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TITLE: **Baseline plasma chemistry model for intense electron beam driven plasmas and preliminary improvement approach***

AUTHORS: P. E. Adamson
Code 6770, Plasma Physics Division, Naval Research Laboratory

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ABSTRACT: The plasma chemistry model from ref [1] is used as the baseline for a DTRA- and NRL-funded effort to update ICEPIC and MEEC with modern plasma chemistry models. Plans for revising the model include **XXX**.

Table 1: Species followed in the baseline gas-chemistry model of ref [1]. All of the molecular-excitation energies listed are with respect to the ground neutral molecular state and similarly for the atomic species with charge state $Z \geq 1$. The energies listed for the atomic ion species with $Z > 1$ are with respect to the ground electronic state of the $Z - 1$ charge state.

Species class	Species state	Excitation energy (eV)
Molecular neutral species (N_2):	$X^1\Sigma$, $A^3\Sigma$, $B^3\Pi$, $W^3\Delta$, $B'^3\Sigma$,	0, 6.17, 7.35, 7.36, 8.17,
	$a'^1\Sigma$, $a^1\Pi$, $w^1\Delta$, $C^3\Pi$	8.40, 8.55, 8.89, 11.0
Molecular ion species (N_2^+):	$X^2\Sigma$, $A^2\Pi$, $B^2\Sigma$	15.6, 16.7, 18.8
Atomic neutral species (N):	$^4S^o$, $^2D^o$, $^2P^o$,	0, 2.39, 2.57,
	$3s\,^4P$, $3s\,^2P$, $2p^4\,^4P$,	10.42, 10.77, 10.95,
	$3p^2\,S^o$, $3p^4\,D^o$, $3p^4\,P^o$, $3p^4\,S^o$,	11.62, 11.79, 11.87, 12.00,
	$3p^2\,D^o$, $3p^2\,P^o$, $3s^2\,D$, $4s^4\,P$,	12.03, 12.15, 12.37, 12.85,
	$4s^2\,P$, $3d^2\,P$, $3d^4\,F$, $3d^4\,P$,	12.92, 12.96, 12.97, 12.98,
	$3d^2\,F$, $3d^4\,D$, $3d^2\,D$	12.99, 13.01, 13.02
Atomic ion species with $Z = 1$ (N^+):	^3P, ^1D, ^1S	14.5, 16.4, 18.6
Atomic ion species with $Z > 1$ ($N^{(Z)}$):	$2 \leq Z \leq 7$	29.6, 47.5, 77.5, 97.9, 552, 667

1 Introduction

The plasma chemistry model used to baseline the DTRA- and NRL-funded update to ICEPIC and MEEC plasma chemistry models is taken from ref [1]. The baseline model includes atomic N and molecular N_2 species listed in Table 1.

2 Neutral N Atom

The neutral N atomic species followed in the baseline plasma chemistry model include the ground state $2s^2 2p^3\ ^4S^o$, the two low–lying meta stable states that share the same electron configuration as the ground state $(1s^2 2s^2 2p^3)$ $N(^2D^o, ^2Po)$, and the first 18 optically allowed excited states. These electronic states and corresponding term symbols are listed in Table 2.

2.1 Electron-Impact Excitation Cross Sections

For the baseline plasma chemistry model, electron-impact excitation cross sections between electronic states of neutral atomic nitrogen listed in Table 2 are taken from BSR calculations by Wang et al.[2] Table 3 describes the file naming schemes and locations of LxCat and raw (BSR output) format data files for cross sections from ref [2], including elastic scattering and electron-impact ionization cross sections which will be described below.

Table 2: Spectroscopic target states of atomic nitrogen for neutral atom excitation, ionization, and elastic scattering cross sections. The indices in the first column of the table are used to catalog the raw BSR and LxCat format data files as described in Table 3.

