Wilkerson, Phys. Rev. A 3, 16 (1971).
[9]M. H. Miller, R. A. Roig, and R. D. Bengtson, Phys. Rev. A 4, 1709 (1971).
[10]A. G. Shenstone, Proc. Phys. Soc. Lond. A 267, 293 (1963).
[11]C. E. Moore, Natl. Bur. Std., Tech. Note No. 36 (U.S. GPO, Washington, D. C., 1945).
[12]G. K. Oertel and L. P. Shomo, Astrophys. J. Suppl. Ser. 16, 175 (1968).
[13]H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Springer, Berlin, 1957).
[14]D. R. Bates and A. Damgaard, Philos. Trans. R. Soc. Lond. A 242, 101 (1949).
[15]K. L. Andrew and K. W. Meissner, J. Opt. Soc. Am. 49, 146 (1959); and C. J. Humphreys, J. Opt. Soc. Am. 54, 1134 (1964).
[16]C. H. Corliss and W. R. Bozman, U.S. Natl. Bur. Std., Monograph No. 53 (U.S. GPO, Washington, D. C., 1962).
[17]M. Z. Khokhlov, Izv. Akad. Nuak SSSR Krym. Astrofiz. Obs. 29, 131 (1963).
[18]I. Y. Y. Slavenas, Opt. Spektrosk. 16, 390 (1964) [Opt. Spectrosc. 16, 214 (1964)].

PHYSICAL REVIEW A VOLUME 7, NUMBER 4 APRIL 1973

Local Thermodynamic Equilibrium of Autoionizing Copper Levels

Roger Assous
Laboratoire des Recherches Physiques Faculté des Sciences, Tour 22, 4 place Jussieu 75230 Paris, Cedex 05, France
(Received 11 September 1972)

The measurements of Allen on autoionized line intensities of copper were carried out again with reference to the electron density N_e of the plasma. The measurements here show a notable deviation of autoionizing-level populations relative to Boltzmann's law, but a much more severe disagreement for an adjacent nonautoionizing level. We encounter a paradoxical situation where Saha's law is assumed for the autoionizing levels when N_e is small, following autoionization theory, but where a deviation from it is observed when N_e is notable, i.e., in the range of low-current atmospheric arcs. Evaluation of the various usual contributions to the population variations cannot account for the observed curves. Other processes must be included in the calculation.

If local thermodynamic equilibrium (LTE) conditions have been largely studied for levels belonging to series converging toward the first ionization potential E_∞^{I} of atoms,[1,2] little is known, as regards complex atoms, about levels lying between the levels E_∞^n of the fundamental configurations of ion in its first degree of ionization. Criteria for LTE conditions are not identical for autoionizing levels which interact with the continuum and for nonautoionizing levels for which this interaction does not exist. More particularly, it has long been known that autoionized lines exhibit very different characteristics when their intensity variations with the electron density of the plasma in which they are emitted are compared with that of nonautoionized lines.[3] This is the conclusion of the measurements of Allen[4] who observed intensity variations of autoionized lines in an arc between copper electrodes, when the intensity of the arc current was varied. However, it is not possible to utilize, for a theoretical interpretation, his measurements or the more recent measurements of Kiselevskii *et al.*,[5] as their measurements of the intensities of the lines refer respectively to the arc current or to the pressure of the plasma. These are not useful parameters. In this work, the intensities of the lines have been measured at various electron densities known from the Stark broadening of copper lines. Also the intensities of autoionized lines were compared not only with the intensity of lines issued from nonautoionizing levels above the first ionization potential but also with the intensity of a line issued from a level situated under this potential.

I. THEORY

A. Autoionizing Levels

In plasmas at low electron densities where collisions play a negligible role in depopulating atomic levels, the theory of autoionization predicts that the population of autoionizing levels is very nearly in equilibrium with the free electrons of the plasma and so may be known by application of the Saha equation.[6] Paradoxically, the situation is not as clear when collisions begin to play a role because then coupling with non-LTE levels could reverse the situation.

