For small values of $T_e (kT_e \ll e\phi_i)$, all collisions become elastic and the term $\kappa g d n v / dx$ approaches zero and can be neglected.

For the ranges of T_e discussed the energy equation reduces to

$$(d/dx)(MNV^3+N_iM_iV_i^3+nmv^3+5nvkT_e +5N_iV_ikT_i+5NVkT_a)=-2EJ. \quad (25)$$

For the case of photoionization, the inelastic energy loss will be smaller than in the electron impact case. Since the inelastic energy loss was shown to be negligible for the regions of interest for electron impact ionization, it will also be negligible for photoionization. Thus the first-order energy equation will be given by Eq. (25) when photoionization dominates as well as when electron impact ionization dominates.

PHYSICAL REVIEW VOLUME 128, NUMBER 3 NOVEMBER 1, 1962

High-Density Corrections in Plasma Spectroscopy*

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(Received May 25, 1962)

The various relationships between spectroscopically measured quantities and the temperature and density of a collision-dominated plasma in local thermal equilibrium are discussed. An internally consistent system of corrections is derived for Saha equations, partition functions, and equations of state on one hand, and line intensities, line profiles, continuum intensities, and optical refractivities. The errors due to remaining uncertainties in these corrections are shown to be usually below 1%. They are therefore negligible compared to those stemming from uncertainties in atomic theory (except for hydrogen or hydrogenic ions) and an order of magnitude smaller than was suggested by discrepancies between previously used corrections to ionization energies of atoms or ions in dense plasmas.

INTRODUCTION

THE concept of local thermal (or thermodynamic) equilibrium plays a vital role in plasma spectroscopy. If it is applicable, all particle distribution functions can be calculated from total densities and temperature, which may both be local functions of time. In other words, the state of the plasma is then fully described by mass density, chemical composition, and temperature. This does not only make it relatively easy to determine the state of the plasma by a few spectroscopic measurements,[1] but also often facilitates the use of such plasmas as spectroscopic light sources for the measurement of atomic parameters[2] like oscillator strengths and line profiles or for the establishment of absolute intensity standards.[3]

Local thermal equilibrium may be expected if collision induced transitions are more frequent than radiative ones, which will in laboratory plasmas usually not lead to thermal equilibrium populations since there one practically never deals with an equilibrium, i.e., blackbody, radiation field. However, often radiative transitions will be negligible, and the level populations will be governed by collision induced processes. If the velocity distribution of the most important reaction partners is Maxwellian (in the nondegenerate case), the principle of detailed balance applies, and the steady-state solution of the rate equations yields the same populations that pertain to a system in complete thermodynamic equilibrium at a temperature equal to the kinetic temperature of the reaction partners.

Since most of these processes are dominated by collisions with electrons, it is their kinetic temperature that is of primary interest. If the relevant velocity distributions at any point and instant are sufficiently close to being Maxwellian and if spatial and time variations are also sufficiently weak as to enable instantaneous and local steady-state populations to be reached, then the assumption of local thermal equilibrium will always be valid as long as radiative rate processes are not important.

THERMODYNAMIC POTENTIALS

Before the distributions over the various possible states are computed for the equivalent thermodynamic equilibrium system, it should be realized that the only quantities which can, at least in principle, be stated without any ambiguity are total number densities N_i of the various chemical species i (hydrogen, helium, etc.) and the temperature. They should, therefore, be chosen as independent variables. Already in the calculation of pressure and internal energy some uncertainty has to be expected, not to mention the distributions over bound

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* Jointly sponsored by the Office of Naval Research and the National Science Foundation.

[1] H. R. Griem, in *Proceedings of the Fifth International Conference on Ionization Phenomena in Gases, 1961* (North-Holland Publishing Company, Amsterdam, 1962), Vol. II, p. 1857.

[2] A. C. Kolb and H. R. Griem, in *Atomic and Molecular Processes*, edited by D. R. Bates (Academic Press Inc., New York, 1962).

[3] R. C. Elton, A. C. Kolb, and H. R. Griem, paper presented at the Optical Society Meeting, Washington, D. C., March, 1962.

states or the various ionization equilibria. (It will be assumed throughout that dissociation of molecules is complete.)

Following the usual practice, as energy levels of the system the unperturbed levels of the constituent atoms or ions will be used with a suitable cutoff. Furthermore, only Coulomb interactions will be considered. One now writes for the free energy (per unit volume), which has an extremum for a thermodynamic equilibrium system of fixed volume and mass, i.e., fixed density or specific volume,

$$F \equiv U - TS = F_0 + F_c. \tag{1}$$

Here F_0 denotes the free energy of the unperturbed system and F_c accounts for the Coulomb interactions.