	State	Term
1	$2s^2 2p^3$	$^4S^o$
2	$2s^2 2p^3$	$^2D^o$
3	$2s^2 2p^3$	$^2P^o$
4	$2s^2 2p^2(^3P)3s$	^4P
5	$2s^2 2p^2(^3P)3s$	^2P
6	$2s2p^4$	^4P
7	$2s^2 2p^2(^3P)3p$	$^2S^o$
8	$2s^2 2p^2(^3P)3p$	$^4D^o$
9	$2s^2 2p^2(^3P)3p$	$^4P^o$
10	$2s^2 2p^2(^3P)3p$	$^4S^o$
11	$2s^2 2p^2(^3P)3p$	$^2D^o$
12	$2s^2 2p^2(^3P)3p$	$^2P^o$
13	$2s^2 2p^2(^1D)3s$	^2D
14	$2s^2 2p^2(^3P)4s$	^4P
15	$2s^2 2p^2(^3P)4s$	^2P
16	$2s^2 2p^2(^3P)3d$	^2P
17	$2s^2 2p^2(^3P)3d$	^4F
18	$2s^2 2p^2(^3P)3d$	^4P
19	$2s^2 2p^2(^3P)3d$	^2F
20	$2s^2 2p^2(^3P)3d$	^4D
21	$2s^2 2p^2(^3P)3d$	^2D

Some details of the BSR model from ref [2]:

- the configuration expansions for each atomic target state contained up to 250 configurations

- the number of pseudostates used to describe ionization processes was limited by a relatively small box size of radius $30a_0$, thus restricting the number of spectroscopic target states that could be accurately modeled to those listed in Table 2

- the close-coupling (CC) expansion includes 690^1 states of atomic nitrogen, with 56 states representing the bound spectrum and the remaining 644 representing the target continuum and some core-excited autoionizing states

- all doublet and quartet target states with total electronic orbital angular momentum $L = 0\check{}4$ are included

- the continuum pseudostates cover the energy regime up to 50 eV above the ionization limit

- the maximum interval in the B-spline grid is $0.65a_0$, which is sufficient to cover electron scattering energies up to 200 eV

- the collision model contained up to 1704 scattering channels, leading to generalized eigenvalue problems with matrix dimensions up to 120,000 in the B-spline basis

- partial waves for total orbital angular momenta $L \leq 25$ were computed numerically resulting in 156 partial waves when spin and parity are taken into account

In order to assess the accuracy and completeness of the BSR results of ref [2], we plan to reproduce them with the UK-molecular R-matrix code suite+ (UKRMol+) B-spline type orbital (BTO)/Gaussian type orbital (GTO) method while varying the following parameters:

- quantum mechanical method for target wave function (Hartree-Fock (HF), complete active space (CAS)-configuration interaction (CI), frozen core (FC)-full CI (FCI), FCI) including the number of configurations in included in the CI,

- basis set size and type in target wave function,

- custom even-tempered versus off-the-shelf basis sets in target wave function,

- extent of the reduced radial range and target-continuum transition,

- continuum BTO/GTO basis size and parameters, and

- B-spline grid interval

2.2 Electron-Impact Ionization

TBD

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[1] note the discrepancy between the total size of the expansion (690) and the sum of the bound and continuum state quantities (56+644=700)

Table 3: Filename structure for example neutral N atom electron-impact excitation, elastic scattering, and electron-impact ionization cross sections stored in LxCat and raw (BSR output) format. The first and second numbers used in the filenames correspond to the indices from the first column of Table 2 for the LHS and RHS N atom species, respectively. Raw data from BSR calculations are stored in the `n_bsr/N_2014_archive` folder. Data files in LxCat format are stored in the `n_bsr/lxcat` folder.

