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Multicomponent transport algorithms for partially ionized mixtures

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ABSTRACT

We investigate iterative methods for solving linear systems arising from the kinetic theory of gases and providing multicomponent transport coefficients of partially ionized plasmas. We consider the situations of weak and strong magnetic fields as well as electron temperature nonequilibrium and the linear systems are investigated in their natural constrained singular symmetric form. Stationary iterative techniques are considered with new more singular formulations of the transport linear systems as well as orthogonal residuals algorithms. The new formulations are derived by considering generalized inverses with nullspaces of increasing dimension. Numerical tests are performed with high temperature air and iterative techniques lead to fast and accurate evaluation of the transport coefficients for all ionization levels and magnetic field intensities.

1. Introduction

Ionized magnetized reactive gas mixtures have many practical applications such as laboratory plasmas, high-speed gas flows, lean flame stabilization or atmospheric phenomena [6,10,13,17,18,32,36,67]. This motivates kinetic theory investigations and the derivation of macroscopic multicomponent plasmas equations. Applications of the Chapman–Enskog theory to partially ionized mixtures in weak and strong magnetic fields in a regime where there is only one temperature have been discussed in particular by Braginsky [6], Bruno, Capitelli and Dangola [8], Chapman and Cowling [13], Devoto [22], Ferziger and Kaper [32], Kaneko [50], for monatomic species, and Giovangigli and Graille [41,43] for polyatomic species. Mixtures of monatomic gases at thermodynamic nonequilibrium with multitemperature transport arising from electron/ions mass ratio asymptotics have been notably investigated by Braginsky [6,7], Chmieleski and Ferziger [16], Daybelge [19], Petit and Darrozes [66], Degond and Lucquin [20,21], Magin and Degrez [56], and a comprehensive multiscale kinetic theory has been presented by Graille, Magin and Massot [47]. Transport properties in multicomponent plasmas have also been investigated with Grad's method by Zhdanov [72].

The conservation equations for partially ionized plasmas derived in these various regimes involve transport fluxes, that is, diffusive mass fluxes, viscous tensors or heat fluxes. These transport fluxes, on the other hand, are expressed in terms of transport coefficients and macroscopic variable gradients. Detailed modeling of multicomponent plasmas thus requires the evaluation of transport coefficients which are functions of the state variables p, T, and $y_1, \ldots, y_n$ and the intensity of the magnetic field B.

Evaluation of the transport coefficients, however, requires solving linear systems associated with linearized Boltzmann equations [8,9,13,32,41,43,45,47,55,60,70,72]. The corresponding transport linear systems can be obtained in their natural constrained singular symmetric form for all the regimes considered [13,32,41,43,47,70]. The systems associated with vector transport relations may also take various forms [23,35,52,58,59,64,73]. Since the size of the linear systems can be relatively large and since transport properties have to be evaluated at each computational cell in space and time, the use of direct

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numerical inversions may become computationally expensive and iterative techniques constitute an interesting and appealing alternative [64,65].

A systematic development of a mathematical and numerical theory of iterative algorithms for evaluating transport coefficients of nonionized polyatomic gas mixtures has been given by Ern and Giovangigli [23,25,28,38]. Various algorithms have been shown to be convergent by using the properties of linearized Boltzmann collision operators, the structure of usual variational approximation spaces associated with species perturbed distribution functions, and the theory of iterative methods for constrained singular symmetric linear systems [23,28,38]. The resulting algorithms have been found to be efficient especially for numerical simulation of reactive flows with complex chemistry [23,25,27–29].

Extensions of these techniques to partially ionized mixtures have been investigated by Giovangigli and Graille [41,43,44] in weak and strong magnetic fields and García Muñoz [36] for nonequilibrium planetary atmospheres. The linear systems in strong magnetic fields are then complex with an imaginary part proportional to the intensity of the magnetic field. Generalized conjugate gradient techniques as well as stationary iterative methods have been discussed [36,41,43,44]. The numerical experiments performed by García Muñoz [36] on multicomponent diffusion matrices in planetary atmospheres have shown in particular that the convergence rates of stationary iterative methods deteriorate as ionization levels increase and these methods become prohibitively slow. Similar results have been reported by Giovangigli and Graille who investigated transport coefficients in magnetized plasmas [43]. The purpose of this paper is now to derive new transport algorithms which converge rapidly for all ionization levels and magnetic field intensities and to perform comprehensive numerical tests with high temperature air to assess the accuracy of the resulting approximate coefficients.

We first review the transport fluxes and the mathematical structure of the transport linear systems in various regimes. We consider the situations of weak and strong magnetic fields as well as that of electron temperature nonequilibrium. We subsequently discuss stationary iterative methods, generalized conjugate gradient techniques, and perform numerical tests with high temperature air.

For stationary methods, we express the solution of transport linear systems in terms of generalized inverses with prescribed range and nullspace [2,4,23,28,37,38,44] and present convergence results for constrained singular symmetric systems [4,28,38,44,51,54,57,61]. We next introduce the more singular formulations of the transport linear systems by considering generalized inverses with nullspaces of increasing dimension. These new formulations can be associated with expansions of symmetric generalized inverses into dyadic products of conjugate directions. These more singular formulations are then used to define new stationary algorithms. The main idea is that the more singular formulations will yield *projected* iterative algorithms with better convergence rates [40]. We next investigate generalized conjugate gradient techniques such as orthogonal residuals algorithms [28,30,31,33,34,44,46,49,54] and discuss the link between the more singular formulations and search directions.

Numerical experiments are performed with high temperature air for varying ionization levels and magnetic field intensities. The air mixture is constituted by the eleven species N_2, O_2, NO, N, O, N_2^+, O_2^+, NO^+, N^+, O^+, and e. Numerical tests are first conducted for stationary iterative techniques in order to evaluate first order and higher order multicomponent diffusion matrices in isotropic and magnetized flows. The numerical experiments confirm the fast convergence rates of the new stationary algorithms for all ionization levels and magnetic field intensities. In particular, accurate low cost approximations are obtained for multicomponent diffusion matrices. Numerical tests are then performed with generalized conjugate gradients algorithms in order to evaluate thermal conductivities and species diffusion velocities. The numerical tests confirm the good convergence rates of generalized conjugate gradient techniques in partially ionized mixtures. These numerical tests with high temperature air finally establish that iterative techniques lead to low cost accurate evaluations of multicomponent transport coefficients for all ionization levels and magnetic field intensities.

The transport linear systems and their mathematical structure is investigated in Sections 2 and 3 for isotropic and anisotropic mixtures, respectively, and in Section 4 for thermodynamic nonequilibrium. Stationary iterative algorithms are investigated in Section 5 and generalized conjugate gradient algorithms in Section 6. Applications to diffusion matrices are presented in Section 7 and applications to thermal conductivities and Stefan–Maxwell equations in Section 8.

2. Transport linear systems in isotropic mixtures

We summarize in this section the transport fluxes and transport linear systems of polyatomic reactive gas mixtures at thermodynamic equilibrium in weak magnetic fields [13,23,32,41,70].

2.1. Transport fluxes

The transport fluxes derived from the kinetic theory of gases can be written in the form [13,32,39,70]

$$\mathbf{\Pi} = -\kappa(\nabla\cdot\boldsymbol{v})I - \eta\left(\nabla\boldsymbol{v} + (\nabla\boldsymbol{v})^t - \frac{2}{3}\eta(\nabla\cdot\boldsymbol{v})I\right), \tag{2.1}$$

$$\mathbf{v}_i = -\sum_{j\in\mathcal{S}} D_{ij}\boldsymbol{d}_j - \theta_i\nabla\log T, \quad i\in\mathcal{S}, \tag{2.2}$$

$$\boldsymbol{q} = -\widehat{\lambda}\nabla T - p\sum_{i\in\mathcal{S}}\theta_i\boldsymbol{d}_i + \sum_{i\in\mathcal{S}}\rho h_i y_i\mathbf{v}_i, \tag{2.3}$$

where $\mathbf{\Pi}$ denotes the viscous tensor, $\mathbf{\nabla} = (\partial_x, \partial_y, \partial_z)^t$ the usual differential operator, $\boldsymbol{I}$ the unit tensor in three dimensions, κ the volume viscosity, η the shear viscosity, $\boldsymbol{v}$ the mass averaged flow velocity, $\mathbf{v}_i, i \in \mathcal{S}$, the species diffusion velocities, $D_{ij}, i,j \in \mathcal{S}$, the multicomponent diffusion coefficients, $\boldsymbol{d}_i, i \in \mathcal{S}$, the species diffusion driving forces, $\theta_i, i \in \mathcal{S}$, the species thermal diffusion coefficients, T the absolute temperature, $\mathcal{S} = \{1, \ldots, n^s\}$ the species indexing set, n^s the number of species, $\boldsymbol{q}$ the heat flux vector, $\widehat{\lambda}$ the partial thermal conductivity, p the pressure, ρ the density, $h_i, i \in \mathcal{S}$, the species enthalpy per unit mass, and $y_i, i \in \mathcal{S}$, the species mass fractions. Note incidentally that the ratio κ/η is not small for polyatomic gases as taken for granted in most books on fluid dynamics and its impact is investigated in [5]. The vectors $\boldsymbol{d}_i, i \in \mathcal{S}$, incorporate the effects of various state variable gradients and external forces and are given by

$$\boldsymbol{d}_i = \frac{\mathbf{\nabla} p_i}{p} - \frac{n_i q_i}{p}(\boldsymbol{E} + \boldsymbol{v} \wedge \boldsymbol{B}), \quad i \in \mathcal{S}, \tag{2.4}$$

where $p_i, i \in \mathcal{S}$, denotes the species partial pressures, $n_i, i \in \mathcal{S}$, the species molar densities, $q_i, i \in \mathcal{S}$, the species molar charges, $\boldsymbol{E}$ the electric field, and $\boldsymbol{B}$ the magnetic field. Alternatively, the diffusion velocities and the heat flux vector may be written in terms of the species thermal diffusion ratios $\chi_i, i \in \mathcal{S}$, and the thermal conductivity λ [70]

$$\mathbf{v}_i = -\sum_{j \in \mathcal{S}} D_{ij}(\boldsymbol{d}_j + \chi_j \mathbf{\nabla} \log T), \quad i \in \mathcal{S}, \tag{2.5}$$

$$\boldsymbol{q} = -\lambda \mathbf{\nabla} T + p \sum_{i \in \mathcal{S}} \chi_i \mathbf{v}_i + \sum_{i \in \mathcal{S}} \rho h_i y_i \mathbf{v}_i, \tag{2.6}$$

or in terms of the constrained diffusion driving forces $\widetilde{\boldsymbol{d}}_i = \boldsymbol{d}_i - y_i \sum_{l \in \mathcal{S}} \boldsymbol{d}_l, i \in \mathcal{S}$. The corresponding governing equations expressing the conservation of species mass, momentum and energy are omitted for brevity and we refer to [13,32,39,70] for more details.

2.2. Transport linear systems

The transport linear systems obtained from the kinetic theory take on either the nonsingular form

$$Ga = b, \tag{2.7}$$

or else the constrained singular form

$$\begin{cases} Ga = b, \\ \langle a, \mathrm{g} \rangle = 0, \end{cases} \tag{2.8}$$

where G denotes the system matrix, b the right-hand side, g the constraint vector and $\langle , \rangle$ the Euclidean scalar product [13,23,32,70]. Both systems are typically associated with the evaluation of a transport coefficient $\mu = \langle a, b' \rangle$ where b' is a given vector.

The transport linear systems are derived from a variational procedure used to solve constrained systems of linearized Boltzmann integral equations. For each transport coefficient, various transport linear systems can be considered, corresponding to different choices of the variational approximation space. The standard choices as well as some reduced transport linear systems are presented in Table 1. In this table, the first column contains the system $Ga = b$; the second, the size of the system n where n^s denotes the number of species and n^p the number of polyatomic species; the third, the constraint $\langle a, \mathrm{g} \rangle = 0$; and the last, the expression of the associated transport coefficient μ. The transport coefficients corresponding to the largest variational space have been denoted by μ, and the ones associated with a reduced variational space have been denoted by $\mu_{[x]}$, where x stands for a simple symbol associated with the reduced variational space. The explicit expressions for all of the system matrices, right-hand sides, and constraint vectors can be found in Ern and Giovangigli [23].

For nonionized mixtures the reduced systems yield approximations for the transport coefficients which are generally within a few percent accuracy of the transport coefficients obtained with the standard systems [23,25]. The accuracy of the corresponding coefficients deteriorates for ionized mixtures since the convergence of the Chapman–Enskog expansion is known to be slower [6,10,13,32]. An extreme situation is that of electrical conductivities which require higher order diffusion coefficients to compensate for the cancellation of significative digits [6,32,43].

2.3. Mathematical structure

For $x, y \in \mathbb{R}^n$ the scalar product is given by $\langle x, y \rangle = \sum_{1 \leqslant k \leqslant n} x_k y_k$ where $x = (x_1, \ldots, x_n)^t, y = (y_1, \ldots, y_n)^t$, and we denote $x^\perp = \{ y \in \mathbb{R}^n ; \langle x, y \rangle = 0 \}$. We denote by $\mathbb{R}^{n,n}$ the set of square matrices of size n, and for $G \in \mathbb{R}^{n,n}$, we write G^t the transpose of G, $N(G)$ the nullspace of G, and $R(G)$ the range of G. We denote $\mathbb{I}$ the unit tensor in $\mathbb{R}^{n,n}$ and for $x, y \in \mathbb{R}^n$, the tensor product matrix $x \otimes y$ is given by $x \otimes y = (x_k y_l)_{1 \leqslant k,l \leqslant n}$.

The sparse transport matrix $db(G)$ is a submatrix formed by diagonals of blocks of G [23]. It can be used as a splitting matrix for stationary methods as well as a preconditioner for generalized conjugate gradients algorithms [23,25]. The definition of the matrix $db(G)$ is reminded in Appendix A. The matrices G and $db(G)$ have a general structure inherited from the properties of Boltzmann linearized collision operators and the properties of usual variational approximation spaces associated

Table 1
Typical transport linear systems for isotropic gases.

System	Size	Constraint	Evaluation
$Ha^\eta = b^\eta$	n^s	–	$\eta = \langle a^\eta, b^\eta\rangle$
$Ka^\kappa = b^\kappa$	$n^s + n^p$	$\langle a^\kappa, \mathsf{k}\rangle = 0$	$\kappa = \langle a^\kappa, b^\kappa\rangle$
$K_{[01]}a^\kappa_{[01]} = b^\kappa_{[01]}$	n^p	–	$\kappa_{[01]} = \langle a^\kappa_{[01]}, b^\kappa_{[01]}\rangle$
$La^{D_k} = b^{D_k}$	$2n^s + n^p$	$\langle a^{D_k}, \mathcal{Y}\rangle = 0$	$D_{kl} = \langle a^{D_k}, b^{D_l}\rangle$
$L_{[e]}a^{D_k}_{[e]} = b^{D_k}_{[e]}$	$2n^s$	$\langle a^{D_k}_{[e]}, \mathcal{Y}_{[e]}\rangle = 0$	$D_{[e]kl} = \langle a^{D_k}_{[e]}, b^{D_l}_{[e]}\rangle$
$\Delta a^{D_k}_{[00]} = b^{D_k}_{[00]}$	n^s	$\langle a^{D_k}_{[00]}, \mathsf{y}\rangle = 0$	$D_{[00]kl} = \langle a^{D_k}_{[00]}, b^{D_l}_{[00]}\rangle$
$L\widehat{a^\lambda} = \widehat{b^\lambda}$	$2n^s + n^p$	$\langle \widehat{a^\lambda}, \mathcal{Y}\rangle = 0$	$\widehat{\lambda} = (p/T)\langle \widehat{a^\lambda}, \widehat{b^\lambda}\rangle$ $\theta_k = -\langle \widehat{a^\lambda}, b^{D_k}\rangle$
$\Lambda a^\lambda = b^\lambda$	$n^s + n^p$	–	$\lambda = (p/T)\langle a^\lambda, b^\lambda\rangle$ $\chi = L^{00\lambda}a^\lambda$
$L_{[e]}\widehat{a^\lambda_{[e]}} = \widehat{b^\lambda_{[e]}}$	$2n^s$	$\langle \widehat{a^\lambda_{[e]}}, \mathcal{Y}_{[e]}\rangle = 0$	$\widehat{\lambda}_{[e]} = (p/T)\langle \widehat{a^\lambda_{[e]}}, \widehat{b^\lambda_{[e]}}\rangle$ $\theta_{[e]k} = -\langle \widehat{a^\lambda_{[e]}}, b^{D_k}_{[e]}\rangle$
$\Lambda_{[e]}a^\lambda_{[e]} = b^\lambda_{[e]}$	n^s	–	$\lambda_{[e]} = (p/T)\langle a^\lambda_{[e]}, b^\lambda_{[e]}\rangle$ $\chi_{[e]} = L^{00\lambda}_{[e]}a^\lambda_{[e]}$

with the transport linear systems [23,26]. In order to simplify the presentation, we frequently assume in this paper that the number of species is $n^s \geqslant 3$. For the nonsingular systems, one can establish that

($\mathbf{G_1}$)*The matrices* $G, 2db(G) - G$, *and* $db(G)$ *are symmetric positive definite for* $n^s \geqslant 1$.
On the other hand, for the singular systems, one can establish that
($\mathbf{G_2}$) *The matrix* G *is symmetric positive semi-definite and its nullspace is* $N(G) = \mathbb{R}\mathsf{z}$. *The nullspace vector* z, *the constraint vector* g *and the right member* b *are such that* $\langle \mathsf{z}, \mathsf{g}\rangle > 0$ *and* $\langle \mathsf{z}, b\rangle = 0$. The matrices $2db(G) - G$ and $db(G)$ *are symmetric positive definite for* $n^s \geqslant 3$.

These properties imply that the transport linear systems are well posed [23,28]. Their solution is also conveniently expressed in terms of symmetric generalized inverses [23,28] as further discussed in Section 5. The singular systems can also be recast into the nonsingular form $a = (G + \alpha \mathsf{g}\otimes\mathsf{g})^{-1}b$ where $\alpha > 0$ and the matrix $G + \alpha\mathsf{g}\otimes\mathsf{g}$ is symmetric positive definite [23,37,38].

3. Transport linear systems in nonisotropic mixtures

We summarize in this section the transport fluxes and transport linear systems for polyatomic reactive gas mixtures at thermodynamic equilibrium in strong magnetic fields [6,13,32,41,43].