Usually the Debye theory can be used to calculate F_c. The principal result of this theory is that each electron and ion in an electrolyte or plasma is effectively surrounded by a spherically symmetrical cloud of shielding charges which modify the Coulomb potential to

$$V_z = (ze/r)\exp(-r/\rho_D), \tag{2}$$

with

$$kT/\rho_D{}^2 = 4\pi e^2 (N_e + \sum z^2 N_i{}^z), \tag{3}$$

where z assumes the value 0 for neutrals, 1 for singly ionized atoms, etc., and where the $N_i{}^z$ are the total densities of the chemical species i in the various ionization stages z.

The potential energy of the charge cloud surrounding an ion of charge z becomes with Poisson's equation for the charge density

$$U_z = -\int r^2 V_z \left[d^2V_z/dr^2 + (2/r) dV_z/dr \right] dr \tag{4}$$
$$= -z^2 e^2 / 2\rho_D,$$

and the contribution of Coulomb interactions to the internal energy (per unit volume) is in this approximation

$$U_c = -(e^2/2\rho_D)(N_e + \sum z^2 N_i{}^z)$$
$$= -e^3 (\pi/kT)^{1/2} (N_e + \sum z^2 N_i{}^z)^{3/2}. \tag{5}$$

Using the equation for the free energy

$$F = U + T\partial F/\partial T, \tag{6}$$

one obtains finally

$$F = F_0 - (e^2/3\rho_D)(N_e + \sum z^2 N_i{}^z)$$
$$= F_0 - (2e^3/3)(\pi/kT)^{1/2}(N_e + \sum z^2 N_i{}^z)^{3/2}. \tag{7}$$

Debye's approximation involves the assumption that on the average electrostatic interactions are small compared with thermal energies. Also, this formula can only be expected to be valid if the Debye sphere contains a large number of charged particles. But it has been shown that this requirement is not too critical and that the Debye theory may be used up to densities fulfilling a certain inequality[4] which for the present purposes is most conveniently written as[5]

$$N_e + \sum N_i{}^z \geq (8\pi \rho_D{}^3)^{-1}. \tag{8}$$

For laboratory plasmas this inequality is practically always fulfilled, e.g., even for a hydrogen plasma at $kT = 1$ eV and $N_e = 10^{19}$ cm^{-3}. But in stellar interiors the Debye theory must usually be replaced by more complicated expressions[4,5] which can also be derived by interpolation between the Debye theory result and that of the so-called ion-sphere model.[6]

IONIZATION ENERGIES

The Saha equation is obtained by extremizing the free energy with respect to an ionization process which changes $N_i{}^z$, $N_i{}^{z+1}$, N_e to $N_i{}^z + \delta N_i{}^z$, $N_i{}^{z+1} + \delta N_i{}^{z+1}$, $N_e + \delta N_e$. Since $\delta N_i{}^{z+1} = -\delta N_i{}^z = \delta N_e$, this extremum is characterized by

$$\partial F/\partial N_e - \partial F/\partial N_i{}^z + \partial F/\partial N_i{}^{z+1} = 0. \tag{9}$$

The corresponding expression for F_0 contains a term $I_i{}^z$, the unperturbed ionization energy of the ith atom or ion in charge state z. Therefore, to correct the Saha equation $I_i{}^z$ must be replaced by $I_i{}^z - \Delta I_i{}^z$, and one has

$$N_e N_i{}^{z+1}/N_i{}^z = (2Z_i{}^{z+1}/Z_i{}^z)(mkT/2\pi\hbar^2)^{3/2}$$
$$\times \exp[-(I_i{}^z - \Delta I_i{}^z)/kT]. \tag{10}$$

Here $Z_i{}^{z+1}$, $Z_i{}^z$ are the partition functions of the subsequent ionization stages, and $\Delta I_i{}^z$ is given by

$$\Delta I_i{}^z = -(\partial F_c/\partial N_e - \partial F_c/\partial N_i{}^z + \partial F_c/\partial N_i{}^{z+1})$$
$$= (z+1)e^2/\rho_D = 2(z+1)e^3(\pi/kT)^{1/2}$$
$$\times (N_e + \sum z^2 N_i{}^z)^{1/2}. \tag{11}$$

For $z=0$, i.e., the ionization of neutral atoms, this reduces to e^2/ρ_D, a result obtained before.[7] For the equilibrium between negative ions ($z=-1$) and atoms and electrons the correction vanishes, as it should since, e.g., in the reaction $\mathrm{H}^- \rightarrow \mathrm{H} + e$ there is no change in the number of free charges. If instead of the free energy the free enthalpy is employed,[8] $\Delta I_z{}^0$ becomes $3e^2/2\rho_D$. However, this corresponds to assuming an ionization equilibrium under constant pressure, which is somewhat unphysical since only total densities (specific volumes) and temperatures can be stated independently of high-density corrections, whereas the pressure is a derived quantity. In other words, the appropriate independent variables are temperature and specific volume, not temperature and pressure.

