Non-equilibrium calculations of atmospheric processes initiated by electron impact.

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Abstract. Electron impact in the atmosphere produces ionisation, dissociation, electronic excitation and vibrational excitation of atoms and molecules. The products can then take part in chemical reactions, recombination with electrons, or radiative or collisional deactivation. While most such processes are fast, some longer-lived species do not reach equilibrium. The electron source (photoelectrons or auroral electrons) also varies over time and longer-lived species can move substantially in altitude by molecular, ambipolar or eddy diffusion. Hence, non-equilibrium calculations are required in some circumstances. Such time-step calculations need to have sufficiently short steps so that the fastest processes are still calculated correctly, but this can lead to computation times that are too large. Hence techniques to allow for longer time steps by incorporating equilibrium calculations are described. Examples are given for results of atmospheric non-equilibrium calculations, including the populations of the vibrational levels of ground state N₂, the electron density and its dependence on vibrationally excited N₂, predictions of nitric oxide density, and detailed processes during short duration auroral events.

1. Introduction
Sunlight produces photoionisation and secondary electrons in the atmosphere. High-energy electrons from the Sun also produce ionisation and secondary electrons in auroral processes. Impact of these secondary electrons on atoms and molecules produces further ionisation, dissociation of molecules, and electronic and vibrational excitation of atoms and molecules. The ions, dissociation products and excited atoms and molecules take part in chemical reactions. Ions, particularly molecular ones produced in the chemical reactions, undergo recombination with free electrons. The excited atoms and molecules can radiatively decay, or be quenched in collisions.

Many of these processes are quite rapid, so that they can be modeled in equilibrium calculations. However, some species and excitation states are longer-lived. They therefore do not reach equilibrium during the daily cycle of sunlight or the shorter time scales of auroral processes. They can also be moved vertically by molecular, ambipolar and eddy diffusion. Thus non-equilibrium calculations are necessary to determine the details of atmospheric processes initiated by electron impact.

The non-equilibrium calculation used here is a “time-step” method, in which the change in the density of each species is calculated for small time steps over the interval of interest. This method fails if the time step is too long for any of the fast reactions. This problem could be solved by reducing the length of the time step, but this may make the overall computation time too long. The solution used...
here is to perform an equilibrium calculation for the faster reactions, or to import results from equilibrium calculations into the time-step calculations.

Various cases in which non-equilibrium calculations have been applied to atmospheric calculations will be reviewed. These include the calculation of the populations of vibrationally excited molecular nitrogen in the atmosphere, the calculation of the atmospheric electron density and its dependence on vibrationally excited N$_2$, the calculation of the atmospheric NO density in auroral conditions, and detailed processes in short duration auroral events.

2. Methods for non-equilibrium calculations

In the time-step calculation the incremental change in density $\Delta[z]$ for each species $z$ is calculated at successive small time steps of $\Delta t$ as

$$\Delta[z] = R[x][y] \Delta t,$$

where $R$ is the rate for the reaction $x + y \rightarrow z + ...$ and $\Delta[x] = \Delta[y] = -\Delta[z]$. To implement this computationally, all density changes for each species $x, y$ and $z$ are summed, and the summation done for all species, before adjusting the densities of the species, so that positive and negative increments cancel before any changes are applied. (In the more straightforward alternative, where the increment is calculated for each reaction in turn, a negative density could be calculated for a reactant in a fast reaction. By summing the values first, the negative changes may be mainly cancelled by positive contributions from other reactions.)

Some reactions may be too fast for this to work, so that negative densities may still be calculated. This can be understood by considering what happens in the case of a very long time step. If a particular reactant is being depleted, then its new value will go negative because the loss rate is assumed to remain constant, whereas the loss rate should decline with time as its population declines. Using smaller time steps results in a smaller reduction, so that the density remains positive. A possible approach to this would be to replace the linear change described in equation (1) with an exponential decline, but an attempt to do this resulted in oscillating density values. Instead, the approach used in this work was to apply the continuity equation for short-lived species.