Denoting the true population of the autoionizing level p by $n(p)$ and the population of another non-specified level q by $n(q)$ we can write for the population rate of the level p if the atom is supposed to have only two ionization levels E_∞^{I}, E_∞^{II} and is in an optically thin plasma:

$$\dot{n}(p) = -n(p)\Big(C(p,c) + \sum_{q\neq p} C(p,q) + \sum_{q<p} A(p,q) + A^a(p,1)\Big) + \sum_{q\neq p} n(q)C(q,p) + N_1^+[N_e\alpha^{\mathrm{res}}(1,p) + C(c,p)]\ . \quad (1)$$

$C(p, c)$ is the ionization probability toward the upper ionization potential E_∞^{II}. $C(c, p)$ is the probability of the inverse—three-body recombination—process. The excitation probability $C(p, q) = N_e \langle vQ(p, q)\rangle$ is the product of the electron density, the electron velocity v, and the excitation cross section $Q(p, q)$, integrated over the Maxwell distribution of the electrons. $C(q, p)$ is the probability of the inverse process. Because of the difference in the nature of autoionizing and nonautoionizing levels belonging to one atomic configuration, elastic collisions will not have an ordinary effect of statistical redistribution of populations between levels of a common configuration but can play the role of an essential factor for populating—or depolating—nonautoionizing from autoionizing levels. So, these elastic collisions will be included in the probability rates $C(p, q)$ and $C(q, p)$, where p and q will belong to a common configuration.

N_e is the electron density of the plasma. $A(p, q)$ and $A^a(p, 1)$ are, respectively, the spontaneous radiative deexcitation and autoionization probabilities. Because the autoionizing levels considered are situated just above E_∞^I, only the first level E_∞^I of the ion (with population N_1^+) is considered as a final state of the ion after autoionization. This fundamental state of the ion is the parent of the free states interacting with the autoionizing levels. We introduce a coefficient $\alpha^{\text{res}}(1, p)$ for the "resonance recombination" which is the inverse process of autoionization. This coefficient is related to the dielectronic recombination coefficient[7] $\alpha^{\text{di}}(1, q)$ from the ion state 1 toward the q state by the relation

$$\alpha^{\text{di}}(1, q) = \alpha^{\text{res}}(1, p)\,\frac{A(p, q)}{A^a(p, 1) + A(p, q)}\ . \tag{2}$$

We neglect radiative recombinations from the continuum situated above E_∞^{II}, because they populate mostly the lower levels.

The probability—integrated over a Maxwellian distribution of atoms—has been calculated for inelastic atom-atom collisions with the expression reported by Drawin[2] and compared with the probability of electron-atom collisions. The ratio of these probabilities does not exceed 3.10^{-4} in our case for an atom temperature $\frac{1}{2}T_e < T_a < T_e$ where T_e is the electron temperature; then atom-atom collision contribution have been neglected. We have not taken into account the process of symmetric ion-atom charge transfer which may be important in certain cases but for which few results are available for excited states of complex atoms, and probably none in the case of multilevel ionization potentials.

The levels p satisfying LTE conditions with free electrons should have a population $n_E(p)$ for which

$$n_E(p)C(p, c) = C(c, p)N_1^+\ ,$$
$$N_e\alpha^{\text{res}}(1, p)N_1^+ = A^a(p, 1)n_E(p)\ . \tag{3}$$

Then

$$\dot{n}(p) = -n(p)\Big(C(p, c) + \sum_{q\neq p} C(p, q) + \sum_{q<p} A(p, q) + A^a(p, 1)\Big) + \sum_{q\neq p} n(q)C(q, p) + n_E(p)[A^a(p, 1) + C(p, c)] = 0\ . \tag{4}$$

$\dot{n}(p) = 0$ because of the high rates of equilibrating processes. With the relationship

$$C(q, p) = [n_E(p)/n_E(q)]\,C(p, q) \tag{5}$$

and the definition

$$b(q) = n(q)/n_E(q)\ , \tag{6}$$

$$b(p) = \frac{A^a(p, 1) + C(p, c) + \sum_q b(q)C(p, q)}{\sum_{q<p} A(p, q) + A^a(p, 1) + C(p, c) + \sum_q C(p, q)}\ . \tag{7}$$

This equation cannot be solved unless we know the populations $n(q)$ of the neighboring levels of p. In low density plasmas, the collisional probabilities $C(p, c)$ and $C(p, q)$ become negligible and we obtain the known relation[6]

$$b(p) = \frac{A^a(p, 1)}{\sum_{q<p} A(p, q) + A^a(p, 1)}\ . \tag{8}$$

When the neighboring levels of the autoionizing level p can be considered in LTE (often true on account of their high principal quantum number n),

$$b(p) = \frac{A^a(p, 1) + C(p, c) + \sum_{q\neq p} C(p, q)}{\sum_{q<p} A(p, q) + A^a(p, 1) + C(p, c) + \sum_{q\neq p} C(p, q)} \tag{9}$$

In the expression (1) the following possible process has been ignored: Spontaneous transitions of the atoms toward free states of equal energy, occurring in the autoionization process may be accompanied by superelastic collisional induced transitions which will leave the ion in its ground state. This is an alternative process for the collisional stabilization of autoionizing states towards discrete states of the atoms, considered by Bates and Dalgarno.[6] This process and its reverse—three-body recombination—is an equilibrating one so it cannot be used to explain any disagreement of the observed population variation law with a Boltzmann-type law.