In the validity regime of the Debye theory, Eq. (11)

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[4] T. H. Berlin and E. W. Montroll, J. Chem. Phys. **20**, 75 (1952).

[5] D. P. Duclos and A. B. Cambel, Z. Naturforsch. **16a**, 711 (1961).

[6] J. C. Stewart and K. D. Pyatt, Air Force Special Weapons Center Technical Report No.-61-71, (unpublished), Vol. I. 1961

[7] O. Theimer, Z. Naturforsch. **12a**, 518 (1957).

[8] G. Traving, *Über die Theorie der Druckverbreiterung von Spektrallinien* (G. Braun, Karlsruhe, 1960).

always results in smaller corrections of the ionization energy than those obtained from a consideration of only nearest-neighbor interactions.[9] Clearly, this is even more true with respect to previously proposed relations in which a nearest-neighbor term is rather arbitrarily added to the Debye or plasma polarization term.[10] The difference of the numerical factor in this polarization term and the present result is due to an inconsistent application of the Debye theory[11] in reference 10. The nearest-neighbor term only comes in at extremely high densities[5,6,12] violating the inequality (8), which hardly ever occurs in laboratory plasmas.

The expression (11) for the lowering of the ionization potential is therefore the general result for single or multiple ionization in a Debye plasma. It is certainly valid in the limit of small $(\Delta I_i^z/kT)$, i.e., small ratios of electrostatic to thermal energies. Uncertainties in ΔI_i^z should at most be of the order $\Delta I_i^z(\Delta I_i^z/kT)$, unless at high densities other corrections come into play, so that the ions can no longer be treated as point charges.[13] Other than that, the relative error of the factor $\exp[-(I_i^z-\Delta I_i^z)/kT]$ in the Saha equation should normally be estimated by $(\Delta I_i^z/kT)^2$, which is a percent or less in almost all cases.

PARTITION FUNCTIONS

It is consistent with the model adopted in this paper to use as partition functions simply

$$Z_i^z=\sum g_{im}^z \exp(-E_{im}^z/kT), \tag{12}$$

where g_{im}^z and E_{im}^z are statistical weights and (unperturbed) excitation energies of the levels m of species i in ionization stage z. The sum should include all levels which fulfill $E_{im}^z \leq I_i^z-\Delta I_i^z$.

The uncertainty inherent in the cutoff procedure will be of the order of the last contributing term, e.g., for hydrogen $2n^2\exp[-I_i^0(1-1/n^2)/kT]\approx 2n^2 \times\exp(-I_i^0/kT)$, if n is the principal quantum number of the last state below the reduced ionization limit. Usually the excited states do not contribute much in Eq. (12), so that the relative error in the partition function $(\Delta Z_i^z/Z_i^z)$ is half as large as this last term. For other neutral atoms or ions on estimates $(n_i^z)^2\approx(z+1)^2 \times I_i^0/(I_i^z-E_{in}^z)\approx I_i^z/\Delta I_i^z$ and accordingly $|\Delta Z_i^z/Z_i^z| \approx(I_i^z/\Delta I_i^z)\exp(-I_i^z/kT)$. In plasmas of sufficiently high electron densities for local thermal equilibrium to exist, this uncertainty in the partition function will only very rarely exceed one-tenth of a percent. It seems, therefore, hardly justified to replace the straightforward cutoff by more involved methods of calculation,[10,14] which are moreover less consistent with the correction of the ionization energy in the Saha equation.

Another error in the partition function is introduced by using the unperturbed energies in Eq. (12). Since the linear Stark effect only spreads the levels without shifting their centers of gravity, the main effect will be due to quadratic Stark effect shifts or, in case of ion lines, also due to shifts caused by plasma polarization.[15] For levels below the reduced ionization limit, such shifts will, at most, be of the order of the difference between two levels whose principal quantum numbers differ by one unit, i.e., $\Delta E_{in}^z<E_{in+1}^z-E_{in}^z\approx 2I_i^z/n^3$. The relative change in the partition function is accordingly with $\exp(\Delta E_{in}^z/kT)\approx 1+\Delta E_{in}^z/kT$ given by

$$|\Delta Z_i^z/Z_i^z|\approx(I_i^z/kT)\ln(I_i^z/\Delta I_i^z)\exp(-I_i^z/kT),$$

using $2\sum 1/n\approx\ln n_{\max}{}^2$ with $n_{\max}{}^2\approx I_i^z/\Delta I_i^z$ and replacing $\exp(-E_{in}^z/kT)$ by $\exp(-I_i^z/kT)$ before the summation or integration. Also this uncertainty will almost always be well below one-tenth of a percent. In general, the over-all theoretical uncertainty in the partition functions will therefore be solely determined by uncertainties in ΔI_i^z, i.e., be of the same order as those in the exponential of the Saha equation.

