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Transport properties of local thermodynamic equilibrium hydrogen plasmas including electronically excited states

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A study of the dependence of transport coefficients (*thermal conductivity, viscosity, electrical conductivity*) of local thermodynamic equilibrium H_2 plasmas on the presence of electronically atomic excited states, H(n), is reported. The results show that excited states with their "abnormal" cross sections strongly affect the transport coefficients especially at high pressure. Large relative errors are found when comparing the different quantities with the corresponding values obtained by using ground-state transport cross sections. The accuracy of the present calculation is finally discussed in the light of the selection of transport cross sections and in dependence of the considered number of excited states.

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I. INTRODUCTION

Transport properties of H_2 thermal plasmas have been calculated by many authors due to their importance in many technological applications [1–4]. The reiteration of these studies is usually justified by the improvement of the input data (*collision integrals*) entering in the relevant equations. Moreover, more recently an effort to understand the role of thermodynamics and kinetics in affecting the data has been reported [5,6]. In all cases the presence of electronically excited states in affecting the transport coefficients has been completely ignored. The justification is the low concentrations of electronically excited states compared to that in the ground state. This point is however a little contradictory when comparing the similar effort made by different authors in the calculation of partition functions and thermodynamic properties of hydrogen species. Inspection of these results in fact shows that the specific heat of hydrogen atoms reaches values orders of magnitude higher than the corresponding translational contribution, thus indicating a role of electronically excited states with high principal quantum numbers in affecting the thermodynamics of hydrogen plasmas [7]. It is indeed true that the specific heat of the single species reaches its maximum when entropic effects shift the equilibrium towards ionization so that excited states should lose their strong effect in determining the total quantities. Despite this, one overlooks that excited states have cross sections dramatically depending on the principal quantum number, so that neglecting excited states in the transport equations could appear a strong approximation.

Many years ago an attempt to estimate the role of excited states in affecting the transport properties of H_2 thermal plasmas was made by one of us [8,9]. The results, which were limited to plasmas operating at atmospheric pressure, showed some dependence of the transport properties on the presence of excited states. This dependence however was too much depending on the selection of collision integrals, the accuracy of which was poor at that time. An *unusual* effect was also observed for the so-called reactive thermal conductivity [9]. This contribution, which represents the diffusion of ionization energy through the temperature gradient existing in the plasma [10], is expressed as a ratio of two determinants, whose order depends on the number of independent chemical reactions occurring in the plasma. Diagonal and nondiagonal terms appear in the equation. The unusual effect observed consisted in the fact that when the complete equation was used, the reactive thermal conductivity appeared practically independent of the presence of excited states with their abnormal cross sections, the reverse being true when only diagonal terms were taken into account. This point has been recently confirmed by our group [11] in a new attempt to shed light on the role of electronically excited states on the reactive thermal conductivity. In this paper, however, we have shown that compensation effects of diagonal and nondiagonal terms for atmospheric plasmas disappear at higher pressures. The increase of pressure shifts the ionization equilibrium to higher temperatures where the electronically excited states start being populated without losing their absolute concentrations.

More recently we have reanalyzed the role of excited states in affecting the viscosity of hydrogen plasmas [12]. In this case too we have shown a strong effect of these states in affecting the viscosity, especially at high pressure. Moreover, we have confirmed the importance of including the off-diagonal terms in the equation for the viscosity. Empirical rules for calculating viscosity must be ruled out; probably one should use, in this case, higher approximations of the Chapman-Enskog method.

To conclude our work we present in this paper the influence of excited states on the translational thermal conductivity of hydrogen plasmas as well as on the contribution of electrons to thermal and electrical conductivity. These last terms require a strong effort in the evaluation of the relevant diffusion and viscosity type transport cross sections. Moreover, the calculation of diffusion transport cross sections for the interaction of H(n)-H(m) based on the resonant excita-

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tion transfer cross sections must be revised when these cross sections become lower than the contribution due to the elastic collision. At the same time, the diffusion-type collision integrals for the interactions $H(n)$-H^+ based on charge transfer cross sections must be refined to include the elastic contribution. The last can be obtained by considering a polarizability model with the dependence of the polarizability on the principal quantum number of excited states.

The complicated nature of the present problem needs to be stressed. The results, based on a set of transport cross sections derived by simple traditional methods, as well as on the use of standard transport equations, could generate the sensation of the completely solved problem. Unfortunately, this is not the case, as will be clear in the following. We therefore anticipate the qualitative nature of the present calculations which should generate further work on the subject.

The paper is organized as follows. Section II deals with the calculation of transport cross sections for excited states (called ‘‘abnormal’’ cross sections). Section III reports the transport coefficients (viscosity, different contributions of the total thermal conductivity, electrical conductivity) calculated with this set of cross sections. The results are always compared with the approximation that calculates the cross sections of excited states equal to the ground state (the so-called ‘‘usual’’ cross sections). Section IV analyzes the accuracy of the present calculations emphasizing, in particular, the empirical approach, making heavy use of crude averaging approximations to obtain the necessary transport collision integrals. Summary and future perspectives are reported in the Conclusions.

II. TRANSPORT CROSS SECTIONS

A. Transport cross sections for ground-state atoms and molecules

Transport cross sections can be calculated as a function of the gas temperature T according to the following equations [13]:

$$\Omega_{ij}^{\ell,s} = \sqrt{\frac{kT}{2\pi\mu_{ij}}}\int_0^{+\infty} e^{-\gamma_{ij}^2}\gamma_{ij}^{2s+3}\sigma^{(\ell)}(g)\,d\gamma, \qquad (1)$$

$$\sigma^{(\ell)}(g) = 2\pi\int_0^{+\infty}[1-\cos^{\ell}(\chi)]\,b\,db, \qquad (2)$$

where $\gamma_{ij}^2 = \mu_{ij}g^2/2kT$, g is the reduced relative velocity, μ is the reduced mass of the colliding particles, χ is the deflection angle, b is the impact parameter, and $\sigma^{(\ell)}$ is the gas-kinetic cross section of order ℓ that can be derived from measurements or computed from the intermolecular potential $V(r)$. In the last case the collision integrals are tabulated for different forms of the intermolecular potential (exponential repulsive, Morse, Lennard-Jones potential) [13]. Simple interpolations among tabulated data furnish the needed collision integrals once the parameters entering in the potential are known.

The considered interactions include neutral-neutral (H_2-H_2, H_2-H, H-H), ion-neutral (H^+-H_2, H^+-H), electron-neutral (e-H, e-H_2) and charged-charged (H^+-e, H^+-H^+, e-e) types.

The relevant collision integrals have been discussed by Gorse and Capitelli [14]. The only difference from the data reported in Ref. [14] is in the charged-charged collision integrals which have been calculated interpolating the numerical values given by Mason *et al.* [15] rather than using the well-known Liboff's equations [16].

