ro-vibrational transition are related to the local kinetic temperature by Boltzmann's law. This implies that the source function of a given vibrational-rotational emission is equal to the Planck function at the local kinetic temperature. However, the assumption of LTE for the vibrational degree of freedom is not valid for many infrared emitting gases at and above mesospheric altitudes (CO_2, O_3, CO, etc.), and, in some cases (NO, NO_2, O_3, etc.) even in the stratosphere. LTE breaks down if non-thermal excitation mechanisms such as photochemical processes, solar pumping, and absorption of upwelling radiation cannot be compensated by collisional relaxation. The resulting non-LTE emissions can affect limb radiances even at tangent heights much lower than the breakdown of LTE occurs. In order to consider the effect of non-LTE within radiative transfer calculations the non-LTE state distribution has to be known. Dedicated non-LTE models for numerous infrared emitting gases calculate the non-LTE vibrational state distribution by solving the statistical equilibrium equation under consideration of collisional, chemical, and radiative processes. In each layer l, the vibrational state distribution is then expressed by the vibrational temperature for each vibrational level m of specie g, or

$$T_{vib,gml} = -hE_{vib,gm}\left[k_B \ln\left(\frac{n_{gml}}{n_{g0l}}\right)\right]^{-1} , \tag{6}$$

where n_{gml} and n_{g0l} are the fractional populations of the state m and the ground state, respectively. Alternatively, the non-LTE state distribution can be expressed by the ratio r_{gml} of the fractional populations of the vibrational level m in non-LTE and in LTE:

$$r_{gml} = \frac{n_{gml}^{NLTE}}{n_{gml}^{LTE}} . \tag{7}$$

The latter representation of non-LTE populations is used internally in the code. Either $T_{vib,gml}$ or r_{gml} profiles are necessary input data for KOPRA non-LTE calculations. The treatment of radiative transfer under non-LTE conditions requires some modifications with respect to LTE regarding a) the non-LTE partition sum, b) the non-LTE source function, and c) the non-LTE absorption coefficient.

3.2 The non-LTE correction to the vibrational partition sum

If vibrational temperatures are provided by the user the conversion of $T_{vib,gml}$ to r_{gml} requires the calculation of the non-LTE vibrational partition sum. The LTE vibrational partition sum, can be expressed according to Boltzmann's law:

$$Q_{gl}^{LTE} = \sum_{\eta} g_{g\eta} \exp\left(-\frac{E_{g\eta}}{k_B T_{kin,l}}\right) , \tag{8}$$

where the sum is over all accessible vibrational-rotational states η with the state energy $E_{g\eta}$ and the degeneracy factor $g_{g\eta}$. If vibrational LTE breaks down, the vibrational states are not distributed according to Boltzmann's law which raises the necessity for non-LTE corrections to the partition sum. Under assumption of rotational LTE (which is valid for most atmospheric species below approx. 120 km) and a negligible vibration-rotation interaction, the non-LTE partition sum can be expressed according to *Edwards et al.* [1] by $Q_{gl}^{NLTE} = f_{Q,gl} Q_{gl}^{LTE}$ with the correction factor

$$f_{Q,gl} = \frac{\sum_m g_{gm} \exp\left(-\frac{E_{vib,gm}}{k_B T_{kin,l}}\right)}{\sum_m g_{gm} \exp\left(-\frac{E_{vib,gm}}{k_B T_{vib,gml}}\right)} . \tag{9}$$

The summation is performed within the code over all vibrational states m for which vibrational temperature profiles are provided. The relation between $T_{vib,gml}$ and r_{gml} is then given by

$$r_{gml} = f_{Q,gl} \frac{\exp\left(-E_{vib,gm}/k_B T_{vib,gml}\right)}{\exp\left(-E_{vib,gm}/k_B T_{kin,l}\right)}. \tag{10}$$

3.3 The non-LTE absorption coefficient

The absorption coefficient $\sigma_{a,gl}$ for a given species g is defined as

$$\sigma_{a,gl}(\nu) = \sum_n \frac{h\nu_n}{c} B_{\eta_1\eta_2} n_{\eta_1 l} \left(1 - \frac{g_{\eta_1} n_{\eta_2}}{g_{\eta_2} n_{\eta_1}}\right) \Phi_{nl}(\nu), \tag{11}$$

where the sum is over all transitions n between the ro-vibrational states η_1 and η_2. $B_{\eta_1\eta_2}$ is the Einstein coefficient for absorption and $\Phi_{nl}(\nu)$ is the profile function. Under conditions of LTE, the ratio $(g_{\eta_1} n_{\eta_2})/(g_{\eta_2} n_{\eta_1})$ is given by the Boltzmann factor Γ at the local kinetic temperature $T_{kin,l}$,