PLASMA PRESSURE

While problems connected with ionization energies and partition functions (which would even diverge without the cutoff) have received wide attention, the related corrections in the equation of state for a high-density plasma are usually ignored. But in many experiments the total plasma pressure is known rather well and can therefore, in conjunction with the equation of state, be used for the determination of plasma densities and temperatures in place of one spectroscopic measurement.

Also the pressure follows from the free energy. It is given by $p=-\partial F_m/\partial V$, where V is the specific volume and F_m the free energy per unit mass. With $F_m=FV$, one therefore obtains for the correction to the ideal gas pressure, using Eq. (7),

$$\begin{aligned}\Delta p=-F_c-V\partial F_c/\partial V=\tfrac{1}{2}F_c\\ =-(e^2/6\rho_D)(N_e+\textstyle\sum z^2N_i^z)\\ =-\tfrac{1}{3}e^3(\pi/kT)^{1/2}(N_e+\textstyle\sum z^2N_i^z)^{3/2},\end{aligned} \tag{13}$$

since F_c is proportional to $V^{-3/2}$.

This is just the generalization for multiple ionization of the well-known result[8] of the Debye–Hückel theory for $z=1$, which can be shown to be the first order correction in a more systematic perturbation theory.[16] [However, the sign of the correction term in Eq. (76) in reference 16 seems to be wrong.] The decrease in the plasma pressure will probably never be more than a few

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[10] G. Ecker and W. Weizel, Ann. Physik **17**, 126 (1956).

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[13] D. P. Duclos, Arnold Engineering Development Center Report AEDC-TN-60-192, 1960 (unpublished); S. G. Brush, J. Nuclear Energy, Part C **4**, 287 (1962).

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[15] H. F. Berg, A. W. Ali, R. Lincke, and H. R. Griem, Phys. Rev. **125**, 199 (1962).

[16] H. S. Green, Nuclear Fusion **1**, 69 (1961).

percent under laboratory conditions, and the errors due to uncertainties in this correction should therefore again be of no importance.

LINE INTENSITIES

In laboratory plasmas, self-absorption and induced emission are usually negligible, except for resonance lines, or can easily be corrected for. Densities N_{im}^z in the appropriate upper states E_{im}^z follow from total densities N_i^z of species i in ionization stage z in case of local thermal equilibrium simply through

$$N_{im}^z = (g_{im}^z/Z_i^z)N_i^z \exp(-E_{im}^z/kT). \qquad (14)$$

The N_i^z can, in turn, be computed from the chemical composition using the appropriate Saha equations, if either total pressure or total density $(\sum N_i^z)$ are known.

For optically thin lines, the intensity is directly proportional to N_{im}^z, i.e., all the theoretical uncertainties entering in the calculation of N_{im}^z (mainly the errors in the reduction of the ionization energies) will be reflected in the calculated intensity. Another source of error is the use of the unperturbed energy E_{im}^z in the Boltzmann factor in Eq. (14). This can be rectified by taking energy levels measured for emission from the plasma. Since essentially only the upper levels are perturbed, the correction ΔE_{im}^z can be obtained from measured line shifts $\Delta\lambda_{im}^z$ as

$$\Delta E_{im}^z = -hc\Delta\lambda_{im}^z(\lambda_{im}^z)^{-2}. \qquad (15)$$

The corresponding relative correction $(\approx \Delta E_{im}^z/kT)$ of the Boltzmann factor is of the order 1% or less for typical conditions in dense plasmas. Often, it will also suffice to use calculated values[17] of $\Delta\lambda_{im}^z$.

Furthermore, line intensities are proportional to the fourth power of the frequency and to the square of the dipole matrix elements. The relative correction for the wavelength shift is obviously $-(4\Delta\lambda_{im}^z/\lambda_{im}^z)$. It may sometimes be as large as 1% and should then be included in the analysis. For allowed transitions, the relative reduction in the square of the dipole matrix elements can be estimated from standard quantum mechanical perturbation theory as $|\Delta E_{im}^z/(E_{in}^z-E_{im}^z)|$ where E_{in}^z is the energy of that neighboring level which gives the largest contribution to the quadratic Stark effect of the upper level. For the stronger lines this reduction will tend to be less than 1%, but in some instances a larger correction may be required. Whenever it becomes appreciable, forbidden lines will appear, and the actual change in the total intensity, including these forbidden components, would be overestimated by the above formula. Therefore the uncertainty in the dipole matrix elements will usually stay well within the error brackets of measurements or calculations of the quantities related to them, namely oscillator strengths and transition probabilities.