1. *Numerical Values*

We shall calculate the contributions to the population of the autoionizing level ($5s\,^2D_{2\,1/2}$) from which is issued the 4866-Å line of Cu. The probability of spontaneous transition towards lower levels is obtained from Bethe's formula[8]:

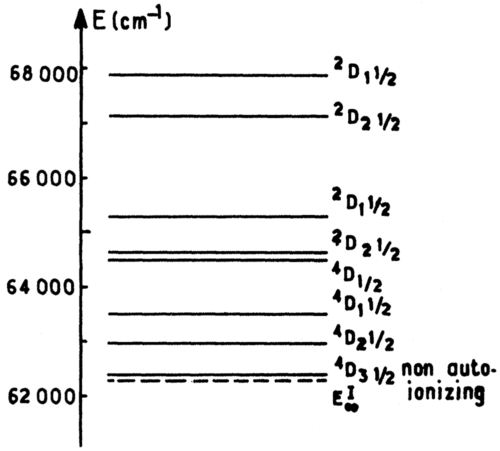

FIG. 1. Cu I: first autoionizing levels of the series $3d^94s\ (^3D)5s$.

$$\sum_{q<p} A(p, q) = 1.66\ \frac{10^{10}}{p^{*4.5}} \simeq 5.10^8 \text{ sec} .$$

We have taken for p^* the effective principal quantum number. The expression of Seaton[9] for the ionization probability integrated over the Maxwell distribution of electrons shows that this contribution is relatively small in the temperature range of our plasma. Although the levels studied cannot yet be considered as hydrogenic, we utilize this approximation for the spontaneous radiative transition coefficient, and for the evaluation of the other rates, as is commonly done in LTE calculations. Since this hypothesis is made for the calculation of the radial parts of all the rates that we compare, one can consider that the relative error on the result is still acceptable. The predominant inelastic contribution from the nearest configuration was calculated with the expression of Seaton, integrated over the Maxwell distribution of the electrons.[10] It has a probability $C(p, q) = 0.7\times10^{10}$ sec^{-1} when $N_e = 10^{16}$cm^{-3}. As we shall see in the next paragraph, elastic collisions give a contribution of the same order.

Using these numerical values and the values $A^a(p, 1) = 2\times10^{11}$ sec^{-1} for the autoionization probability corresponding to the experimental breadth 8.7 cm^{-1} of the level $5s\,^2D_{5/2}$ known from the line[4] at 4866 Å (Table I), we see in Eq. (7) that $b(p) > 0, 9$ whatever the equilibrium state of the neighboring levels. This means that the population of this autoionizing level should still obey the Saha equation at an electron density $N_e = 10^{16}$ cm^{-3}. We see in Fig. 2 that this could be expected only at densities greater by a factor 4 or 5.

B. Adjacent Nonautoionizing Level

The variation of population of the level (^3D) $5s\,^4D_{7/2}$ from which is issued the transition at 4275 Å was measured. This level is free from interaction with other bound configurations, as is seen from the Ritz diagram of the series.[11] Furthermore, it is not autoionizing since the 4275-Å line is sharp. The level energy scheme of copper (Fig. 1) shows that autoionizing and nonautoionizing levels of the configuration $3d^94s5s$ lie near each other (500 cm^{-1} in some cases) but levels of the configuration $3d^94s5p$ are found some 8000 cm^{-1} higher. This disposition of the configurations could favor elastic collisions to populate or depopulate the nonautoionizing state from the near autoionizing ones, within the configuration $4s5s$, relative to inelastic collisions with levels of the configuration $4s5p$. This can be seen by considering the probability rates on the processes. Elastic collisions contribute through two terms, the dipole term[12]:

$$N_e\,\bar{v}Q^{\text{el}}_{\text{dip}} = 38.8\,\bar{v}^{1/3}\,\frac{a_0{}^2e^{4/3}}{(\pi\hbar)^{2/3}}\ \frac{f_{ij}}{(\Delta E/E_H)^{4/3}}\,N_e ,$$

where f_{ij} is the oscillator strength of the transition $4s$-$5p$ calculated in the hydrogenic approximation of Bates and Damgaard,[13] ΔE and E_H are, respectively, the energy of this transition and the hydrogen potential ionization, $\bar{v}$ is the mean value of the electron velocity, a_0 is the radius of the first Bohr orbit, and e the charge of the electron. The quadrupole term, integrated over the Maxwell distribution of the electrons, does not depend on the energy and may be written[14]

$$N_e\,\langle vQ^{\text{el}}_{\text{quad}}\rangle = 6.05\times10^{-8}\,\beta N_e \simeq 3\times10^9 \text{ sec}^{-1} ,$$

where β is a quantity involving the squared radius of the atom in the excited state and a coupling coefficient of the atomic term assumed in LS coupling, although this hypothesis is only approximative. This coupling coefficient involves a sum over J' of the line strengths for transitions going from the level $5s\,^4D_{7/2}$ to the levels of permitted S and J' ($\Delta J = 0, \pm 2$) of the same configuration. The numerical value has been calculated for $N_e = 10^{16}$ cm^{-3}. Because of the great energy interval between the level $5s\,^4D_{7/2}$ and those of the configuration $4s5p$, the dipole term is negligible and the inelastic contribution is smaller than the quadrupole term. Again, ionization probabilities toward E^{II}_∞ are small and ionization toward E^{I}_∞ does not occur since we are concerned here with a nonautoionizing level. Following these evaluations, and on account of the predominance of elastic collisions we could expect the population $n(q)$ to be nearly proportional to that of the near autoionizing levels p of the configuration $4s5s$. The curve of Fig. 2(e) shows that this is not observed and that some other process must be considered.

C. LTE Criteria

The criteria of Drawin differ from those of Griem by a factor ψ_1^{-1} tabulated in Ref. 2.

Applying these criteria to the level $4d^{10}6s\,^2S_{1/2}$, chosen because it exhibits small configuration interactions with other levels, as it appears from the Ritz diagram of its series,[11] we obtain a minimum electron density $N_e = 2\times10^{14}$ cm^{-3} to ensure partial LTE of the level. As will be shown in Sec. II, the electron density of our plasma varies between 4×10^{15} and 4×10^{16} cm^{-3}, and thus verifies the criteria of partial LTE for the high levels belonging to series converging towards E_∞^{I}. Unfortunately, it was not possible to verify experimentally the validity of Boltzmann's law between these high levels. The only pair of well-isolated lines we have in the spectral range observed is the pair 4480 Å-3825 Å, but this latter line falls at the limit of transmission of the glass prism of our spectrograph and thus could not be measured with acceptable accuracy.

However, this investigation was conducted on the ion levels $4f\,^3H_5^0$ and $4f\,^3P_2^0$ from which are issued two neighboring lines at 4931 Å. No Boltzmann-like law has been observed between these levels and the $6s\,^2S_{1/2}$ level mentioned above. Thus, no determination of the temperature of the plasma was possible from the measurement of the ratio of line intensities in successive ionization degrees.

II. EXPERIMENTAL METHOD

Our apparatus has been described elsewhere.[15] It consists essentially of an ordinary electric arc placed in a vessel where a partial vacuum can be made, with an argon flow from the observation window of the vessel to the pump. A grid of 1-mm spacing was placed in front of the plasma and gave ten horizontal images, which were focalized with an adequate magnitude on the vertical slit of the spectrograph (Huet 44 model). The Abel inversion of the observed intensities of these ten images could be obtained with a computer program. Step filters cannot be used with an inhomogeneous source, so, we supposed a linear reprocity curve for the Kodak Panchromatic films used to determine their characteristic curve, with the aid of a Pointolite lamp of known color temperature. True profiles were assumed to be of Voigt type and the intensities A determined without planimetry with the formula

$$A = hpE\ ,$$

where p is a parameter deduced from the width h at one-half, and the width b at one-tenth, the maximum intensity, with the aid of a curve found in Ref. 16. h and b are readily measured by superposition of a semilog paper on the densitometer profile. E is the intensity at the maximum of the line, as deduced from the characteristic curve. Nevertheless the measurements do not reach a great accuracy, essentially because of the relatively low accuracy of the photographic method, particularly for narrow lines. This explains the relative great scattering of points obtained for various arc currents (Fig. 2).