To implement this, the positive and negative contributions to $\Delta[z]$, $\Delta[z_p]$ and $\Delta[z_n]$, are summed and the next value of $[z]$ is calculated by solving the continuity equation, in which the gain $\Delta[z_p]$ is assumed equal to the new value of the population $[z]'$ multiplied by the loss rate in the current interval, $\Delta[z_n]/[z]$, giving:

$$[z]' = \frac{\Delta[z_p]}{\Delta[z_n]}. \quad (2)$$

This allows longer intervals to be used, hence reducing computation time.

The implementation of these methods is illustrated in figure 1. The densities calculated for atmospheric O$^+$($^4$S), O$^+$($^3$D) and O$^+$($^3$P), produced by sunlight and subsequent reactions [1], at 150 km, noon, solar maximum and 65ºN, are shown for 72 seconds, starting with all densities at zero. For 0.001 s intervals, the densities of O$^+$($^3$D) and O$^+$($^3$P) reach equilibrium in about 0.1 s, whereas the density of O$^+$($^4$S) is still rising at 72 s. For 1 s intervals, the straight forward application of equation (1) fails, as negative densities are calculated. When equation (2) is used for O$^+$($^3$D) and O$^+$($^3$P) densities, the equilibrium values are very close to the 0.001 time-step values. Thus it is possible to run a time-step calculation with longer time steps, by using equation (2) for species that have relatively high loss rates. This approach is used in calculations of atmospheric electron and NO densities reviewed below.

In some cases it may be better to run an equilibrium calculation to evaluate the population of a particular reactant and import it into a time-step calculation. This will be explained where it is used in the examples below.
Figure 1. A comparison of O* densities in time-step calculations using 0.001 s intervals and 1.0 s intervals. Values for the shorter time step are shown for O*(^4S) (—), O*(^2D) (— —) and O*(^2P) (— — —), with the first 10 values marked (● ● ●) for each species. Densities calculated at 1 s intervals, using equation (2) for O*(^2D) and O*(^2P), are shown for 1–50 s for O*(^4S) (□), O*(^2D) (○) and O*(^2P) (△).

3. Examples of non-equilibrium calculations

3.1. Vibrationally excited nitrogen

Vibrationally excited ground state nitrogen is important in atmospheric calculations via its role in reducing the electron density [2]. The reaction:

\[ \text{N}_2(v') + O^* \rightarrow \text{NO}^* + \text{N}(^4S) \]  \hspace{1cm} (R1)

is significantly enhanced, by a factor of up to hundreds, if the nitrogen is vibrationally excited to \( v' > 1 \). As molecular ions recombine with electrons at much higher rates than atomic species, the calculated electron density is reduced when vibrationally excited \( \text{N}_2 \) is considered, as the rate of \( \text{NO}^* \) production and so subsequent recombination is increased.
In addition to direct excitation, electron impact can produce vibrational excitation of the ground state of N\(_2\) by producing excited electronic states that radiatively decay into levels of the ground state. It also produces excitation of N\(_2\)\((\nu' = 4)\) indirectly by its role in the production of N\(^4\(S\)) (by dissociation) and NO (by ionisation, leading to subsequent reactions), which then combine in the reaction [3]:

\[
N(^4S) + NO \rightarrow N_2(\nu' = 4) + O .
\] (R2)

As radiative decay of the vibrational levels of the ground state of nitrogen is relatively slow, loss processes are mainly determined by reaction (R1) and collisional interactions. Excitation can be gained or lost by conversion from or to translational motion in VT (vibrational-translational) transitions, while it can be exchanged between molecules in VV (vibrational-vibrational) transitions, where one molecule gains excitation energy and another loses it when they collide [4]. At higher altitudes where collisions are less frequent, the population of N\(_2\)\((\nu' > 0)\) is reduced by molecular diffusion downwards [5]. The long-lived O\(^4\(S\)) ions and balancing electrons also move vertically by ambipolar diffusion [6], affecting the density of O\(^+\) in reaction (R1).