3.1. Transport fluxes

In the presence of strong magnetic fields, the transport fluxes are not anymore isotropic [6,13,32,41,43]. Denoting by $\boldsymbol{B}$ the magnetic field, $B = \|\boldsymbol{B}\|$ the magnetic field intensity, and $\boldsymbol{\mathcal{B}} = \boldsymbol{B}/B$ the unitary vector, we introduce for any three dimensional vector $\mathbf{x}$ the associated vectors

$$\mathbf{x}^\parallel = (\mathbf{x}\cdot\boldsymbol{\mathcal{B}})\boldsymbol{\mathcal{B}}, \quad \mathbf{x}^\perp = \mathbf{x} - \mathbf{x}^\parallel, \quad \mathbf{x}^\odot = \boldsymbol{\mathcal{B}}\wedge\mathbf{x}.$$

The vectors $\mathbf{x}^\parallel, \mathbf{x}^\perp$ and $\mathbf{x}^\odot$ are mutually orthogonal and obtained from $\mathbf{x}$ by applying the linear operators $\boldsymbol{\mathcal{B}}\otimes\boldsymbol{\mathcal{B}}, I - \boldsymbol{\mathcal{B}}\otimes\boldsymbol{\mathcal{B}}$ and $R(\boldsymbol{\mathcal{B}})$ where $R(\boldsymbol{\mathcal{B}})$ is the rotation matrix such that $R(\boldsymbol{\mathcal{B}})\mathbf{x} = \boldsymbol{\mathcal{B}}\wedge\mathbf{x}$. In strong magnetic fields, the viscous tensor $\boldsymbol{\Pi}$ is found in the form

$$\begin{aligned}\boldsymbol{\Pi} = {}& -\kappa(\nabla\cdot\boldsymbol{v})\mathbf{I} - \eta_1\mathsf{S} - \eta_2(R(\boldsymbol{\mathcal{B}})\mathsf{S} - \mathsf{S}R(\boldsymbol{\mathcal{B}})) - \eta_3(\langle \mathsf{S}\boldsymbol{\mathcal{B}}, \boldsymbol{\mathcal{B}}\rangle\boldsymbol{\mathcal{B}}\otimes\boldsymbol{\mathcal{B}} - R(\boldsymbol{\mathcal{B}})\mathsf{S}R(\boldsymbol{\mathcal{B}}))\\ & - \eta_4(\mathsf{S}\boldsymbol{\mathcal{B}}\otimes\boldsymbol{\mathcal{B}} + \boldsymbol{\mathcal{B}}\otimes\boldsymbol{\mathcal{B}}\mathsf{S} - 2\langle \mathsf{S}\boldsymbol{\mathcal{B}}, \boldsymbol{\mathcal{B}}\rangle\boldsymbol{\mathcal{B}}\otimes\boldsymbol{\mathcal{B}}) - \eta_5(\boldsymbol{\mathcal{B}}\otimes\boldsymbol{\mathcal{B}}\mathsf{S}R(\boldsymbol{\mathcal{B}}) - R(\boldsymbol{\mathcal{B}})\mathsf{S}\boldsymbol{\mathcal{B}}\otimes\boldsymbol{\mathcal{B}}),\end{aligned} \tag{3.1}$$

where $\mathsf{S} = \nabla\boldsymbol{v} + \nabla\boldsymbol{v}^t - \frac{2}{3}(\nabla\cdot\boldsymbol{v})\mathbf{I}$ denotes the strain rate tensor, κ the volume viscosity, and $\eta_j, 1 \leqslant j \leqslant 5$, the shear viscosities. The species diffusion velocities $\mathbf{v}_i, i \in \mathcal{S}$, are found in the form

$$\mathbf{v}_i = -\sum_{j\in\mathcal{S}}\left(D^\parallel_{ij}\boldsymbol{d}^\parallel_j + D^\perp_{ij}\boldsymbol{d}^\perp_j + D^\odot_{ij}\boldsymbol{d}^\odot_j\right) - \theta^\parallel_i(\nabla\log T)^\parallel - \theta^\perp_i(\nabla\log T)^\perp - \theta^\odot_i(\nabla\log T)^\odot, \tag{3.2}$$

where $D^{\parallel}_{ij}, D^{\perp}_{ij}$, and $D^{\odot}_{ij}, i,j \in \mathcal{S}$, are the species diffusion coefficients parallel, perpendicular and transverse to the magnetic field, and $\theta^{\parallel}_i, \theta^{\perp}_i, \theta^{\odot}_i, i \in \mathcal{S}$, the species thermal diffusion coefficients parallel, perpendicular and transverse to the magnetic field. The heat flux $\boldsymbol{q}$ can be written similarly in the form

$$\boldsymbol{q} = -\widehat{\lambda}^{\parallel}(\boldsymbol{\nabla} T)^{\parallel} - \widehat{\lambda}^{\perp}(\boldsymbol{\nabla} T)^{\perp} - \widehat{\lambda}^{\odot}(\boldsymbol{\nabla} T)^{\odot} - p\sum_{i\in\mathcal{S}}\left(\theta^{\parallel}_i \boldsymbol{d}^{\parallel}_i + \theta^{\perp}_i \boldsymbol{d}^{\perp}_i + \theta^{\odot}_i \boldsymbol{d}^{\odot}_i\right) + \sum_{i\in\mathcal{S}} \rho y_i h_i \mathbf{v}_i, \tag{3.3}$$

where $\widehat{\lambda}^{\parallel}, \widehat{\lambda}^{\perp}$, and $\widehat{\lambda}^{\odot}$ are the partial thermal conductivities parallel, perpendicular and transverse to the magnetic field.

The species diffusion velocities and the heat flux can also be rewritten in terms of the thermal diffusion ratios $\chi^{\parallel}_i, \chi^{\perp}_i$, and $\chi^{\odot}_i, i \in \mathcal{S}$, and the thermal conductivities $\lambda^{\parallel}, \lambda^{\perp}$, and $\lambda^{\odot}$ [41,43]

$$\begin{aligned}\mathbf{v}_i = &-\sum_{j\in\mathcal{S}} D^{\parallel}_{ij}\left(\boldsymbol{d}^{\parallel}_j + \chi^{\parallel}_j(\boldsymbol{\nabla}\log T)^{\parallel}\right) - \sum_{j\in\mathcal{S}} D^{\perp}_{ij}\left(\boldsymbol{d}^{\perp}_j + \chi^{\perp}_j(\boldsymbol{\nabla}\log T)^{\perp} + \chi^{\odot}_j(\boldsymbol{\nabla}\log T)^{\odot}\right)\\ &-\sum_{j\in\mathcal{S}} D^{\odot}_{ij}\left(\boldsymbol{d}^{\odot}_j + \chi^{\perp}_j(\boldsymbol{\nabla}\log T)^{\odot} - \chi^{\odot}_j(\boldsymbol{\nabla}\log T)^{\perp}\right),\end{aligned} \tag{3.4}$$

$$\boldsymbol{q} = -\lambda^{\parallel}(\boldsymbol{\nabla} T)^{\parallel} - \lambda^{\perp}(\boldsymbol{\nabla} T)^{\perp} - \lambda^{\odot}(\boldsymbol{\nabla} T)^{\odot} + p\sum_{i\in\mathcal{S}}(\chi^{\parallel}_i \mathbf{v}^{\parallel}_i + \chi^{\perp}_i \mathbf{v}^{\perp}_i + \chi^{\odot}_i \mathbf{v}^{\odot}_i) + \sum_{i\in\mathcal{S}} \rho_i y_i h_i \mathbf{v}_i. \tag{3.5}$$

The corresponding governing equations expressing the conservation of species mass, momentum and energy are omitted for brevity and we refer to [13,32,41] for more details.

3.2. Transport linear systems

The transport linear systems associated with the transport coefficients parallel to the magnetic field are real and identical to that of isotropic mixtures already investigated in Section 2. These system are not further considered in this section. On the other hand, the transport linear systems associated with anisotropic coefficients are complex, vector products with the magnetic field having been replaced by multiplications with imaginary numbers [32,41]. The transport linear systems obtained from the kinetic theory take on either the regular form

$$(G + iG')a = b, \tag{3.6}$$

or else the constrained singular form

$$\begin{cases}(G + iG')a = b,\\ \langle a, \mathrm{g}\rangle = 0,\end{cases} \tag{3.7}$$

where $i^2 = -1, G, G' \in \mathbb{R}^{n,n}$ denotes the system matrices, $b \in \mathbb{R}^n$ the right-hand side, $\mathrm{g} \in \mathbb{R}^n$ the constraint vector, and $\langle , \rangle$ the Hermitian scalar product. The real part G is the matrix already obtained for isotropic mixtures whereas the imaginary part G' is proportional to the intensity of the magnetic field. Both systems are typically associated with the evaluation of the transport coefficient $\mu^{\perp} + i\mu^{\odot} = \langle a, b'\rangle$, where $b' \in \mathbb{R}^n$ is a given vector.

The transport linear systems corresponding to the first usual Sonine/Wang-Chang Uhlenbeck polynomial expansions are presented in Table 2. The explicit expressions of the systems coefficients are detailed in references [23,43]. The successive approximations in the Chapman–Enskog expansion of transport coefficients are still known to converge more slowly in plasmas than in neutral mixtures [6,8,10]. Note that the variational framework for a direct evaluation of the thermal conductivity and the thermal diffusion ratios [24,23] has been generalized to the anisotropic case [44].

Table 2
Typical transport linear systems for nonisotropic gases.

Systems	Size	Constraint	Coefficients
$Ha^{\eta 1} = b^{\eta}$	n^s	–	$\eta_1 + i\eta_2 = \frac{1}{2}\langle a^{\eta 1} + a^{\eta 2}, b^{\eta}\rangle$
$(H + 2iH')a^{\eta 2} = b^{\eta}$			$\eta_1 + \eta_3 = \langle a^{\eta 1}, b^{\eta}\rangle$
$(H + iH')a^{\eta 3} = b^{\eta}$			$\eta_4 + i\eta_5 + \eta_1 + i\eta_2 = \langle a^{\eta 3}, b^{\eta}\rangle$
$(L + iL')a^{D_j} = b^{D_j}$	$2n^s + n^p$	$\langle a^{D_j}, \mathcal{Y}\rangle = 0$	$D^{\perp}_{ij} + iD^{\odot}_{ij} = \langle a^{D_j}, b^{D_i}\rangle$
$(\Lambda + i\Lambda')a^{D_j}_{[00]} = b^{D_j}_{[00]}$	n^s	$\langle a^{D_j}_{[00]}, \mathrm{y}\rangle = 0$	$D^{\perp}_{[00]ij} + iD^{\odot}_{[00]ij} = \langle a^{D_j}_{[00]}, b^{D_i}_{[00]}\rangle$
$(L + iL')\widehat{a^{\lambda}} = \widehat{b^{\lambda}}$	$2n^s + n^p$	$\langle \widehat{a^{\lambda}}, \mathcal{Y}\rangle = 0$	$\widehat{\lambda}^{\perp} + i\widehat{\lambda}^{\odot} = (p/T)\langle \widehat{a^{\lambda}}, \widehat{b^{\lambda}}\rangle$
			$\theta^{\perp}_i + i\theta^{\odot}_i = -\langle \widehat{a^{\lambda}}, b^{D_i}\rangle$
$(\Lambda + i\Lambda')a^{\lambda} = b^{\lambda}$	$n^s + n^p$	–	$\lambda^{\perp} + i\lambda^{\odot} = (p/T)\langle a^{\lambda}, b^{\lambda}\rangle$
			$\chi^{\perp} + i\chi^{\odot} = L^{00\lambda}a^{\lambda}$
$(\Lambda_{[\mathrm{e}]} + i\Lambda'_{[\mathrm{e}]})a^{\lambda}_{[\mathrm{e}]} = b^{\lambda}_{[\mathrm{e}]}$	n^s	–	$\lambda^{\perp}_{[\mathrm{e}]} + i\lambda^{\odot}_{[\mathrm{e}]} = (p/T)\langle \alpha^{\lambda}_{[\mathrm{e}]}, b^{\lambda}_{[\mathrm{e}]}\rangle$
			$\chi^{\perp}_{[\mathrm{e}]} + i\chi^{\odot}_{[\mathrm{e}]} = L^{00\lambda}_{[\mathrm{e}]}a^{\lambda}_{[\mathrm{e}]}$

3.3. Mathematical structure

For $x, y \in \mathbb{C}^n$ the Hermitian scalar product is given by $\langle x, y\rangle = \sum_{1\leqslant k\leqslant n} x_k \bar{y}_k$ where $x = (x_1, \ldots, x_n)^t, y = (y_1, \ldots, y_n)^t$, and the nondegenerate nondefinite bilinear symmetric form (x, y) naturally associated with complex symmetric matrices is given by $(x, y) = \sum_{1\leqslant k\leqslant n} x_k y_k$. The real x and imaginary y parts $x, y \in \mathbb{R}$, of a complex number $z \in \mathbb{C}, z = x + iy$, are written $x = \Re z$ and $y = \Im z$. When A is a real linear subspace $A \subset \mathbb{R}^n$, we denote by $A + iA$ the corresponding complex linear space $\{z \in \mathbb{C}^n,\ z = x + iy,\ x, y \in A\}$. If A is a real subspace, we denote by $A^\perp$ the orthogonal complement with respect to the Euclidean product whereas when B is a complex subspace, we denote by $B^\perp$ the orthogonal complement with respect to the nondegenerate bilinear form $(,)$. Note that if B has a basis of real vectors, the orthogonal complement is equivalently defined with the Hermitian scalar product. This is notably the case with the constraint $\langle a, \mathrm{g}\rangle = 0$ which can also be written $(a, \mathrm{g}) = 0$ since g is real. When $a, b \in \mathbb{C}^n$, the tensor product matrix $a \otimes b$ has components $a_k b_l, 1 \leqslant k, l \leqslant n$ and for any $x \in \mathbb{C}^n$ we have $a \otimes b\, x = a(b, x)$.

The following results have been obtained from the properties of Boltzmann linearized operators under general assumptions on the variational approximation spaces after properly structuring the complex transport linear systems [41]. For the nonsingular systems, the matrix G satisfies (G_1) whereas the imaginary part is such that

$(\mathbf{G}_1')$ *The matrix G' is real diagonal.*

On the other hand, for the singular systems, the matrix G satisfies (G_2) wheras the imaginary part is such that

$(\mathbf{G}_2')$ *The matrix G' is real and given by $G' = Q\mathcal{D}'P$ where P and Q are the projector matrices $Q = P^t = I - \mathrm{g} \otimes \mathrm{z}/\langle \mathrm{z}, \mathrm{g}\rangle$ and $\mathcal{D}'$ is diagonal.*

It is easily deduced from $(\mathrm{G}_1)(\mathrm{G}_1')$ and $(\mathrm{G}_2)(\mathrm{G}_2')$ that $N(G + iG') = \{0\}$ in the regular case, $N(G + iG') = \mathbb{C}\mathrm{z}$ in the singular case, and that the transport linear systems are well posed [41,43,44]. Their solution may conveniently be expressed in terms of symmetric generalized inverses as further discussed in Section 5. The singular systems can also be recast into the nonsingular form $a = \left(G + iG' + \alpha \mathrm{g} \otimes \mathrm{g}\right)^{-1} b$ where $\alpha > 0$ and the matrix $G + \alpha \mathrm{g} \otimes \mathrm{g}$ is symmetric positive definite [23,44].

4. Transport linear systems in a two-temperature plasma

We summarize in this section the transport fluxes and the transport linear systems in the situation of electron temperature nonequilibrium. We only considered a two-temperature plasma and refer to Capitelli et al. [11,12], Nagnibeda and Kustova [60], and Kustova [53] for more general desequilibriums as state-to-state models.

Two-temperature plasmas are relevant for many scientific and industrial application as for instance lean flame stabilization by pulsed high voltage discharges [18]. The Knudsen number Kn and the square root of the mass ratio $(m_e/m_h)^{1/2}$, where m_h denotes a typical heavy species mass, are usually of the same order of magnitude [16,20,21,47,56,66]. The corresponding Boltzmann equations then have a natural scaling already discussed by Petit and Darrozes [66], Degond and Lucquin [20,21], Magin and Degrez [56], and Graille, Magin, and Massot [47]. The species $\mathcal{S} = \mathcal{H} \cup \{\mathrm{e}\}$ must be partitioned between the heavy species $\mathcal{H}$ and the electrons e and Graille, Magin and Massot have established that the proper reference velocity is the heavy species velocity $\boldsymbol{v}_h$ in order to derive $\mathcal{O}(\mathrm{Kn})$ accurate electron governing equations with the Kolesnikov effect [47]. The infinite mass approximation with Dirac masses, previously used by several authors, may also be avoided in the Chapman–Enskog procedure and entropy production has been shown to be nonnegative for the resulting multicomponent flow model [47].

4.1. Heavy species transport fluxes

In the limit of zero electron mass, there are no polarization effects for the heavy species and the corresponding transport fluxes can be written [47]

$$\mathbf{\Pi}_h = -\kappa(\nabla \cdot \boldsymbol{v}_h)\mathbf{I} - \eta\left(\nabla \boldsymbol{v}_h + (\nabla \boldsymbol{v}_h)^t - \frac{2}{3}(\nabla \cdot \boldsymbol{v}_h)\mathbf{I}\right), \tag{4.1}$$

$$\mathbf{v}_i = -\sum_{j\in\mathcal{H}} D_{ij}\widehat{\boldsymbol{d}}_j - \theta_i \nabla \log T_h, \quad i \in \mathcal{H}, \tag{4.2}$$

$$\boldsymbol{q}_h = -\widehat{\lambda}_h \nabla T_h - p_h \sum_{i\in\mathcal{H}} \theta_{hi}\widehat{\boldsymbol{d}}_i + \sum_{i\in\mathcal{H}} \rho h_i y_i \mathbf{v}_i, \tag{4.3}$$

where $\mathbf{\Pi}_h$ is the heavy species viscous tensor, $\boldsymbol{v}_h$ the heavy species mass averaged flow velocity, $\mathbf{v}_i, i \in \mathcal{H}$, the heavy species diffusion velocities, $\widehat{\boldsymbol{d}}_i, i \in \mathcal{H}$, the heavy species effective diffusion driving forces, T_h the heavy species temperature, $\mathcal{H}$ the set of heavy species indices, $\boldsymbol{q}_h$ the heavy species heat flux, $h_i, i \in \mathcal{H}$, the heavy species enthalpy per unit mass, and $y_i, i \in \mathcal{H}$, the heavy species mass fractions. The vectors $\widehat{\boldsymbol{d}}_i$ incorporate the effects of various state variable gradients and forces and are given by

$$\widehat{\boldsymbol{d}}_i = \frac{\nabla p_i}{p_h} - \frac{n_i q_i}{p_h}(\boldsymbol{E} + \boldsymbol{v}_h \wedge \boldsymbol{B}) - \frac{n_i \boldsymbol{F}_{ie}}{p_h}, \quad i \in \mathcal{H}, \tag{4.4}$$

where $p_i, i \in \mathcal{H}$, denotes the heavy species partial pressures, p_h the heavy species total pressure, $q_i, i \in \mathcal{H}$, the heavy species molar charges, and $\boldsymbol{F}_{ie}, i \in \mathcal{H}$, the average force of electrons acting on the ith heavy species. This force can be expanded in the form

$$\boldsymbol{F}_{ie} = -p_e\Big(\alpha_{ie}^{\parallel}\boldsymbol{d}_e^{\parallel} + \alpha_{ie}^{\perp}\boldsymbol{d}_e^{\perp} + \alpha_{ie}^{\odot}\boldsymbol{d}_e^{\odot} + \chi_{ie}^{\parallel}\boldsymbol{\nabla}\log T_e^{\parallel} + \chi_{ie}^{\perp}\boldsymbol{\nabla}\log T_e^{\perp} + \chi_{ie}^{\odot}\boldsymbol{\nabla}\log T_e^{\odot}\Big), \quad i \in \mathcal{H}, \tag{4.5}$$

where p_e is the electron partial pressure, and $\alpha_{ie}^{\parallel}, \alpha_{ie}^{\perp}, \alpha_{ie}^{\odot}, \chi_{ie}^{\parallel}, \chi_{ie}^{\perp}$ and $\chi_{ie}^{\odot}, i \in \mathcal{H}$, are second order coupling coefficients [47]. In particular, the influence of electron temperature and partial pressure on the heavy species is mediated through the force terms $\boldsymbol{F}_{ie}, i \in \mathcal{H}$. The heavy species diffusion velocities and heat flux may also be written in terms of the heavy species thermal diffusion ratios $\chi_i, i \in \mathcal{H}$, and the heavy species thermal conductivity λ_h as for isotropic gas mixtures [47].

4.2. Electron transport fluxes

The electron transport fluxes present polarization effects in the presence of strong magnetic fields. The second order electron diffusion velocity is found in the form [47]

$$\mathbf{v}_e = -D_{ee}^{\parallel}\boldsymbol{d}_e^{\parallel} - D_{ee}^{\perp}\boldsymbol{d}_e^{\perp} - D_{ee}^{\odot}\boldsymbol{d}_e^{\odot} - \theta_e^{\parallel}(\boldsymbol{\nabla}\log T_e)^{\parallel} - \theta_e^{\perp}(\boldsymbol{\nabla}\log T_e)^{\perp} - \theta_e^{\odot}(\boldsymbol{\nabla}\log T_e)^{\odot} - \sum_{i\in\mathcal{H}}\Big(\alpha_{ie}^{\parallel}\boldsymbol{d}_i^{2\parallel} + \alpha_{ie}^{\perp}\boldsymbol{d}_i^{2\perp} + \alpha_{ie}^{\odot}\boldsymbol{d}_i^{2\odot}\Big), \tag{4.6}$$

where $D_{ee}^{\parallel}, D_{ee}^{\perp}$ and $D_{ee}^{\odot}$ are the electron diffusion coefficients parallel, perpendicular and transverse to the magnetic field, and $\theta_e^{\parallel}, \theta_e^{\perp}$ and $\theta_e^{\odot}$ the electron thermal diffusion coefficients parallel, perpendicular and transverse to the magnetic field. In this equation, the electron diffusion driving force $\boldsymbol{d}_e$ and the second order diffusion driving forces $\boldsymbol{d}_i^2, i \in \mathcal{H}$, are given by

$$\boldsymbol{d}_e = \frac{\boldsymbol{\nabla}p_e}{p_e} - \frac{n_e q_e}{p_e}(\boldsymbol{E} + \boldsymbol{v}_h \wedge \boldsymbol{B}), \quad \boldsymbol{d}_i^2 = -n_i\mathbf{v}_i, \quad i \in \mathcal{H}. \tag{4.7}$$

Similarly, the electron heat flux can be decomposed in the form

$$\boldsymbol{q}_e = -\widehat{\lambda}_e^{\parallel}(\boldsymbol{\nabla}T_e)^{\parallel} - \widehat{\lambda}_e^{\perp}(\boldsymbol{\nabla}T_e)^{\perp} - \widehat{\lambda}_e^{\odot}(\boldsymbol{\nabla}T_e)^{\odot} - p_e\Big(\theta_e^{\parallel}\boldsymbol{d}_e^{\parallel} + \theta_e^{\perp}\boldsymbol{d}_e^{\perp} + \theta_e^{\odot}\boldsymbol{d}_e^{\odot}\Big) - p_e\sum_{i\in\mathcal{H}}\Big(\chi_{ie}^{\parallel}\boldsymbol{d}_e^{2\parallel} + \chi_{ie}^{\perp}\boldsymbol{d}_e^{2\perp} + \chi_{ie}^{\odot}\boldsymbol{d}_e^{2\odot}\Big) + \rho_e h_e\mathbf{v}_e, \tag{4.8}$$

where $\widehat{\lambda}_e^{\parallel}, \widehat{\lambda}_e^{\perp}$ and $\widehat{\lambda}_e^{\odot}$ are the electron partial thermal conductivities parallel, perpendicular and transverse to the magnetic field. In particular, the influence of heavy species temperature and partial pressures on the electron transport fluxes is mediated through the second order diffusion driving forces $\boldsymbol{d}_i^2, i \in \mathcal{H}$. Similar expressions can also be written in terms of the thermal diffusion ratios and the electron thermal conductivity but are omitted for the sake of brevity as well as the governing equations [47].