A. Determination of the Electron Density N_e

In order to avoid demixing effects in the plasma, no testing element has been added to measure N_e; copper lines themselves were employed for this purpose. Up to $N_e = 1.1\times10^{16}$ cm^{-3}, the electron density of the plasma was determined by measuring the width of the line at 4022 Å ($5d\,^2D_{3/2}$-$4p\,^2P_{1/2}$), which is both intense and sufficiently broad at relatively low electron densities. The width of this line was calculated following Griem's theory of Stark effect with the aid of an already existing computer program.[17,18] Over this electron density, which corresponds roughly to a width of 2 Å, the line exhibits an induced linear Stark effect because its width begins to reach the spectral distance of the interacting level closest to the upper level $5d\,^2D_{3/2}$. Using the approximate linearity of the variation of Stark broadening with N_e, greater N_e were determined by measuring the width of the 4480-Å line, which is not affected by this inductive effect. Strictly speaking, using Stark broadening to determine N_e presupposes that LTE conditions are verified. With this hypothesis, we derived the temperature from the Saha equation. The variation of T with N_e is relatively slow, as we see in the abscissa scale of Fig. 1; furthermore, Stark broadening is not highly sensitive to temperature, so that any moderate deviation from partial LTE conditions does not seem to introduce significant errors.

B. Interpretation

The characteristics and the identifications of the lines of which the intensity has been measured are presented in Table I. The points representing the intensity ratio of two transitions, which is proportional to the population ratio of their upper level, are plotted in Fig. 2 against N_e and T corresponding to various current intensities of the arc. For comparison, the Boltzmann ratios are drawn in

TABLE I. Cu I observed lines. E_∞^{I} designates the level $3d^{10}\,^1S_0$; E_∞^{II} designates the configuration $3d^9 4s\,(^3D, ^1D)$. The breadth of the levels is due to autionization.

λ (Å)	Identification	Breadth (cm^{-1})	Ionization potential
4480	$3d^{10}\,4p\,^2P_{1/2}$-$3d^{10}\,6s\,^2S_{1/2}$	sharp	E_∞^{I}
4275	$4s\,(^3D)\,4p\,^4P_{5/2}$-$4s\,(^3D)5s\,^4D_{7/2}$	sharp	E_∞^{II}
4177	$4s\,(^3D)\,4p\,^4P_{5/2}$-$4s\,(^3D)5s\,^4D_{5/2}$	6,5	E_∞^{II}
4259	$4s\,(^3D)\,4p\,^4P_{3/2}$-$4s\,(^3D)5s\,^4D_{3/2}$	2,5	E_∞^{II}
4866	$4s\,(^1D)\,5s\,^2D_{5/2}$-$4s\,(^1D)5s\,^2D_{5/2}$	8,7	E_∞^{II}