B. Transport cross sections of excited states

We limit our description to the interactions $H(n)$-H^+, $H(n)$-$H(m)$, and e-$H(n)$. The interaction of molecular hydrogen and excited atomic hydrogen can be disregarded due to the practical disappearance of hydrogen molecules in the temperature range where the electronically excited states of hydrogen atoms start being populated.

For the present calculations we need the collision integrals of different orders, depending on the different approximations used in the Chapman-Enskog method. To this end we have used a recursive formula [13]

$$\Omega^{\ell,s+1} = T\frac{\partial\Omega^{\ell,s}}{\partial T} + \left(s+\frac{3}{2}\right)\Omega^{\ell,s}. \qquad (3)$$

Note also that we have used the *reduced collision integrals*, i.e., the collision integrals normalized to the rigid sphere model.

1. The interaction $H(n)$-$H(n)$

Viscosity-type collision integrals, $\Omega^{(2,2)*}$, for the interaction $H(n)$-$H(n)$ up to $n=5$ have been calculated by Celiberto *et al.* [17] by using potential-energy curves obtained by configuration interaction method. The data have been interpolated at different temperatures and then extrapolated to $n=12$ with suitable fitting procedures [18].

Diffusion-type collision integrals, $\Omega^{(1,1)*}$, up to $n=5$ have been obtained by integrating the momentum transfer cross sections reported by Celiberto *et al.* [17]. These data have been extrapolated up to $n=12$ with the same procedure described previously.

The recursive formula (3) has been then used for the collision integrals $\Omega^{(1,2)}_{H(n)\text{-}H(n)}$ and $\Omega^{(1,3)}_{H(n)\text{-}H(n)}$. A sample of viscosity-type collision integrals has been reported in Fig. 1 as a function of $n'=2-1/n^2$, n being the principal quantum number of atomic hydrogen.

2. The interaction $H(n)$-$H(m)$

Let us start with the diffusion-type collision integrals. These collision integrals contain two contributions, one coming from the *resonant excitation exchange* $\Omega_{et}^{(\ell,s)*}$, i.e., by the process

$$H(n)+H(m)\rightarrow H(m)+H(n),$$

the other one by the *elastic contribution* $\Omega_{el}^{(\ell,s)*}$.

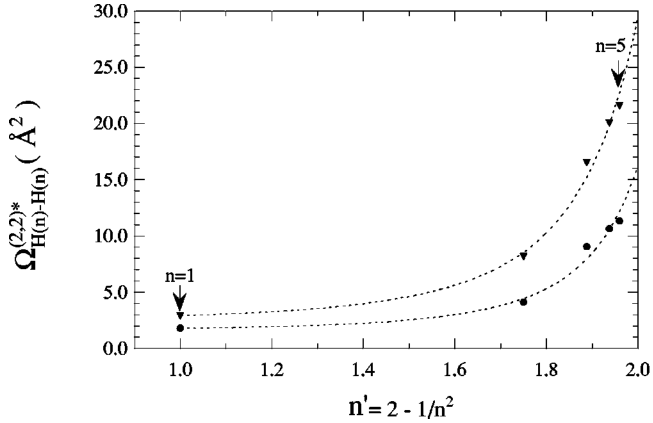

FIG. 1. Viscosity-type collision integrals as a function of $n'=(2-1/n^2)$, for H(n)-H(n) interactions, at $T=10^4$ (triangles) and 2×10^4 K (circles). Circles and triangles represent data of Celiberto *et al.* [17]

The contribution coming from the excitation transfer process has been calculated by Capitelli *et al.* [11]. The elastic contribution has been estimated by averaging the corresponding diagonal (not affected by excitation transfer process) contributions H(n)-H(n), H(m)-H(m) according to the simple formula

$$\Omega^{(\ell,s)*}_{H(n)\text{-H}(m)el}(T)=\tfrac{1}{2}\left(\Omega^{(\ell,s)*}_{H(n)\text{-H}(n)}+\Omega^{(\ell,s)*}_{H(m)\text{-H}(m)}\right). \tag{4}$$

Finally the diffusion-type collision integrals have been calculated according to the following equation:

$$\Omega^{(\ell,s)*}_{\text{H}(n)\text{-H}(m)}(T)=\sqrt{(\Omega^{(\ell,s)}_{et}*)^2+(\Omega^{(\ell,s)}_{el}*)^2}. \tag{5}$$

In general, excitation transfer process dominates the diffusion-type collision integrals; the elastic contribution starts being predominant for large differences in the $n-m$ values.

Viscosity-type collision integrals (not affected by the excitation transfer process) have been obtained by a simple average,

$$\Omega^{(2,2)*}_{H(n)\text{-H}(m)}(T)=\tfrac{1}{2}\left(\Omega^{(2,2)*}_{\text{H}(n)\text{-H}(n)}+\Omega^{(2,2)*}_{\text{H}(m)\text{-H}(m)}\right). \tag{6}$$

3. *The interaction* H(n)-H$^+$

The diffusion-type collision integrals have been calculated, as in the case of H(n)-H(n) interaction, by averaging the contribution from *resonant charge transfer* and *elastic collision*.

The contribution due to charge transfer has been calculated by Capitelli *et al.* [8,11] and fitted according to the following expression:

$$\Omega^{(1,1)*}_{\text{H}(n)\text{-H}^+ct}(T)=\exp[f_1 n'^{f_2}T'^{f_3}+\exp(f_4 n'-f_5)] \tag{7}$$

with $T'=T/1000$, $f_1=3.519$, $f_2=0.77$, $f_3=-2.732\times10^{-2}$, $f_4=15.9$, $f_5=30.3$. The corresponding $\Omega^{(1,2)}_{\text{H}(n)\text{-H}^+ct}$ and $\Omega^{(1,3)}_{\text{H}(n)\text{-H}^+ct}$ collision integrals have been obtained by the recursive formula (3).

To estimate the contribution due to elastic collision we have used a polarizability model including the dependence of polarizability on the principal quantum number n. The following equation can be used:

$$\Omega^{(1,1)*}_{\text{H}(n)\text{-H}^+pol}(T)=425.4Z\frac{\alpha^{1/2}_{pol}}{T}, \tag{8}$$

where Z represents the ion charge and α_{pol} is the atom polarizability expressed in Å^3. The dependence of α_{pol} on the principal quantum number n has been obtained by [19]

$$\alpha_{pol}=\tfrac{1}{8}a_0^3 n^4[17n^2-3(n_1-n_2)^2-9m^2+19], \tag{9}$$

where the *parabolic quantum numbers* n_1 and n_2 are defined as

$$\begin{cases} n_1=n-\ell-1 \\ n_2=\ell-|m| \end{cases} \Rightarrow n_1-n_2=n-2\ell-1-|m|. \tag{10}$$

The total diffusion collision integrals have been obtained by averaging the charge transfer and polarizability contributions according to the following equation:

$$\Omega^{(\ell,s)*}_{\text{H}(n)\text{-H}^+}(T)=\sqrt{(\Omega^{(\ell,s)}_{ct}*)^2+(\Omega^{(\ell,s)}_{pol}*)^2}. \tag{11}$$

As in the case of H(n)-H(n) interaction, the diffusion-type collision integrals are dominated by resonant charge exchange cross sections, the elastic (polarizability) contribution not exceeding 10%.