4.3. Transport linear systems

The kinetic theory investigations of Graille, Magin and Massot [47] have shown that the transport linear systems associated with the heavy species are similar to that of isotropic mixtures investigated in Section 2 with the indexing set $\mathcal{S}$ replaced by $\mathcal{H}$. In particular, these systems share the same mathematical structure already investigated in Section 2. On the other hand, the small transport linear systems associated with electrons are similar to that of the nonisotropic mixtures obtained in Section 3 without singularities [47].

Since we are interested in iterative solutions of the transport linear systems associated with a large number of species, only the mathematical structure of the heavy species transport linear systems – associated with the main computational costs – and similar to that presented in Section 2 is therefore relevant in the nonequilibrium case. We do not repeat the corresponding table of transport linear systems since they formally corresponds to changing the indexing set from $\mathcal{S}$ to $\mathcal{H}$.

Investigating the corresponding linear systems is important in several respects. Two-temperature plasmas are first relevant for various scientific and industrial applications. Investigating the heavy species transport linear systems considerably broadens the applicability of the new algorithms investigated in the next sections. In addition, the resulting linear systems obtained by suppressing the electron from the species list are especially relevant for a number of computational studies. We will establish in particular that the numerical difficulties found for increasing ionization rates are *not* associated with electron. Finally, the acceleration techniques obtained with more singular formulations of the transport linear systems will also be efficient for the heavy species.

5. Generalized inverses and stationary iterative techniques

We express the solution of transport linear systems in terms of generalized inverses with prescribed range and nullspace [23,28,38,41,44] and review projected stationary iterative techniques in order to solve constrained singular symmetric systems [23,28,38,44]. We next introduce the more singular formulations of the transport linear systems as well as expansions of symmetric generalized inverses into dyadic products of conjugate directions.

5.1. Generalized inverses and transport linear systems

The transport linear systems associated with partially ionized gas mixtures can be written in the general form

$$\begin{cases} \mathcal{G}a = b, \\ a \in \mathscr{C}, \end{cases} \tag{5.1}$$

where $\mathcal{G} \in \mathbb{K}^{n,n}, \mathscr{C}$ is a linear subspace of $\mathbb{K}^n, a, b \in \mathbb{K}^n$ are vectors and $\mathbb{K}$ denotes $\mathbb{R}$ or $\mathbb{C}$. In the isotropic case, we have $\mathbb{K} = \mathbb{R}, \mathcal{G} = G$, and either $\mathscr{C} = \mathbb{R}^n$ in the regular case or else $\mathscr{C} = \mathrm{g}^\perp$ and $N(\mathcal{G}) = \mathbb{R}\mathrm{z}$ in the singular case. In the nonisotropic case, we have $\mathbb{K} = \mathbb{C}, \mathcal{G} = G + iG'$, and either $\mathscr{C} = \mathbb{C}^n$ in the regular case or else $\mathscr{C} = \mathrm{g}^\perp + i\mathrm{g}^\perp$ and $N(\mathcal{G}) = \mathbb{C}\mathrm{z}$ in the singular case.

The solutions of the transport linear systems may naturally be expressed in terms of generalized inverses with prescribed range and nullspace [23,28,38,44]. More specifically, if $\mathcal{G} \in \mathbb{K}^{n,n}$ is a matrix and $\mathscr{C}$ and $\mathscr{S}$ two subspaces of $\mathbb{K}^n$ such that $N(\mathcal{G}) \oplus \mathscr{C} = \mathbb{K}^n$ and $R(\mathcal{G}) \oplus \mathscr{S} = \mathbb{K}^n$, then there exists a unique matrix $\mathcal{Z}$ such that $\mathcal{G}\mathcal{Z}\mathcal{G} = \mathcal{G}, \mathcal{Z}\mathcal{G}\mathcal{Z} = \mathcal{Z}, N(\mathcal{Z}) = \mathscr{S}$, and $R(\mathcal{Z}) = \mathscr{C}$ [2,4,39]. This matrix $\mathcal{Z}$ is termed the generalized inverse of $\mathcal{G}$ with prescribed range $\mathscr{C}$ and nullspace $\mathscr{S}$ and is also such that $\mathcal{G}\mathcal{Z} = P_{R(\mathcal{G}),\mathscr{S}}$ and $\mathcal{Z}\mathcal{G} = P_{\mathscr{C},N(\mathcal{G})}$ where for any complementary spaces $R \oplus S = \mathbb{K}^n, P_{R,S}$ denote the projector onto R parallel to S. First order multicomponent diffusion matrices can notably be expressed as generalized inverses of Stefan–Maxwell like matrices [38,41,44]. The well posedness of the transport linear systems (5.1) is addressed in the following proposition and its solution a is related to generalized inverses [23,28,38,44].

Proposition 5.1. *Let $\mathcal{G} \in \mathbb{K}^{n,n}$ be a matrix and $\mathscr{C}$ be a subspace of $\mathbb{K}^n$. The constrained linear system (5.1) is well posed, i.e., admits a unique solution a for any $b \in R(\mathcal{G})$, if and only if*

$$N(\mathcal{G}) \oplus \mathscr{C} = \mathbb{K}^n. \tag{5.2}$$

In this situation, for any subspace $\mathscr{S}$ such that $R(\mathcal{G}) \oplus \mathscr{S} = \mathbb{K}^n$, the solution a can be written $a = \mathcal{Z}b$, where $\mathcal{Z}$ is the generalized inverse of $\mathcal{G}$ with prescribed range $\mathscr{C}$ and nullspace $\mathscr{S}$.

The well posedness condition is easily obtained in the real and complex cases since the constraint vector g is such that $\langle \mathrm{z}, \mathrm{g} \rangle \neq 0$. An important property is that the proper generalized inverses are symmetric [28,44]. In the real case (2.8) the proper generalized inverse Z of G is the one with range $\mathrm{g}^\perp$ and nullspace $\mathbb{R}\mathrm{g}$ and we then have $GZ = \mathbb{I} - \mathrm{g} \otimes \mathrm{z}/\langle \mathrm{g}, \mathrm{z} \rangle$ and $ZG = \mathbb{I} - \mathrm{z} \otimes \mathrm{g}/\langle \mathrm{g}, \mathrm{z} \rangle$. In the complex case (3.7) the proper generalized inverse $\mathcal{Z}$ of $\mathcal{G} = G + iG'$ is the one with range $\mathrm{g}^\perp + i\mathrm{g}^\perp$ and nullspace $\mathbb{C}\mathrm{g}$ and we have $\mathcal{G}\mathcal{Z} = \mathbb{I} - \mathrm{g} \otimes \mathrm{z}/\langle \mathrm{g}, \mathrm{z} \rangle$ and $\mathcal{Z}\mathcal{G} = \mathbb{I} - \mathrm{z} \otimes \mathrm{g}/\langle \mathrm{g}, \mathrm{z} \rangle$. Both generalized inverses are shown to be symmetric and Z and $\Re\mathcal{Z}$ are positive semi-definite with nullspace $\mathbb{R}\mathrm{g}$ [23,28,44]. In the real singular situation the transport linear systems can be recast into the nonsingular form $a = (G + \alpha \mathrm{g} \otimes \mathrm{g})^{-1} b$ where $\alpha > 0$ and the matrix $G + \alpha \mathrm{g} \otimes \mathrm{g}$ is then symmetric positive definite, and, in the complex case, we may similarly write $a = (G + iG' + \alpha \mathrm{g} \otimes \mathrm{g})^{-1} b$ [23,37,38,44]. However, the singular formulations are more suited to iterative techniques [23].

5.2. Projected iterative algorithms

For a matrix $\mathcal{T} \in \mathbb{C}^{n,n}, \sigma(\mathcal{T})$ and $\rho(\mathcal{T})$ denote respectively the spectrum and the spectral radius of $\mathcal{T}$, and we also define $\gamma(\mathcal{T}) = \max\{|\lambda|;\ \lambda \in \sigma(\mathcal{T}),\ \lambda \neq 1\}$. A matrix $\mathcal{T}$ is said to be convergent when $\lim_{i\to\infty} \mathcal{T}^i$ exists not necessarily being zero [61]. A matrix $\mathcal{T} \in \mathbb{C}^{n,n}$ is convergent if and only if either $\rho(\mathcal{T}) < 1$ or $\rho(\mathcal{T}) = 1, 1 \in \sigma(\mathcal{T}), \gamma(\mathcal{T}) < 1$, and $\mathcal{T}$ has only elementary divisors corresponding to the eigenvalue 1, that is, $N(I - \mathcal{T}) \cap R(I - \mathcal{T}) = \{0\}$ [4,39,57,61,63].

Next, for a matrix $\mathcal{G} \in \mathbb{C}^{n,n}$, the decomposition

$$\mathcal{G} = \mathcal{M} - \mathcal{W}, \tag{5.3}$$

is a splitting if the matrix $\mathcal{M}$ is invertible. In order to solve the linear system $\mathcal{G}a = b$, where $b \in \mathbb{C}^n$, the splitting (5.3) induces the iterative scheme

$$z_{i+1} = \mathcal{T} z_i + \mathcal{M}^{-1} b, \quad i \geqslant 0, \tag{5.4}$$

where $\mathcal{T} = \mathcal{M}^{-1}\mathcal{W}$. When $b \in R(\mathcal{G})$, we have $\mathcal{M}^{-1} b \in R(I - \mathcal{T})$, and the behavior of the sequence of iterates (5.4) is given in the next lemma [4,40,57].

Lemma 5.2. *Let $\mathcal{T} \in \mathbb{K}^{n,n}$ and let $c \in \mathbb{K}^n$ such that $c \in R(I - \mathcal{T})$. Then the iterative scheme $z_{i+1} = \mathcal{T} z_i + c, i \geqslant 0$, converges for any $z_0 \in \mathbb{K}^n$ if and only if $\mathcal{T}$ is convergent. In this situation, the limit $\lim_{i\to\infty} z_i = z_\infty$ is given by $z_\infty = \bar{z}_\infty + P_{N(I-\mathcal{T}),R(I-\mathcal{T})} z_0$ where $\bar{z}_\infty$ is the unique solution of $(I - \mathcal{T})\bar{z}_\infty = c$ such that $\bar{z}_\infty \in R(I - \mathcal{T})$.*

We are now interested in solving the constrained singular system (5.1) by stationary iterative techniques. These techniques provide iterates which depend linearly on the right-hand side b, and this property may be important for some applications, as for instance for multicomponent diffusion matrices. For a given splitting $\mathcal{G} = \mathcal{M} - \mathcal{W}$ and for $b \in R(\mathcal{G})$, assuming that the iteration matrix $\mathcal{T} = \mathcal{M}^{-1}\mathcal{W}$ is convergent, the iterates (5.4) will converge for any z_0. When the matrix $\mathcal{G}$ is singular, we have $\rho(\mathcal{T}) = 1$ since $\mathcal{T} z = z$ for $z \in N(\mathcal{G})$, and neither the iterates $\{z_i;\ i \geqslant 0\}$ nor the limit z_∞ are guaranteed to be in the constrained space $\mathscr{C}$. In order to overcome these difficulties, we use a projected iterative scheme [38]

$$z'_{i+1} = \mathcal{P}\mathcal{T}z'_i + \mathcal{P}\mathcal{M}^{-1}b, \quad i \geqslant 0, \tag{5.5}$$

where $\mathcal{P} = P_{\mathscr{C},N(\mathcal{G})}$ is the projector matrix onto the subspace $\mathscr{C}$ along $N(\mathcal{G})$. All the corresponding iterates $\{z'_i;\ i \geqslant 0\}$ then satisfy the constraint $z'_i \in \mathscr{C}$. The spectral radius of the iteration matrix $\mathcal{P}\mathcal{T}$ associated with (5.5) can then be estimated by using a theorem of Neumann and Plemmons [61] which states that $\rho(\mathcal{P}\mathcal{T}) = \gamma(\mathcal{T})$ when $\mathcal{T}$ is convergent. This estimate can also be deduced by investigating directly the spectrum of $\mathcal{P}\mathcal{T}$ and the corresponding eigenvectors using the following result [28,44].

Theorem 5.3. *Let $\mathcal{T} \in \mathbb{K}^{n,n}$ be a matrix such that $R(I-\mathcal{T}) \cap N(I-\mathcal{T}) = \{0\}$. Let $\mathscr{C}$ be a subspace complementary to $N(I-\mathcal{T})$, i.e., such that $N(I-\mathcal{T}) \oplus \mathscr{C} = \mathbb{K}^n$, and let also $\mathcal{P}$ be the oblique projector matrix onto the subspace $\mathscr{C}$ along $N(I-\mathcal{T})$. Then we have*

$$\sigma(\mathcal{P}\mathcal{T}) = \begin{cases} (\sigma(\mathcal{T}) \setminus \{1\}) \cup \{0\}, & \text{if } N(I-\mathcal{T}) \neq \{0\}, \\ \sigma(\mathcal{T}), & \text{if } N(I-\mathcal{T}) = \{0\}, \end{cases}$$

and the matrices $\mathcal{T}$ and $\mathcal{P}$ satisfy the relation $\mathcal{P}\mathcal{T} = \mathcal{P}\mathcal{T}\mathcal{P}$. In addition, if $\lambda \neq 1$ and $x \neq 0$ are such such that $\mathcal{T}x = \lambda x$, then $y = \mathcal{P}x$ is an eigenvector for the product $\mathcal{P}\mathcal{T}$ associated with the eigenvalue λ, that is, $\mathcal{P}\mathcal{T}y = \lambda y$.

In order to obtain convergent iteration matrices – and therefore convergent projected iterative schemes for the transport linear systems in the real case – we may then use Keller's theorem [51].

Theorem 5.4. *Let $G \in \mathbb{R}^{n,n}$ be a symmetric matrix and let $G = M - W$ be a splitting such that M is symmetric and $M + W$ is positive definite. Then $T = M^{-1}W$ is convergent if and only if G is positive semi-definite.*

Combining then Keller's theorem, the spectral Theorem 5.3, and the mathematical structure resulting from the kinetic theory of gases, we may use in the real situation the splitting matrices

$$M = db(G) + \operatorname{diag}(\sigma_1, \ldots, \sigma_n), \tag{5.6}$$

where $db(G)$ is the sparse transport matrix and $\sigma_1, \ldots, \sigma_n$ are any nonnegative factors. Indeed, $M + W = 2db(G) - G + 2\operatorname{diag}(\sigma_1, \ldots, \sigma_n)$, and we deduce that $M + W$ is positive definite from $(G_1 - G_2)$, so that Keller's theorem can be used. The convergence of projected iterative algorithms and the asymptotic expansion of generalized inverses are then obtained [28]. On the other hand, in the complex case, in order to obtain an iterative scheme with convergence properties valid for any matrix G', that is, for any magnetic field intensity B, we may include the full imaginary part iG' of $\mathcal{G}$ in the splitting matrix $\mathcal{M}$

$$\mathcal{M} = db(G) + \operatorname{diag}(\sigma_1, \ldots, \sigma_n) + iG'. \tag{5.7}$$

Then $\mathcal{M} = M + iG'$ and $G = M - W$ is a splitting of the real matrix G. This can be done in practice since the inverse of the matrix $\mathcal{M} = M + iG'$ is easily expressed in terms of the inverse of $M + i\mathcal{D}'$ when G' is in the form $G' = Q\mathcal{D}'P$ [44]. Note that Keller's theorem cannot be applied directly as in the real case since $\mathcal{G}$ is not Hermitian when G' is nonzero [44]. The convergence and properties of the projected iterative algorithms (5.5) when applied to the real or complex symmetric constrained singular systems (5.1) are summarized in the following statement [28,44].

Theorem 5.5. *Let $\mathcal{G} = G + iG'$ where G, G' are real symmetric matrices, G is positive semi-definite and $G'N(G) = 0$. Let $\mathcal{C} \subset \mathbb{R}^n$ be a subspace complementary to $N(G)$ and let $\mathscr{C} = \mathcal{C} + i\mathcal{C}$. Consider a splitting $G = M - W$, assume that M is symmetric and that $M + W$ is positive definite, so that M is also symmetric positive definite. Define $\mathcal{M} = M + iG', \mathcal{G} = \mathcal{M} - \mathcal{W}$, so that $\mathcal{W} = W$, and $\mathcal{T} = \mathcal{M}^{-1}\mathcal{W}, T = M^{-1}W$. Let $\mathcal{P} = P$ be the oblique projector matrix onto the subspace $\mathcal{C}$ along $N(G)$. Let also $b \in R(\mathcal{G}), z_0 \in \mathbb{C}^n, z'_0 = \mathcal{P}z_0$, and consider for $i \geqslant 0$ the iterates $z_{i+1} = \mathcal{T}z_i + M^{-1}b$ as in (5.4) and $z'_{i+1} = \mathcal{P}\mathcal{T}z'_i + \mathcal{P}M^{-1}b$ as in (5.5). Then $z'_i = \mathcal{P}z_i$ for all $i \geqslant 0$, the matrices $\mathcal{T}, \mathcal{P}\mathcal{T}, T$, and PT are convergent, $\rho(T) = \rho(\mathcal{T}) = 1$ when $\dim(N(G)) \geqslant 1, \rho(\mathcal{P}\mathcal{T}) = \gamma(\mathcal{T}) < 1, \rho(PT) = \gamma(T) < 1$, and*

$$\gamma(\mathcal{T}) \leqslant \gamma(T), \tag{5.8}$$

so that the convergence rate is never worse in the magnetized case $G' \neq 0$. Moreover, we have the following limits

$$\lim_{i\to\infty} z'_i = \mathcal{P}(\lim_{i\to\infty} z_i) = a = \sum_{0\leqslant j<\infty} (\mathcal{P}\mathcal{T})^j \mathcal{P}\mathcal{M}^{-1}b, \tag{5.9}$$

where a is the unique solution of (5.1). Moreover, each partial sum $\mathcal{Z}_i, i \geqslant 1$, given by $\mathcal{Z}_i = \sum_{0\leqslant j\leqslant i-1} (\mathcal{P}\mathcal{T})^j \mathcal{P}\mathcal{M}^{-1}\mathcal{P}^t$ is symmetric and $\lim_{i\to\infty} \mathcal{Z}_i = \mathcal{Z}$ where

$$\mathcal{Z} = \sum_{0\leqslant j<\infty} (\mathcal{P}\mathcal{T})^j \mathcal{P}\mathcal{M}^{-1}\mathcal{P}^t, \tag{5.10}$$

is the symmetric generalized inverse of $\mathcal{G}$ with prescribed nullspace $N(\mathcal{Z}) = \mathcal{C}^\perp + i\mathcal{C}^\perp$ and range $R(\mathcal{Z}) = \mathscr{C} = \mathcal{C} + i\mathcal{C}$. Similar properties hold in the real case where $G' = Z' = 0$ and $Z = \sum_{0\leqslant j<\infty} (PT)^j PM^{-1}P^t$ is real and is the generalized inverse of G with prescribed range $R(Z) = \mathcal{C}$ and nullspace $N(Z) = \mathcal{C}^\perp$, and each iterate $Z_i = \sum_{0\leqslant j<i-1} (PT)^j PM^{-1}P^t$ is positive semi-definite with $R(Z_i) = \mathcal{C}$.