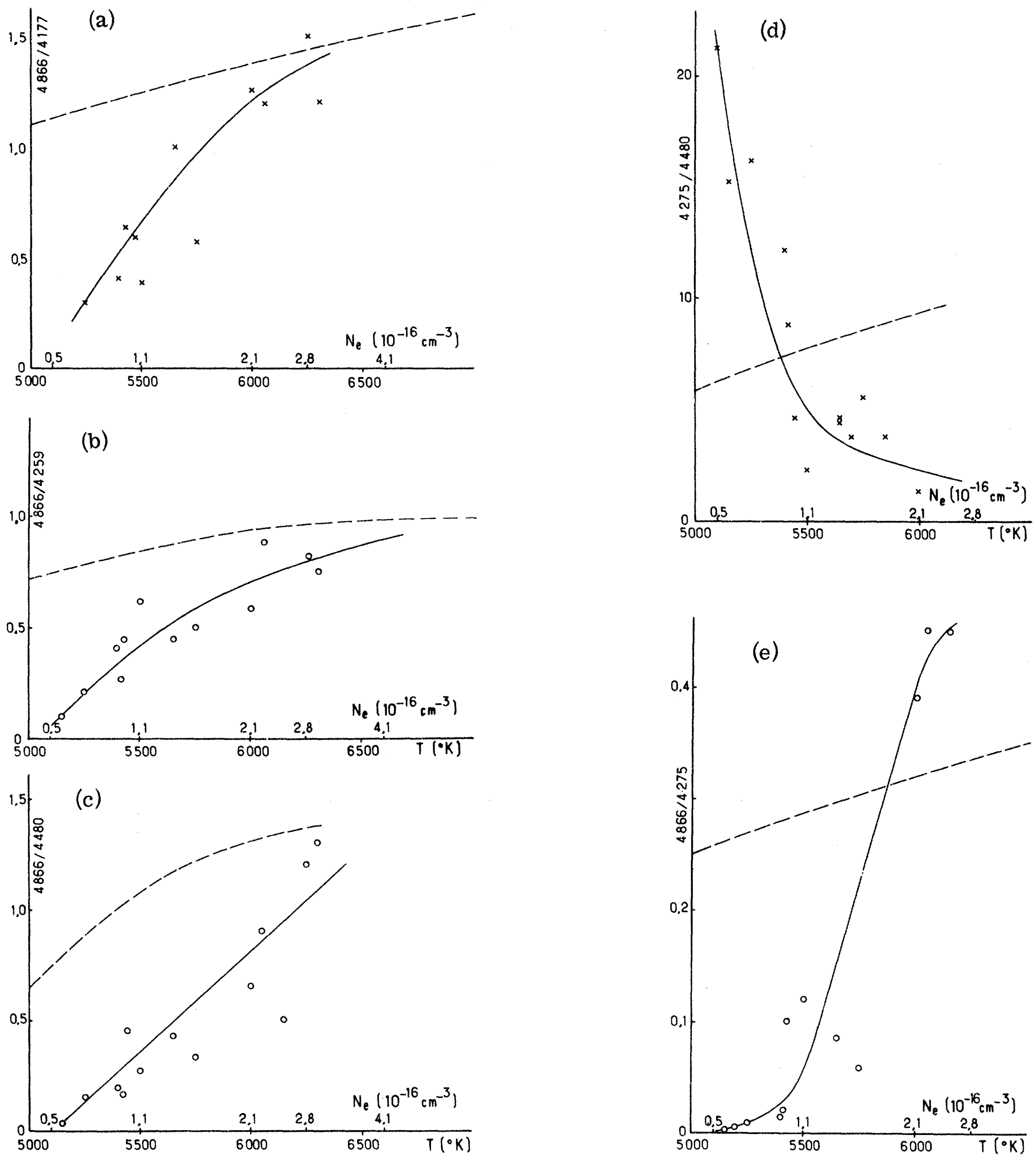

FIG. 2. Line intensity ratios for various N_e, T: dotted line, Boltzmann's law; dashed line, interpolation curve of experimental points. (a) 4866 Å/4177 Å; (b) 4866 Å/4259 Å; (c) 4866 Å/4480 Å; (d) 4275 Å/4480 Å; (e) 4866 Å/4275 Å.

these figures. The most striking feature in these curves is that the populations of the autoionizing and the nonautoionizing levels behave very differently, as already pointed out by Allen. But one conclusion of our measurements is that the principal intensity anomalies are not shown by autoionized lines but the nonautoionized 4275-Å line. This results from the comparison of the experimental interpolated curves with the Boltzmann distributions drawn in Fig. 2 from the known variation T. In these figures, the scales of the experimental and Boltzmann curves are identical, but the origin in the ordinate scale is arbitrary. The last ones are set as limits of experimental ones on account of the increasing effect of collisions. In Figs. 2(d)–2(e) (nonautoionized line) no agreement is possible. The agreement of the autoionized line variations with the Boltzmann law is far from being close. Nevertheless the deviation which exceeds 50% in the first part of some curves decreases when $N_e \simeq 4\times10^{16}$ cm^{-3}. For all these lines, the slope of the experimental curve is greater than that of the Boltzmann curve. Consideration of the variation in the width of the 4866-Å line gives some indications about the relative contributions of collisions and autoionization to the broadening on the line. As N_e becomes greater as it reaches the value 2×10^{16} cm^{-3}, the width of the level conserves its low N_e value, i.e., 8.7 cm^{-1}, which corresponds to a linewidth of about 2 Å; above this value of N_e, the width increases, which is the indication that the collisional broadening exceeds, say, 10% of the autoionization width. For $N_e=2\times10^{16}$ cm^{-3}, our calculated contribution $C(p, q)$ is about 1.5×10^{10} sec^{-1}, which represents 10% of $A^a(p, 1)$. The agreement is acceptable; however, this calculated value could be further increased by a configuration interaction $4s5s\times4s4d$, as suggested by Wilson[19] to explain some anomalies in the observed widths of the levels of the ^2D term.