The viscosity-type collision integrals, not affected by resonant charge transfer cross sections, have been obtained by extrapolating the corresponding values calculated in Ref. [17] for $n\leqslant5$ to $n=12$. Their dependence as a function of T' and n' is given by

$$\Omega^{(2,2)*}_{H(n)\text{-H}^+}(T)=\exp[g_1 n'^{g_2}T'^{g_3}+\exp(g_4 n'-g_5)] \tag{12}$$

with $T'=T/1000$, $g_1=4.0349$, $g_2=0.9$, $g_3=-3.442\times10^{-1}$, $g_4=15.6$, $g_5=30.25$.

4. *The interaction* e-H(n)

Momentum transfer cross sections, $\sigma^{mt}_{e\text{-H}(n)}$, for the collision e-H(n) have been calculated by Ignjatovic *et al.* [20] using the partial wave method.

Their cross sections $[a_0^2]$ have been fitted as a function of energy $E[eV]$ and of the principal quantum number n by the following expression:

$$\sigma^{mt}_{e\text{-H}(n)}(E)=\frac{A}{E}\ln[1+Bn^4E^2][1+C\exp(-D\sqrt{E})]. \tag{13}$$

The relevant parameters A, B, C, and D have been reported in Table 9 of Ref. [20]. The momentum transfer cross sections have been transformed in diffusion-type collision integrals by direct integration of Eq. (1).

The recursive formula (3) has been used for obtaining the other collision integrals $\Omega^{(\ell,s)*}_{e\text{-H}(n)}$ $2\leqslant s\leqslant5$. The viscosity-type

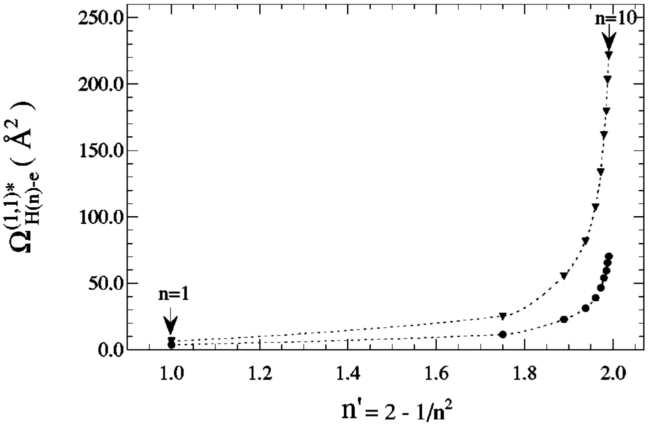

FIG. 2. Diffusion-type collision integrals as a function of $n' = (2-1/n^2)$, for e-H(n) interactions, at $T=10^4$ (triangles) and 2×10^4 K (circles), obtained by integration of cross section data from Ref. [20].

collision integrals $\Omega^{(2,2)*}_{e\text{-H}(n)}$ have been considered equal to the $\Omega^{(1,1)*}_{e\text{-H}(n)}$ ones, while the collision integrals of the order $\Omega^{(2,s)*}_{e\text{-H}(n)}$ have been again calculated by the recursive formula. A sample of results is reported in Fig. 2

III. TRANSPORT COEFFICIENTS

Transport coefficients have been calculated by using the third approximation of the Chapman-Enskog method for the electron component and the first nonvanishing approximation for heavy components (i.e., the first approximation for viscosity and the second one for the contribution of the heavy components to the thermal conductivity) [21].

Saha and Boltzmann laws have been used for calculating the equilibrium composition of the plasma (H_2, H, H^+, e) and the concentration of excited states of atomic hydrogen in the different principal quantum number n [H(n)] (see Capitelli *et al.* [11]). In general we have considered 12 electronically excited states; at high pressure we have reduced the number of excited states to 7 to take into account the decrease of the number of electronically excited states with increasing the pressure as discussed in Ref. [11].

A. Thermal conductivity

The total thermal conductivity λ_{tot} of a local thermodynamic equilibrium (LTE) plasma has been calculated by adding the different contributions, i.e.,

$$\lambda_{tot}=\lambda_h+\lambda_e+\lambda_{int}+\lambda_r, \tag{14}$$

where the members on the right-hand side of the equation represent, respectively, the translational contribution of heavy particles, the translational contribution of electrons, the contribution of internal degrees of freedom, and the reactive thermal conductivity.

The first term can be expressed through the second approximation of the Chapman-Enskog method according to the following equation:

$$\lambda_h=4\begin{vmatrix} L_{11} & \dots & L_{1\mu} & \chi_1 \\ \vdots & & \vdots & \vdots \\ L_{\mu 1} & \dots & L_{\mu\mu} & \chi_\mu \\ \chi_1 & \dots & \chi_\mu & 0 \end{vmatrix} \Bigg/ \begin{vmatrix} L_{11} & \dots & L_{1\mu} \\ \vdots & & \vdots \\ L_{\mu 1} & \dots & L_{\mu\mu} \end{vmatrix}. \tag{15}$$

Elements of the determinants are expressed as a function of temperature, collision integrals, and mass of the species (explicit equations can be found in Ref. [13]). The order of the determinant is controlled by the number of chemical species (μ) considered in the calculation. In the present case we consider up to 15 species [H_2, H^+, e, H(n)].

Figure 3(a) reports the ratio λ^a_h/λ^u_h, i.e., the ratio between the translational thermal conductivity values calculated with the abnormal cross sections λ^a_h and the corresponding results calculated with the usual cross sections λ^u_h as a function of temperature for different pressures. The temperature range considered in the different figures is $10^4 \leqslant T \leqslant 3\times10^4$ K. For $T<10^4$ K the presence of excited states does not alter the results.

Inspection of Fig. 3(a) shows that the differences in the ratio λ^a_h/λ^u_h strongly increase with the pressure. By defining a relative error as $err=|\lambda^a_h-\lambda^u_h|/\lambda^a_h\times100$ we can appreciate that the maximum error in the curves is 7%, 40%, and 240% for 1, 10, and 100 atm, respectively.