The projected iterative algorithms (5.5) applied to the transport linear systems have been successful for accurate evaluation of multicomponent diffusion matrices in nonionized gas mixtures [23,25,27,28,38]. When applied to partially ionized mixtures, these algorithms have been found efficient at low ionization levels [36,44]. The convergence rates are insensitive to the intensity of the magnetic when the whole complex part iG' is included in the splitting matrix $\mathcal{M} = M + iG'$ as shown by the estimate (5.8).

However, as investigated by García Muñoz [36] for planetary atmosphere and reported by Giovangigli and Graille for high temperature air [44], the corresponding convergence rates deteriorate when ionization levels increase and then convergence becomes prohibitively slow. The solution of this problem requires introducing new formulations of the transport linear systems investigated in the following section. The stationary projected iterative algorithms will then be performed with the new formulations.

5.3. Generalized inverses and conjugate directions

We consider in this section the transport linear system in the real singular case (2.8) under assumption (G_2) and we write $\mathrm{z}_1 = \mathrm{z}$ and $\mathrm{g}_1 = \mathrm{g}$. The matrix G is symmetric positive semi-definite, $N(G) = \mathbb{R}\mathrm{z}_1, \langle \mathrm{z}_1, \mathrm{g}_1\rangle > 0$, and we denote by Z the generalized inverse of G with prescribed nullspace $N(Z) = \mathbb{R}\mathrm{g}_1$ and range $R(Z) = \mathrm{g}_1^\perp$. Letting $Q = P^t = \mathbb{I} - \mathrm{g}_1 \otimes \mathrm{z}_1/\langle \mathrm{g}_1, \mathrm{z}_1\rangle$, we have the relations $GZ = Q, ZG = P$, and Z is symmetric positive semi-definite. We now select $\mathrm{z}_2^* \in \mathbb{R}^n$ such that $\mathrm{z}_2^* \notin \mathbb{R}\mathrm{z}_1$ and define

$$\mathrm{z}_2 = \mathrm{z}_2^* - \frac{\langle \mathrm{z}_2^*, \mathrm{g}_1\rangle}{\langle \mathrm{z}_1, \mathrm{g}_1\rangle}\mathrm{z}_1, \quad \mathrm{g}_2 = G\mathrm{z}_2. \tag{5.11}$$

Note that $\langle \mathrm{z}_2, \mathrm{g}_2\rangle > 0$ since $\langle \mathrm{z}_2, \mathrm{g}_2\rangle = \langle \mathrm{z}_2, G\mathrm{z}_2\rangle$ and $\mathrm{z}_2 \notin N(G) = \mathbb{R}\mathrm{z}_1$, and by construction we have $\langle \mathrm{z}_2, \mathrm{g}_1\rangle = 0$ and $\langle \mathrm{z}_1, \mathrm{g}_2\rangle = 0$, so that $\mathrm{g}_2 \notin \mathbb{R}\mathrm{g}_1$. We then introduce

$$G_2 = G - \frac{\mathrm{g}_2 \otimes \mathrm{g}_2}{\langle \mathrm{z}_2, \mathrm{g}_2\rangle}, \quad Z_2 = Z - \frac{\mathrm{z}_2 \otimes \mathrm{z}_2}{\langle \mathrm{z}_2, \mathrm{g}_2\rangle}, \tag{5.12}$$

$$P_2 = \mathbb{I} - \frac{\mathrm{z}_1 \otimes \mathrm{g}_1}{\langle \mathrm{z}_1, \mathrm{g}_1\rangle} - \frac{\mathrm{z}_2 \otimes \mathrm{g}_2}{\langle \mathrm{z}_2, \mathrm{g}_2\rangle}, \quad Q_2 = \mathbb{I} - \frac{\mathrm{g}_1 \otimes \mathrm{z}_1}{\langle \mathrm{z}_1, \mathrm{g}_1\rangle} - \frac{\mathrm{g}_2 \otimes \mathrm{z}_2}{\langle \mathrm{z}_2, \mathrm{g}_2\rangle}, \tag{5.13}$$

and by a direct calculation we obtain that $G_2Z_2 = Q_2, Z_2G_2 = P_2$. Since $\langle G_2x, x\rangle = \langle Gw, w\rangle$ where $w = x - \mathrm{z}_2\langle x, \mathrm{g}_2\rangle/\langle \mathrm{z}_2, \mathrm{g}_2\rangle$, it is easily deduced that G_2 is positive semi-definite and $N(G_2) = \mathrm{span}\{\mathrm{z}_1, \mathrm{z}_2\}$. Proceeding similarly for Z_2 we obtain that Z_2 is positive semi-definite and $N(Z_2) = \mathrm{span}\{\mathrm{g}_1, \mathrm{g}_2\}$. In particular, Z_2 is the generalized inverse of G_2 with prescribed nullspace $N(Z_2) = \mathrm{span}\{\mathrm{g}_1, \mathrm{g}_2\}$ and range $R(Z_2) = \mathrm{span}\{\mathrm{g}_1, \mathrm{g}_2\}^\perp$. Letting $a_2 = Z_2b, b_2 = Q_2b$, we obtain after some algebra the new transport linear system

$$\begin{cases} G_2a_2 = b_2, \\ \langle a_2, \mathrm{g}_1\rangle = \langle a_2, \mathrm{g}_2\rangle = 0. \end{cases} \tag{5.14}$$

It is easily checked that $N(G_2) \oplus \mathrm{span}\{\mathrm{g}_1, \mathrm{g}_2\}^\perp = \mathbb{R}^n$ and $b_2 \in R(G_2)$ so that that the system (5.14) is well posed from Proposition 5.1. Its unique solution is thus given by $a_2 = Z_2b$ and the solution of the original system a can then be written

$$a = a_2 + \frac{\langle \mathrm{z}_2, b\rangle}{\langle \mathrm{z}_2, \mathrm{g}_2\rangle}\mathrm{z}_2. \tag{5.15}$$

The main idea is that the projected iterative algorithm applied to the more singular system (5.14) may involve a matrix P_2T_2 with a lower spectral radius than that of PT by properly selecting z_2^*.

Let indeed $G = M - W$ be a splitting with M and $M + W$ symmetric positive definite and $T = M^{-1}W$. The matrix T is symmetric with respect to the scalar product $\langle\!\langle x, y\rangle\!\rangle = \langle Mx, y\rangle$ since $\langle\!\langle Tx, y\rangle\!\rangle = \langle Wx, y\rangle$ so that T has only real eigenvalues and a basis of right eigenvectors orthonormal with respect to $\langle\!\langle , \rangle\!\rangle$. Moreover, $\rho(T) \subset (-1, 1]$ since T is convergent. Let us assume – as a typical example – that z_2^* is an eigenvector associated with an eigenvalue $1 - \epsilon$ of T so that $G\mathrm{z}_2^* = \epsilon M\mathrm{z}_2^*$ with $\mathrm{z}_2^* \neq 0$. Assume also that ϵ is small so that this eigenvalue is the *worse*. All eigenvalues different from unity and different from the isolated eigenvalue $1 - \epsilon$ are assumed to be in $(-\alpha, \alpha)$ with $0 < \alpha < 1 - \epsilon$. From the spectral Theorem 5.3 we know that $1 - \epsilon$ is also an eigenvalue of the matrix PT with eigenvector $P\mathrm{z}_2^*$ and that all nonzero eigenvalue of PT are similarly nonunity eigenvalues of T. Defining z_2 and g_2 as in (5.11), we have $\mathrm{span}\{\mathrm{z}_1, \mathrm{z}_2\} = \mathrm{span}\{\mathrm{z}_1^*, \mathrm{z}_2^*\}$ and $\mathrm{g}_2 = G\mathrm{z}_2 = G\mathrm{z}_2^*$. Then z_2^* can be taken of order unity but $\mathrm{g}_2 = G\mathrm{z}_2^* = \epsilon M\mathrm{z}_2^*$ is small, say $\mathcal{O}(\epsilon)$. From the expressions (5.12) we obtain that $G - G_2 = \mathcal{O}(\epsilon)$ and $Z - Z_2 = \mathcal{O}(1/\epsilon)$. Since G and G_2 are close, upon writing $G = M - W$ and $G_2 = M_2 - W_2, T = M^{-1}W, T_2 = M_2^{-1}W_2$, where M and M_2 are symmetric positive definite, we may let $M_2 \simeq M, W_2 \simeq W$. On the other hand, it is established [44,40] that

$$\gamma(T) = \sup\left\{\frac{|\langle Wx, x\rangle|}{\langle Mx, x\rangle}; x \in \mathbb{R}^n,\ x \neq 0, \langle M\mathrm{z}_1, x\rangle = 0\right\},$$

$$\gamma(T_2) = \sup\left\{\frac{|\langle W_2x, x\rangle|}{\langle M_2x, x\rangle}; x \in \mathbb{R}^n, x \neq 0, \langle M_2\mathrm{z}_1, x\rangle = \langle M_2\mathrm{z}_2, x\rangle = 0\right\}.$$

This results from the symmetry of T with respect to the scalar product $\langle\!\langle x, y\rangle\!\rangle = \langle Mx, y\rangle$ since $\langle\!\langle Tx, y\rangle\!\rangle = \langle Wx, y\rangle$ so that $|\langle Wx, x\rangle|/\langle Mx, x\rangle$ is the corresponding Rayleigh quotient, with a similar argument for T_2. Moreover, we have the relation

$\langle\langle z_1, z_2^* \rangle\rangle = 0$ since these vectors are associated with different eigenvalues so that $\langle Mz_1, z_2^* \rangle = 0$. The maximum value of the Rayleigh quotient $|\langle Wx, x\rangle|/\langle Mx, x\rangle$ for $\gamma(T)$ is then obtained with $x = z_2^*$ since we have assumed that $1 - \epsilon$ is the worse eigenvalue. We then see that this bad eigenvalue $1 - \epsilon$ of T associated with the vector z_2^* is eliminated when estimating $\gamma(T_2)$ since $N(G_2) = N(\mathbb{I} - T_2) = \mathrm{span}\{z_1, z_2\}$ contains z_2^*. More specifically, the relevant vectors to be considered for $\gamma(T_2)$ are now orthogonal to $M_2 z_1$ and $M_2 z_2$ and are thus orthogonal $M_2 z_2^*$, and this excludes the vector z_2^*. In addition, from Theorem 5.3, all eigenvectors of $P_2 T_2$ associated with nonzero eigenvalues of $P_2 T_2$ are projections of eigenvectors of T_2 in such a way that the components of such eigenvectors of T_2 along $\mathrm{span}\{z_1, z_2\}$ are eliminated by P_2.

In the asymptotic situation where ϵ is small, a connection may be made with deflation techniques that have been introduced for solving invertible nearly singular systems. These methods separate the solution component along an approximate nullvector from its orthogonal complement and have notably been investigated by Chan [14,15] and Stewart [69]. The framework associated with transport linear systems is quite different since we investigate exactly singular systems, with a special symmetric structure inherited from mathematical physics, and we are interested in symmetric generalized inverses and solution by stationary iteration techniques. Moreover the vectors under concern are eigenvalue of the iteration matrix T or equivalently of the symmetric-definite pencil $G - \lambda M$ and not of the original matrix G. Nevertheless, we can make a parallel with these techniques in the asymptotic situation where ϵ is small since the projector P_2 has a larger nullspace than P and Z_2 is a more stable component of the generalized inverse Z. We may then term Z_2 a deflated generalized inverse and similarly $P_2 T_2$ an iteration matrix with a deflated spectrum since the bad eigenvalue $1 - \epsilon$ in PT has been eliminated from $P_2 T_2$.

In practice, however, the eigenvalues of T different from unity are not necessarily close to unity or either to -1. We may still obtain a spectral radius of the iteration matrix $\rho(P_2 T_2)$ significantly lower than the radius of $\rho(PT)$ by eliminating the worse eigenvalue, provided it is clearly separated from the other eigenvalues. To this aim, it is sufficient that $\mathrm{span}\{z_1^*, z_2^*\}$ contain an approximation of the corresponding eigenvector. In other words, the spectrum modification can be very effective and robust provided we can approximate the eigenvector associated with the worse eigenvalue and that the Rayleigh quotients associated with T and T_2 are approximately similar. This will notably be the case for the transport linear systems associated with multicomponent diffusion in partially ionized mixtures, even though the eigenvalues of the corresponding iteration matrices are not close to unity or minus unity.

It is possible to generalize this construction and to expand the matrices G and Z into tensor products of conjugate directions. We may then introduce the corresponding more singular formulations of the transport linear systems [40]. This generalization may be used to suppress a group of worse eigenvalues of the matrix T. We summarize here this construction and refer to [40] for more details and for the mathematical aspects.

Let $z_i^*, 1 \leqslant i \leqslant n$, be a basis of $\mathbb{R}^n$ with $z_1^* = z$, and define for convenience $z_1 = z_1^* g_1 = g, G_1 = G, Z_1 = Z, P_1 = P, Q_1 = Q$. One can then construct inductively for $k \geqslant 2$

$$z_k = z_k^* - \sum_{1 \leqslant j \leqslant k-1} \frac{\langle z_k^*, g_j \rangle}{\langle z_j, g_j \rangle} z_j, \quad g_k = G_{k-1} z_k, \tag{5.16}$$

$$G_k = G_{k-1} - \frac{g_k \otimes g_k}{\langle z_k, g_k \rangle}, \quad Z_k = Z_{k-1} - \frac{z_k \otimes z_k}{\langle z_k, g_k \rangle}. \tag{5.17}$$

These vectors $z_i, g_i, 1 \leqslant i \leqslant n$, are such that $\langle z_i, g_i \rangle > 0, z_i = Z_{i-1} g_i, 1 \leqslant i \leqslant n, \langle z_i, g_j \rangle = 0$ if $i \neq j, 1 \leqslant i, j \leqslant n$. Moreover, for $0 \leqslant k \leqslant n$ we have the relations $G_k Z_k = Q_k, Z_k G_k = P_k$, where P_k is the projector onto $\mathrm{span}\{g_1, \ldots, g_k\}^\perp$ parallel to $\mathrm{span}\{z_1, \ldots, z_k\}$, and Q_k is the projector onto $\mathrm{span}\{z_1, \ldots, z_k\}^\perp$ parallel to $\mathrm{span}\{g_1, \ldots, g_k\}$. In addition, G_k and Z_k are symmetric positive semi-definite, $N(G_k) = \mathrm{span}\{z_1, \ldots, z_k\}, R(G_k) = \mathrm{span}\{z_1, \ldots, z_k\}^\perp$, and Z_k is the generalized inverse of G_k with prescribed nullspace $N(Z_k) = \mathrm{span}\{g_1, \ldots, g_k\}$ and range $R(Z_k) = \mathrm{span}\{g_1, \ldots, g_k\}^\perp$. Finally, we have $g_i = G z_i, z_i = Z g_i, 2 \leqslant i \leqslant n, g^\perp = \mathrm{span}\{z_2, \ldots, z_n\}$, the directions $z_i, 2 \leqslant i \leqslant n$, are conjugate for G, the directions $g_i, 2 \leqslant i \leqslant n$ are conjugate for Z, and we have the decompositions

$$G = \sum_{2 \leqslant i \leqslant n} \frac{g_i \otimes g_i}{\langle z_i, g_i \rangle}, \quad Z = \sum_{2 \leqslant i \leqslant n} \frac{z_i \otimes z_i}{\langle z_i, g_i \rangle}. \tag{5.18}$$

Letting $b_k = Q_k b$, we can then generalize the transport linear systems (2.8) and (5.14) – corresponding respectively to $k = 1$ and $k = 2$ – in the form

$$\begin{cases} G_k a_k = b_k, \\ \langle a_k, g_l \rangle = 0, \quad 1 \leqslant l \leqslant k. \end{cases} \tag{5.19}$$

This system is well posed, its solution is $a_k = Z_k b$, and we have the expansion

$$a = a_k + \sum_{1 \leqslant l \leqslant k} \frac{\langle z_l, b \rangle}{\langle z_l, g_l \rangle} z_l. \tag{5.20}$$

5.4. Conjugate directions in the anisotropic situation

We consider in this section the transport linear system in the complex singular case (3.7) under assumptions $(G_2)(G_2')$ and we write $z = z_1$ and $g = g_1$. The matrix $\mathcal{G}$ is in the form $\mathcal{G} = G + iG'$, where G, G' are symmetric, G positive semi-definite,

$N(G) = \mathbb{R}z_1, G'z_1 = 0$, and we denote by $\mathcal{Z}$ the generalized inverse of $G + iG'$ with prescribed nullspace $N(\mathcal{Z}) = \mathbb{C}g_1$ and range $R(\mathcal{Z}) = g_1^\perp + ig_1^\perp$. We have the relations $\mathcal{G}\mathcal{Z} = Q, \mathcal{Z}\mathcal{G} = P$, where $Q = P^t = \mathbb{I} - g \otimes z/\langle g, z\rangle$, and $\mathcal{Z}$ is symmetric. However, a conjugate directions expansion cannot be performed as easily as in the real case since the nondegenerate bilinear form $(,)$ naturally associated with complex symmetric matrices is nondefinite in $\mathbb{C}^n$. We may indeed encounter breakdowns arising from zero scalar product in the decomposition into conjugate directions. In order to avoid such problems we have to restrict the vectors $z_i^*, 1 \leqslant i \leqslant n$, to be *real* vectors.

Let thus assume that $z_1 = z_1^*$ and $z_2^* \in \mathbb{R}^n, z_2^* \notin \mathbb{R}z_1$ and define z_2 and g_2 by letting

$$z_2 = z_2^* - \frac{(z_2^*, g_1)}{(z_1, g_1)} z_1, \quad g_2 = \mathcal{G}z_2. \tag{5.21}$$

Then we have $z_2 \in \mathbb{R}^n, g_2 \in \mathbb{C}^n, (z_2, g_1) = 0, (g_2, z_1) = 0, \Re(z_2, g_2) = \langle Gz_2, z_2\rangle \neq 0$ since $z_2 \notin N(G) = \mathbb{R}z_1$. Moreover $\mathcal{Z}g_2 = \mathcal{Z}\mathcal{G}z_2 = z_2$ since $(z_2, g_1) = 0$ and $\operatorname{span}\{z_1, z_2\} = \operatorname{span}\{z_1^*, z_2^*\}$. Defining then

$$\mathcal{G}_2 = \mathcal{G} - \frac{g_2 \otimes g_2}{(z_2, g_2)}, \quad \mathcal{Z}_2 = \mathcal{Z} - \frac{z_2 \otimes z_2}{(z_2, g_2)}, \tag{5.22}$$

$$\mathcal{Q}_2 = \mathbb{I} - \frac{g_1 \otimes z_1}{(z_1, g_1)} - \frac{g_2 \otimes z_2}{(z_2, g_2)}, \quad \mathcal{P}_2 = \mathbb{I} - \frac{z_1 \otimes g_1}{(z_1, g_1)} - \frac{z_2 \otimes g_2}{(z_2, g_2)}, \tag{5.23}$$

a direct calculation yields the relations $\mathcal{G}_2\mathcal{Z}_2 = \mathcal{Q}_2, \mathcal{Z}_2\mathcal{G}_2 = \mathcal{P}_2$, and $\mathcal{P}_2$ is the projector onto $\operatorname{span}\{g_1, g_2\}^\perp$ parallel to $\operatorname{span}\{z_1, z_2\}$, $\mathcal{Q}_2$ is the projector onto $\operatorname{span}\{z_1, z_2\}^\perp$ parallel to $\operatorname{span}\{g_1, g_2\}$. After some algebra it is shown that $\mathcal{Z}_2$ is the generalized inverse of $\mathcal{G}_2$ with prescribed nullspace $N(\mathcal{Z}_2) = \operatorname{span}\{g_1, g_2\}$ and range $R(\mathcal{Z}_2) = \operatorname{span}\{g_1, g_2\}^\perp$. Letting $b_2 = \mathcal{Q}_2 b$, we obtain the new transport linear system

$$\begin{cases} \mathcal{G}_2 a_2 = b_2, \\ (a_2, g_1) = (a_2, g_2) = 0. \end{cases} \tag{5.24}$$

This system is well posed and its unique solution is given by $a_2 = \mathcal{Z}_2 b$ and the solution of the original system a can be written

$$a = a_2 + \frac{(z_2, b)}{(z_2, g_2)} z_2. \tag{5.25}$$

One may investigate more closely the structure of the matrices $\Re(\mathcal{G}_2)$ and $\Im(\mathcal{G}_2)$ when $\Im(\mathcal{G}_1) = G'$ is in the form $G' = Q\mathcal{D}'P$. After some lengthy algebra, thanks to $z_2 \in \mathbb{R}^n$, one can establish that

$$\Re(\mathcal{G}_2) = G - \frac{Gz_2 \otimes Gz_2}{\langle Gz_2, z_2\rangle} + \frac{r_2 \otimes r_2}{\langle Gz_2, z_2\rangle m^2},$$
$$\Im(\mathcal{G}_2) = (\mathbb{I} - s_1 \otimes z_1 - s_2 \otimes z_2)\mathcal{D}'(\mathbb{I} - z_1 \otimes s_1 - z_2 \otimes s_2),$$

where $m^2 = (Gz_2, z_2)^2 + (G'z_2, z_2)^2, \mathcal{D}'$ is the diagonal matrix such that $G' = Q\mathcal{D}'P$, and where $r_2 = (G'z_2, z_2)Gz_2 - (Gz_2, z_2)G'z_2, s_1 = g_1/\langle z_1, g_1\rangle s_2 = \big(mGz_2 + (Gz_2, z_2)Gz_2 + (G'z_2, z_2)G'z_2\big)/m(m + (Gz_2, z_2))$. As a consequence, $\Im(\mathcal{G}_2)$ shares a similar form with $\Im(\mathcal{G}_1)$ and the inverse of $M + i\Im(\mathcal{G}_2)$ is easily expressed in terms of the inverse of $M + i\mathcal{D}'$ as described in Giovangigli and Graille [44]. These expressions simplify when $(G'z_2, z_2) = 0$ and $m = (Gz_2, z_2)$ which sometimes happens in practice.