As the energy spectrum of secondary electrons is related to incident sunlight [7], electron impact rates vary with time for calculations of daytime processes. Auroral processes have much smaller time scales, of seconds to minutes. Hence a time-step calculation is required to model the populations of the ground-state vibrational levels of N\(_2\), given the mix of processes described above. However, the populations of the excited electronic states are determined by radiative decays that are generally much faster and cover a wide range of different probabilities. Hence a statistical equilibrium calculation [8] is best for determining the populations of the excited states. However, because the populations of the excited states are not greatly affected by those of the ground state (as most nitrogen molecules in the atmosphere are in level \(\nu'' = 0\) and because the excitation probabilities to excited states are assumed to be very similar for different levels of the ground state), the populations of the excited states can be determined in a statistical equilibrium calculation and then used as inputs in the time-step calculation for the levels of the ground state. For example, if the population of N\(_2\)[A\(^3\Sigma_u^+(\nu')\)] has been calculated by statistical equilibrium, the rate of the radiative decay into level \(\nu''\) of the ground state, \(i.e.\) for A\(^3\Sigma_u^+(\nu') \rightarrow X^1\Sigma_g^+(\nu'')\), can be calculated for an interval \(\Delta t\) of the time-step calculation.

This mix of statistical-equilibrium and time-step methods was applied in the calculation of the populations of vibrational levels of N\(_2\) in auroral conditions and the consequent enhancement of reaction (R1) [2]. Calculations were made for a 6-minute aurora applied to a normal atmosphere at noon and at midnight. The electron density at noon was calculated to validate the model that was then applied for the auroral processes.

An example of the results is shown in figure 2, giving the calculated populations of the ground state vibrational levels for an IBC III\(^+\) aurora at noon, and the vibrational temperatures calculated for selected ranges of the vibrational levels. The results show the distributions to be more extended at higher \(\nu''\) than in previous work, with higher vibrational temperatures for \(\nu'' > 4\) than generally reported previously.

3.2. Calculations of the electron density

The time-step calculation of the electron density developed for the previous example has been applied in investigations of the parameters that determine the calculated electron density, including the rate for reaction (R1) [9] and the electron impact cross sections for vibrational excitation of N\(_2\) [10]. The calculated values are compared with the International Reference Ionosphere (IRI), which is an empirical model based on a wide range of measurements [11]. In each investigation a time-step simulation was run for the interval from 4am until noon at 0.1 s intervals, with the contribution from
Figure 2. (a) Predicted absolute density of \(N_2[X(\nu'')]\), as a function of the vibrational quantum number \((\nu'')\) and four different altitudes, for the daytime plus a 6-minute aurora (IBC III*). For purposes of comparison, the Boltzmann population at 350 km is also shown. (b) Relative vibrational distributions (to the population at \(\nu'' = 0\)) for each of the four altitudes, as a function of the vibrational quantum number. For purposes of comparison, the Boltzmann population of \(N_2\) appropriate for an altitude of 130 km is also shown. (c) The electron temperature and the effective vibrational temperatures of the \(N_2\) vibrational distribution as a function of altitude and for selected ranges of vibrational levels of the \(X\)-state. The 0–2 vibrational temperature for daytime only is also shown (“day 0–2”).

the excited electronic states of \(N_2\) imported from the output of a statistical equilibrium calculation for photoelectron impact. The dependence on the rate of reaction (R1) is now considered as an example.

There are two sets of published rates for reaction (R1) in the atmosphere. A set of values by Van Zandt and O’Malley [12] gives the rate for all \(\nu'\) at various temperatures. A more recent set uses rates of St. Maurice and Torr [13] for \(N_2(\nu'' = 0)\) as a function of temperature which were specified as appropriate for ionospheric conditions, multiplied by enhancement factors of Schmeltekopf et al. [14] for each value of \(\nu'\). In figure 3 the electron densities calculated using the rates of Van Zandt and O’Malley are compared with the IRI, while the same comparison is made in figure 4 using the rates of St. Maurice and Torr with the enhancement factors of Schmeltekopf et al. In each case the model is run with and without the enhancement due to vibrationally excited \(N_2\) being included. For both sets of rates, it is seen that the electron density is overestimated, especially for the rates of Van Zandt and O’Malley, when the enhancement is not included. When the enhancement is taken into account, the electron density is underestimated in the region of the peak density, for both sets, but more so for the
rates of Van Zandt and O’Malley. Hence it is shown that the enhancement of reaction (R1) due to vibrationally excited N\textsubscript{2} needs to be included in calculations of the electron density and that the rates of St. Maurice and Torr combined with the enhancement factors of Schmeltekopf \textit{et al.} give a more accurate result than the rates of Van Zandt and O’Malley.