Process		LHS Index	RHS Index	Format	Filename
Electron-Impact Excitation	$e^- + N[(2s^2 2p^3)\,^4S^o] \rightarrow e^- + N[(2s^2 2p^3)\,^2D^o]$	1	2	LxCat BSR	`tr_001_002_lxcat` `tr_001_002`
	$e^- + N[(2s^2 2p^3)\,^2D^o] \rightarrow e^- + N[(2s2p^4)\,^4P]$	2	6	LxCat BSR	`tr_002_006_lxcat` `tr_002_006`
Elastic Scattering	$e^- + N[(2s^2 2p^3)\,^4S^o]$	1	1	LxCat BSR	`tr_001_001_lxcat` `tr_001_001`
	$e^- + N[(2s^2 2p^3)\,^2D^o]$	2	2	LxCat BSR	`tr_002_002_lxcat` `tr_002_002`
Electron-Impact Ionization	$e^- + N[(2s^2 2p^3)\,^4S^o] \rightarrow e^- + e^- + N[(2s^2 2p^3)\,^4S^o]^+$	1	N/A	LxCat BSR	`ion_001_lxcat` `ion_001`
	$e^- + N[(2s^2 2p^3)\,^2D^o] \rightarrow e^- + e^- + N[(2s^2 2p^3)\,^2D^o]^+$	2	N/A	LxCat BSR	`ion_002_lxcat` `ion_002`

Table 4: Collision strengths $\Omega(i,j)$.

i	j	$\Omega(i,j)$
^{3}P	^{1}D	2.98
^{3}P	^{1}S	0.395
^{1}D	^{1}S	0.410

Table 5: Nitrogen ion electron-impact excitation cross section files.

Process	Cross Section File
$e^- + N\left[(2s^22p^2)\ ^3P\right]^+ \rightarrow e^- + N[(2s^22p^2)\ ^1D]^+$	`np_henry/tr_001_002_lxcat`
$e^- + N\left[(2s^22p^2)\ ^3P\right]^+ \rightarrow e^- + N[(2s^22p^2)\ ^1S]^+$	`np_henry/tr_001_003_lxcat`

2.3 Elastic Scattering

TBD

3 Singly-Ionized Nitrogen Ion

For the singly ionized atomic nitrogen ion species, the states considered are the ground state N^+ (^3P) and the two low–lying meta stable states that share the same electron configuration as the ground state $(1s^22s^22p^2)$ N^+ $(^1D,\ ^1S)$.

3.1 Electron-Impact Excitation Cross Sections

Cross sections for the two processes considered,

$$e^- + N\left[(2s^22p^2)\ ^3P\right]^+ \rightarrow e^- + N[(2s^22p^2)\ ^1D]^+ \tag{1}$$

$$e^- + N\left[(2s^22p^2)\ ^3P\right]^+ \rightarrow e^- + N[(2s^22p^2)\ ^1S]^+ \tag{2}$$

are calculated using the approach from references [3] and [4]:

$$\sigma_j = \left[\left(1.197\times10^{-15}\right)/g_iE\right]\Omega(1,j) \tag{3}$$