It should be noted that the small effect observed at 1 atm is due to a compensation effect between diagonal and off-diagonal terms in the whole representation of the translational thermal conductivity of the heavy components [see Eq. (15)]; this compensation disappears when we consider only the diagonal terms in Eq. (15). In this case, in fact, the relative error reaches a value of 160% when comparing the translational thermal conductivity calculated with the two sets of collision integrals.

The compensation between diagonal and nondiagonal terms disappears at high pressure as a result of the shifting of the ionization equilibrium towards higher temperatures, where excited states are more easily populated. The results of Fig. 3(a) have been obtained by considering in all cases 12 excited states. However, as pointed out in the Introduction, the number of excited states to be considered in the partition function should decrease with increasing pressure. As in Ref. [11], applying a very simple cutoff criterion, we have estimated to $n=7$ the maximum principal quantum number to be considered at 100 atm. As expected, the differences in λ^a_h/λ^u_h strongly decrease when reducing the total number of excited states [see the dotted line in Fig. 3(a)]. The relative error can reach in this case a value of 42%.

Let us now consider the effect of excited states on the translational thermal conductivity of free electrons. In this case we have used the third approximation of the Chapman-Enskog method. The relevant equations can be written as [21]

$$\lambda_e=\frac{75}{8}10^{16}n_e k\left(\frac{2\pi kT_e}{m_e}\right)^{1/2}\frac{q^{22}}{q^{11}q^{22}-(q^{12})^2}, \tag{16}$$

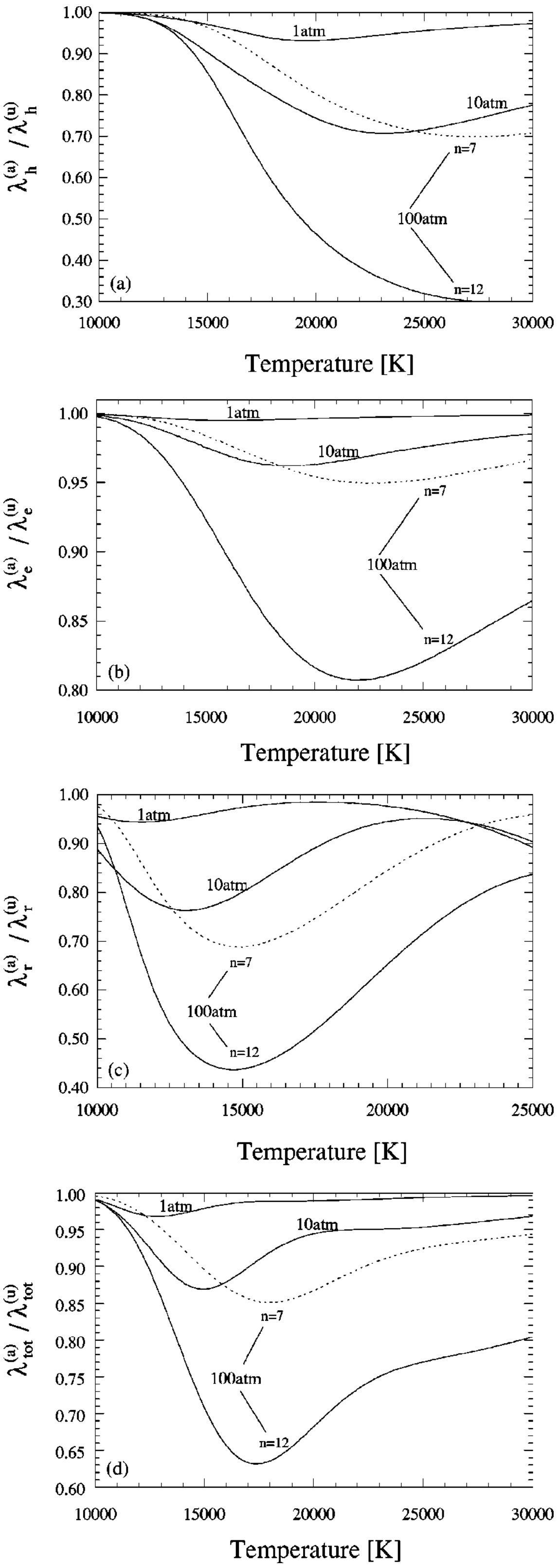

FIG. 3. Ratio between transport coefficients calculated by using *abnormal* (*a*) and *usual* (*u*) collision integrals, as a function of temperature, at different pressures and for different number of atomic levels. (a) Translational thermal conductivity of heavy particles; (b) translational thermal conductivity of electrons; (c) reactive thermal conductivity; (d) total thermal conductivity.

$$q^{11}=8\sqrt{2}n_e Q_{ee}^{(2,2)*}+8\sum_{j=1}^{\mu-1} n_j\left(\frac{25}{4}Q_{ej}^{(1,1)*}-15Q_{ej}^{(1,2)*}+12Q_{ej}^{(1,3)*}\right), \tag{17}$$

$$q^{12}=8\sqrt{2}n_e\left(\frac{7}{4}Q_{ee}^{(2,2)*}-2Q_{ee}^{(2,3)*}\right)+8\sum_{j=1}^{\mu-1} n_j\left(\frac{175}{16}Q_{ej}^{(1,1)*}-\frac{315}{8}Q_{ej}^{(1,2)*}+57Q_{ej}^{(1,3)*}-30Q_{ej}^{(1,4)*}\right), \tag{18}$$

$$q^{22}=8\sqrt{2}n_e\left(\frac{77}{16}Q_{ee}^{(2,2)*}-7Q_{ee}^{(2,3)*}+5Q_{ee}^{(2,4)*}\right)+8\sum_{j=1}^{\mu-1} n_j\left(\frac{1225}{64}Q_{ej}^{(1,1)*}-\frac{735}{8}Q_{ej}^{(1,2)*}+\frac{399}{2}Q_{ej}^{(1,3)*}-210Q_{ej}^{(1,4)*}+90Q_{ej}^{(1,5)*}\right), \tag{19}$$

where m_e, T_e, n_e represent the electron mass, density, and temperature of electrons, respectively, and $Q_{ij}^{(\ell,s)*}=\pi\Omega_{ij}^{(\ell,s)*}$.

The presence of excited states affects only the interaction of electrons with H(n). Figure 3(b) reports the ratio λ_e^a/λ_e^u calculated with the two sets of collision integrals as a function of temperature at different pressures. We observe that the excited states increase their influence with increasing the pressure. The relative error, defined as $err=|\lambda_e^a-\lambda_e^u|/\lambda_e^a\times 100$, reaches maximum values of 0.5%, 4%, and 25% for 1, 10, and 100 atm, respectively. The last deviation reduces to 5% when considering only seven excited states [see the dotted line in Fig. 3(b)].

