

FIG. 3. The difference between the computed velocity autocorrelation function and an exponential one according to the Enskog theory versus the number of mean collision times for 108 particles at V/V_0 of 20, 3, and 1.6.

2 and 3). They lead to the positive structure in the velocity autocorrelation function which extends to about 20 collision times. An effort to find an explanation of this long memory effect (long compared to the relaxation time of 1.5 collision times) is underway. An attempt was made to associate the positive correlation with an initially energetic particle which creates a hot and low-density region which persists for a long time. More details must be worked out in order to verify this mechanism.

At still higher densities the particles surround-

ing any one particle are more densely packed. The major effect of these neighbors is therefore to reflect the particles, leading to the negative structure in the autocorrelation function discovered earlier⁷ and discussed recently in terms of backscattering⁸ (see Fig. 3). This negative correlation increases with increasing density and ultimately results in the vanishing of the diffusion coefficient in the crystalline phase.

*Work performed under the auspices of the U. S. Atomic Energy Commission.

¹E. G. D. Cohen, J. R. Dorfman, M. H. Ernst, L. S. Garcia-Colin, and J. V. Sengers, in *Lectures in Theoretical Physics*, 1966 (to be published).

²B. J. Alder and T. E. Wainwright, *J. Chem. Phys.* **31**, 459 (1959).

³S. Chapman and T. G. Cowling, *The Mathematical Theory of Nonuniform Gases* (University Press, Cambridge, England, 1939).

⁴C. Longuet-Higgins and J. A. Pople, *J. Chem. Phys.* **25**, 884 (1956).

⁵J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, in *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954).

⁶B. J. Alder and T. E. Wainwright, in *The Many-Body Problem*, edited by J. Percus (Interscience Publishers, Inc., New York, 1963).

⁷B. J. Alder and T. E. Wainwright, in *Transport Processes in Statistical Mechanics*, edited by I. Prigogine (Interscience Publishers, Inc., New York, 1958).

⁸J. H. Dymond and B. J. Alder, *J. Chem. Phys.* **45**, 2061 (1966).

INFLUENCE OF ELECTRON CORRELATIONS ON A PLASMA-BROADENED LYMAN-ALPHA LINE*

Earl W. Smith

Department of Physics and Astronomy, University of Florida, Gainesville, Florida

(Received 8 May 1967)

In a previous paper,¹ the relaxation techniques developed by Zwanzig² and Fano³ were used to study the broadening of spectral lines originating from neutral atoms in a plasma. In the relaxation theory, the plasma is represented by three weakly coupled subsystems: an excited atom, a gas of N ions, and a gas of N electrons. In Ref. 1 a calculation of the Lyman-alpha line was made, treating the electron subsystem as an ideal gas of electrons. The purpose of this paper is to present the results of the correction of this ideal-gas approximation.

As in most line-broadening theories, the ions

are regarded as infinitely massive classical particles over the time of interest (static-ion approximation). The weak coupling interaction between the atom and its thermal bath of ions and electrons is taken to be a dipole-field interaction which has the form $e\vec{R} \cdot (\vec{\mathcal{E}}_e + \vec{\mathcal{E}}_i)$, where \vec{R} is the position of the atomic electron while $\vec{\mathcal{E}}_e$ and $\vec{\mathcal{E}}_i$ represent the electric fields produced by the electrons and ions, respectively. It is further assumed that the three subsystems are statistically independent and the plasma density matrix is given by a product of density matrices for the atom, the electrons, and the

ions,³ $\rho^{(a)}\rho^{(e)}\rho^{(i)}$. With these assumptions it is found that the line shape for dipole radiation is¹

$$I(\omega) = \int Q(\vec{\mathcal{E}})J(\omega, \vec{\mathcal{E}})d^3\mathcal{E}, \quad (1)$$

where $Q(\vec{\mathcal{E}})$ is the probability of finding an ion field $\vec{\mathcal{E}}$ at the atom and $J(\omega, \vec{\mathcal{E}})$ is the line shape resulting from the electron-atom interaction in the presence of the static electric field $\vec{\mathcal{E}}$. In the relaxation theory, ω is a complex variable, $\omega = \tilde{\omega} + i\epsilon$, whose real part $\tilde{\omega}$ is the true frequency and whose imaginary part ϵ is taken to be the natural half-width for the line under consideration.