As in the real case, upon introducing the splittings $\mathcal{G} = \mathcal{M} - \mathcal{W}$ and $\mathcal{G}_2 = \mathcal{M}_2 - \mathcal{W}_2$, and the corresponding iteration matrices $\mathcal{T} = \mathcal{M}^{-1}\mathcal{W}, \mathcal{T}_2 = \mathcal{M}_2^{-1}\mathcal{W}_2$, we may expect the spectral radius of the iteration matrix $\mathcal{P}_2\mathcal{T}_2$ to be lower than that of $\mathcal{P}\mathcal{T}$ by properly selecting the vector z_2^* by eliminating any isolated worse eigenvalue of $\mathcal{T}$. This procedure can also be generalized as in the real case provided that $z_i^*, 1 \leqslant i \leqslant n$, form a basis of *real* vectors but the details are omitted and we refer to [40].

6. Orthogonal residuals algorithms

Conjugate gradients-type methods – used with preconditioning – are among the most effective iterative procedures for solving Hermitian systems [46,49,54]. Projected conjugate gradients methods have been introduced in particular to solve real symmetric constrained singular semi-definite systems arising from multicomponent transport [23,25,28,38]. For general linear systems, however, one cannot obtain short recurrence algorithms which globally minimize some error norm over the corresponding Krylov subspaces unless the matrix has certain rather special spectral properties [30]. Complex symmetric systems have been investigated motivated by electromagnetic applications [3,31,33,34,43,44]. In particular, projected orthogonal residuals algorithms have been investigated in order to solve the complex symmetric constrained singular systems arising from magnetized multicomponent transport [31,43,44]. These algorithms reduce to projected conjugate gradients methods in the absence of magnetization, that is, when the imaginary part of the system matrix vanishes.

We investigate in this section orthogonal residuals techniques and the links with expansions into conjugate directions obtained in the previous section.

6.1. Projected orthogonal directions

We consider a matrix in the form $\mathcal{G} = G + iG'$ where G, G' are real symmetric matrices, G is positive semi-definite and $G'N(G) = 0$, a vector $b \in R(\mathcal{G})$, a subspace $\mathcal{C} \subset \mathbb{R}^n$ complementary to $N(G)$ and $\mathscr{C} = \mathcal{C} + i\mathcal{C}$. The projector onto $\mathscr{C}$ parallel to $N(G) + iN(G) = N(G + iG')$ coincide with the projector onto $\mathcal{C}$ parallel to $N(G)$ and is denoted by $\mathcal{P}$. The projected preconditioned orthogonal residuals algorithm can be described as follows [31,44].

Assume that $M \in \mathbb{R}^{n,n}$ is hermitian positive definite. Let $z_0 \in \mathbb{C}^n$, be an initial guess, $z'_0 = \mathcal{P}z_0, r'_0 = b - \mathcal{G}z'_0, p'_0 = \mathcal{P}M^{-1}r'_0$. If $\langle \mathcal{G}p'_0, p'_0\rangle = 0$ we stop at step 0, whereas if $\langle \mathcal{G}p'_0, p'_0\rangle \neq 0$ we define $\sigma'_0 = \langle r'_0, p'_0\rangle / \langle \mathcal{G}p'_0, p'_0\rangle$, $v'_{00} = \langle \mathcal{G}M^{-1}\mathcal{G}p'_0, p'_0\rangle / \langle \mathcal{G}p'_0, p'_0\rangle$, and $p'_1 = \mathcal{P}M^{-1}\mathcal{G}p'_0 - v'_{00}p'_0, z'_1 = z'_0 + \sigma'_0 p'_0$, and $r'_1 = r'_0 - \sigma'_0 \mathcal{G}p'_0$. Assume now by induction that for $k \geqslant 1$ we have defined $\{p'_i\}_{0\leqslant i\leqslant k}, \{z'_i\}_{0\leqslant i\leqslant k}, \{r'_i\}_{0\leqslant i\leqslant k}$, with $\prod_{0\leqslant i\leqslant k-1}\langle \mathcal{G}p'_i, p'_i\rangle \neq 0, r'_i = b - \mathcal{G}z'_i, 0 \leqslant i \leqslant k$, and

$$\langle M^{-1}r'_i, r'_j\rangle = 0, \quad 0 \leqslant j < i \leqslant k, \tag{6.1}$$

$$\langle \mathcal{G}p'_i, p'_j\rangle = 0, \quad 0 \leqslant j < i \leqslant k, \tag{6.2}$$

$$\langle r'_i, p'_j\rangle = 0, \quad 0 \leqslant j < i \leqslant k, \tag{6.3}$$

$$\mathcal{K}_i = \mathrm{span}(r'_0, \ldots, r'_i), = \mathrm{span}(r'_0, \ldots, (\mathcal{G}M^{-1})^i r'_0), \quad 0 \leqslant i \leqslant k, \tag{6.4}$$

$$\mathcal{K}'_i = \mathrm{span}(p'_0, \ldots, p'_i) = \mathcal{P}M^{-1}\mathcal{K}_i, \quad \mathcal{K}_i = \mathcal{H}\mathcal{K}'_i, \quad 0 \leqslant i \leqslant k, \tag{6.5}$$

where $\dim(\mathcal{K}_i) = i + 1$ for $0 \leqslant i \leqslant k - 1$ and where $\mathcal{H} = \mathbb{I} - \sum_{1\leqslant i,j\leqslant p}\gamma_{ij} z_i \otimes Mz_j$ and $(\gamma_{ij})_{1\leqslant i,j\leqslant p}$ is the inverse of the matrix $\big(\langle Mz_i, z_j\rangle\big)_{1\leqslant i,j\leqslant p}$ and $\dim(\mathcal{K}_i) = \dim(\mathcal{K}'_i) = i + 1$ for $0 \leqslant i \leqslant k - 1$. Then $\langle \mathcal{G}p'_k, p'_k\rangle = 0$ if and only if $r'_k = 0$ and in this situation we stop at step k. On the other hand if $\langle \mathcal{G}p'_k, p'_k\rangle \neq 0$ we introduce the solution $v'_{k0}, \ldots, v'_{kk}$ of the linear systems

$$\begin{pmatrix} \langle \mathcal{G}p'_0, p'_0\rangle & & & \\ \langle \mathcal{G}p'_0, p'_1\rangle & \langle \mathcal{G}p'_1, p'_1\rangle & & \\ \vdots & \vdots & \ddots & \\ \langle \mathcal{G}p'_0, p'_k\rangle & \langle \mathcal{G}p'_1, p'_k\rangle & \ldots & \langle \mathcal{G}p'_k, p'_k\rangle \end{pmatrix} \begin{pmatrix} v'_{k0} \\ v'_{k1} \\ \vdots \\ v'_{kk} \end{pmatrix} = \begin{pmatrix} \langle \mathcal{G}M^{-1}\mathcal{G}p'_k, p'_0\rangle \\ \langle \mathcal{G}M^{-1}\mathcal{G}p'_k, p'_1\rangle \\ \vdots \\ \langle \mathcal{G}M^{-1}\mathcal{G}p'_k, p'_k\rangle \end{pmatrix}, \tag{6.6}$$

we define $\sigma'_k = \langle r'_k, p'_k\rangle / \langle \mathcal{G}p'_k, p'_k\rangle$ and we set

$$p'_{k+1} = \mathcal{P}M^{-1}\mathcal{G}p'_k - \sum_{0\leqslant j\leqslant k} v'_{kj}p'_j, \quad z'_{k+1} = z'_k + \sigma'_k p'_k, \quad r'_{k+1} = r'_k - \sigma'_k \mathcal{G}p'_k. \tag{6.7}$$

Theorem 6.1. *The projected preconditioned orthogonal residuals algorithm is well defined and converges in at most rank$(\mathcal{G})$ steps towards the unique solution a of $\mathcal{G}a = b$ and $a \in \mathscr{C}$. Moreover, the iterates $z'_k, k \geqslant 1$, are the projections of the iterates $z_k, k \geqslant 1$, of the corresponding unprojected algorithm* [44].

When the magnetic part G' vanishes and $\mathcal{G} = G$ is symmetric positive semi-definite we recover the projected version of the preconditioned conjugate gradient algorithm [31,28] and other preconditioning techniques are discussed in Giovangigli and Graille [44].

6.2. Conjugate directions versus conjugate gradients

When applied to a symmetric positive semi-definite matrix G the projected orthogonal residuals algorithm yield the projected conjugate gradient algorithm for singular systems [31,44]. Starting form $x_0 = 0$, the approximate solution is then obtained in the form

$$p'_0 \frac{\langle r'_0, p'_0\rangle}{\langle Gp'_0, p'_0\rangle} + \cdots + p'_l \frac{\langle r'_l, p'_l\rangle}{\langle Gp'_l, p'_l\rangle},$$

where $l + 1$ is the dimension of the subspace spanned by the vectors $(GM^{-1})^k b, k \geqslant 0$. Thanks to the symmetry of G we have the classical relations $\langle r'_l, p'_l\rangle = \langle r'_0, p'_l\rangle = \langle b, p'_l\rangle$ where $b = \mathcal{P}^t b = r'_0$ in such a way that the generalized inverse Z has been approximated in the form

$$\frac{p'_0 \otimes p'_0}{\langle Gp'_0, p'_0\rangle} + \cdots + \frac{p'_l \otimes p'_l}{\langle Gp'_l, p'_l\rangle}.$$

An important difference with the expansion into conjugate directions (5.18) is therefore that the fixed subspaces $\mathrm{span}\{z_1, \ldots, z_k\}, k \geqslant 1$, have been replaced by the projected preconditioned Krylov subspaces $\mathcal{P}M^{-1}\ \mathrm{span}\{b, \ldots, (GM^{-1})^i b\}, i \geqslant 0$, which depend on b. In addition, the algorithm associated with the expansion (5.18) is linear whereas orthogonal residuals algorithms are non linear. Finally, we obtain with the orthogonal residuals algorithm the important relations $\langle M^{-1}r'_i, r'_j\rangle = 0, 0 \leqslant i, j \leqslant l$. Since the more singular formulation is associated with a decomposition of the generalized inverse Z in the form

$$Z = \frac{z_2 \otimes z_2}{\langle G z_2, z_2 \rangle} + Z_2,$$

we also conclude that using the more singular formulation (5.14) (5.15) with projected conjugate gradients then constrain the first projected search direction p'_0 to be the vector z_2 and the subsequent directions are next chosen in the Krylov subspaces associated with G_2. Using the more singular formulations thus automatically leads to deflated conjugate gradient techniques introduced to solve invertible nearly singular systems [68]. Note however, that the framework associated with transport linear systems is quite different since we consider exactly singular systems, that we are interested in a constrained solution obtained upon projecting the search directions, and that in practice the vectors z_2 are not quasi nullvectors.

Similarly, in the complex magnetized case, starting from $z_0 = 0$, the approximate solution is then obtained in the form

$$p'_0 \frac{\langle r'_0, p'_0 \rangle}{\langle \mathcal{G} p'_0, p'_0 \rangle} + \cdots + p'_l \frac{\langle r'_l, p'_l \rangle}{\langle \mathcal{G} p'_l, p'_l \rangle}, \tag{6.8}$$

where $l+1$ is the dimension of the subspace spanned by the vectors $(\mathcal{G}M^{-1})^k b, k \geqslant 0$. When $\mathcal{G}$ is not Hermitian, we do not have a simple relation between $\langle r'_i, p'_i \rangle$ and $\langle r'_0, p'_i \rangle$ where $r'_0 = \mathcal{P} b = b$. The more complex relation between $\langle r'_i, p'_i \rangle$ and the scalar products $\langle r'_0, p'_0 \rangle, \ldots, \langle r'_0, p'_i \rangle$ is investigated in [40]. However, when z_2 is a real vector, we have $(\mathcal{G} z_2, z_2) = \langle \mathcal{G} z_2, z_2 \rangle$ and from the decomposition

$$\mathcal{Z} = \frac{z_2 \otimes z_2}{(\mathcal{G} z_2, z_2)} + \mathcal{Z}_2,$$

we conclude that using a projected orthogonal residuals algorithm with the more singular formulation (5.24) (5.25) constrain the first projected search direction p'_0 to be the real direction z_2 and the subsequent directions are next chosen in the Krylov subspaces associated with $\mathcal{G}_2$.

7. Application to diffusion matrices

We investigate in this section the use of stationary iterative techniques in order to evaluate multicomponent diffusion matrices. Evaluating diffusion coefficients is usually required for implicit time marching techniques. We discuss the expansions of diffusion matrices obtained by using projected iterative algorithms with both the natural and the more singular formulations of the transport linear systems. We also consider first order and higher order diffusion matrices as well as isotropic and magnetized mixtures.

In order to assess the accuracy of the resulting algorithms, numerical experiments are performed with high temperature air. The corresponding mixture is constituted by the $n^s = 11$ species N_2, O_2, NO, N, O, N_2^+, O_2^+, NO^+, N^+, O^+, and e. The Thermodynamic properties have been estimated from Gupta, Yos, Thomson and Lee [48] and the collision integrals from Wright, Bose, Palmer, and Levin [71]. We have considered typical mixtures with

$$X_{N_2} = X_{O_2} = X_{NO} = X_N = X_O = 0.2(1 - 10x),$$
$$X_{N_2^+} = X_{O_2^+} = X_{NO^+} = X_{N^+} = X_{O^+} = x, \quad X_e = 5x,$$

and the ionization parameter x is such that $0 \leqslant x \leqslant 0.1$. The corresponding ionization level or degree is then $X_e = 5x$. The accuracy of the asymptotic expansions is investigated as depending on the ionization parameter x and the intensity of the magnetic field B. The species mass fractions are denoted by $y_1, \ldots, y_{n^s}$ and are such that $y_k > 0, k \in \mathcal{S}$, and $\sum_{k \in \mathcal{S}} y_k = 1$. In all the numerical experiments, the pressure is taken to be $p = 0.1$ atm and the temperature $T = T_h = 10,000$ K. Using other pressures or temperatures would not significantly modify the accuracy of the asymptotic expansions. Similar results have also been obtained for other choices of the mixture mole fractions.

7.1. The real first order matrix

We investigate in this section the evaluation of the first order diffusion matrix $D_{[00]}$. The corresponding n^s systems presented in Table 1 are of size $n = n^s$ and in the form

$$\begin{cases} \Delta a^{D_k}_{[00]} = b^{D_k}_{[00]}, \\ \langle a^{D_k}_{[00]}, y \rangle = 0, \end{cases} \quad k \in \mathcal{S}, \tag{7.1}$$

and the first order diffusion coefficients are then evaluated from

$$D_{[00]kl} = \langle a^{D_k}_{[00]}, b^{D_l}_{[00]} \rangle, \quad k, l \in \mathcal{S}. \tag{7.2}$$

The Stefan–Maxwell matrix Δ can be written [13,32,38,39]

$$\Delta_{kk} = \sum_{\substack{l\in\mathcal{S}\\ l\neq k}} \frac{X_k X_l}{\mathcal{D}_{kl}}, \quad k\in\mathcal{S}, \quad \Delta_{kl} = -\frac{X_k X_l}{\mathcal{D}_{kl}}, \quad k,l\in\mathcal{S},\ k\neq l,$$

where $X_1,\dots,X_n^s$ are the species mole fractions, $\mathcal{D}_{kl}, k,l\in\mathcal{S}$, the species binary diffusion coefficients, and the constraint vector y is the mass fractions vector $\mathrm{y}=(y_1,\dots,y_n^s)^t$. The matrix Δ is symmetric positive semi-definite with nullspace $N(\Delta)=\mathbb{R}\mathrm{u}, R(\Delta)=\mathrm{u}^\perp$, where $\mathrm{u}=(1,\dots,1)^t\in\mathbb{R}^{n^s}$, $2\mathrm{diag}(\Delta)-\Delta$ is positive definite when $n^s\geqslant 3$ and Δ is a singular M-matrix [38,62]. The right hand sides $b_{[00]}^{D_k}, k\in\mathcal{S}$, are given by

$$b_{[00]}^{D_k} = \mathrm{e}^k - \mathrm{y}, \quad k\in\mathcal{S},$$

where $\mathrm{e}^k, k\in\mathcal{S}$, are the standard basis vectors of $\mathbb{R}^{n^s}$ and $b_{[00]i}^{D_k}=\delta_{ki}-\mathrm{y}_i, i,k\in\mathcal{S}$. Since $b_{[00]}^{D_k}\in R(\Delta), k\in\mathcal{S}$, and $\langle \mathrm{u},\mathrm{y}\rangle = 1$, the transport linear systems (7.1) are well posed and from $D_{[00]kl}=\langle \Delta a_{[00]}^{D_k}, a_{[00]}^{D_l}\rangle$ and the symmetry of Δ, we obtain the symmetry of $D_{[00]}$. We also have $D_{[00]kl}=\langle a_{[00]}^{D_k}, b_{[00]}^{D_l}\rangle = \langle a_{[00]}^{D_k}, \mathrm{e}^l\rangle$ since $\langle a_{[00]}^{D_k},\mathrm{y}\rangle = 0$ and $D_{[00]kl}=a_{[00]l}^{D_k}=a_{[00]k}^{D_l}$. The transport linear systems (7.1) imply the matrix relations $\Delta D_{[00]}=Q$, and $D_{[00]}\mathrm{y}=0$ where $Q=\mathbb{I}-\mathrm{y}\otimes\mathrm{u}=[b_{[00]}^{D_1},\dots,b_{[00]}^{D_{n^s}}]$. After some algebra it is easily obtained that $D_{[00]}$ is the generalized inverse of Δ with prescribed nullspace $\mathbb{R}\mathrm{y}$ and range $\mathrm{y}^\perp$ and for $\alpha>0$ we have $D_{[00]}=(\Delta+\alpha\mathrm{y}\otimes\mathrm{y})^{-1}-(1/\alpha)\mathrm{u}\otimes\mathrm{u}$ [37,38].

As a direct application of Section 5, from the convergence of the projected iterative algorithm applied to (7.1), or equivalently from the expansion of generalized inverses (5.10), we deduce that upon using the splitting $\Delta=M-W$, with $M=\mathcal{D}$ and

$$\mathcal{D} = \mathrm{diag}\left(\frac{\Delta_{11}}{1-y_1},\dots,\frac{\Delta_{n^s,n^s}}{1-y_{n^s}}\right), \tag{7.3}$$

and letting $T=M^{-1}W$ and $P=Q^t=\mathbb{I}-\mathrm{u}\otimes\mathrm{y}$, we have the convergent asymptotic expansion [38]

$$D_{[00]} = \sum_{0\leqslant j<\infty} (PT)^j PM^{-1}P^t. \tag{7.4}$$

In the first term $PM^{-1}P^t$ the matrix M^{-1} corresponds to the Hirschfelder-Curtiss approximation and the projector operation P to the addition of a species independent mass conservation corrector [38,64,65]. The next approximation of $D_{[00]}$ with two terms is more interesting since it is much more accurate and still yields $(n^s)^2$ coefficients within $\mathcal{O}\left((n^s)^2\right)$ operations [29,38].