Let us now examine the reactive thermal conductivity. This contribution has been extensively analyzed in Ref. [11]. The main conclusions follow the trend illustrated for λ_h and λ_e in the present paper. In particular, Fig. 3(c) reports the ratio λ_r^a/λ_r^u as a function of temperature at different pressures. The relative error, again defined as $err=|\lambda_r^a-\lambda_r^u|/\lambda_r^a\times 100$, reaches maximum values of 40%, 37%, and 120% for 1, 10, and 100 atm, respectively. In the last case the maximum error reduces to 47% when inserting seven excited states.

Finally we want to point out that the larger contribution to λ_{int} comes from the vibrational and rotational degrees of freedom of the molecular H_2. Electronically excited states of atomic hydrogen should contribute to the thermal conductivity when the reactive thermal conductivity considers only the ionization from the ground state, i.e., when use is made of the usual collision integrals. This means that in the temperature range 10^4–3×10^4 K the internal contribution of molecules disappears, while the internal contribution due to the electronically excited states is already inserted in λ_r.

Now we compare the total thermal conductivity calculated according to the two sets of collision integrals. Figure 3(d) reports the ratio $\lambda_{tot}^a/\lambda_{tot}^u$ as a function of temperature

TABLE I. Total thermal conductivity ($\mathrm{W\,m^{-1}\,K^{-1}}$) in the temperature range (10^4–3×10^4 K), at different pressures and for different number of atomic excited levels.

T	$P=1$ atm $n=12$	$P=10$ atm $n=12$	$P=100$ atm $n=7$
10000	$3.813\times10^{+0}$	$3.543\times10^{+0}$	$3.742\times10^{+0}$
11000	$4.419\times10^{+0}$	$4.106\times10^{+0}$	$4.024\times10^{+0}$
12000	$5.038\times10^{+0}$	$4.700\times10^{+0}$	$4.477\times10^{+0}$
13000	$5.825\times10^{+0}$	$5.248\times10^{+0}$	$5.035\times10^{+0}$
14000	$6.640\times10^{+0}$	$5.759\times10^{+0}$	$5.641\times10^{+0}$
15000	$6.987\times10^{+0}$	$6.313\times10^{+0}$	$6.241\times10^{+0}$
16000	$6.541\times10^{+0}$	$6.905\times10^{+0}$	$6.801\times10^{+0}$
17000	$5.565\times10^{+0}$	$7.386\times10^{+0}$	$7.327\times10^{+0}$
18000	$4.598\times10^{+0}$	$7.583\times10^{+0}$	$7.842\times10^{+0}$
19000	$3.942\times10^{+0}$	$7.443\times10^{+0}$	$8.362\times10^{+0}$
20000	$3.614\times10^{+0}$	$7.075\times10^{+0}$	$8.869\times10^{+0}$
21000	$3.529\times10^{+0}$	$6.657\times10^{+0}$	$9.329\times10^{+0}$
22000	$3.601\times10^{+0}$	$6.330\times10^{+0}$	$9.711\times10^{+0}$
23000	$3.774\times10^{+0}$	$6.155\times10^{+0}$	$1.001\times10^{+1}$
24000	$4.012\times10^{+0}$	$6.139\times10^{+0}$	$1.024\times10^{+1}$
25000	$4.297\times10^{+0}$	$6.258\times10^{+0}$	$1.043\times10^{+1}$
26000	$4.615\times10^{+0}$	$6.484\times10^{+0}$	$1.063\times10^{+1}$
27000	$4.963\times10^{+0}$	$6.794\times10^{+0}$	$1.086\times10^{+1}$
28000	$5.335\times10^{+0}$	$7.167\times10^{+0}$	$1.116\times10^{+1}$
29000	$5.730\times10^{+0}$	$7.591\times10^{+0}$	$1.152\times10^{+1}$
30000	$6.148\times10^{+0}$	$8.055\times10^{+0}$	$1.195\times10^{+1}$

TABLE II. Viscosity [$\mathrm{Kg\,m^{-1}\,s^{-1}}$] in the temperature range (10^4–3×10^4 K), at different pressures and for different number of atomic excited levels.

T	$P=1$ atm $n=12$	$P=10$ atm $n=12$	$P=100$ atm $n=7$
10000	9.371×10^{-5}	1.012×10^{-4}	1.041×10^{-4}
11000	8.764×10^{-5}	1.075×10^{-4}	1.135×10^{-4}
12000	7.105×10^{-5}	1.084×10^{-4}	1.219×10^{-4}
13000	5.043×10^{-5}	1.012×10^{-4}	1.283×10^{-4}
14000	3.281×10^{-5}	8.641×10^{-5}	1.309×10^{-4}
15000	2.056×10^{-5}	6.796×10^{-5}	1.285×10^{-4}
16000	1.299×10^{-5}	5.054×10^{-5}	1.207×10^{-4}
17000	8.647×10^{-6}	3.662×10^{-5}	1.082×10^{-4}
18000	6.294×10^{-6}	2.653×10^{-5}	9.336×10^{-5}
19000	5.088×10^{-6}	1.960×10^{-5}	7.827×10^{-5}
20000	4.528×10^{-6}	1.502×10^{-5}	6.459×10^{-5}
21000	4.331×10^{-6}	1.208×10^{-5}	5.308×10^{-5}
22000	4.347×10^{-6}	1.025×10^{-5}	4.387×10^{-5}
23000	4.493×10^{-6}	9.161×10^{-6}	3.674×10^{-5}
24000	4.723×10^{-6}	8.564×10^{-6}	3.134×10^{-5}
25000	5.010×10^{-6}	8.300×10^{-6}	2.733×10^{-5}
26000	5.340×10^{-6}	8.267×10^{-6}	2.440×10^{-5}
27000	5.704×10^{-6}	8.396×10^{-6}	2.231×10^{-5}
28000	6.096×10^{-6}	8.642×10^{-6}	2.086×10^{-5}
29000	6.513×10^{-6}	8.977×10^{-6}	1.991×10^{-5}
30000	6.952×10^{-6}	9.381×10^{-6}	1.934×10^{-5}

for different pressures. The relative error in this case assumes the values of 3%, 15%, and 60% for $p=1$, 10, and 100 atm, respectively; the last error reduces to 18% when inserting seven excited states.