In the first part of the curves of Fig. 2(a)–2(c), where N_e is smaller, these collisional contributions may be neglected in comparison with $A^a(p;1)$ as we showed, Eq. (7) gives $b(p)>0.9$ corresponding to a near-Boltzmann-like curve, which is not observed in these curves. Since this disagreement cannot be attributed to the collisional contribution, one may suggest other process as ion-atom resonant charge transfer, which can become important when the ionization potential is small.[20] If one considers ionization of the level p toward $E_\infty^{\rm I}$ through its interaction with the continuum states, the energy interval for this process appears to be small and so resonant charge transfer could become an important process, and should be necessarily included in the calculation.

The author is indebted to Dr. O. Bely for his valuable observations about this work.

[1] J. Richter, Tenth International Conference on Ionization Phenomena in Gases, Oxford, England, 1971 (unpublished).
[2] H. W. Drawin, Z. Phys. **228**, 99 (1969).
[3] E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge U. P., London, 1963), p. 374.
[4] C. W. Allen, Phys. Rev. **39**, 42 (1932); Phys. Rev. **39**, 55 (1932).
[5] L. I. Kiselevskii and V. N. Snopko, Opt. Spektrosk. 17, 637 (1964) [Opt. Spectrosc. 17, 347 (1964)].
[6] D. R. Bates and A. Dalgarno, in *Atomic and Molecular Processes*, edited by D. R. Bates (Academic, New York, 1962).
[7] A. Burgess, Astrophys. J. **138**, 776 (1964).
[8] H. A. Bethe and E. E. Salpeter, in *Handbuch der Physik*, edited by S. Flügge (Springer, Berlin, 1957), Vol. 35.
[9] M. J. Seaton, Planet. Space Sci. **12**, 55 (1964).
[10] J. T. Jefferies, *Spectral Line Formation* (Blaisdell, Waltham, Mass., 1968).
[11] A. G. Shenstone, Philos. Trans. R. Soc. Lond. A **241**, 37 (1948).
[12] H. Van Regemorter, C.R. Acad. Sci. (Paris) **257**, 63 (1963).
[13] D. R. Bates and A. Damgaard, Philos. Trans. R. Soc. Lond. A **242**, 101 (1949).
[14] S. Sahal-Bréchot and H. Van Regemorter, Ann. Astrophys. 27, 432 (1964).
[15] R. Assous, J. Opt. Soc. Am. **62**, 544 (1972).
[16] H. C. Van de Hulst, Bull. Astron. Inst. Neth. **10**, 75 (1946).
[17] R. Assous, J. Phys. (Paris) **29**, 877 (1968).
[18] R. Assous, C.R. Acad. Sci. (Paris) **267**, 325 (1968).
[19] M. Wilson, J. Phys. B **2**, 524 (1969).
[20] D. R. Bates, in Ref. 6.

PHYSICAL REVIEW A VOLUME 7, NUMBER 4 APRIL 1973

Modified Hund's Rule for *jj* Coupling*

T. E. H. Walker and J. T. Waber
Department of Materials Science, Northwestern University, Evanston, Illinois 60201
(Received 6 November 1972)

New Hund's rules are proposed for atoms for *jj* coupling. It is found that two distinct rules are needed depending on the relative values of j_i and l_i for interacting electrons.

I. INTRODUCTION

In almost all cases, the state of lowest energy deriving from a particular atomic-orbital configuration is given correctly by Hund's rules.[1] These rules predict that the states of highest multiplicity are the lowest in energy, and of these the lowest is that state of highest L. It is important to recognize that Hund's rules are not a general ordering rule for excited states. In fact, for all two-electron configurations ll', the relative ordering of the resulting ^1L and ^3L states alternates for decreasing L. Hund's rules assume LS coupling, in which the spin and orbital angular momenta are separately quantized and their interaction is small compared to the electron repulsion. There is no reason to suppose that the same rules can be taken over directly to jj coupling. Indeed, since for any ll' configuration with $l, l'>0$ there are four different jj configurations, it is clear that Hund's rules for LS coupling are insufficiently general for the problem.

The properties of $(j)^n$ configurations have been investigated at some length[2,3] in connection with the shell model of nuclear structure. There are also important differences between the nuclear and