CONTINUUM INTENSITIES

The formulas for continuous emission from optically thin plasmas in local thermal equilibrium are best derived from the continuous absorption coefficients which, in principle, can be calculated from quantum mechanics, even though this has only been done for one-electron (bound or free) systems. The emission is then found by multiplication with the Kirchhoff–Planck function, correcting for stimulated emission. This expresses the emission in terms of the densities in the appropriate lower states.

To obtain the formulas for continuous emission in their usual form, one eliminates these densities through Boltzmann factors and the Saha equation. This results, e.g., for hydrogen or hydrogenic ions in the well-known[18] (except for the factor containing ΔI_i^z) formula

$$\epsilon_{i\nu}^z = \frac{8e^4h(z+1)}{3(3\pi)^{1/2}m_e^2c^3}\left(\frac{I_i^z}{kT}\right)^{1/2} \left[\bar{g}_f \exp\left(\frac{I_i^z}{m^2kT}\right) + 2\left(\frac{I_i^z}{kT}\right)\sum_{n=l}^{m}\frac{\bar{g}_b}{n^3}\exp\left(\frac{I_i^z}{n^2kT}\right)\right] \times N_eN_i^{z+1}\exp\left(\frac{-\Delta I_i^z}{kT}\right)\exp\left(-\frac{h\nu}{kT}\right). \qquad (16)$$

Here $\bar{g}_f$ and $\bar{g}_b$ are free-free and free-bound Gaunt factors, which are of order one and have been tabulated.[19] The principal quantum number l of the lowest contributing state is determined by the requirement $h\nu \leq I_i^z(1/l^2-1/m^2)$, where the value of $m\approx m+1$ is usually not at all critical. A logical choice is the principal quantum number of that state for which the Stark broadening becomes of the order of the difference between neighboring levels (Inglis-Teller limit[20]). There is little ambiguity in this method because, e.g., a change of m by one unit only means calling a certain feature near the series limit a line or a piece of the continuum, without any change of the total intensity in the corresponding frequency band. This follows (if also line intensities are expressed in terms of electron and ion densities) from the asymptotic behavior of line oscillator strengths.

For intermediate frequencies, which are only somewhat larger than $I_i^z[1/(m-1)^2-1/m^2]/h$, absorption edges will tend to be quite close to each other. Then the average intensity can be calculated by replacing the sum over n by an integral. This leads with

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[17] H. R. Griem, M. Baranger, A. C. Kolb, and G. Oertel, Phys. Rev. **125**, 177 (1962); see also H. R. Griem, Phys. Rev. **128**, 515 (1962).

[18] H. Maecker and T. Peters, Z. Physik **139**, 448 (1954); see also W. Finckelnburg and H. Maecker, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1957), Vol. 22; and W. Finckelnburg and T. Peters, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1957), Vol. 38.

[19] W. C. Karzas and R. Latter, Astrophys. J. Suppl. No. 55, 167 (1961).

[20] D. R. Inglis and E. Teller, Astrophys. J. **90**, 439 (1939).

$1/l^2 = h\nu/I_i^z + 1/m^2$ to

$$\epsilon_{i\nu}^z \approx \frac{8e^4 h(z+1)}{3(3\pi)^{1/2} m_e^2 c^3}\left(\frac{I_i^z}{kT}\right)^{1/2} \times \bar{g}_f \exp\left(\frac{I_i^z}{m^2 kT}\right) N_e N_i^{z+1} \exp\left(\frac{-\Delta I_i^z}{kT}\right), \quad (17)$$

i.e., the factor $\exp(-h\nu/kT)$ cancels out. In practice, Eq. (17) can also be applied for $h\nu \lesssim I_i^z[1/(m-1)^2 - 1/m^2]$, because the sum in Eq. (16) disappears and $\exp(-h\nu/kT)$ is then usually near unity.

The continuous spectrum of hydrogen or hydrogenic ions due to bremsstrahlung and recombination radiation is therefore essentially flat for frequencies that are smaller or at least not much larger than $I_i^z[1/(m-1)^2 - 1/m^2]/h$. For this reason, theoretical uncertainties analogous to those encountered in case of line radiation will mostly cancel here. The same should be true for the case of large frequencies, where Eq. (16) must be used. The lower bound-state wave functions enter here, but as for the lines, errors due to perturbations of these states tend to be negligible.