Numerical values of the total thermal conductivity, at different pressures, as a function of temperature, have been reported in Table I. Note that we have reported for $p=100$ atm the values calculated by including in the relative equations seven excited states. This selection should be pre-

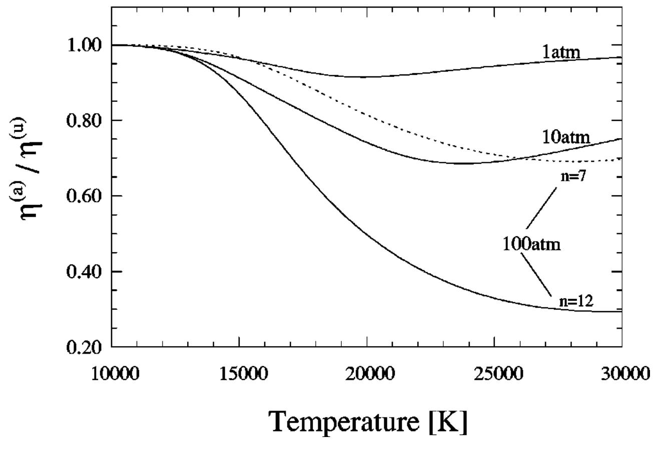

FIG. 4. Ratio between the viscosity values calculated by using *abnormal* (a) and *usual* (u) collision integrals, as a function of temperature, at different pressures and for different number of atomic levels.

TABLE III. Electrical conductivity ($\mathrm{S\,m^{-1}}$) in the temperature range [10^4–3×10^4 K], at different pressures and for different number of atomic excited levels.

T	$P=1$ atm $n=12$	$P=10$ atm $n=12$	$P=100$ atm $n=7$
10000	$1.783\times10^{+3}$	$8.918\times10^{+2}$	$3.389\times10^{+2}$
11000	$2.871\times10^{+3}$	$1.741\times10^{+3}$	$7.473\times10^{+2}$
12000	$3.994\times10^{+3}$	$2.858\times10^{+3}$	$1.409\times10^{+3}$
13000	$5.073\times10^{+3}$	$4.130\times10^{+3}$	$2.346\times10^{+3}$
14000	$6.073\times10^{+3}$	$5.447\times10^{+3}$	$3.534\times10^{+3}$
15000	$6.978\times10^{+3}$	$6.734\times10^{+3}$	$4.921\times10^{+3}$
16000	$7.785\times10^{+3}$	$7.954\times10^{+3}$	$6.439\times10^{+3}$
17000	$8.505\times10^{+3}$	$9.095\times10^{+3}$	$8.023\times10^{+3}$
18000	$9.158\times10^{+3}$	$1.016\times10^{+4}$	$9.622\times10^{+3}$
19000	$9.766\times10^{+3}$	$1.116\times10^{+4}$	$1.120\times10^{+4}$
20000	$1.035\times10^{+4}$	$1.210\times10^{+4}$	$1.274\times10^{+4}$
21000	$1.092\times10^{+4}$	$1.299\times10^{+4}$	$1.423\times10^{+4}$
22000	$1.148\times10^{+4}$	$1.385\times10^{+4}$	$1.566\times10^{+4}$
23000	$1.204\times10^{+4}$	$1.468\times10^{+4}$	$1.704\times10^{+4}$
24000	$1.260\times10^{+4}$	$1.549\times10^{+4}$	$1.837\times10^{+4}$
25000	$1.317\times10^{+4}$	$1.628\times10^{+4}$	$1.965\times10^{+4}$
26000	$1.374\times10^{+4}$	$1.706\times10^{+4}$	$2.088\times10^{+4}$
27000	$1.433\times10^{+4}$	$1.784\times10^{+4}$	$2.208\times10^{+4}$
28000	$1.493\times10^{+4}$	$1.860\times10^{+4}$	$2.324\times10^{+4}$
29000	$1.555\times10^{+4}$	$1.936\times10^{+4}$	$2.436\times10^{+4}$
30000	$1.618\times10^{+4}$	$2.011\times10^{+4}$	$2.546\times10^{+4}$

ferred to that which considers $n=12$, as discussed in Ref. [11].

B. Viscosity

The influence of electronically excited states on the viscosity has been recently discussed. We have used the first approximation of the Chapman-Enskog method which assumes a form very similar to Eq. (15) [13].

The results are in line with those discussed for the heavy particle translational contribution to the total thermal conductivity. In particular, Fig. 4 reports the ratio η^a/η^u as a function of temperature for different pressures. As in the case of translational thermal conductivity the viscosity values calculated with the abnormal cross sections are less than the corresponding values calculated with the usual cross sections. The maximum relative error in this case assumes the values of 9%, 48%, and 250% for $p=1$, 10, and 100 atm, respectively; the last error becoming 45% when inserting seven excited states.

Again we observe larger deviations when the off-diagonal terms in the viscosity equation are neglected in the calculation. As an example, at 1 atm the maximum error increases from 9% to 100%. Numerical values of viscosity at different pressures are presented in Table II. Again for $p=100$ atm we report only the values calculated including seven excited states.

C. Electrical conductivity

Electrical conductivity (Table III) has been calculated by using the third approximation of the Chapman-Enskog method which can be written as [21]

$$\sigma_e=\frac{3}{2}e^2n_e^2\left(\frac{2\pi}{m_ekT_e}\right)^{1/2}\frac{q^{11}q^{22}-(q^{12})^2}{q^{00}[q^{11}q^{22}-(q^{12})^2]+q^{01}(q^{12}q^{02}-q^{01}q^{22})+q^{02}(q^{01}q^{12}-q^{02}q^{11})}, \tag{20}$$

$$q^{00}=8n_e\sum_{j=1}^{\mu-1}n_jQ_{ej}^{(1,1)*}, \tag{21}$$

$$q^{01}=8n_e\sum_{j=1}^{\mu-1}n_j\left(\frac{5}{2}Q_{ej}^{(1,1)*}-3Q_{ej}^{(1,2)*}\right), \tag{22}$$

$$q^{02}=8n_e\sum_{j=1}^{\mu-1}n_j\left(\frac{35}{8}Q_{ej}^{(1,1)*}-\frac{21}{2}Q_{ej}^{(1,2)*}+6Q_{ej}^{(1,3)*}\right). \tag{23}$$

The presence of electronically excited states can affect σ_e through the collisions e-H(n). The trend of the electrical conductivity follows that one described for the contribution of electrons to the thermal conductivity as can be appreciated in Fig. 5 where we have reported σ_e^a/σ_e^u. The relative error calculated as before increases from 1% at 1 atm to 45% at 100 atm. The last error reduces to 10% when only seven states are considered. The results at 1 atm are similar to those reported in Ref. [20], being however different at 10 atm. This is probably due to the simplified equation used in Ref. [20] for the calculation of the electrical conductivity.

IV. COMMENTS

The results reported in the previous sections indicate a strong dependence of the transport coefficients of LTE H_2 plasmas on the presence of electronically excited states. This conclusion is reached when comparing the transport coefficients calculated with the two sets of collision integrals. A natural question arises on the accuracy of the presented results which, of course, depend on the adopted set of collision integrals for excited states as well as on the number of excited states existing in the plasma.