3.3. Calculations of nitric oxide density
Nitric oxide is a minor constituent of the upper atmosphere, but is important because of its role in infrared emission [15]. Recently the NO density in the upper atmosphere has been measured by the Student Nitric Oxide Explorer (SNOE) satellite [16]. NO is generated by reactions of ions and nitrogen atoms, N(4\textsc{S}) and N(\textsc{2D}), that are produced either by photoionisation and photodissociation by sunlight, or by electron impact by photoelectrons and auroral secondary electrons. These processes do not reach chemical equilibrium below about 130 km due to molecular and eddy diffusion of N(4\textsc{S}) atoms and NO molecules. Hence a time-step simulation is useful in modeling the NO density over a period of several days.

As the calculations need to be performed down to an altitude of about 70 km (to include for the effects of eddy diffusion) the atmospheric densities are much higher than in the calculations for electron density, which had a minimum altitude of 130 km. This requires much smaller time steps (than 0.1 s) for a straight forward time step calculation, and hence an unreasonably long computation time for a simulation of several days. The computation time was reduced by applying the continuity equation (2) for fast processes, as described in section 2, allowing time steps of 0.5 or 1.0 s to be used.

One postulated source of NO in the upper atmosphere is the reaction [17]:

\[
\text{N}_2[A^3\Sigma_u^+] + O \rightarrow \text{NO} + \text{N}(\textsc{2D})
\]  
(R3)
and a current investigation [18] is to determine the contribution of this reaction to the production of NO in the upper atmosphere. As the $N_2[A^3Σ_u^+]$ can be produced by direct excitation or by radiative decay from other excited states of $N_2$ and is depleted by radiative decay, chemical and collisional processes, with a wide range of time scales, its population is more easily determined in a statistical equilibrium calculation [8] than a time-step simulation. The option of applying equation (2) as part of the time-step simulation was not used because of the large number of levels in the electronic states of $N_2$ and the much larger number of radiative transitions between these levels. This would greatly increase the computation time for the simulation. Hence the population is determined in a statistical equilibrium calculation and then imported into the time-step simulation. This is only possible because the NO density is relatively small compared to the main atmospheric constituents ($O_2$, $N_2$ and $O$), so that the reverse reactions of $N_2[A^3Σ_u^+] + NO$ [19] are small compared to the other reactions which deplete $N_2[A^3Σ_u^+]$ and which are taken into account in the statistical equilibrium calculation.

An example of the application of the time-step simulation, as used by Campbell et al. [18], to the calculation of NO densities is shown in figure 5, where the calculated values are compared with the maximum NO density measured by the SNOE satellite at 106 ± 1.6 km, shown by the vertical line. The calculated values are for a simulation for 4.5 days of the daily sunlight cycle plus (as postulated in similar work [20]) an auroral energy flux of 0.5 erg.cm$^2$.s$^{-1}$ and for the same simulation with an IBC II* aurora (27 erg.cm$^2$.s$^{-1}$) applied for 1 hour at the end. Each case is run with and without the contribution of reaction (R3). It can be seen that inclusion of reaction (R3) increases the calculated NO density by a factor of about 3. The agreement with the measured value is not definitive, as the actual auroral conditions are not known, but it is seen that the observed maximum value can be calculated using plausible input parameters.

4. Non-equilibrium calculations of auroral processes
Infrared emission from NO is important in the heat balance of the upper atmosphere and provides a means of remote sensing of NO densities. The accepted sources [21] for this emission are nightglow, produced by radiative decay following the collisional excitation:

![Figure 5](image-url)  
**Figure 5.** Calculated values of NO density compared with the maximum observed value (•) at 106 km. The calculated values are for 4.5 days of sunlight plus an auroral energy flux of 0.5 erg.cm$^2$.s$^{-1}$ with (●) and without (○) the $N_2[A^3Σ_u^+] + O$ contribution, and with the addition of an IBC II* aurora for one hour, with (■) and without (▲) the $N_2[A^3Σ_u^+] + O$ contribution.
and the chemiluminescent reaction, for $\nu' = 0, 1, \ldots, 12$,

$$\text{N}_2\text{D} + \text{O}_2 \rightarrow \text{NO}(\nu') + \text{O}. \quad (R5)$$

Recent measurements [22] of the vibrational excitation cross sections for NO at low impact energy, i.e.

$$\text{NO}(\nu'' = 0) + e^- \rightarrow \text{NO}(\nu') + e^- (\nu' = 1, 2, 3), \quad (R6)$$

have enabled calculations of the infrared emission due to electron impact to be made.