$$\Gamma = \exp\left(-\frac{hc\nu}{k_B T_{kin,l}}\right). \tag{12}$$

Under vibrational non-LTE, the absorption coefficient can then be related to the LTE band absorption coefficients $\sigma_{a,gkl}^{LTE}$ of all vibrational bands k between the levels m_1 and m_2 by

$$\sigma_{a,gl}^{NLTE}(\nu) = \sum_k \alpha_{gkl} \sigma_{a,gkl}^{LTE} \tag{13}$$

where α_{gkl} is defined as

$$\alpha_{gkl} = \frac{r_{gm_1l} - r_{gm_2l}\Gamma}{1 - \Gamma}. \tag{14}$$

3.4 The non-LTE source function

A general form of the source function for a single ro-vibrational transition can be written

$$J_{nl} = 2hc^2\nu^3 \left(\frac{g_{\eta_1} n_{\eta_2}}{g_{\eta_2} n_{\eta_1}} \exp\left(\frac{hc\nu}{k_B T_{kin,l}}\right) - 1\right)^{-1}, \tag{15}$$

which is equal to the Planck function for LTE conditions. Under vibrational non-LTE, the source function for the vibrational band k can be expressed by r_{gm_1l} and r_{gm_2l}:

$$J_{gkl}^{NLTE} = 2hc^2\nu^3 \left(\frac{r_{gm_1l}}{r_{gm_2l}} \exp\left(\frac{hc\nu}{k_B T_{kin,l}}\right) - 1\right)^{-1}. \tag{16}$$

The term $J_{gl}\sigma_{a,gl}$ in Eq. 5 then has to be substituted by

$$J_{gl}\sigma_{a,gl} = \sum_k J_{gkl}^{NLTE} \sigma_{a,gkl}^{NLTE}. \tag{17}$$

3.5 Rotational non-LTE

Rotational non-LTE occurs at high altitudes, where collisional thermalization of the rotational state distribution is slower than spontaneous emission. The inclusion of rotational non-LTE in atmospheric radiance calculation becomes necessary for species with high concentrations in the upper atmosphere (above 120 km), such as NO [2]. The radiative transfer equation under conditions of rotational non-LTE can be derived from the vibrational non-LTE case by substitution of the vibrational levels m by ro-vibrational states m, j and vibrational bands k by ro-vibrational lines n. Thus, under conditions of rotational non-LTE, the expressions for absorption coefficient and source function are given by

$$\sigma_{a,gl}^{NLTE}(\nu) = \sum_n \alpha_{gnl} \sigma_{a,gnl}^{LTE} \, , \; \alpha_{gnl} = \frac{r_{gm_1j_1l} - r_{gm_2j_2l}\Gamma}{1-\Gamma}, \tag{18}$$

$$J_{nl}^{NLTE} = 2hc^2\nu^3 \left(\frac{r_{gm_1j_1l}}{r_{gm_2j_2l}} \exp\left(\frac{hc\nu}{k_B T_{kin,l}} \right) - 1 \right)^{-1}, \tag{19}$$

$$J_{gl}\sigma_{a,gl} = \sum_n J_{gnl}^{NLTE} \sigma_{a,gnl}^{NLTE}, \tag{20}$$

where r_{gmjl} is defined according to Eq. 7 as the the ratio of the non-LTE populations and LTE populations of the ro-vibrational state m, j, respectively.

4 Wavenumber interpolation

The absorption coefficients are calculated in the modules abco_m and addlin_m for each pair of Curtis-Godson temperatures and pressures (i.e. for each layer of the forward model) on a layer-specific wavenumber grid. This means, however, that during the radiative transfer where the atmospheric layers are linked an interpolation in wavenumber has to be performed.

At the beginning of the radiative transfer the common wavenumber grid for all layers of the line-of-sight is determined. Then an interpolation to this grid is performed only once for each absorption coefficient in each layer and the subsequent calculations for radiative transfer and derivative calculation are performed exclusively on the common grid. By this scheme the frequent interpolation of two different grids to their common grid (and the determination of this grid) is avoided (avoid 'if's to search the common grid inside the loop over wavenumbers).

Bibliography

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[2] B. Funke and M. López-Puertas, “Nonlocal thermodynamic equilibrium vibrational, rotational, and spin state distribution of NO(ν= 0,1,2) under quiescent atmospheric conditions,” *J. Geophys. Res.* **105**(D4), pp. 4409–4426, 2000.