Plasma Spectroscopy

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Preface

This book is meant as a reference source for spectroscopic research in experimental plasma physics and the physics of stellar atmospheres. It may also serve as a text for a special graduate course in physics or astronomy, as it contains an introduction to the general theory of quantitative spectroscopy, numerical results of this theory and their derivation, and a description of experimental techniques and results. Applications of theoretical and experimental methods to the determination of plasma conditions or atomic parameters are equally stressed. The extensive tabulations of oscillator strengths, continuum emission coefficients, and line broadening parameters should aid in laboratory experiments or quantitative analyses of stellar spectra. For ease of reference, the tables are grouped together after the text. The problems attached to the fifteen chapters are designed as guides to a quantitative understanding of methods and applications; the solutions appear at the end of the book.

Quantitative spectroscopic techniques can be applied to many problems in laboratory plasma physics, astronomy, and related fields. Most of the methods require a knowledge of atomic spectroscopy, which has been treated in a number of books (see the bibliography below). Accordingly, the reader of this book is assumed to have sufficient familiarity with the theory of atomic spectra. Furthermore, the reader should have been exposed to quantum-mechanical perturbation theory and to certain aspects of statistical mechanics.

Although the original literature on plasma spectroscopy has developed to an impressive size, no comprehensive and critical review has been attempted heretofore. For this reason, there will without doubt be omissions and errors in this book, especially in the tabulated material. (The author would be grateful if such defects were pointed out to him.) The reader will also notice that in some areas much remains to be done. Here the hope is that careful measurements and theoretical investigations can be stimulated to remedy this situation in the future.

The author was introduced to this challenging subject by his teachers, W. Lochte-Holtgreven and A. Unsöld, at Kiel University. The present book has grown out of work done by the plasma physics groups at the University of Maryland and the U.S. Naval Research Laboratory for the last six or seven years. Thanks are due many colleagues at both institutions and several students for numerous suggestions and valuable criticism. Mrs. Joan Haugen painstakingly typed the manuscript, and Mrs. Christel Siahatgar prepared most of the extensive tables. Very special thanks go to these two ladies and to the author's wife for their help, patience, and encouragement.

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Contents

Classical Radiation Theory

1

Most of the electromagnetic radiation emitted by gaseous plasmas stems from atomic processes. Plasma spectroscopy is therefore based on atomic and plasma physics and requires mainly an understanding of quantum theory and the statistical mechanics of ionized gases. In both fields the basic theory is well known. However, much detailed work remains to be done to elucidate the nature of numerous approximate treatments and to assess the ranges of applicability and the degree of approximation that has been achieved.

Because of the merging of different branches of physics, an unusually close interplay between theory and experiment is mandatory. In this respect, plasma spectroscopy tends to follow the example of astrophysics. Since the development of stars is decisively influenced by radiative energy transfer and since electromagnetic radiation is by far the most important carrier of information available to them, astronomers have developed applications of the theory of radiation to these two problems, which predominate in plasma spectroscopy as well.

Astronomers have felt compelled to resume work on applications of quantum theory to atomic physics; plasma spectroscopists also must contribute to the improvement of our knowledge and command of atomic radiation theory. Besides methods for the determination of plasma parameters and the investigation of radiative transfer and energy loss problems, a third main objective of plasma spectroscopy is therefore to help in the establishment of a reliable system of atomic parameters.

The difficulties in applications of quantum mechanics are hardly ever of a basic nature. However, experiments are indispensable because precise calculations are often practically impossible, even with modern electronic computers, or because no reliable error estimate can be made for a completed calculation. Both to see more clearly the remaining problems and also to appreciate the power and reliability of plasma spectroscopy as a tool, it is best to follow the development of radiation theory, before the combination with statistical mechanics and more specific applications are taken up.