where g_i is the initial state statistical weight ($g_i = 9$) and $\Omega(1,j)$ is the collision strength for the final state. Although the collision strengths have energy dependence as shown in Figure 1, we will use the constant values given in Table 4 consistent with the approach in ref [3]. The relevant cross sections are stored in LxCat format in the files listed in Table 5. *Note: ref [4] also provides approaches for computing electron-impact excitation cross sections for six optically allowed N^+ transitions to triplet states as well as excitations to Rydberg-states that are not included in this baseline plasma chemistry model.*
Improvements: TBD
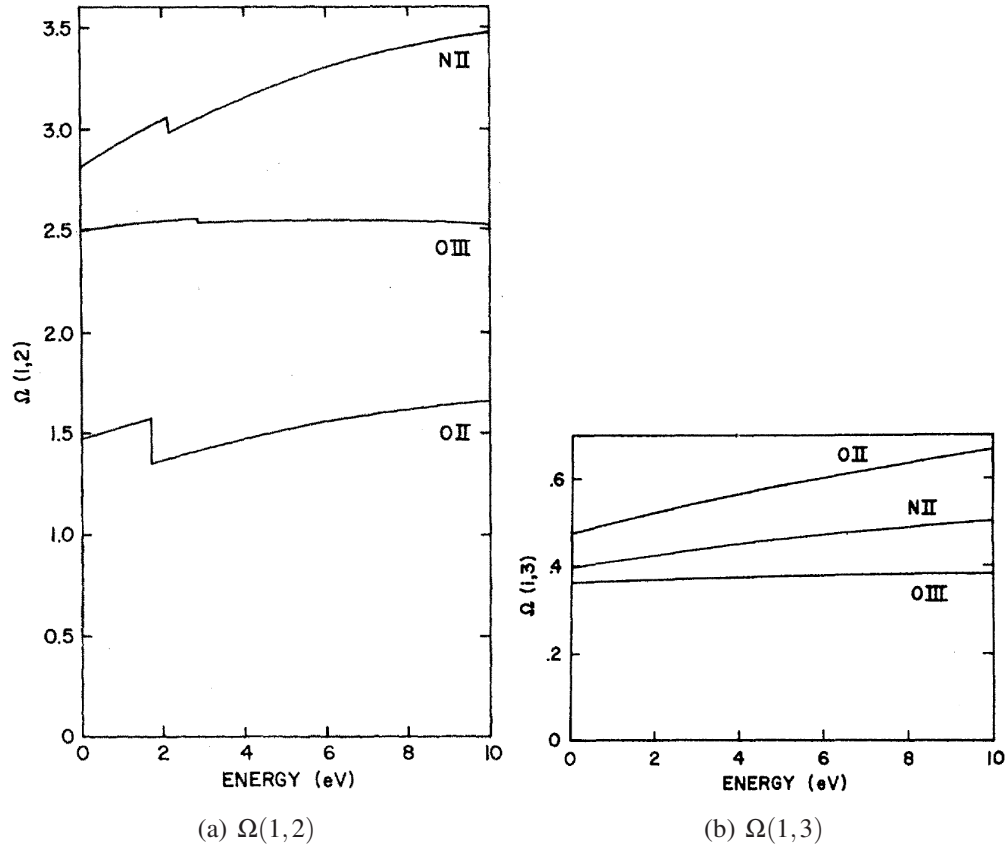
3.2 Electron-Impact Ionization Cross Sections

TBD

(a) $\Omega(1,2)$

(b) $\Omega(1,3)$

Figure 1: Energy variation of collision strengths for electrons incident on N^+, O^+, and O^{++} ions from ref [3].

3.3 Elastic Scattering Cross Sections

<mark>TBD</mark>

4 Ionized Atomic Nitrogen ($Z > 1$)

The ground electronic states of ionized atomic nitrogen with charge state $Z > 1$ are also contained in the model. None of the $Z > 1$ species have low–lying electronic levels that share the same ground– state–electron configuration.

4.1 Electron-Impact Excitation Cross Sections

<mark>TBD</mark>

4.2 Electron-Impact Ionization Cross Sections

<mark>TBD</mark>

4.3 Elastic Scattering Cross Sections

<mark>TBD</mark>

5 Molecular neutral species (N$_2$)

<mark>TBD</mark>

6 Molecular ion species (N$_2^+$)

<mark>TBD</mark>

7 Summary

Table 6: Neutral N atom plasma chemistry model–baseline and preliminary improvement approach.

Process	Baseline	Preliminary Improvement Approach
Electron-Impact Excitation	BSR[2]	Reproduce ref [2] BSR results with the UKRMol+ BTO/GTO method; explore impact of varying: - quantum mechanical method for target wave function (HF, CAS-CI, FC-FCI, FCI) including the number of configurations in included in the CI, - basis set size and type in target wave function, - custom even-tempered versus off-the-shelf basis sets in target wave function, - extent of the reduced radial range and target-continuum transition, - continuum BTO/GTO basis size and parameters, and B-spline grid interval
Electron-Impact Ionization		
Elastic Scattering		

Table 7: Singly-ionized N atom plasma chemistry model–baseline and preliminary improvement approach.

Electron-Impact Excitation
Electron-Impact Ionization
Elastic Scattering

Table 8: Ionized N atom (Z > 1) plasma chemistry model–baseline and preliminary improvement approach.