These points need some comments. Let us consider first the most important interactions that affect our results. In the case of heavy particle components (translational thermal conductivity and viscosity) the viscosity-type collision integrals for the interaction H(n)-H$^+$ have a large role in affecting the results. These collision integrals have been obtained by extrapolating to $n>5$ the collision integrals calculated in Ref. [8] by adiabatically averaging the contribution coming from the different potential curves arising in a particular collision. In turn the potential curves of H_2^+ are exact, since the hydrogen molecular ion is one of the few examples treated exactly by quantum mechanics. The problem in this case is the extrapolation of the results to higher n. A completely

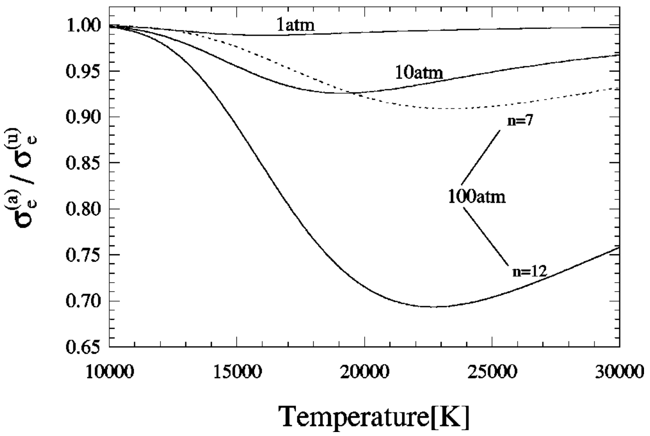

FIG. 5. Ratio between the electrical conductivity values calculated by using *abnormal* (*a*) and *usual* (*u*) collision integrals, as a function of temperature, at different pressures and for different number of atomic levels.

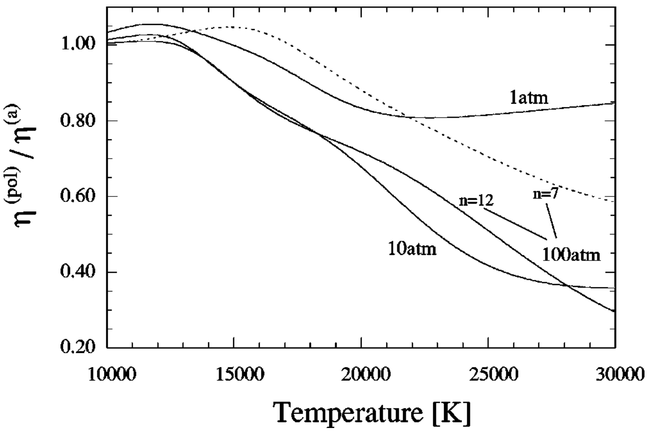

FIG. 6. Ratio between the viscosity values calculated by using $\Omega^{(2,2)*}_{H(n)\text{-}H^+}$ based on the polarizability model (pol), and *abnormal* (*a*) collision integrals, as a function of temperature, at different pressures and for different number of atomic levels.

different way to calculate the viscosity-type collision integrals should be to calculate them with a polarizability model taking into account the dependence of the polarizability on the principal quantum number. A comparison of collision integrals calculated in this way with the corresponding ones used in the present work shows that the polarizability model gives a much stronger dependence of collision integrals on *n* specially for $n>5$. At the same time the viscosity data obtained by the transport cross sections from polarizability model are lower than the corresponding values used in the bulk of the present work (see Fig. 6). Again the differences become more and more important with increasing the pressure, thus emphasizing the need for further studies on viscosity-type collision integrals for the interaction $H(n)$-H^+. Differences in the viscosity values are well evident also at 1 atm.

Another set of collision integrals which can affect the viscosity is that relative to the interaction $H(n)$-$H(n)$. These collision integrals have been calculated taking into account only a few potentials in each interaction. As an example, the interaction between $H(2)$-$H(2)$ species occurs adiabatically through a lot of $^{1,3}\Sigma$, $^{1,3}\Pi$, $^{1,3}\Delta$ states [22], while the collision integrals calculated in Ref. [17] include only the contribution coming from the states $^1\Sigma_g^+$ and $^1\Pi_g$. The difference in the two sets of collision integrals does not exceed a factor of 1.7 which can be taken as an indication of the accuracy of our collision integrals. These differences do not propagate in the calculated viscosity values for the temperature and pressure ranges considered in the present paper.

Note, however, that when dealing with the interaction of excited states, inelastic and reactive terms [23,24] can affect the results. Insertion of these effects should increase the transport cross sections exalting in any case the role of excited states in affecting the results. Similar considerations apply to the translational thermal conductivity of heavy components.

The dependence of the reactive thermal conductivity on the collision integrals has been examined in detail in Ref. [11] where we have shown that this term mainly depends on the diffusion-type collision integrals for the interaction $H(n)$-H^+. In the present study we have taken into account in this collision also the contribution coming from the polarizability. A comparison of λ_r, calculated by using in both cases abnormal collision integrals with and without the polarizability contribution, shows no appreciable differences, thus meaning that the charge transfer cross sections dominate the diffusion-type collision integrals.

The contribution of electrons to the thermal and electrical conductivity depends on the collision integrals for the interaction e-$H(n)$. The quantum mechanical calculation of the momentum transfer cross sections performed by Ignjatovic and Mihajlov [20] seems adequate for the present aim. Also in this case we have neglected in the transport cross sections the effects due to inelastic and reactive collisions which strongly increase with *n*. Moreover, the use of the present calculations to higher pressures can be open to question due to the many body effects neglected by Ignjatovic and Mihajlov [20] (e.g., see Ref. [25]).

Let us now examine the effect of the number of excited states on the transport properties. This point has been partially discussed above where we have shown calculations performed by considering excited states up to $n=7$ for $p=100$ atm. This problem derives by the finite number of excited states existing in the plasma. Several cutoff criteria have been proposed in the literature to truncate the partition function of an atom. Despite this, till now no universal criterion existed. All the criteria however indicate that the number of excited states to be considered in a plasma decreases with increasing the electron density or the total pressure. In Ref. [11] we have calculated an approximate number of excited states at 100 atm of 7 by using a very simple criterion, i.e., by considering excited states with a classical Bohr radius not exceeding the interparticle distance.

At higher pressures, of course, the number of excited states should further decrease. However, increasing the pressure the ionization equilibrium is shifted to higher temperatures so that the concentration of excited states with low principal quantum number can be sufficient to affect the transport properties. This point can be better appreciated by looking at the behavior of the different quantities at 1000 atm (see Fig. 7). In this case we have reported the different quantities by varying the number of excited states. We can see that in this case already the first excited state $(n=2)$ affects the results. Of course, the 1000 atm case presents other problems linked to nonideality of the plasma under these conditions [4,25].