1-1 Electromagnetic equations

The rationalized mks system of units is used unless specifically stated otherwise. (However, working equations will usually be written in such a way that cgs units can be used as well.) The vacuum values of dielectric constant and magnetic permeability in the mks system are $\epsilon_0 = (4\pi \times 9 \times 10^9)^{-1} = 8.85 \times 10^{-12}$ C^2 N^{-1} m^{-2} and $\mu_0 = 4\pi \times 10^{-7} = 12.57 \times 10^{-7}$ W A^{-1} m^{-1}. The newton is the unit of force (1 N = 10^5 dyn); the weber is the unit of magnetic flux (1 W m^{-2} = 10^4 G). The units of charge and current are coulomb and ampere, respectively, and one also has $(\epsilon_0\mu_0)^{-1/2} = c \approx 3 \times 10^8$ m/sec.

Maxwell's equations

$$\operatorname{curl} \mathbf{E} + \dot{\mathbf{B}} = 0 \tag{1-1a}$$

$$\operatorname{div} \mathbf{B} = 0 \tag{1-1b}$$

$$\operatorname{curl} \mathbf{H} - \dot{\mathbf{D}} = \mathbf{j} \tag{1-1c}$$

$$\operatorname{div} \mathbf{D} = \rho \tag{1-1d}$$

and Lorentz's force law

$$\mathbf{F} = \rho\mathbf{E} + \mathbf{j} \times \mathbf{B} \tag{1-2}$$

form the basis of classical radiation theory. If ρ is the density of all charges, one has simply (in vacuum)

$$\mathbf{B} = \mu_0 \mathbf{H} \tag{1-3a}$$

$$\mathbf{D} = \epsilon_0 \mathbf{E} \tag{1-3b}$$

Furthermore, the current density is for charges of one sign

$$\mathbf{j} = \rho \mathbf{v} \tag{1-4}$$

where $\mathbf{v}$ is the mean velocity.

It is convenient to introduce vector and scalar potentials through

$$\mathbf{B} = \text{curl}\, \mathbf{A} \tag{1-5a}$$

$$\mathbf{E} = -\,\text{grad}\, \varphi - \dot{\mathbf{A}} \tag{1-5b}$$

This choice automatically fulfills the first two of Maxwell's equations. In addition, one postulates the foll6wing Lorentz condition

$$\text{div}\, \mathbf{A} = -\epsilon_0 \mu_0 \dot{\varphi} \tag{1-6}$$

Substitution into the last two of Maxwell's equations, with curl curl $\mathbf{A}$ = grad div $\mathbf{A} - \nabla^2 \mathbf{A}$ (in cartesian coordinates), yields

$$\frac{1}{c^2} \ddot{\mathbf{A}} - \nabla^2 \mathbf{A} = \mu_0 \rho \mathbf{v} \tag{1-7a}$$

$$\frac{1}{c^2} \ddot{\varphi} - \nabla^2 \varphi = \frac{1}{\epsilon_0} \rho \tag{1-7b}$$

A special solution of these inhomogeneous wave equations is obtained from a generalization of the Coulomb potential as

$$\mathbf{A}(\mathbf{r}'',t) = \frac{\mu_0}{4\pi} \int \frac{\rho' \mathbf{v}'}{|\mathbf{r}'' - \mathbf{r}'|}\, d\tau' \tag{1-8a}$$

$$\varphi(\mathbf{r}'',t) = \frac{1}{4\pi\epsilon_0} \int \frac{\rho'}{|\mathbf{r}'' - \mathbf{r}'|}\, d\tau' \tag{1-8b}$$

where ρ', $\mathbf{v}'$ are to be taken at $\mathbf{r}'$ and $t' = t - |\mathbf{r}'' - \mathbf{r}'|/c$, the integration being over all points characterized by $\mathbf{r}'$. That the "retarded" potentials in Eqs. (1-8a) and (1-8b) obey the wave equations (1-7a) and (1-7b) can be seen as follows: Any function of $t' = t - |\mathbf{r}'' - \mathbf{r}'|/c$ divided by $|\mathbf{r}'' - \mathbf{r}'|$ presents a spherical wave emerging from $\mathbf{r}'$, that is, is a solution of the homogeneous wave equation for $\mathbf{r}'' \neq \mathbf{r}'$. On substitution of the potentials into the wave equations, therefore, only points $\mathbf{r}'$ near $\mathbf{r}''$ contribute to the left-hand side. The remaining integrals over a small sphere with radius r surrounding $\mathbf{r}''$ are of the order r^2 (times the local charge or current density) and therefore their second spatial derivatives are of the order 1. But the second time derivatives divided by c^2 vanish as