Electron-Impact Excitation
Electron-Impact Ionization
Elastic Scattering

A R-matrix Method Considerations

In R-matrix methods, the scattering problem is divided into inner and outer regions separated by a sphere of radius $r = a$ upon which the energy-dependent R-matrix is constructed. In the inner region, quantum chemistry methods, such as HF and post-HF methods found in codes such as General Atomic and Molecular Electronic Structure System (GAMESS)[5] and Gaussian[6], are used to produce full scattering energy-independent wavefunctions for the target molecule and for the target molecule plus the scattering electron. The form of the inner region wavefunction is

$$\Psi_k = \hat{A} \sum_{i,j} c_{ijk} \Phi_i^N \eta_j + \sum_m b_{mk} X_m^{N+1} \tag{4}$$

The first of the two terms in equation 4 is a sum over products of the target wavefunctions, Φ_i^N, and the continuum orbitals, η_j, where c_{ijk} is the coefficient for the ith, jth, kth term. N labels the target wavefunction (N electrons in the target atom). The second term, called the L^2 term, is necessary to describe polarisation/correlation and resonance formation. This involves forming a wavefunction of the target molecule plus the scattering electron (hence the $N+1$ label) using occupied and virtual target orbitals, the X_m^{N+1}, where b_{mk} is the coefficient for the mth, kth term. A crucial assumption applied when selecting the target model is that the target wavefunction is entirely contained within the R-matrix sphere. In the outer region, the R-matrix is propagated to a large radius (typically on the order of 100 a_0), then used to calculate K- and T-matrices which give scattering quantities such as eigenphases, cross-sections, and resonances.

The quality of R-matrix calculations are highly dependent on several factors:

1. the amount of electron correlation captured by the quantum chemistry treatment used to compute the target wavefunction, Ψ

2. the size, nature, and quality of the atomic basis set used in #1 (also affects amount of electron correlation included in the model)

3. inclusion of polarization/correlation and excited states in the scattering model

4. number of continuum basis functions used to represent the continuum orbitals, X

A.1 Target model

The simplest *ab initio* quantum chemistry treatment in common usage is the HF method, in which electrons only interact with the mean averaged field of other electrons and nuclei. The corresponding HF wavefunction is represented by a single configuration. On the other end of the accuracy scale is the FCI method, which includes all possible electron configurations constructed from all available molecular orbitals (MOs) subject only to the constraints of the Pauli Principle and total symmetry, giving the best possible wavefunctions for a given basis set. Intermediate between these is CAS-CI where only a subset of the available HF MOs are in the "active space" of the FCI method. A special variant of the CAS-CI method is the FC-FCI model where the core MOs are always doubly occupied and the remaining electrons are active in all the other orbitals.

UKRMol+ calculations are carried out with GTO basis sets, of which one of the most widely used families is the (aug)-cc-pVNZ by Dunning.[7] They are attractive as they are designed for converging post-Hartree–Fock calculations systematically to the complete basis set limit using empirical extrapolation techniques. For first- and second-row atoms, the basis sets are cc-pVNZ where N=D,T,Q,5,6,... (DZ=double-zeta, TZ=triple-zeta, etc.). The 'cc-p', stands for 'correlation-consistent polarized,' and the 'V' indicates they are valence-only basis sets. As N increases, the basis includes successively larger shells of polarization (correlating) functions (d, f, g, etc.). If prefixed by 'aug-', the basis set is an augmented version with added diffuse functions (Rydberg-like orbitals). For example, aug-cc-pVDZ is the augmented correlation-consistent polarized valence-only double-zeta Dunning basis set.

There are three major factors to consider when settling on the quantum chemistry model and basis set for R-matrix calculations:

1. accuracy of resulting energy levels (vertical excitation energies) and target properties (e.g. permanent and transition dipole moments) for all molecular states of interest

2. computational tractability when used, in conjunction with a continuum basis, in a scattering calculation.