Non-equilibrium calculations are required in this application for two reasons. The NO density increases with time due to auroral impact, as shown in figure 5. The second reason is that the vibrational levels of NO are excited by impact of thermal electrons, as well as auroral electrons. The excitation rates due to thermal electrons depend on their density and temperature, both of which change during auroral impact, therefore requiring a non-equilibrium calculation.

The increase of NO density calculated for an IBC II+ aurora is plotted in figure 6 for a 30-minute time interval, along with the calculated density of N$_2$D atoms. It can be seen that the N$_2$D atoms reach equilibrium quickly, while the NO density continues to increase. Consequently the ratio of infrared emission due to the NO(1→0) transition following from electron impact increases relative to that due to chemiluminescence, as also shown in figure 6.

**Figure 6.** Logarithm (base 10) of the calculated densities of NO and N$_2$D atoms and the ratio of electron impact to chemiluminescent production of the (1→0) emission from NO as a function of time, at an altitude of 150 km.

The impact of auroral secondary electrons produces ionisation and corresponding free electrons, thus increasing the electron density. The electron temperature also increases, as the secondary electrons produced in the ionisation process initially have a substantially higher temperature. The
temperature is calculated by assuming that a particular energy of 0.45 eV per ionisation event is imparted to the kinetic energy of the free electrons. Their temperature is determined by applying conservation of energy, by finding the electron temperature at which the energy flow into the electrons is equal to the energy which they lose in producing excitation and in other cooling processes. The calculated electron density and temperature and the N(2D) density, for a particular observed aurora [21], are shown in figure 7, all plotted as a function of time. The strength of the aurora is indicated by the intensity of the observed 557.7 nm emission. It can be seen that while the N(2D) density follows the auroral input fairly closely, the electron density shows a time lag in its response.

As the electron density is proportionally larger, relative to the N(2D) density, after a temporary increase in auroral input, it is to be expected that the ratio of electron impact excitation to chemiluminescence (which is proportional to the N(2D) density) will increase. This forms the basis of an ongoing investigation into the possibility of using electron impact excitation of NO as a means of remote sensing of auroral processes and NO density.

![Figure 7](image)

**Figure 7.** The strength of the aurora (indicated by the observed 557.7 nm emission), and the calculated values of the density of N(2D) atoms, the electron density and the electron temperature, plotted as a function of time at an altitude of 120 km.

### 5. Conclusions

The need for non-equilibrium calculations in atmospheric modeling is described. Two methods of combining equilibrium and non-equilibrium calculations are described as a means of reducing computation time in time-step calculations. One of these, where the continuity equation is solved for fast reactions at each time step, is validated in a sample calculation. Some examples using non-equilibrium methods in atmospheric calculations are reviewed, including time-step calculations of the populations of the vibrational levels of the ground state of N₂. These require importation of the populations of the excited states of N₂ determined in a statistical-equilibrium calculation. Calculations of the atmospheric electron density, using the same mix of non-equilibrium and statistical equilibrium calculations, are used to show that one set of rate constants for the reaction of vibrationally excited N₂ with O⁺ leads to substantially better results than another. Predictions of NO density in the atmosphere require non-equilibrium calculations, but also both of the equilibrium calculations (i.e. statistical equilibrium for the excited states of N₂ and the use of the continuity equation for fast reactions). These
calculations, with plausible auroral input, are used to predict an atmospheric density of NO which is similar to the maximum measured value. Finally time-step calculations are used to predict the NO, N(^2)D) and electron densities and electron temperatures in short duration auroral events. The results indicate that the electron impact contribution to infrared emissions in aurora is not a linear function of the auroral strength, and so may provide a means of remote sensing of auroral processes and NO density.

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