To crudely evaluate the remaining uncertainities, one may consider the effects of Debye shielding. Semiclassical arguments indicate that the relevant distances from the nuclei are of the order $r_{i\nu}^z \approx 4^{1/3}(z+1)^{-1}(I_i^z/h\nu)^{2/3}a_0$, where a_0 is the Bohr radius of the hydrogen atom. [One simply equates $m_e v^2/r$ with $(z+1)e^2/r^2$ and assumes that the emitted frequencies $\omega = 2\pi\nu$ are of the order of the angular velocity v/r of the radiating electron at the near point.] Whenever $r_{i\nu}^z$ is smaller than the Debye radius ρ_D by some factor, the relative reduction in the free-free radiation is thus estimated by $2r_{i\nu}^z/\rho_D$, because this radiation is proportional to the square of the effective charge at the distance $r_{i\nu}^z$ from the nucleus. (Only the free-free radiation is important at low frequencies, i.e., large $r_{i\nu}^z$.) Frequencies of interest in plasma spectroscopy are generally larger than $I_i^z/10h$, and $r_{i\nu}^z$ will therefore usually be smaller than $4^{1/3}(z+1)^{-1}10^{2/3}a_0$, which is less than $4(z+1)^{-1}\times 10^{-8}$ cm or two or more orders of magnitude smaller than typical Debye radii in dense laboratory plasmas. Only in extreme cases, this or an equivalent correction will be necessary. Then classical theory is usually applicable, and the effects due to electron-electron correlations can be calculated in a consistent manner.[21]

Normally the formulas described in this section will properly predict the continua from one-electron systems, except for the details in the neighborhood of absorption edges. The choice of the reduction in the series limit I_i^z/m^2 is not critical and the formulas will often also be applicable to more-electron systems if the contributing levels are nearly hydrogenic. Finally, it should be emphasized that the apparent reduction in the series limit due to the merging of lines has no logical connection with the reduction in the ionization energy from the Coulomb interaction term in the thermodynamic potential. The latter is generally the most important high-density correction in Eqs. (16) and (17), even though it is usually smaller and never larger than the reduction of the series limit.[22]

The appearance of the factor $\exp(-\Delta I_i^z/kT)$ in the continuum formulas can only be avoided by an *ad hoc* assumption.[23] That it must be included, can also be seen from the fact that the emission at frequency ν is proportional to the density of electrons in a velocity interval centered around v_n which is determined by the photoelectric equation $\frac{1}{2}m_e v_n^2 + E_n' = h\nu$. Here E_n', the binding energy of the electron in the lower state, is given by $I_i^z/n^2 - \Delta I_i^z$ and therefore $\frac{1}{2}m_e v_n^2$ by $h\nu - I_i^z/n^2 + \Delta I_i^z$. Since the number of electrons in the proper velocity range is proportional to $\exp(-\frac{1}{2}m v_n^2/kT)$, one immediately obtains the exponential factors in the continuum formula, including the factor $\exp(-\Delta I_i^z/kT)$. If this correction factor is inserted, and if Eq. (11) is used for ΔI_i^z, the precision in calculated continuum intensities will be comparable to that obtainable for total line intensities, again apart from errors stemming from uncertainties in atomic or ionic wave functions in case of systems other than hydrogen, ionized helium, etc.

STARK PROFILES

The profiles of spectral lines emitted by dense plasmas in local thermal equilibrium are strongly influenced by the electric fields produced by electrons and ions surrounding the emitting atoms or ions. The theory of this Stark broadening has recently been developed to a stage[17,24] where linewidths and line shifts can be calculated to a precision of 10 to 20% (in terms of the widths), assuming that one knows the electron density and that no multiple ionization exists. The extension to multiple ionization is trivial,[1] but some discussion of the meaning of the term "electron density" is indicated.

If the Unsöld correction,[9] i.e., the nearest-neighbor approximation, or still larger reductions of the ionization potential[10] were used to calculate electron densities, e.g., from known total pressures and temperatures, one would clearly overestimate the Stark broadening. This follows because no independent perturbing charge is generated in the plasma if an electron just passes from one atom to the nearest ion. This only happens when the electron has enough energy to escape the potential well

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of any individual ion, which occurs at the reduced ionization energy obtained from the Debye theory.