The rescaled errors of the various iterates associated with the classical expansion (7.4) are presented in Fig. 1 for the ionization parameter $x=10^{-4}, x=10^{-3}$, and $x=10^{-2}$. These errors are calculated with the Frobenius matrix norm $\|A\|^2=\sum_{1\leqslant i,j\leqslant n} a_{ij}^2$ and rescaled by the initial error. We can see that the convergence rates deteriorate as the ionization parameter x increases as first investigated by García Muñoz [36] for planetary atmospheres. In particular, the convergence behavior for $x=10^{-2}$, one of the worse case encountered, is not satisfactory.

We also investigated a splitting matrix M taking into account the line and column corresponding to the electron in Δ. Assuming that the electron is the n^sth species, this matrix M is defined by $M_{ij}=\mathcal{D}_{ij}$ if $i\neq n^s$ and $j\neq n^s$, and $M_{ij}=\Delta_{ij}$ otherwise. However, it only *marginally* improved the bad convergence rates observed with increasing ionization levels, suggesting that the small coefficients in Δ and the large coefficient in $D_{[00]}$ associated with electron [42] are not at the origin of the problem. This has been confirmed by investigating the heavy species first order diffusion matrix associated with nonequilibrium models – where the electron species is simply suppressed – which yielded similar results as those presented in Fig. 1.

In order to improve the convergence rates for increasing ionization levels, we have used the *more singular* formulation (5.14) with the vector u_2^* defined by $(\mathrm{u}_2)_k^*=1$ if $k\in\mathcal{I}$ and $(\mathrm{u}_2)_k^*=0$ otherwise, where $\mathcal{I}$ denotes the set of ionized species. Letting $y_c=\sum_{k\in\mathcal{I}} y_k$ the resulting vector u_2 is such that $(\mathrm{u}_2)_k=1-y_c$ if $k\in\mathcal{I}$ and $(\mathrm{u}_2)_k=-y_c$ otherwise. Defining $\mathrm{u}_1=\mathrm{u}$,

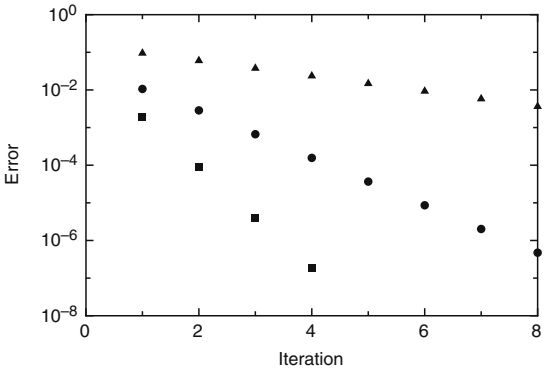

Fig. 1. Reduced errors of first order classical approximate diffusion matrices for various ionized mixtures; ■ $x=10^{-4}$, • $x=10^{-3}$, and ▲ $x=10^{-2}$.

$\mathsf{y}_1 = \mathsf{y}, \mathsf{y}_2 = \Delta\mathsf{u}_2, \Delta_2 = \Delta - \mathsf{y}_2 \otimes \mathsf{y}_2/\langle \mathsf{u}_2, \mathsf{y}_2\rangle (D_{[00]})_2 = D_{[00]} - \mathsf{u}_2 \otimes \mathsf{u}_2/\langle \mathsf{u}_2, \mathsf{y}_2\rangle$, we then have $\Delta_2 (D_{[00]})_2 = Q_2$ where $Q_2 = Q - \mathsf{u}_2 \otimes \mathsf{y}_2/\langle \mathsf{u}_2, \mathsf{y}_2\rangle$ and $N((D_{[00]})_2) = \mathrm{span}\{\mathsf{y}_1, \mathsf{y}_2\}$. The more singular formulation associated with (7.1) can then be written

$$\begin{cases} \Delta_2 (a^{D_k}_{[00]})_2 = (b^{D_k}_{[00]})_2, \\ \left\langle (a^{D_k}_{[00]})_2, \mathsf{y}_1 \right\rangle = \left\langle (a^{D_k}_{[00]})_2, \mathsf{y}_2 \right\rangle = 0, \end{cases} \quad k \in \mathcal{S}, \tag{7.5}$$

where $(b^{D_k}_{[00]})_2 = Q_2 b^{D_k}_{[00]}$ and $(D_{[00]})_2$ may equivalently be defined by $(D_{[00]})_{2kl} = \left\langle (a^{D_k}_{[00]})_2, (b^{D_l}_{[00]})_2 \right\rangle = 0, k, l \in \mathcal{S}$. We next set $\Delta_2 = M_2 - W_2$, where M_2 is a diagonal matrix, as for instance $M_2 = \mathcal{D}_2$ with

$$\mathcal{D}_2 = \mathrm{diag}\left(\frac{(\Delta_2)_{11}}{1 - (\mathsf{y}_1)_1 - (\mathsf{y}_2)_1}, \ldots, \frac{(\Delta_2)_{n^s n^s}}{1 - (\mathsf{y}_1)_{n^s} - (\mathsf{y}_2)_{n^s}} \right). \tag{7.6}$$

When all mass fractions are positive the coefficients $(\Delta_2)_{kk}$ and $(Q_2)_{kk} = 1 - (\mathsf{y}_1)_k - (\mathsf{y}_2)_k$ are always positive provided there are at least two neutral and two ionized species in the mixture. Upon letting $T_2 = M_2^{-1} W_2$ and $P_2 = Q_2^t = \mathbb{I} - \mathsf{u}_1 \otimes \mathsf{y}_1/\langle \mathsf{u}_1, \mathsf{y}_1\rangle - \mathsf{u}_2 \otimes \mathsf{y}_2/\langle \mathsf{u}_2, \mathsf{y}_2\rangle$ we have the expansion

$$D_{[00]} = \frac{\mathsf{u}_2 \otimes \mathsf{u}_2}{\langle \mathsf{u}_2, \mathsf{y}_2\rangle} + \sum_{0 \leqslant j < \infty} (P_2 T_2)^j P_2 M_2^{-1} P_2^t. \tag{7.7}$$

The resulting errors of the successive approximations are presented in Fig. 2 for the ionization parameter $x = 10^{-4}, x = 10^{-3}$, and $x = 10^{-2}$. These results show the much better convergence behavior of the modified iterates (7.7).

An eigenvalue analysis indeed reveals that there is one relatively isolated bad eigenvalue of the matrix T associated with the classical expansion (7.4) when the ionization degree increases. The corresponding eigenvectors further suggest the use of the vector u_2^* defined by $(\mathsf{u}_2)_k^* = 1$ if $k \in \mathcal{I}$ and $(\mathsf{u}_2)_k^* = 0$ otherwise. That is, this eigenvector is approximately in $\mathrm{span}\{\mathsf{u}_1^*, \mathsf{u}_2^*\} = \mathrm{span}\{\mathsf{u}_1, \mathsf{u}_2\}$. This eigenvalue may be associated with the small values of the binary diffusion coefficients between positively charged ions as already analyzed by García Muñoz [36]. This also explains why bad convergence rates are still observed for the heavy species diffusion matrices without electron. In Fig. 3 are then presented the errors associated with the classical and new expansions of the heavy species first order diffusion matrices for $x = 10^{-2}$. This figure confirms that the modified formulation also improve the convergence rates for the heavy species first order diffusion matrices.

Finally, using a more singular formulation with the matrices Δ_3 and $(D_{[00]})_3$ and a nullspace of dimension 3 did not significantly improved the convergence rates. After elimination of the worse eigenvalue of T there usually remains a group of several 'quasi largest' similar eigenvalues in T_2 which cannot be taken into account with one single extra nullspace vector.

7.2. The complex first order matrix

We investigate in this section the evaluation of the first order magnetized diffusion matrix $D^{\perp}_{[00]} + iD^{\odot}_{[00]}$. The first order diffusion matrix parallel to the magnetic field can be evaluated as in the previous section. The corresponding n^s systems presented in Table 2 are of size $n = n^s$ and written

$$\begin{cases} (\Delta + i\Delta')a^{D_k}_{[00]} = b^{D_k}_{[00]}, \\ \langle a^{D_k}_{[00]}, \mathsf{y}\rangle = 0, \end{cases} \quad k \in \mathcal{S}, \tag{7.8}$$

where $i^2 = -1$ and Δ' is the magnetized part of the complex Stefan–Maxwell matrix. This matrix is in the form $\Delta' = (\mathbb{I} - \mathsf{y} \otimes \mathsf{u})\mathcal{D}'(\mathbb{I} - \mathsf{u} \otimes \mathsf{y})$ and $\mathcal{D}'$ is the diagonal matrix such that $\mathcal{D}'_{kk} = n_k q_k B/p$ where B denotes the intensity of the magnetic field, $n_k, k \in \mathcal{S}$, the species mole per unit volume, $q_k, k \in \mathcal{S}$, the species molar charges, and p the pressure [43]. The first order diffusion coefficients are then evaluated from

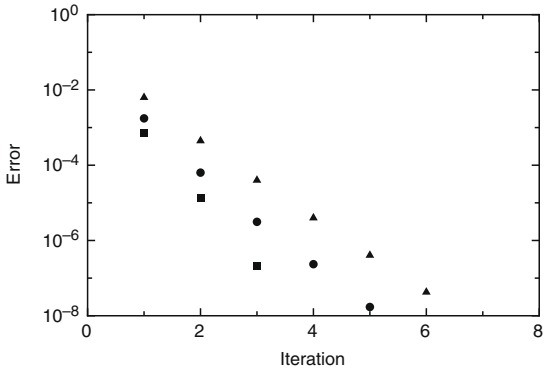

Fig. 2. Reduced errors of first order new approximate diffusion matrices for various ionized mixtures; ■ $x = 10^{-4}$, • $x = 10^{-3}$, and ▲ $x = 10^{-2}$.

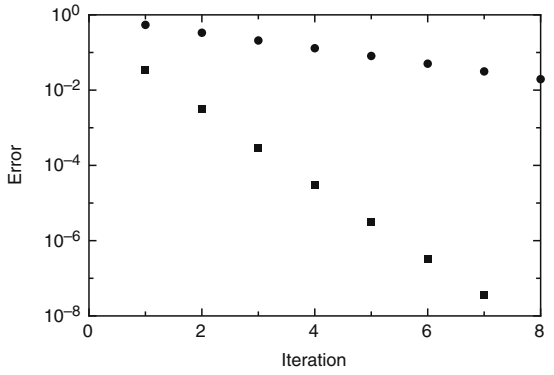

Fig. 3. Reduced errors of heavy species first order approximate diffusion matrices for $x = 10^{-2}$; • classical expansion with Δ, ■ new expansion with Δ_2.

$$D^{\perp}_{[00]kl} + iD^{\odot}_{[00]kl} = \langle a^{D_k}_{[00]}, b^{D_l}_{[00]} \rangle, \quad k, l \in \mathcal{S}. \tag{7.9}$$

The symmetry properties of $D^{\perp}_{[00]}$ and $D^{\odot}_{[00]}$ as well as the nullspace and range of $D^{\perp}_{[00]kl} + iD^{\odot}_{[00]kl}$ are derived as in the real case and the details are omitted. As in the isotropic case, the transport linear systems imply the matrix relations $(\Delta + i\Delta')(D^{\perp}_{[00]} + iD^{\odot}_{[00]}) = Q$ and $(D^{\perp}_{[00]} + iD^{\odot}_{[00]})\mathrm{y} = 0$. The matrix $\Delta + i\Delta'$ is such that $N(\Delta + i\Delta') = \mathbb{C}\mathrm{u}, R(\Delta + i\Delta') = \mathrm{u}^{\perp} + i\mathrm{u}^{\perp}, D^{\perp}_{[00]} + iD^{\odot}_{[00]}$ is the generalized inverse of $\Delta + i\Delta'$ with prescribed nullspace $\mathbb{C}\mathrm{y}$ and range $\mathrm{y}^{\perp} + i\mathrm{y}^{\perp}$, and for $\alpha > 0$, we have $D^{\perp}_{[00]} + iD^{\odot}_{[00]} = (\Delta + i\Delta' + \alpha \mathrm{y} \otimes \mathrm{y})^{-1} - (1/\alpha)\mathrm{u} \otimes \mathrm{u}$ [43].

As a direct application of the stationary iterative algorithms introduced in Section 5, we deduce that, upon using the splitting $\Delta + i\Delta' = \mathcal{M} - \mathcal{W}$ where $\mathcal{M} = \mathcal{D} + i\Delta'$ and $\mathcal{D}$ is the diagonal matrix (7.3) and letting $\mathcal{T} = \mathcal{M}^{-1}\mathcal{W}, \mathcal{P} = P = \mathbb{I} - \mathrm{u} \otimes \mathrm{y}$, we have the convergent asymptotic expansion

$$D^{\perp}_{[00]} + iD^{\odot}_{[00]} = \sum_{0 \leqslant j < \infty} (\mathcal{P}\mathcal{T})^j \mathcal{P}\mathcal{M}^{-1}\mathcal{P}^t.$$

Since $\Delta' = (\mathbb{I} - \mathrm{y} \otimes \mathrm{u})\mathcal{D}'(\mathbb{I} - \mathrm{u} \otimes \mathrm{y})$ and $\mathcal{D}'$ is diagonal, the inverse of the matrix $\mathcal{M} = \mathcal{D} + i\Delta'$ is easily expressed in terms of the inverse of the diagonal matrix $\mathcal{D} + i\mathcal{D}'$ and the iterates are easily evaluated [43,44]. Various approximations can then be obtained by truncating this convergent series. The first approximation $\mathcal{P}\mathcal{M}^{-1}\mathcal{P}^t$ generalizes the Hirschfelder-Curtiss approximation with a mass corrector to the magnetized case [43]. The errors associated with the classical expansion are similar to that of Fig. 1 and are omitted.

In order to improve the convergence rates for increasing ionization levels, we have used the *more singular* formulation (5.24) with the vector u_2. Note incidentally that the simplifying property $\langle \Delta' \mathrm{u}_2, \mathrm{u}_2 \rangle = 0$ holds when the total charge is zero. Defining $\mathrm{u}_1 = \mathrm{u}, \mathrm{y}_1 = \mathrm{y}, \mathrm{y}_2 = (\Delta + i\Delta')\mathrm{u}_2, (\Delta + i\Delta')_2 = (\Delta + i\Delta') - \mathrm{y}_2 \otimes \mathrm{y}_2/(\mathrm{u}_2, \mathrm{y}_2)$, and $(D^{\perp}_{[00]} + iD^{\odot}_{[00]})_2 = (D^{\perp}_{[00]} + iD^{\odot}_{[00]}) - \mathrm{u}_2 \otimes \mathrm{u}_2/\langle \mathrm{u}_2, \mathrm{y}_2 \rangle$, we have $(\Delta + i\Delta')_2(D^{\perp}_{[00]} + iD^{\odot}_{[00]})_2 = \mathcal{Q}_2$ where $\mathcal{Q}_2 = \mathcal{Q} - \mathrm{u}_2 \otimes \mathrm{y}_2/\langle \mathrm{u}_2, \mathrm{y}_2 \rangle$ and $N\Big((D^{\perp}_{[00]} + iD^{\odot}_{[00]})_2\Big) = \mathrm{span}\{\mathrm{y}_1, \mathrm{y}_2\}$. The more singular formulation can then be written

$$\begin{cases} (\Delta + i\Delta')_2 (a^{D_k}_{[00]})_2 = (b^{D_k}_{[00]})_2, \\ \Big((a^{D_k}_{[00]})_2, \mathrm{y}_1\Big) = \Big((a^{D_k}_{[00]})_2, \mathrm{y}_2\Big) = 0, \end{cases} \quad k \in \mathcal{S}, \tag{7.10}$$

where $(b^{D_k}_{[00]})_2 = \mathcal{Q}_2 b^{D_k}_{[00]}$ and $(D^{\perp}_{[00]} + iD^{\odot}_{[00]})_2$ may equivalently be defined by $(D^{\perp}_{[00]} + iD^{\odot}_{[00]})_{2kl} = \Big\langle (a^{D_k}_{[00]})_2, (b^{D_l}_{[00]})_2 \Big\rangle = 0, k, l \in \mathcal{S}$. Upon letting $(\Delta + i\Delta')_2 = \mathcal{M}_2 - \mathcal{W}_2$ and $\mathcal{M}_2 = \mathcal{D}_2 + i\Delta'$ where $\mathcal{D}_2$ is the diagonal matrix (7.6), and $\mathcal{T}_2 = \mathcal{M}_2^{-1}\mathcal{W}_2, \mathcal{P}_2 = \mathcal{Q}_2^t = \mathbb{I} - \mathrm{u}_1 \otimes \mathrm{y}_1/\langle \mathrm{u}_1, \mathrm{y}_1 \rangle - \mathrm{u}_2 \otimes \mathrm{y}_2/\langle \mathrm{u}_2, \mathrm{y}_2 \rangle$, we have the expansion

$$D^{\perp}_{[00]} + iD^{\odot}_{[00]} = \frac{\mathrm{u}_2 \otimes \mathrm{u}_2}{(\mathrm{u}_2, \mathrm{y}_2)} + \sum_{0 \leqslant j < \infty} (\mathcal{P}_2\mathcal{T}_2)^j \mathcal{P}_2 \mathcal{M}_2^{-1} \mathcal{P}_2^t. \tag{7.11}$$

The errors corresponding to the new expansion are presented in Fig. 4 for $x = 10^{-4}, x = 10^{-3}$, and $x = 10^{-2}$ and $B = 10^3$ mT. The errors are calculated with the complex Frobenius matrix norm $\|A\|^2 = \sum_{1 \leqslant i,j \leqslant n} |a_{ij}|^2$ and are rescaled by the initial error. These results show the good convergence behavior of the modified iterates (7.11).

7.3. Higher order diffusion matrices

We investigate in this section the evaluation of higher order approximations of diffusion matrices, also accounting for the energy of the molecules. The corresponding n^s linear systems presented in Table 1 are of size $n = 2n^s + n^p$, where n^p denotes the number of polyatomic species, and are written

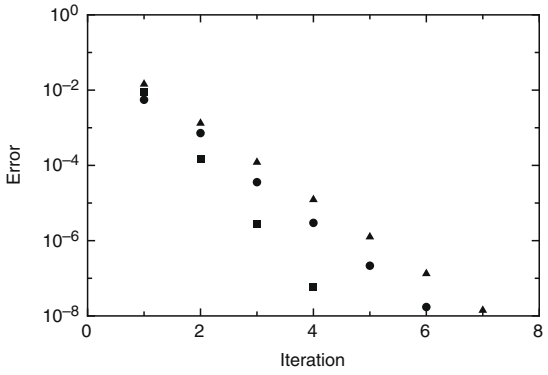

Fig. 4. Reduced errors of first order magnetized new approximate diffusion matrices for various ionized mixtures and $B = 10^3$ mT; ■ $x = 10^{-4}$, • $x = 10^{-3}$, and ▲ $x = 10^{-2}$.

$$\begin{cases} La^{D_k} = b^{D_k}, \\ \langle a^{D_k}, \mathcal{Y} \rangle = 0, \end{cases} \quad k \in \mathcal{S}. \tag{7.12}$$

The diffusion coefficients are then given by

$$D_{kl} = \langle a^{D_k}, b^{D_l} \rangle, \quad k, l \in \mathcal{S}. \tag{7.13}$$

The coefficients of the matrix L are intricate expressions involving collision integrals and internal energy relaxation times that are detailed in references [23,43]. The matrix L is symmetric positive semi-definite, $N(L) = \mathbb{R}\mathcal{U}, R(L) = \mathcal{U}^\perp$, and $2db(L) - L$ is positive definite when $n^s \geqslant 3$. Upon partitioning $\mathbb{R}^{2n^s+n^p}$ into $\mathbb{R}^{n^s} \times \mathbb{R}^{n^s+n^p}$, the nullspace vector $\mathcal{U}$, the constraint vector $\mathcal{Y}$, and the right hand sides $b^{D_k}, k \in \mathcal{S}$, are given by

$$\mathcal{U} = \begin{pmatrix} \mathsf{u} \\ 0 \end{pmatrix}, \quad \mathcal{Y} = \begin{pmatrix} \mathsf{y} \\ 0 \end{pmatrix}, \quad b^{D_k} = \begin{pmatrix} b^{D_k}_{[00]} \\ 0 \end{pmatrix}, \quad k \in \mathcal{S}, \tag{7.14}$$

where 0 denote the zero vector in $\mathbb{R}^{n^s+n^p}$, and $\mathsf{u}, \mathsf{y}, b^{D_k}_{[00]}, k \in \mathcal{S}$, have been defined in the previous section. The right hand sides $b^{D_k}, k \in \mathcal{S}$, can also be written

$$b^{D_k} = \mathsf{e}^k - \mathcal{Y}, \quad k \in \mathcal{S},$$

where $\mathsf{e}^k, k \in \mathcal{S}$, are the standard basis vectors of $\mathbb{R}^{2n^s+n^p}$. Since $b^{D_k} \in R(L), k \in \mathcal{S}$, and $\langle \mathcal{U}, \mathcal{Y} \rangle = 1$, the transport linear systems (7.12) are well posed and from $D_{kl} = \langle La^{D_k}, a^{D_l} \rangle$ and the symmetry of L, we deduce the symmetry of D. We also have $D_{kl} = \langle a^{D_k}, b^{D_l} \rangle = \langle a^{D_k}, \mathsf{e}^l \rangle$ since $\langle a^{D_k}, \mathcal{Y} \rangle = 0$ in such a way that $D_{kl} = a^{D_k}_l = a^{D_l}_k, 1 \leqslant k, l \leqslant n^s$.