The microfield function $Q(\vec{\mathcal{E}})$ is known⁴ and $J(\omega, \vec{\mathcal{E}})$ is evaluated by the Zwanzig-Fano relaxation techniques. In Ref. 1, $J(\omega, \vec{\mathcal{E}})$ is given by

$$J(\omega, \vec{\mathcal{E}}) = -\pi^{-1} \text{Im Tr}_a \{ \vec{d} \cdot [\omega - \mathcal{L}(\omega)]^{-1} (\rho^{(a)} \vec{d}) \}, \quad (2)$$

where \vec{d} is the atomic-dipole operator, $\mathcal{L}(\omega)$ is an effective Liouville operator for the atom,

and the trace is over states of the atom.

The Hamiltonian which is used in the present evaluation of $J(\omega, \vec{\mathcal{E}})$ has the form

$$H = H_a + H_e + e\vec{R} \cdot (\vec{\mathcal{E}}_e + \vec{\mathcal{E}}), \quad (3)$$

where H_a is the Hamiltonian for an unperturbed atom, H_e is an electron Hamiltonian which consists of a kinetic energy term plus an effective electron potential function,¹ and $\vec{\mathcal{E}}$ is a vector having the same magnitude and direction as the ion field. In Ref. 1, $\mathcal{L}(\omega)$ is expanded in a perturbation series based on an unperturbed Liouville operator L_0 , which corresponds to the Hamiltonian $(H_a + H_e)$, and a perturbation L_1 , which corresponds to the interaction $e\vec{R} \cdot (\vec{\mathcal{E}}_e + \vec{\mathcal{E}})$.

The eigenstates $|a\rangle$, $|b\rangle$, and $|c\rangle$ of H_a will be used in evaluating the trace in Eq. (2); the energy difference between the states $|a\rangle$ and $|b\rangle$, divided by \hbar , is called ω_{ab} and a variable $\Delta\omega_{ab} = \omega - \omega_{ab}$ is defined. Denoting the z component of \vec{R} by R^z , a second-order evaluation of $[\omega - \mathcal{L}(\omega)]$ gives¹

$$[\omega - \mathcal{L}(\omega)]_{ab, a'b'} = \Delta\omega_{ab} \delta_{aa'} \delta_{bb'} - (e\mathcal{E}/\hbar) (R_{aa'}^z \delta_{bb'} - R_{b'b}^z \delta_{aa'}) - \hbar^{-2} \langle L_1 (\hbar\omega - L_0)^{-1} L_1 \rangle_{ab, a'b'}, \quad (4)$$

where $\langle M \rangle$ denotes $\text{Tr}_e \{ M \rho^{(e)} \}$ which is an operator in the atomic subsystem. After considerable algebra one finds

$$\begin{aligned} \langle L_1 (\hbar\omega - L_0)^{-1} L_1 \rangle_{ab, a'b'} = & -(2ime^4/3)(8\pi m/kT)^{1/2} \{ \sum_c [\delta_{bb'} R_{ac} \cdot R_{ca'} G(\Delta\omega_{cb}) \\ & + \delta_{aa'} R_{b'c} \cdot R_{cb} G(-\Delta\omega_{ac})] - R_{aa'} \cdot R_{b'b} [G(\Delta\omega_{ab'}) + G(-\Delta\omega_{a'b})] \}, \end{aligned} \quad (5)$$

where m and n are the mass and density of the electrons and $G(\Delta\omega)$ is an integral discussed below.

The right-hand side of Eq. (5) represents a second-order electron-atom interaction. The integral $G(\Delta\omega)$ represents a frequency dependence which is a result of the time dependence in a quadratic Stark interaction between the atom and the time-varying electron field. (See Sec. 5B of Ref. 1 for a more detailed discussion of this point.) It has been found that the difference between the calculations made with an ideal gas of electrons and the corrected cal-

culations reported in this Letter lies entirely in the G integral.