Also for Stark-broadening calculations Eq. (11) should therefore be used to correct the Saha equation. However, some uncertainties will be introduced by the contribution of highly excited atoms or ions, which will roughly increase the number of broadening electronic charges by one unit for each excited state with a Bohr-radius larger than the mean distance $N_e^{-1/3}$ between electrons. The effective electron density is thereby increased by a factor $1+\sum N_{in}^z/N_e \approx 1+\sum 2n^2(N_i^z/Z_i^zN_e) \times\exp(-E_{in}^z/kT)$. The sum should be extended from $n_{\min}\approx[I_i^z/(z+1)e^2N_e^{1/3}]^{1/2}$ to $n_{\max}\approx[I_i^z/\Delta I_i^z]$. This correction is usually only a few percent or less and therefore barely significant in view of the other errors in line broadening calculations.

Most high-density corrections are already included in the Stark broadening theory.[24] In the treatment of the quasi-static broadening by slowly moving ions, field-strength distribution functions[25,26] are employed that have been corrected for ion-ion correlations and Debye shielding by electrons. And for the electron impact broadening of overlapping lines a logarithmic cutoff is introduced at or near the Debye radius which, as in the case of ion broadening, only accounts for shielding by electrons, i.e., the term $\sum z^2N_i^z$ in Eq. (3) is dropped. Only in case of the impact broadening of isolated lines will high-density corrections usually be negligible, since here distant collisions do not contribute anyway.

OPTICAL REFRACTIVITY

Besides from absolute line and continuum intensities or from the profiles of Stark broadened lines, electron densities can be determined from measurements of the refractive index of a plasma.[27–29] At small fractional ionization the contribution from ground-state atoms or ions must be subtracted, which can be done empirically since the wavelength dependence of this contribution is quite different from that of the electrons. But already at a degree of ionization of 10% electrons begin to dominate.

In the frequency range of interest for plasma spectroscopy and for the electron densities occurring in laboratory experiments, the refractive index n deviates only very slightly from unity, and one can simply use

$$n-1=-N_e'e^2/2\pi m_e\nu^2 \tag{18}$$

for the electron contribution. Also here it should be investigated whether one is consistent in identifying the value of N_e' in Eq. (18) with that occurring in the corrected Saha equation. Obviously, some of the bound electrons in high-lying excited states will be practically indistinguishable from the free electrons. One should therefore set

$$N_e'=N_e+\sum N_{in}^z, \tag{19}$$

extending the sum over all levels fulfilling $I_i^z-\Delta I_i^z-E_{in}^z<h\nu$. For hydrogenic systems, this correction will be of the order

$$\begin{aligned}\sum N_{in}^z &\approx (N_i^z/Z_i^z)\sum 2n^2\exp(-E_{in}^z/kT)\approx(N_i^z/Z_i^z)\\ &\quad\times\exp[-(I_i^z-\Delta I_i^z)/kT]\sum 2n^2\approx\tfrac{2}{3}(N_i^z/Z_i^z)\\ &\quad\times\exp[-(I_i^z-\Delta I_i^z)/kT](n_{\max}^3-n_{\min}^3),\end{aligned}$$

neglecting the splitting between the relevant levels. The principal quantum number of the lowest contributing term is $n_{\min}\approx[I_i^z/(h\nu+\Delta I_i^z)]^{1/2}$, and $n_{\max}$ must be chosen as $n_{\max}\approx[I_i^z/\Delta I_i^z]^{1/2}$ to avoid counting the same electron twice. One therefore has finally

$$N_e'=N_e+\tfrac{2}{3}\sum\left[\left(\frac{I_i^z}{\Delta I_i^z}\right)^{3/2}-\left(\frac{I_i^z}{h\nu+\Delta I_i^z}\right)^{3/2}\right]\times\left(\frac{N_i^z}{Z_i^z}\right)\exp\left(-\frac{I_i^z-\Delta I_i^z}{kT}\right), \tag{20}$$

where the sum is now only over the various chemical species and ionization stages whose total densities are N_i^z. Normally, the correction in the electron density will be in or below the percent range, and uncertainties due to errors in this correction should therefore be negligible even compared to the high inherent precision of this method.

Another correction stems from the remaining interactions between the electrons. In the classical theory for bound electrons the term ν^2 in Eq. (18) is just replaced by $\nu^2-\nu_0^2$, where ν_0 is the resonance frequency of the system. Similarly, these interactions can easily be accounted for by subtracting the square of the Langmuir plasma frequency. However, this correction is just compensated by the Lorentz polarization correction,[30] and the deviation of the refractive index from unity becomes simply

$$n-1=-\frac{N_ee^2}{2\pi m_e\nu^2}\left\{1+\tfrac{2}{3}\sum\left[\left(\frac{I_i^z}{\Delta I_i^z}\right)^{3/2}-\left(\frac{I_i^z}{h\nu+\Delta I_i^z}\right)^{3/2}\right]\times\left(\frac{N_i^z}{Z_i^zN_e}\right)\exp\left(-\frac{I_i^z-\Delta I_i^z}{kT}\right)\right\}. \tag{21}$$