Upon defining the blocks $a^D = [a^{D_1}, \ldots, a^{D_{n^s}}]$ and $b^D = [b^{D_1}, \ldots, b^{D_{n^s}}]$, the linear systems yield the matrix relations $La^D = b^D$ and $\mathcal{Y}^t a^D = 0$. We introduce the rectangular matrix $\Pi = (\mathbb{I}_{n^s}, \mathcal{O})^t \in \mathbb{R}^{2n^s+n^p, n^s}$, the projectors $\mathcal{Q} = \mathcal{P}^t = \mathbb{I}_n - \mathcal{Y} \otimes \mathcal{U}, \mathsf{Q} = \mathsf{P}^t = \mathbb{I}_{n^s} - \mathsf{y} \otimes \mathsf{u}$, and we have the block decompositions

$$a^D = \begin{pmatrix} D \\ X \end{pmatrix}, \quad b^D = \begin{pmatrix} \mathsf{Q} \\ \mathcal{O} \end{pmatrix}, \quad \Pi = \begin{pmatrix} \mathbb{I}_{n^s} \\ \mathcal{O} \end{pmatrix}, \quad \mathcal{Q} = \begin{pmatrix} \mathsf{Q} & \mathcal{O}^t \\ \mathcal{O} & \mathbb{I}_{n^s+n^p} \end{pmatrix}, \tag{7.15}$$

where $\mathcal{O}$ denotes the zero matrix in $\mathbb{R}^{n^s+n^p, n^s}$, X a matrix in $\mathbb{R}^{n^s+n^p, n^s}$, and $\mathbb{I}_s$ the unit matrix of size s. Denoting by $\mathcal{Z}$ the generalized inverse of L with nullspace $\mathcal{Y}$ and range $\mathcal{Y}^\perp$, we have $L\mathcal{Z} = \mathcal{Q}, \mathcal{Z}L = \mathcal{P}, N(\mathcal{Z}) = \mathbb{R}\mathcal{Y}, R(\mathcal{Z}) = \mathcal{Y}^\perp$, and $a^{D_k} = \mathcal{Z}b^{D_k}, k \in \mathcal{S}$. As a consequence, we have $b^D = \mathcal{Q}\Pi, D = \Pi^t a^D$, and $a^D = \mathcal{Z}b^D = \mathcal{Z}\mathcal{Q}\Pi = \mathcal{Z}\Pi$, so that $D = \Pi^t a^D = \Pi^t \mathcal{Z}\Pi$.

Projected stationary iterative algorithms can be used for solving (7.12) with splittings in the form $L = \mathcal{M} - \mathcal{W}$ and $\mathcal{M} = db(L) + \mathrm{diag}(\sigma_1, \ldots, \sigma_n)$ [23]. We then have the convergent asymptotic expansion

$$a^D = \sum_{0 \leqslant j < \infty} (\mathcal{P}\mathcal{T})^j \mathcal{P}\mathcal{M}^{-1} b^D, \tag{7.16}$$

and the higher order matrix D is then evaluated from $D = \Pi^t a^D$. The iterates $(a^D)^j$, $j \geqslant 0$, satisfy $(a^D)^{j+1} = \mathcal{P}\mathcal{T}(a^D)^j + \mathcal{P}\mathcal{M}^{-1}b^D$ and only involve the product of the matrix $\mathcal{P}\mathcal{T} \in \mathbb{R}^{2n^s+n^p, 2n^s+n^p}$ by $(a^D)^j \in \mathbb{R}^{2n^s+n^p, n^s}$. The iterates can also be deduced from the expansion (5.10) of the generalized inverse $\mathcal{Z}$ since $a^D = \mathcal{Z}b^D$ and $b^D = \mathcal{Q}b^D$. Using $b^D = \mathcal{Q}\Pi$, we also obtain the identity

$$D = \Pi^t \left(\sum_{0 \leqslant j < \infty} (\mathcal{P}\mathcal{T})^j \mathcal{P}\mathcal{M}^{-1}\mathcal{P}^t \right) \Pi,$$

but the iterates must be taken on the block a^D prior to evaluate D.

In order to improve the convergence rates for increasing ionization levels, we have used the *more singular* formulation (5.14) with the vector $\mathcal{U}_2$ defined by

$$\mathcal{U}_2 = \begin{pmatrix} \mathrm{u}_2 \\ 0 \end{pmatrix}, \tag{7.17}$$

where $\mathrm{u}_2 \in \mathbb{R}^{n^s}$ has been defined for first order matrices. Upon letting $\mathcal{U}_1 = \mathcal{U}, \mathcal{Y}_1 = \mathcal{Y}, \mathcal{Y}_2 = L\mathcal{U}_2, L_2 = L - \mathcal{Y}_2 \otimes \mathcal{Y}_2 / \langle \mathcal{U}_2, \mathcal{Y}_2 \rangle, \mathcal{Z}_2 = \mathcal{Z} - \mathcal{U}_2 \otimes \mathcal{U}_2 / \langle \mathcal{U}_2, \mathcal{Y}_2 \rangle$, and $a_2^D = a^D - \mathcal{U}_2 \otimes \mathrm{u}_2 / \langle \mathcal{U}_2, \mathcal{Y}_2 \rangle$, we have $L_2 \mathcal{Z}_2 = \mathcal{Q}_2, a_2^D = \mathcal{Z}_2 b^D, b_2^D = \mathcal{Q}_2 b^D$ where $\mathcal{Q}_2 = \mathcal{Q} - \mathcal{Y}_2 \otimes \mathcal{U}_2 / \langle \mathcal{U}_2, \mathcal{Y}_2 \rangle$ and $N(\mathcal{Z}_2) = \mathrm{span}\{\mathcal{Y}_1, \mathcal{Y}_2\}$. The more singular formulation can then be written

$$\begin{cases} L_2 a_2^{D_k} = b_2^{D_k}, \\ \langle a_2^{D_k}, \mathcal{Y}_1 \rangle = \langle a_2^{D_k}, \mathcal{Y}_2 \rangle = 0, \end{cases} \quad k \in \mathcal{S}. \tag{7.18}$$

Letting $L_2 = \mathcal{M}_2 - \mathcal{W}_2, \mathcal{M}_2 = db(L_2) + \mathrm{diag}(\sigma_1, \ldots, \sigma_n)$, where $\sigma_i, 1 \leqslant i \leqslant n$, are nonnegative weights, $\mathcal{T}_2 = \mathcal{M}_2^{-1} \mathcal{W}_2$ and $\mathcal{P}_2 = \mathcal{Q}_2^t = \mathbb{I} - \mathcal{U}_1 \otimes \mathcal{Y}_1 / \langle \mathcal{U}_1, \mathcal{Y}_1 \rangle - \mathcal{U}_2 \otimes \mathcal{Y}_2 / \langle \mathcal{U}_2, \mathcal{Y}_2 \rangle$, we have the expansion

$$a_2^D = \sum_{0 \leqslant j < \infty} (\mathcal{P}_2 \mathcal{T}_2)^j \mathcal{P}_2 \mathcal{M}_2^{-1} b_2^D. \tag{7.19}$$

Finally we have $D = \mathrm{u}_2 \otimes \mathrm{u}_2 / \langle \mathcal{U}_2, \mathcal{Y}_2 \rangle + \Pi^t a_2^D$ or equivalently

$$D = \frac{\mathrm{u}_2 \otimes \mathrm{u}_2}{\langle \mathcal{U}_2, \mathcal{Y}_2 \rangle} + \Pi^t \sum_{0 \leqslant j < \infty} (\mathcal{P}_2 \mathcal{T}_2)^j \mathcal{P}_2 \mathcal{M}_2^{-1} \mathcal{P}_2^t \Pi. \tag{7.20}$$

Only these modified formulations yield satisfactory results for all ionization levels. The resulting errors of the successive approximations of D are presented in Fig. 5 for the ionization parameter $x = 10^{-4}, x = 10^{-3}$, and $x = 10^{-2}$. In the numerical experiments, the matrix L has been evaluated following the approximations presented in [23]. The rotational relaxation times for internal energy of the polyatomic ionized molecules have been approximated as the relaxation time of the corresponding neutral molecules [1]. The results presented in Fig. 5 show that good convergence rates are also observed for higher order matrices. The improvement of the convergence rates is exhibited in Fig. 6 where the convergence history of the expansions obtained from L and L_2 are presented. We have also experimented the more singular formulation with the matrix L_3 and various vectors $\mathcal{U}_3$ but no significant improvements have been obtained. The errors presented in Fig. 6 corresponds to the vector $\mathcal{U}_3 = (0_{n^s}, \mathrm{u}_2, 0_{n^p})^t$ with straightforward notation.

In the magnetized case, we have to solve the n^s complex systems

$$\begin{cases} (L + iL')\, a^{D_k} = b^{D_k}, \\ \langle a^{D_k}, \mathcal{Y} \rangle = 0, \end{cases} \quad k \in \mathcal{S}, \tag{7.21}$$

where $L' = (\mathbb{I} - \mathcal{Y} \otimes \mathcal{U})\, \mathsf{L}' (\mathbb{I} - \mathcal{U} \otimes \mathcal{Y})$, and L' is a diagonal matrix given in [43]. The matrix $L + iL'$ is complex symmetric, $N(L + iL') = \mathbb{C}\mathcal{U}$, and $R(L + iL') = \mathcal{U}^\perp + i\mathcal{U}^\perp$. Introducing the generalized inverse $\mathcal{Z}$ of $L + iL'$ with nullspace $\mathbb{C}\mathcal{Y}$ and range $\mathcal{Y}^\perp + i\mathcal{Y}^\perp$ we have as in the real case the relations $b^D = \mathcal{Q}\Pi, a^D = \mathcal{Z}\Pi$. Upon using splittings in the form $L + iL' = \mathcal{M} - \mathcal{W}$ with $\mathcal{M} = db(L) + \mathrm{diag}(\sigma_1, \ldots, \sigma_n) + iL'$, we obtain the expansion

$$D^\perp + iD^\odot = \Pi \left(\sum_{0 \leqslant j < \infty} (\mathcal{P}\mathcal{T})^j \mathcal{P} \mathcal{M}^{-1} \mathcal{P}^t \right) \Pi^t,$$

but the convergence rates of these expansions decrease as ionization levels increase. As in the real case, we have to use a more singular formulation in order to obtain a better convergence behavior for higher ionization levels. These expansions

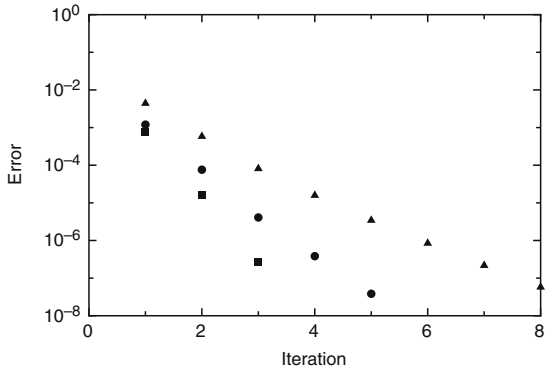

Fig. 5. Reduced errors of higher order new approximate diffusion matrices for various ionized mixtures; ■ $x = 10^{-4}$, • $x = 10^{-3}$, and ▲ $x = 10^{-2}$.

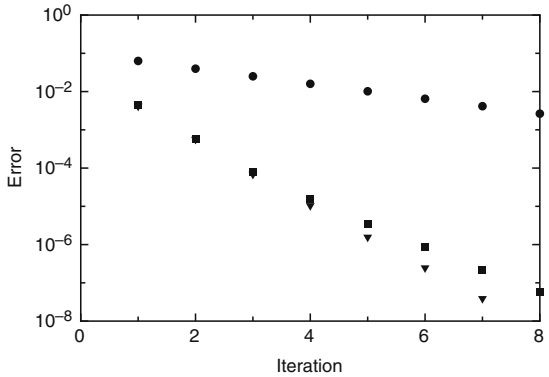

Fig. 6. Reduced errors of higher order approximate diffusion matrices for $x = 10^{-2}$; • classical expansion with L, ■ new expansion with L_2, ▼ new expansion with L_3.

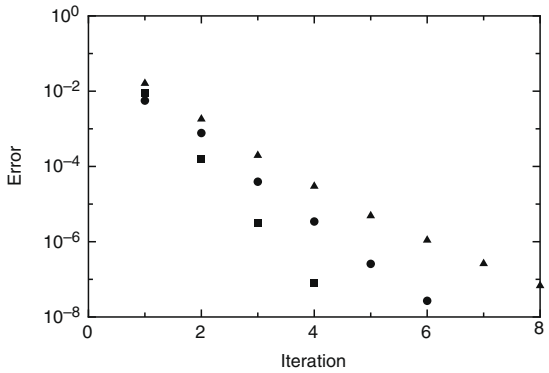

Fig. 7. Reduced errors of higher order magnetized new approximate diffusion matrices for various ionized mixtures and $B = 10^3$ mT; ■ $x = 10^{-4}$, • $x = 10^{-3}$, and ▲ $x = 10^{-2}$.

are similar to those of the real case and the details are omitted. The resulting errors of the successive approximations of $D^{\perp} + iD^{\odot}$ are presented in Fig. 7 for $B = 10^3$ mT and $x = 10^{-4}, x = 10^{-3}$, and $x = 10^{-2}$. These results show that the good convergence rates observed for isotropic higher order matrices also hold for magnetized higher order matrices.

The higher order effects usually have a minor impact on the diffusion matrix of neutral species mixtures [23]. They have a more important impact, however, on ionized mixtures. Our numerical tests for high temperature air have shown that the relative error in matrix norms $\|D^{\parallel} - D^{\parallel}_{[00]}\|/\|D^{\parallel}\|$, $\|D^{\perp} - D^{\perp}_{[00]}\|/\|D^{\perp}\|$, and $\|D^{\odot} - D^{\odot}_{[00]}\|/\|D^{\parallel}\|$, can be large for ionization levels above 10^{-3}. In addition, higher order effects due to the energy of the molecules are always important, even for weakly ionized mixtures, in order to evaluate the electrical conductivities [6,8–10,32].

8. Application to thermal conductivity and Stefan–Maxwell equations

We investigate in this section iterative techniques in order to evaluate the thermal conductivity coefficients and the species diffusion velocities. Both problems can be solved by using generalized conjugate gradient techniques. We consider both the isotropic case as well as the nonisotropic magnetized case. In order to assess the accuracy of the resulting algorithms, numerical experiments are again performed with high temperature air. In contrast with stationary techniques, it is found that generalized conjugate gradient techniques are efficient for all ionization levels and magnetic field intensities.

8.1. Transport linear systems associated with λ and χ

The linear system associated with the thermal conductivity presented in Table 1 is of size $n = n^s + n^p$ and written in the form

$$\Lambda a^{\lambda} = b^{\lambda}, \tag{8.1}$$

where the coefficients of the matrix Λ are intricate expressions that are detailed in reference [23]. This system can directly be obtained from a variational formulation in the isotropic as well as in the magnetized case [24,43]. The matrix Λ is symmetric

positive definite [23] and the thermal conductivities and the thermal diffusion ratios are evaluated from the following products [23,43]

$$\lambda = \frac{p}{T}\langle a^\lambda, b^\lambda\rangle, \quad \chi = L^{00\lambda} a^\lambda, \tag{8.2}$$

where $L^{00\lambda}$ is the upper right block of L of size $n^s \times (n^s + n^p)$ in such a way that L has the block decomposition

$$L = \begin{pmatrix} \Lambda & L^{00\lambda} \\ L^{\lambda 00} & \Lambda \end{pmatrix}. \tag{8.3}$$

The coefficients of the matrices $L^{00\lambda}$ and $L^{00\lambda} = (L^{00\lambda})^t$ are given in [23] and the rescaled thermal diffusion ratios $\widetilde{\chi}$ are also obtained from the rescaled version $\widetilde{L}^{00\lambda}$ of the block $L^{00\lambda}$ [29]. More specifically, if $\widetilde{L}^{00\lambda}$ is the matrix such that $\mathrm{diag}(X_1, \ldots, X_{n^s})\widetilde{L}^{00\lambda} = L^{00\lambda}$ then we have $X_i\widetilde{\chi}_i = \chi_i, i \in \mathcal{S}$, where $\widetilde{\chi}$is evaluated from $\widetilde{\chi} = \widetilde{L}^{00\lambda} a^\lambda$.

In the nonisotropic case, the linear system associated with the thermal conductivities presented in Table 2 is written in the form

$$(\Lambda + i\Lambda')a^\lambda = b^\lambda, \tag{8.4}$$

where Λ' is a diagonal matrix given in [43]. The thermal conductivities and the thermal diffusion ratios are then given by the following products

$$\lambda^\perp + i\lambda^\odot = \frac{p}{T}\langle a^\lambda, b^\lambda\rangle, \quad \chi^\perp + i\chi^\odot = L^{00\lambda} a^\lambda, \tag{8.5}$$

and the rescaled thermal diffusion ratios are similarly obtained from the rescaled block $\widetilde{L}^{00\lambda}$ [29].

In the numerical experiments, the matrices Λ, Λ' and $L^{00\lambda}$ have been evaluated as described in Section 7.3. The isotropic systems (8.1) have been solved with a conjugate gradients technique and the magnetized systems (8.4) by using an orthogonal residuals technique. In both situations, a diagonal preconditionning matrix has been used. In Fig. 8 are presented the convergence history for various values of the ionization parameter $x = 10^{-4}, x = 10^{-3}$, and $x = 10^{-2}$ without magnetization. The errors are defined by $|\lambda - \lambda^k|/\lambda$ where λ is the thermal conductivity and λ^k the kth iterate. In Fig. 9 are presented the convergence history for $x = 10^{-2}$ and $B = 10^3$ mT for $\lambda = \lambda^\parallel, \lambda^\perp$, and $\lambda^\odot$. The errors are defined similarly by $|\lambda^\parallel - \lambda^{\parallel k}|/\lambda^\parallel, |\lambda^\perp - \lambda^{\perp k}|/\lambda^\perp$, and $|\lambda^\odot - \lambda^{\odot k}|/|\lambda^\odot|$. These figures shows the good behavior of the generalized conjugate gradient techniques for all ionization levels and magnetic field intensities.

The numerical simulations with partially ionized air have also shown that three iterations are generally required in order to evaluate the thermal diffusion ratios with a good accuracy whereas two iterates are generally sufficient for the thermal conductivities.

8.2. Stefan–Maxwell equations

When an explicit time marching technique is used to compute a multicomponent flow then only the diffusion velocities are required. When fractional steps are used, the diffusion velocities are also sufficient if the 'diffusion time step' is taken to be explicit. In this situation, some type of Stefan–Maxwell equations can be solved by using orthogonal residuals algorithms and the evaluation of the diffusion coefficients can be avoided.

The particular form of the Stefan–Maxwell equations depends on the order of accuracy of the diffusion velocities and on magnetization. As a general rule, the Stefan–Maxwell equations are easily derived from the transport linear systems upon multiplying on the right by the proper diffusion driving force vectors.

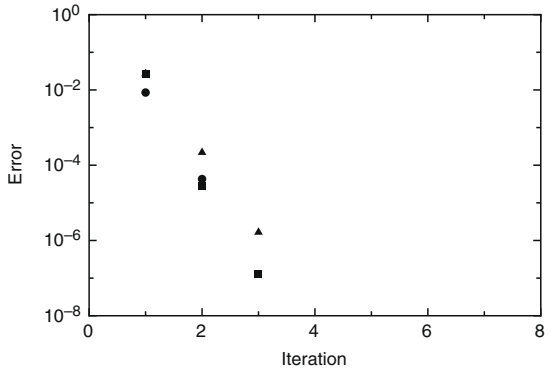

Fig. 8. Reduced errors for conjugate gradient approximate thermal conductivities λ and various ionized mixtures; ■ $x = 10^{-4}$, • $x = 10^{-3}$, and ▲ $x = 10^{-2}$.