$$\frac{\omega^2 r^2}{c^2} = \left(\frac{2\pi r}{\lambda}\right)^2$$

where ω is a frequency characterizing the time variations of ρ or $\rho\mathbf{v}$, and λ is the wavelength of the corresponding radiation. Also, $\rho'(\mathbf{r}',t')$ and $\mathbf{v}'(\mathbf{r}',t')$ approach $\rho(\mathbf{r}'',t)$ and $\mathbf{v}(\mathbf{r}'',t)$, so that the remaining integrals become just the well-known static solutions which indeed satisfy Eqs. (1-7*a*) and (1-7*b*) without the terms involving the time derivative. That the potentials also obey Lorentz's condition [Eq. (1-6)] follows simply from the equation of continuity:

$$\operatorname{div}(\rho\mathbf{v}) + \dot{\rho} = 0 \tag{1-9}$$

The retarded potentials are, of course, special solutions of the wave equations. To obtain the general solution, solutions of the homogeneous wave equations must be added. For the present purposes, one can assume that only the vector potential contains such solutions obeying the homogeneous wave equation and the simplified Lorentz condition, namely,

$$\frac{1}{c^2}\ddot{\mathbf{A}} - \nabla^2\mathbf{A} = 0 \tag{1-10a}$$

$$\operatorname{div}\mathbf{A} = 0 \tag{1-10b}$$

The corresponding fields $\mathbf{B} = \operatorname{curl}\mathbf{A}$ and $\mathbf{E} = -\dot{\mathbf{A}}$ represent transverse waves, and the required solutions of the inhomogeneous wave equations are therefore superpositions of transverse waves to the fields derived from the retarded potentials in Eqs. (1-8*a*) and (1-8*b*).

1-2 Fields from moving point charges

In spectroscopy one is concerned with radiation whose wavelength is very much greater than the classical electron radius

$$r_0 = \frac{e^2}{4\pi\epsilon_0 mc^2} \approx 2.82 \times 10^{-5}\ \text{Å}$$

Therefore the structure of the electron is of no consequence; i.e., it can always be replaced by a point charge with total charge $e = \int \rho\, d\tau$ and mass m. Accordingly, the objective is to express fields and potentials in terms of total charge e and velocity $\mathbf{v}$ of the electron and then to see under which conditions electromagnetic radiation is produced. For this purpose, one needs to study the fields produced by moving or, more precisely, by accelerated point charges.

Some care must be taken in the evaluation of the retarded potentials produced by such point charges. In general, the integral $\int \rho' \, d\tau'$ does not equal the total charge, because the retarded times are different for different volume elements. One may first consider the contribution to the total charge e for all points that are between radii r and $r + dr$, measured from the point at which one wants to know the potentials. To the charge $\rho'(\mathbf{r}',t') \, d\tau' = \rho' \, d\sigma \, dr$ actually present at time t' one must add a term that compensates for the difference of the charges streaming through the elements of surface $d\sigma$ at r and $r + dr$, respectively, in the times $t - t' = r/c$ and $t - t' - dt' = (r + dr)/c$. If $\mathbf{r}$ is the vector from the field point to the source point, this difference is $-\rho'\mathbf{v}' \cdot \mathbf{r} \, d\sigma \, dr/cr$. That is,

$$de = \left(1 + \frac{\mathbf{v}' \cdot \mathbf{r}}{cr}\right) \rho' \, d\sigma \, dr$$

is the charge that must be assigned to $d\tau'$ in order to account for the total charge. Transformation from the volume element $d\tau' = d\sigma \, dr$ to the element of charge de in Eqs. (1-8a) and (1-8b) then yields Lienard's and Wiechert's retarded potentials for point charges,

$$\mathbf{A}(t) = \frac{\mu_0}{4\pi} \frac{e\mathbf{v}}{r + \mathbf{r} \cdot \mathbf{v}/c}\bigg|_{t-r/c} \qquad (1\text{-}11a)$$

$$\varphi\,(t) = \frac{1}{4\pi\epsilon_0} \frac{e}{r + \mathbf{r} \cdot \mathbf{v}/c}\bigg|_{t-r/c} \qquad (1\text{-}11b)$$

Here $\mathbf{v}$, $\mathbf{r}$, and $r = |\mathbf{r}|$ must all be taken at the retarded time $t - r/c$.