The correction term is almost always only a few percent or less. Then the accuracy of this formula will be better than a tenth of a percent as long as $|n-1|$ itself is below 10^{-3}, which is generally the case at optical frequencies. Even though Eq. (20) was only derived for hydrogen

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and other one-electron systems, it may also be used for other species as long as only states with large principal quantum numbers contribute significantly to the correction term in Eq. (21), which is the normal situation. The dependence of $n-1$ on the applied frequency is in dense plasmas usually not significantly changed by the influence of magnetic fields. Their various effects have been subject of intense studies in connection with the propagation of electromagnetic waves in plasmas.[30]

SUMMARY

It is observed that temperature, mass density, and chemical composition are the appropriate independent variables for the thermodynamic description of a collision-dominated plasma in local thermal equilibrium, and that the Debye approximation can be used at plasma densities occurring in laboratory experiments. The reduction in the ionization potential ΔI_i^0 of neutral atoms is therefore $\Delta I_i^0=e^2/\rho_D$ and that of z-times ionized systems $\Delta I_i^z=(z+1)e^2/\rho_D$ with the Debye radius $\rho_D=[kT/4\pi(N_e+\sum z^2N_i^z)]^{1/2}$. If a simple cutoff consistent with this value of ΔI_i^z is employed in the partition functions and if a pressure correction

$$\Delta p=-\tfrac{1}{6}(e^2/\rho_D)(N_e+\sum z^2N_i^z)$$

is introduced into the ideal gas law, then the remaining uncertainties in calculated densities N_e and N_i^z due to errors in these high-density corrections are estimated to be of the order of $(\Delta I_i^z/kT)^2$, which is typically below 1%.

On the other hand, if calculated line intensities are corrected empirically for the dependence on the fourth power of the frequency and on the Boltzmann factor, they will only be uncertain by about $|\Delta E_{im}^z/(E_{in}^z-E_{im}^z)|$. Here ΔE_{im}^m is the average Stark shift of the upper level and E_{in}^z the energy of that level which contributes most to the shift. For the stronger lines also this uncertainty is usually below 1%, to which one has to add the error in the transition probability for the unperturbed line.

The situation for continuum intensities is similar, provided one multiplies the usual expression by a factor $\exp(-\Delta I_i^z/kT)$ and uses in addition the Inglis–Teller relation for the depression of the series limits. Then, again apart from uncertainties in the atomic theory for other than one-electron systems, the remaining errors due to high-density corrections should be of the order $4^{1/3}(z+1)^{-1}(I_i^z/h\nu)^{2/3}a_0/\rho_D$, which is once more only 1% or less for frequencies of interest in plasma spectroscopy. Somewhat larger uncertainties must be expected in the neighborhood of absorption edges or in situations where negative-ion or even molecular continua are important.

Stark-broadening calculations have theoretical errors of the order of 10% for hydrogen and hydrogenic-ion lines as well as for many other lines, and contain most of the high-density corrections. Occasionally, another correction should be made to account for the additional broadening by highly excited atoms or ions. Then uncertainties caused by the difficulty to clearly distinguish between free and bound electrons are negligible, provided the reduction ΔI_i^z in the ionization energies is used consistently.

The interferometric measurement of the optical refractivity is capable of much higher precision for the determination of electron densities. Here errors in the theory stay well below 1% if corrections for the contribution of highly excited atoms or ions are applied.

In conclusion, theoretical errors entering quantitative relationships in plasma spectroscopy can be kept below a percent, as far as they stem from uncertainties in the various high-density corrections. Since errors in atomic theory tend to be considerably larger, local thermal equilibrium plasmas are therefore very useful for precision measurements of atomic parameters, mainly oscillator strengths and damping constants, and also as absolute intensity standards if gases with known atomic properties are employed.

To estimate the errors introduced by the only approximate validity of the assumption of local thermal equilibrium, one can use as a guide the results of a recent calculation for hydrogen.[31] Here densities in excited states were calculated relative to an assumed Maxwell–Boltzmann distribution of free electrons, considering all collisional processes involving electrons and also radiative recombination and decay. But radiative excitation and ionization were left out, as is appropriate for an optically thin plasma. The principal conclusion is that at least partial thermal equilibrium (for the higher lying excited states) can still be expected at surprisingly low electron densities. Moreover, deviations of the populations of lower lying states from thermal equilibrium values will often be considerably smaller than indicated by such calculations for optically thin plasmas, since radiation from these levels may actually be trapped. Then the radiation field approaches that of a blackbody in the relevant frequency bands, and one may well have local thermal equilibrium throughout.

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