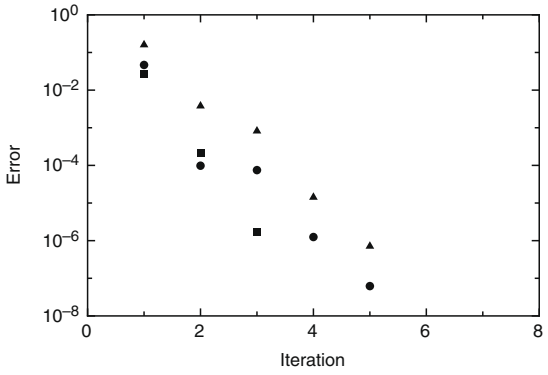

Fig. 9. Reduced errors for orthogonal residuals approximate thermal conductivities $\lambda^{\parallel}, \lambda^{\perp}$, and $\lambda^{\odot}$ and $x = 10^{-2}$.

In the real isotropic case, multiplying on the right the system (7.1) by the species diffusion driving forces vector $\boldsymbol{d}_k$, and summing over k, letting $\mathbf{v}_{[00]} = (\mathbf{v}_{[00]1}, \ldots, \mathbf{v}_{[00]n^s})^t$, $\boldsymbol{d} = (\boldsymbol{d}_1, \ldots, \boldsymbol{d}_{n^s})^t$, and $\mathbf{v}_{[00]i} = -\sum_{j\in\mathcal{S}} D_{[00]ij}\boldsymbol{d}_j$, we obtain the classical Stefan–Maxwell relations

$$\begin{cases} -\Delta\mathbf{v}_{[00]} = \boldsymbol{d} - \mathrm{y}\sum\limits_{l\in\mathcal{S}} \boldsymbol{d}_l, \\ \langle \mathbf{v}_{[00]}, \mathrm{y}\rangle = 0. \end{cases} \tag{8.6}$$

The right-hand side $Q\boldsymbol{d} = \boldsymbol{d} - \mathrm{y}\sum_{l\in\mathcal{S}}\boldsymbol{d}_l$ is the constrained diffusion driving forces vector whose components $\boldsymbol{d}_i - y_i\langle \boldsymbol{d}, \mathrm{u}\rangle, i \in \mathcal{S}$, sum up to zero. The corresponding equations with Soret effects are obtained in a similar way by using the modified diffusion driving forces vector $\boldsymbol{d} + \chi\boldsymbol{\nabla}\log T$ where $\chi = (\chi_1, \ldots, \chi_n^s)^t$ is the thermal diffusion ratios vector. The Stefan–Maxwell equations can then be solved by a projected conjugate gradient method in each spatial direction.

In the nonisotropic case, a complex form of the Stefan–Maxwell equations is obtained [43] by multiplying the system (7.8) on the right by the complex vector $\boldsymbol{d}_k^{\perp} - i\boldsymbol{d}_k^{\odot}$ and summing over $k \in \mathcal{S}$. Letting $\mathbf{v}_{[00]}^{\perp} = (\mathbf{v}_{[00]1}^{\perp}, \ldots, \mathbf{v}_{[00]n^s}^{\perp})^t$ and $\mathbf{v}_{[00]}^{\odot} = (\mathbf{v}_{[00]1}^{\odot}, \ldots, \mathbf{v}_{[00]n^s}^{\odot})^t$, the complex form of the Stefan–Maxwell equations is found in the form [43]

$$\begin{cases} -(\Delta + i\Delta')(\mathbf{v}_{[00]}^{\perp} - i\mathbf{v}_{[00]}^{\odot}) = \boldsymbol{d}_i^{\perp} - i\boldsymbol{d}_i^{\odot} - \mathrm{y}\sum\limits_{l\in\mathcal{S}}(\boldsymbol{d}_l^{\perp} - i\boldsymbol{d}_l^{\odot}), \\ \langle \mathbf{v}_{[00]}^{\perp} - i\mathbf{v}_{[00]}^{\odot}, \mathrm{y}\rangle = 0. \end{cases} \tag{8.7}$$

The proper modifications of the complex Stefan–Maxwell equations in the presence of Soret effects correspond to including the temperature gradient terms in the diffusion driving forces as discussed in [43]. The nonisotropic magnetized Stefan–Maxwell equation can then be solved by an orthogonal residuals method in each spatial direction [43,44].

The Stefan–Maxwell equations between the species diffusion velocity vectors $\mathbf{v}_{[00]1}, \ldots, \mathbf{v}_{[00]n^s}$, and the diffusion driving forces $\boldsymbol{d}_1, \ldots, \boldsymbol{d}_{n^s}$, that are vectors of $\mathbb{R}^3$, only involve scalar coefficients. Upon decomposing these vectors with the canonical basis of $\mathbb{R}^3$, and it is sufficient to consider the case of scalar diffusion velocities $\mathrm{v}_{[00]1}, \ldots, \mathrm{v}_{[00]n^s}$ and scalar diffusion driving forces $d_1, \ldots, d_n$, real for isotropic systems, and complex for magnetized systems. In the numerical tests, we have arbitrary selected a scalar diffusion driving force vector proportional to the charge per unit volume $(X_1q_1, \ldots, X_{n^s}q_{n^s})^t$. Other arbitrary selected diffusion driving forces yielded similar convergence behavior.

In Fig. 10 are presented the convergence history without magnetization $B = 0$ for the ionization parameter $x = 10^{-4}, x = 10^{-3}$, and $x = 10^{-2}$. The errors are defined by $\|\mathrm{v}_{[00]} - \mathrm{v}_{[00]}^k\|/\|\mathrm{v}_{[00]}\|$ where $\mathrm{v}_{[00]} = (\mathrm{v}_{[00]1}, \ldots, \mathrm{v}_{[00]n^s})^t$ is the scalar diffusion velocity, $\mathrm{v}_{[00]}^k = (\mathrm{v}_{[00]1}^k, \ldots, \mathrm{v}_{[00]n^s}^k)^t$ the kth iterate, and $\|a\|$ denotes the Euclidean norm of $a \in \mathbb{R}^n$. Similarly, in Fig. 11 are presented the convergence history for $x = 10^{-2}$ and $B = 10^3$ mT for $\mathrm{v}_{[00]} = \mathrm{v}_{[00]}^{\parallel}, \mathrm{v}_{[00]}^{\perp}$, and $\mathrm{v}_{[00]}^{\odot}$. The errors are defined similarly by $\|\mathrm{v}_{[00]}^{\parallel} - \mathrm{v}_{[00]}^{k\parallel}\|/\|\mathrm{v}_{[00]}^{\parallel}\|, \|\mathrm{v}_{[00]}^{\perp} - \mathrm{v}_{[00]}^{k\perp}\|/\|\mathrm{v}_{[00]}^{\perp}\|$, and $\|\mathrm{v}_{[00]}^{\odot} - \mathrm{v}_{[00]}^{k\odot}\|/\|\mathrm{v}_{[00]}^{\odot}\|$. These figures show the good behavior of the generalized conjugate gradient techniques for various ionization levels and magnetic field intensities. These methods are able to solve the linear systems in their original form and numerical experiments show that using the more singular Stefan–Maxwell system associated with $(\mathrm{v}_{[00]})_2$ more or less introduces a shift of one iterate in the error estimates in agreement with the fact that with the more singular formulation there is one additional already prescribed search direction [40]. This is in agreement with the fact that the worse eigenvalue of the iteration matrix T is generally not close to unity and the corresponding eigenvector is not a quasi nullvector for Δ.

Higher order Stefan–Maxwell equations are easily derived from the transport linear systems and can also be rewritten in terms of Schur complements. In the isotropic case, the higher order Stefan–Maxwell equations are obtained by multiplying the linear system (7.12) on the right by $\boldsymbol{d}_k$ and then summing over $k \in \mathcal{S}$. Upon defining $\boldsymbol{\mathfrak{v}}_l = -\sum_{k\in\mathcal{S}} a_l^{D_k}\boldsymbol{d}_k, 1 \leqslant l \leqslant n, \boldsymbol{\mathfrak{v}} = (\boldsymbol{\mathfrak{v}}_1, \ldots, \boldsymbol{\mathfrak{v}}_n)^t$, where $n = 2n^s + n^p$, or equivalently $\boldsymbol{\mathfrak{v}} = -\sum_{k\in\mathcal{S}} a^{D_k}\boldsymbol{d}_k = -a^D\boldsymbol{d}$, we have $\boldsymbol{\mathfrak{v}} \in (\mathbb{R}^3)^n$ and the higher order Stefan–Maxwell equations are found in the form

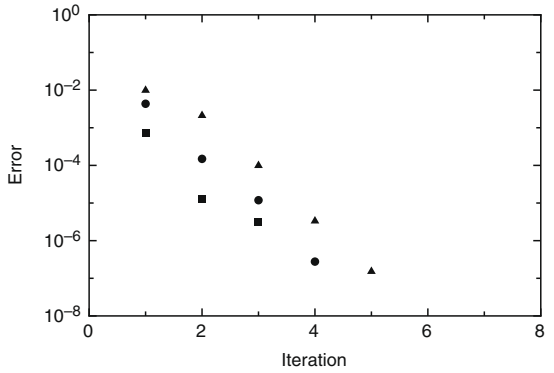

Fig. 10. Reduced errors for conjugate gradient approximate diffusion velocities $\mathbf{v}_i$ and various ionized mixtures; ■ $x = 10^{-4}$, • $x = 10^{-3}$, and ▲ $x = 10^{-2}$.

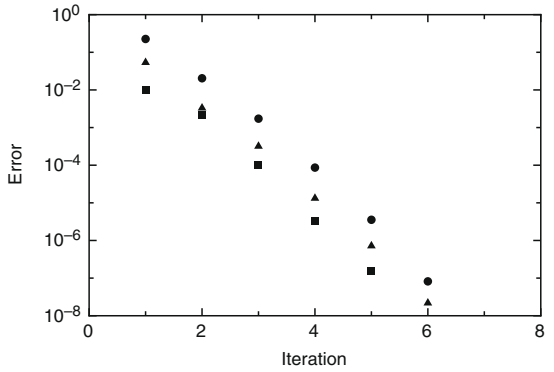

Fig. 11. Reduced errors for conjugate gradient approximate nonisotropic diffusion velocities with $x = 10^{-2}$; ■ $\mathrm{v}^{\parallel}$, • $\mathrm{v}^{\perp}$, and ▲ v°.

$$\begin{cases} -L\mathfrak{v} = b^D\boldsymbol{d}, \\ \langle \mathfrak{v}, \mathcal{Y}\rangle = 0. \end{cases} \tag{8.8}$$

Upon partitionning $(\mathbb{R}^3)^{2n^s+n^p}$ into $(\mathbb{R}^3)^{n^s} \times (\mathbb{R}^3)^{n^s+n^p}$ and similarly $\mathbb{R}^{2n^s+n^p}$ into $\mathbb{R}^{n^s} \times (\mathbb{R}^3)^{n^s+n^p}$ we have the block decompositions

$$\mathfrak{v} = \begin{pmatrix} \mathbf{v} \\ \mathbf{r} \end{pmatrix}, \quad b^D\boldsymbol{d} = \begin{pmatrix} Q\boldsymbol{d} \\ 0 \end{pmatrix}, \quad \mathcal{Y} = \begin{pmatrix} \mathrm{y} \\ 0 \end{pmatrix}, \tag{8.9}$$

so that $\mathbf{v} = \Pi^t\mathfrak{v}$ and $\langle \mathfrak{v}, \mathcal{Y}\rangle = \langle \mathbf{v}, \mathrm{y}\rangle = 0$ where $\mathbf{v} = (\mathbf{v}_1, \ldots, \mathbf{v}_{n^s})^t$ are the diffusion velocities $\mathbf{v}_i = -\sum_{j\in\mathcal{S}} D_{ij}\boldsymbol{d}_j$. Moreover, using the block decomposition (8.3) of the matrix L, and that of $\mathfrak{v}$, we obtain that $\Delta\mathbf{v} + L^{00\lambda}\mathbf{r} = Q\boldsymbol{d}$ and $L^{\lambda 00}\mathbf{v} + \Lambda\mathbf{r} = 0$. We may then write $\mathbf{r} = -\Lambda^{-1}L^{\lambda 00}\mathbf{v}$ and finally eliminate $\mathbf{r}$ to obtain the alternative form of the higher order Stefan–Maxwell equations only involving the velocity vector $\mathbf{v}$

$$-\left(\Delta - L^{00\lambda}\Lambda^{-1}L^{\lambda 00}\right)\mathbf{v} = Q\boldsymbol{d}. \tag{8.10}$$

These equations show that, in comparison with the first order velocities $\mathbf{v}_{[00]}$, the higher order diffusion velocities $\mathbf{v}$ require to modify the matrix Δ by the corrective terms $-L^{00\lambda}\Lambda^{-1}L^{\lambda 00}$. Similar Schur complements have been investigated in various kinetic frameworks, notably by Muckenfusss and Curtiss [59] and Monchick, Munn, and Mason [58]. However, from a numerical point of view, evaluating the product of the matrix $\Delta - L^{00\lambda}\Lambda^{-1}L^{\lambda 00}$ by a vector is costly since it requires solving a linear system with the matrix Λ. Therefore, iterative methods are more conveniently designed with the matrix L than with the Schur complement $\Delta - L^{00\lambda}\Lambda^{-1}L^{\lambda 00}$. In other words, since Λ is a full matrix, the formulation (8.8) with the enlarged velocity vector $\mathfrak{v}$ is more interesting for iterative techniques than the alternative formulation (8.10) only involving the diffusion velocities $\mathbf{v}$.

Higher order Stefan–Maxwell equations have also been investigated by Kolesnikov and Tirskiy [52], Galkin [35], and Magin and Degrez [56] by using vectorial perturbed distribution functions. More specifically, instead of deriving the usual scalar transport linear systems that are next multiplied by the proper diffusion driving forces, it is also possible to consider vectorial species perturbed distribution functions and next to derive the transport linear systems for the diffusion velocities as

elegantly done by Kolesnikov and Tirskiy. The resulting higher order Stefan–Maxwell linear equations derived from both methods are easily shown to be equivalent after some matrix manipulations. Similar equations have also been obtained in the framework of nonequilibrium thermodynamics by Zhdanov and Tirskiy [73].

In addition, the modifications required in order to take into account Soret effects simply corresponds to adding the temperature gradient terms in the diffusion driving forces [43]. These higher order Stefan–Maxwell equations have been generalized to the complex nonisotropic case including Soret effects but the details are omitted [43]. Finally the convergence rates observed for the higher order Sefan–Maxwell equations has been found similar to that of first order Stefan–Maxwell equations and the details are omitted.

9. Conclusion

We have investigated iterative algorithms for solving transport linear systems in partially ionized plasmas. A new formulation of the transport linear systems has been introduced associated with generalized inverses with nullspaces of increasing dimensions. New stationary algorithms as well as generalized conjugate gradient techniques have been considered. The behavior and accuracy of the resulting algorithms has been assessed by comprehensive numerical tests with high temperature air. These algorithms yield low cost accurate approximations of the transport coefficients for all ionization levels and magnetic field intensities and are relevant to multicomponent reactive plasmas numerical simulations.

Appendix A. Bloc structure of the transport linear systems

The transport linear systems are derived from a variational procedure used to solve constrained systems of linearized Boltzmann integral equations. The finite dimensional functional space used in the variational procedure can generally be written $\mathcal{A} = \text{span}\{\xi^{rk},\ (r,k) \in \mathcal{B}\}$, where $\xi^{rk}, (r,k) \in \mathcal{B}$, are basis functions. Here $\mathcal{B}$ denotes the set of basis function indices which has n elements. In the notation (r,k) the index k refers to the species and the index r to the function type that is considered. The basis functions ξ^{rk} are generally expressed in terms of the Laguerre–Sonine polynomials and the Wang Chang and Uhlenbeck polynomials in the internal energy, thus accounting for the polyatomic nature of the molecules [23].

The set $\mathcal{B}$ can be used as a natural indexing set and the components of any vector $x \in \mathbb{R}^n$ are then denoted by $x = (x_k^r)_{(r,k)\in\mathcal{B}}$. We can correspondingly write $G = (G_{kl}^{rs})_{(r,k),(s,l)\in\mathcal{B}}$ the coefficients of the matrix G. For any function type r, we consider the subset $\mathcal{S}_r \subset \mathcal{S}$ given by $\mathcal{S}_r = \{k \in \mathcal{S},\ (r,k) \in \mathcal{B}\}$ and we denote by n_r the number of elements of $\mathcal{S}_r$. Note that $\mathcal{S}_r$ may differ from $\mathcal{S}$ since some types of functions do not appear for certain species. For instance, functions in the internal energy must not be considered for the monatomic species. The transport linear system matrix $G = (G_{kl}^{rs})_{(r,k),(s,l)\in\mathcal{B}}$ in $\mathbb{R}^{n,n}$ can then be partitioned into the blocks $G^{rs} = (G_{kl}^{rs})_{k\in\mathcal{S}_r, l\in\mathcal{S}_s}$ of size $n_r * n_s$. For instance, for the thermal conductivity, the indexing set is given by $\mathcal{B}^\lambda = \{10\} \times \mathcal{S} \cup \{01\} \times \mathcal{P}$, where $\mathcal{P}$ is the set of polyatomic species indices, and $\mathcal{B}^\lambda$ has $n = n^s + n^p$ elements. Thus, the system matrix $\Lambda \in \mathbb{R}^{n^s+n^p,n^s+n^p}$ admits the block decomposition

$$\Lambda = \begin{pmatrix} \Lambda^{1010} & \Lambda^{1001} \\ \Lambda^{0110} & \Lambda^{0101} \end{pmatrix},$$

with $\Lambda^{1010} \in \mathbb{R}^{n^s,n^s}$, $\Lambda^{1001} \in \mathbb{R}^{n^s,n^p}$, $\Lambda^{0110} \in \mathbb{R}^{n^p,n^s}$, and $\Lambda^{0101} \in \mathbb{R}^{n^p,n^p}$. The matrix $\big(\text{diag}(G^{rs})\big)_{kl} = G_{kl}^{rs}\delta_{kl}, (r,k),(s,l) \in \mathcal{B}$, is defined as the diagonal of the rectangular block G^{rs}.

The sparse transport matrix is then formed by the diagonals of all the rectangular blocks G^{rs} of G. This matrix is denoted by $db(G) \in \mathbb{R}^{n,n}$ and can be written

$$db(G)_{kl}^{rs} = G_{kl}^{rs}\delta_{kl}, \quad (r,k),(s,l) \in \mathcal{B}, \tag{A.1}$$

where δ_{kl} is the Kronecker symbol. With respect to the matrix Λ for instance, we have the block decomposition

$$db(\Lambda) = \begin{pmatrix} \text{diag}(\Lambda^{1010}) & \text{diag}(\Lambda^{1001}) \\ \text{diag}(\Lambda^{0110}) & \text{diag}(\Lambda^{0101}) \end{pmatrix}.$$

The matrices G and $db(G)$ have a general mathematical structure inherited from the properties of the Boltzmann linearized collision operator and the properties of the variational approximation spaces associated with the transport linear systems [23].

Appendix B. Zero mass fractions

Zero mass fractions lead to artificial singularities in the transport linear systems which are eliminated by considering rescaled versions of the original systems [23]. Provided the diffusion matrix is replaced by the flux diffusion matrix $\widetilde{D}_{kl} = y_k D_{kl}, k,l \in \mathcal{S}$, it is proven in [23] that all the transport coefficients are smooth rational functions of the mass fractions and admit finite limits when some mass fractions become arbitrarily small. Moreover, the iterative algorithms obtained for positive mass fractions can be rewritten in terms of a rescaled system matrix that is still defined for nonnegative mass fractions and yield the same sequence of iterates [23]. This result establishes rigorously the validity of a common practice in

numerical calculations, which consists in evaluating transport properties of a given gas mixture by first adding to all the species mass fractions a very small number, typically lower than the machine precision.

Even though the singularities disappear by using the flux diffusion matrix $C = \mathrm{diag}(y_1, \ldots, y_{n^s})D$ we have still evaluated the numerical errors with the Frobenius norm of the original symmetric diffusion matrices D for the sake of simplicity. In addition, similar convergence behaviors have been observed with the errors measured through the matrix C.

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