3. spatial extent of the target wavefunction (it must fit inside the R-matrix sphere as this is the basic assumption of the method)

Thus, succesful R-matrix calculations require a delicate balancing act because

- diffuse functions are often necessary to accurately represent certain excited states,

- diffuse functions require a larger R-matrix sphere, and

- the size of the R-matrix sphere impacts the amount of computational resources required as a larger sphere drives the need to include many more continuum functions in the basis.

Furthermore, a large target and continuum basis can also cause issues with numerical linear dependence which can manifest itself in the inner region as unphysical bound states or R-matrix poles.

A.2 Scattering model

In a CC scattering model, a CAS-CI target state is used, and the L^2 functions are formed by adding one more electrons to the active space. The CC-FCI method has demonstrated the advantage that it allows a balanced treatment of the target and scattering problems.

A.3 Continuum model

The UKRMol+ suite uses GTOs for the continuum basis, but the Gaussian radial part of the continuum basis is replaced with B-splines to overcome numerical linear dependence problems. The GTOs and BTOs are mixed freely. The corresponding BTOs have the form:

$$\mathscr{B}(r)_{i,l,m} = \frac{B(r)}{r} X_{lm}(\Omega) \tag{5}$$

where $\mathscr{B}_i(r)$ is the ith radial B-spline and $X_{lm}(\Omega)$ is the real spherical harmonic. UKRMol+ is currently the only R-matrixcode employing B-splines in the continuum model where the target molecule is represented by atom-centered GTO wave functions from standard quantum chemistry methods. This offers the opportunity to model a wide variety of atomic and molecular systems.

In a reduced radial range ($5a_0$), GTOs are used to represent the continuum without linear dependency problems and to give a good representation over a wide energy range. The long distance part of the continuum wave function is represented by BTOs, and the quality of the radial wave function is controlled easily by the density of the knots and the order of the B-splines.

B   NIST Database of N Atom Electronic States

For the neutral N atom, 369 levels are available on NIST.[8] For N(II), 183 levels are available. To illustrate, a sample of the data set for neutral N atom is printed in Table **??**.

Table 9: Sample of available neutral N atom energy levels on NIST.[8]

Configuration	Term	J	Level (eV)	Uncertainty (eV)	Reference
2s2.2p2.(3P).3d	4F	3/2	12.9766982		
		5/2	12.9790452		
		7/2	12.9832470		
		9/2	12.989300		
2s2.2p2.(3P).3d	2F	5/2	12.9948284		
2s2.2p2.(3P).3d	4P	5/2	12.9966571		
		3/2	13.000949		
2s2.2p2.(3P).3d	2F	7/2	13.0036300		
2s2.2p2.(3P).3d	4P	1/2	13.004219		
2s2.2p2.(3P).3d	4D	1/2	13.016403		
		3/2	13.017878		
		5/2	13.019401		
		7/2	13.0205228		
2s2.2p2.(3P).3d	2D	3/2	13.0332040		
		5/2	13.0361585		
2s2.2p2.(3P).4p	2S*	1/2	13.2015646		
2s2.2p2.(3P).4p	4D*	1/2	13.2363956		
		3/2	13.2388264		
		5/2	13.2433050		
		7/2	13.2500219		
2s2.2p2.(3P).4p	4P*	1/2	13.2638889		
		3/2	13.2658172		
		5/2	13.2709051		
2s2.2p2.(3P).4p	2D*	3/2	13.2889719		
		5/2	13.2976903		
2s2.2p2.(3P).4p	4S*	3/2	13.3215592		
2s2.2p2.(3P).4p	2P*	1/2	13.3392700		
		3/2	13.3442063		
2s2.2p2.(3P).5s	4P	1/2	13.6149816		
		3/2	13.6204725		
		5/2	13.6291688		
2s2.2p2.(3P).5s	2P	1/2	13.6426904		
		3/2	13.6511355		
2s2.2p2.(3P).4d	4F	3/2	13.6623957		
		5/2	13.6645955		

C Acknowledgments

Insert acknowledgements.

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