The fields produced by a moving point charge follow from Eqs. (1-5a) and (1-5b), finally, as

$$\mathbf{E} = -\frac{e}{4\pi\epsilon_0} \left\{ \left(1 - \frac{v^2}{c^2}\right)\left(\mathbf{r} + \frac{\mathbf{v}r}{c}\right) - \frac{1}{c^2} \mathbf{r} \times \left[\left(\mathbf{r} + \frac{\mathbf{v}r}{c}\right) \times \dot{\mathbf{v}}\right]\right\} \left(r + \frac{\mathbf{v} \cdot \mathbf{r}}{c}\right)^{-3} \qquad (1\text{-}12a)$$

$$\mathbf{B} = \frac{\mathbf{E} \times \mathbf{r}}{rc} \qquad (1\text{-}12b)$$

(For details of the derivation, see, for example, Heitler's book listed in the Bibliography at the end of the chapter.) At great distances only the term containing the acceleration $\dot{\mathbf{v}}$ is significant, because it decays as $1/r$, as compared with the $1/r^2$ dependence of the first term. The magnetic field is always transverse, but the electric field becomes purely transverse only at great distances, i.e., in the wave zone. There the Poynting vector is proportional to $\mathbf{r}/r^3$, and the energy flux (radiation) is the same through any surface enclosing the charge.

1-3 Emission of dipole radiation

The fields from a system of point charges are simply obtained from the superposition of fields produced by single charges, because Maxwell's equations are linear. Usually one is interested in the radiation from a small number of closely spaced point charges e_k that are positioned at $\mathbf{r}_k = \bar{\mathbf{r}} + \mathbf{x}_k$, where $\bar{\mathbf{r}}$ is a vector denoting the position of the center of charge and $\mathbf{x}_k$ the vector describing the displacement of charge k from this center. Assuming $|\bar{\mathbf{r}}| \gg |\mathbf{x}_k|$ and $v/c \ll 1$, one then derives from Eqs. $(1=12a)$ and $(1=12b)$ for the part of the field that vanishes only as $1/r$

$$\mathbf{E} = \frac{1}{4\pi\epsilon_0}\,\bar{\mathbf{r}} \times \frac{\bar{\mathbf{r}} \times \Sigma e_k \ddot{\mathbf{x}}_k}{c^2|\bar{\mathbf{r}}|^3} \tag{1-13a}$$

$$\mathbf{B} = \frac{1}{4\pi\epsilon_0}\,\frac{\bar{\mathbf{r}} \times \Sigma e_k \ddot{\mathbf{x}}_k}{c^3|\bar{\mathbf{r}}|^2} \tag{1-13b}$$

These fields are therefore proportional to the second time derivative of the electric dipole moment $\Sigma e_k \mathbf{x}_k$ associated with the system of charges. If the differences in the retarded times for the various charges are taken into account and all quantities are calculated to the first order in v/c, one obtains an additional term that is proportional to the quadrupole moment, etc. But in plasma spectroscopy one can practically always neglect these terms because emitting electrons only very rarely approach relativistic energies.

The Poynting vector corresponding to the dipole radiation field is

$$\begin{aligned}\mathbf{S} = \mathbf{E} \times \mathbf{H} &= \frac{-1}{(4\pi)^2\epsilon_0}\,\frac{|\bar{\mathbf{r}} \times \Sigma e_k \ddot{\mathbf{x}}_k|^2\bar{\mathbf{r}}}{c^3|\bar{\mathbf{r}}|^5} \\ &= \frac{-1}{(4\pi)^2\epsilon_0}\,\frac{|\Sigma e_k \ddot{\mathbf{x}}_k|^2\bar{\mathbf{r}}\sin^2\theta}{c^3|\bar{\mathbf{r}}|^3}\end{aligned} \tag{1-14}$$