The integral which appears in the ideal gas case, referred to as G_0 , is given by¹

$$G_0(\Delta\omega) = \int_0^\infty \exp\{is\hbar\Delta\omega/kT\} (s^2 + is)^{-1/2} ds. \quad (6)$$

When electron correlations are considered, it is found that a correction term is added to the integrand in Eq. (6). The evaluation of this correction term requires the use of a radial distribution function; the linearized Debye-Hückel function⁵ was used for this purpose, and the resulting G is

$$G(\Delta\omega) = \int_0^\infty \exp\{is\hbar\Delta\omega/kT\} [(s^2 + is)^{-1/2} - \pi^{1/2} \alpha \exp\{\alpha^2(s^2 + is)\} \text{Erfc}\{\alpha(s^2 + is)^{1/2}\}] ds, \quad (7)$$

where Erfc is the complementary error function. The parameter α is given by $\gamma/2\pi^{1/2}\lambda_D$, where λ_D and λ are the Debye length⁵ and the thermal wavelength $h/(2\pi mkT)^{1/2}$ for electrons. Since the ratio λ/λ_D is a measure of the importance of particle correlations, we expect the electron correlations to be totally negligible in the limit $\alpha \rightarrow 0$. Taking this limit in Eq. (6), the term in brackets becomes $(s^2 + is)^{-1/2}$, hence $G(\Delta\omega)$ reduces to the ideal gas result $G_0(\Delta\omega)$.

It is interesting to note that, for any finite α , the ideal-gas term, $(s^2 + is)^{-1/2}$, will always dominate the Erfc term for small values of s . That is, correlations are negligible for short times or large $\Delta\omega$. We note further that $(s^2 + is)^{-1/2}$ is the large- s asymptote of the Erfc term. This implies that the electron correlations will always be important for very long times, or small $\Delta\omega$. Further analysis shows that the Erfc term begins to be important for values of s on the order of $1/\alpha$; since $\alpha \approx \hbar\omega_p/kT$, where ω_p is the plasma frequency, we may use the well-known property of Fourier transforms,

$$\Delta\omega\Delta t \gtrsim 1 \quad (8)$$

to infer that correlations will be important only for $|\Delta\omega| < \omega_p$.

The most striking feature of the integrand in Eq. (7) is the rapidity with which it vanishes as s increases. For times shorter than $1/\omega_p$ the ideal-gas term is strongly dominant, but for times on the order of $1/\omega_p$ and larger, the correlation term increases rapidly and "cuts off" the ideal-gas term. In the impact theories, the collisions of long duration are said to be unimportant because they are distant and therefore shielded because of the electron correlations; in these theories, the influence of long-duration collisions is approximated by means of an impact-parameter cutoff at the Debye length. While the cut-off behavior of the integrand in Eq. (7) is by no means as sharp as the impact-parameter cutoff used in the impact theories, it does verify that such a cutoff should provide a good approximation to the effects of electron correlations.

Since $G(\Delta\omega)$ is a complex function of the complex variable $\Delta\omega$, it is convenient to write

$$G(\Delta\omega) = G_r(\Delta\tilde{\omega}) - iG_i(\Delta\tilde{\omega}),$$

where $\Delta\tilde{\omega}$ is the frequency separation from the center of the natural line and both G_r and G_i are real functions of the real variable $\Delta\tilde{\omega}$.

There is no analog for G_i in the impact theories for hydrogen lines, hence we can use only G_r when comparing with these theories.

Since electron correlations are relatively unimportant in the line wings, it is not surprising that, as before,¹ G_r resembles the results obtained by Lewis^{1,6} in this region,

$$G_r(\Delta\tilde{\omega}) \sim -0.577 - \ln(\hbar\Delta\tilde{\omega}/4kT). \quad (9)$$

In the impact theories, the Lewis cutoff is used for values of $|\Delta\tilde{\omega}|$ larger than v_{av}/λ_D , where v_{av} is the average electron velocity. For $|\Delta\tilde{\omega}|$ smaller than v_{av}/λ_D , one expects the usual binary-collision impact theories to be valid. In this range, $G_r(\Delta\tilde{\omega})$ has the form

$$G_r(\Delta\tilde{\omega}) \approx -\ln\alpha - \text{const.} \quad (10)$$

The corresponding integral in the impact theories is given by Eq. (30) of Ref. 8; noting that the parameter y_{\min} used in that paper is just 10.7α , we have

$$\frac{1}{2} \int_{y_{\min}}^{\infty} \frac{\exp(-y)}{y} dy \approx -\ln\alpha - 1.47. \quad (11)$$

While Eqs. (10) and (11) agree qualitatively, it is not possible to make a definitive quantitative comparison without additional analysis of the function $G_r(\Delta\tilde{\omega})$. Work is now in progress on this point and will be reported in a future paper.