Another interesting point deals with the accuracy of the present calculations with respect to the Chapman-Enskog approximation used in the present work. Let us first discuss the viscosity and the translational thermal conductivity of the heavy components. We have used for these quantities the first nonvanishing approximations of the method given in the determinantal form of the type of Eq. (15). These approximations are very accurate when neglecting the presence of excited states. In the presence of excited states with their abnormal transport cross sections these approximations could not be sufficient. A signal in this direction is given by the strong differences occurring when neglecting the off-

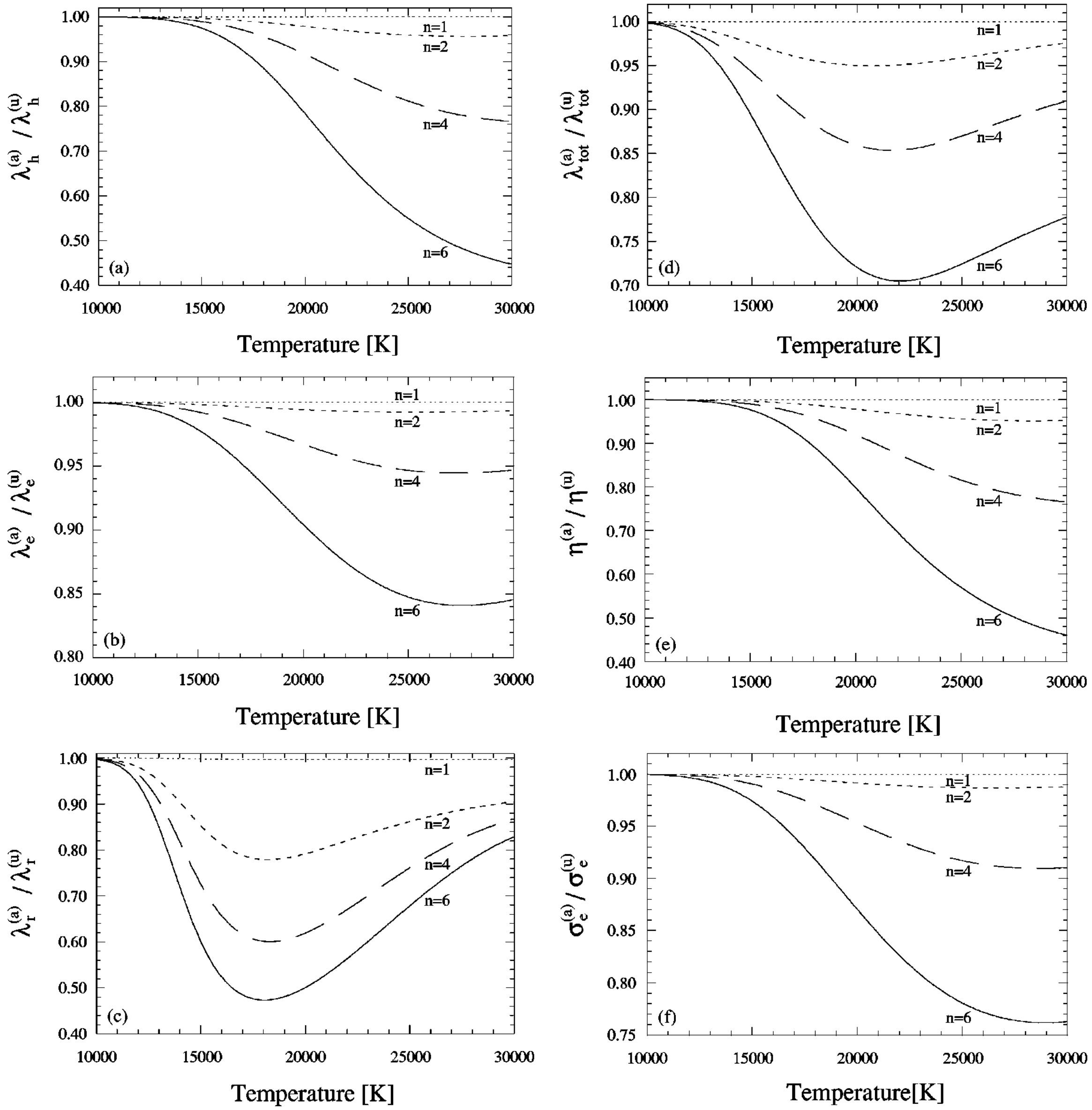

FIG. 7. Ratio between transport coefficients calculated by using *abnormal* (*a*) and *usual* (*u*) collision integrals at pressure of 1000 atm, as a function of temperature, and for different number of atomic levels. (a) Translational thermal conductivity of heavy particles; (b) translational thermal conductivity of electrons; (c) reactive thermal conductivity; (d) total thermal conductivity; (e) viscosity; (f) electrical conductivity.

diagonal terms in these approximations.

A similar conclusion could be extended to the reactive thermal conductivity. Probably a better formulation of the Butler-Brokaw equation could be necessary when considering electronically excited states.

Finally the electron properties (thermal and electrical conductivity) calculated in the present work with the third approximation of the Chapman-Enskog method could require higher approximations due to the strong differences in the collision frequency between electron-ground state and electron-excited state interactions.

The final answer to the role of excited states in affecting the transport properties of a LTE plasma should be an experimental validation of these quantities. At the moment the experiments [26] have been limited to atmospheric plasmas, for which the inclusion of excited states does not alter apparently the situation. Our calculations at 1 atm are in good agreement with the existing theoretical and experimental values. To conclude this section again we want to point out the semiempirical nature of the selected transport cross sections, indicating a qualitative validity of the present transport coefficient calculations.

V. CONCLUSIONS

In the present paper we have shown the dependence of transport coefficients of LTE (local thermodynamic equilibrium) atomic hydrogen plasmas on the presence of electronically excited states. Our results emphasize the importance of these states in affecting the transport coefficients especially at high pressure. This point can open new perspectives in the understanding of transport coefficients for high temperature plasmas.

The present results must be regarded at this stage of the development from the qualitative point of view. Future improvements should consider both an improvement of the transport cross sections as well as a better theory for the calculation of the number of excited states in the actual plasma. In particular, more advanced quantum mechanical methods should be used to calculate the relevant cross sections especially at high pressure when many body interactions cannot be neglected. Higher approximations of the Chapman-Enskog method should also be used to improve the present results. The proposed improvements, while increasing the accuracy of the present results, should not affect their qualitative validity.

Dedicated experiments at high pressure will be welcome to validate the present theoretical values. Extension of these ideas to divertor plasmas and/or to unusual astrophysical situations as well as to nonequilibrium situations should be encouraged.

ACKNOWLEDGMENTS

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