where θ is the angle between the direction of observation and the second derivative of the dipole moment. Since $\bar{\mathbf{r}}$ is a vector pointing toward the system of charges, the minus sign indicates that the Poynting vector is in a direction away from the system, which is as it should be. Integration of $\mathbf{S}$ over a closed surface containing all charges k finally yields the radiated power

$$P_e = \frac{1}{6\pi\epsilon_0 c^3}\,|\Sigma e_k \ddot{\mathbf{x}}_k|^2 \tag{1-15}$$

which is the quantity of primary interest in quantitative spectroscopy.

The harmonic oscillator with $\Sigma e_k \mathbf{x}_k = e\mathbf{x}(t) = e\mathbf{x}_0 \cos \omega_0 t$ is the simplest model of a radiating dipole. It emits an average power

$$P_e = \frac{e^2\omega_0^4}{6\pi\epsilon_0 c^3}\overline{|x(t)|^2} = \frac{e^2\omega_0^4}{12\pi\epsilon_0 c^3}|\mathbf{x}_0|^2 \tag{1-16}$$

According to Eq. (1-13a), the electric vector is at right angles to the direction of observation and in the plane containing this direction and that of $\mathbf{x}_0$. The directional dependence of the emitted intensity is given by the factor $\sin^2\theta$ in Eq. (1-14), with θ now being the angle between $\mathbf{x}_0$ and the radius vector. (Note also the very strong frequency dependence, which suggests that short-wavelength line radiation will be rather strong.)

1-4 Absorption by harmonic oscillators

Harmonic oscillators not only emit electromagnetic radiation but also may extract energy from incident waves. If the wave field is decomposed into Fourier components, the equation of motion for the oscillator becomes

$$\ddot{\mathbf{x}} + \omega_0^2\mathbf{x} = \frac{e}{m}\mathbf{E}_\omega \cos(\omega t + \delta_\omega) \tag{1-17}$$

where δ_ω is the phase of the wave. Assuming that at $t = 0$ only the free oscillation is excited, one obtains the solution

$$\mathbf{x}(t) = \frac{e}{m}\mathbf{E}_\omega \frac{\cos(\omega t + \delta_\omega) - \cos(\omega_0 t + \delta_\omega)}{\omega_0^2 - \omega^2} + \mathbf{x}_0 \sin(\omega_0 t + \varphi) \tag{1-18}$$

The absorbed power follows from the rate of work done on the harmonic oscillator as

$$\begin{aligned} dP_a &= e\dot{\mathbf{x}}(t)\cdot\mathbf{E}_\omega \cos(\omega t + \delta_\omega) \\ &= \frac{e^2}{m}E_\omega^2\left[-\frac{\omega}{\omega_0^2-\omega^2}\sin(\omega t + \delta_\omega) + \frac{\omega_0}{\omega_0^2-\omega^2}\sin(\omega_0 t + \delta_\omega)\right] \\ &\quad \times \cos(\omega t + \delta_\omega) + e\mathbf{E}_\omega\cdot\mathbf{x}_0\omega_0\cos(\omega_0 t + \varphi)\cos(\omega t + \delta_\omega) \end{aligned} \tag{1-19}$$

In the time average, the term with $\omega/(\omega_0^2 - \omega^2)$ vanishes. If the phases δ_ω in the incoming light wave are random, the last term also disappears. Using well-known trigonometric formulas and again assuming the phases δ_ω to be random, the average absorbed power thus becomes

$$\begin{aligned} d\bar{P}_a &= \frac{e^2}{2m}E_\omega^2\frac{\omega_0}{\omega_0^2-\omega^2}\frac{1}{\tau}\int_0^\tau \sin[(\omega_0-\omega)t]\,dt \\ &= \frac{e^2}{2m}E_\omega^2\frac{\omega_0}{\omega_0+\omega}\frac{1}{\tau}\frac{1-\cos[(\omega_0-\omega)\tau]}{(\omega_0-\omega)^2} \end{aligned} \tag{1-20}$$