The change in the line shape due to the correction for electron correlations is illustrated in Fig. 1 which plots the Lyman- α line for

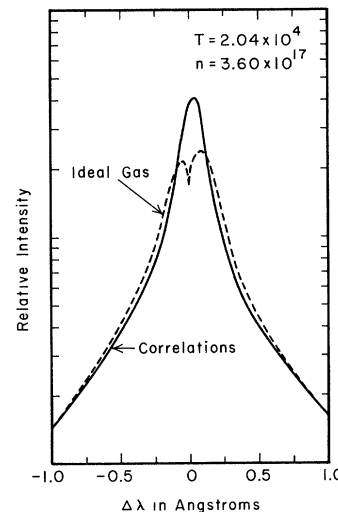


FIG. 1. An illustration of the influence of electron correlations on Lyman- α profiles calculated by the relaxation theory.

hydrogen as calculated by the relaxation theory. The unphysical dip which appeared in the ideal-gas calculations is removed, as anticipated by Griem,⁷ when the correlations are included. From Fig. 1 it is clear that the electron correlations produce an observable alteration of the line only in the region $|\Delta\lambda| < \Delta\lambda_p$, where $\Delta\lambda_p$ is related to the plasma frequency by $\omega_p = 2\pi c \Delta\lambda_p / \lambda_0^2$ and λ_0 is the unperturbed Lyman- α wavelength.

In Fig. 2, the corrected relaxation profile is compared with a profile calculated by the impact theory. For $|\Delta\lambda|$ larger than 0.5 \AA , the relaxation profile shows a small asymmetry favoring the red wing; this asymmetry is due to the induced dipole nature of the electron-atom interaction as discussed in Ref. 1.

Near the center of the line, the relaxation theory produces a broader profile than the impact theory. Some, but not all, of this broadening is due to a difference in the microfield functions used in averaging over ion fields. The impact-theory profile in Fig. 2 was calculated with a modification of Ecker's microfield function⁸ while the more recent Mozer-Baranger⁴ functions have been used in the relaxation-theory calculations. The author has recalculated the impact-theory profile using the Mozer-Baranger functions and it is found that the profile should be somewhat wider between 0.2 and 1.0 \AA . Since the Mozer-Baranger microfield functions provide a better description of the ion correlations than do Ecker's functions, and since correlations are important for the weak-

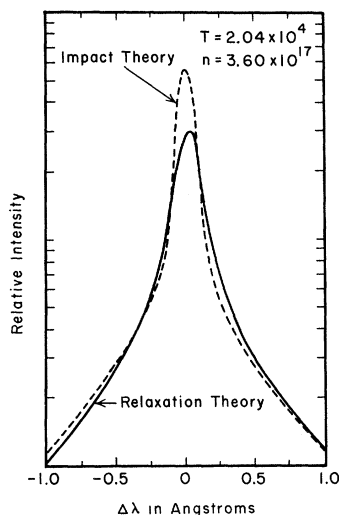


FIG. 2. A comparison of Lyman- α profiles obtained by the corrected relaxation theory and by the impact theory.

er interactions, it is not surprising that the line profile is altered in the line center where weak perturbations dominate the broadening.

After the impact-theory profile is recalculated with the Mozer-Baranger microfield function, it is found that the relaxation-theory profile is still somewhat broader near the line center and the intensity at the center is lower than that obtained by the impact theory. This may again be traced to the difference in the treatment of the weaker electron-atom interactions. In the impact theory, electron correlations are approximated by means of an impact-parameter cutoff at the Debye length while the smoother "cutoff" in the relaxation theory allows the weak collisions to produce a small amount of additional broadening.

In Fig. 2, the intensity at the center of the impact-theory profile is about twice that obtained by the relaxation theory. Although this is a rather large difference, it must be noted that the Lyman- α line has a strong central component which is dominated by electron broadening and the half-width of this line is much smaller than the plasma frequency. This effect should be considerably reduced in the Lyman- β line which is dominated by ion broadening in the center. In the Balmer series, the half-widths are larger than the plasma frequency and the electron correlations should again be less significant. It nevertheless seems likely that the relaxation theory will produce an intensity slightly lower than that obtained by the impact theory at the centers of all neutral-hydrogen lines; recent experiments^{9,10} indicate that this could provide a better agreement between theory and experiment.

It should also be noted that the relaxation profile in Fig. 2 shows a small shift of the line center which is not observed in the impact theory (for hydrogen). For the temperature and density stated, this shift is about 0.03 \AA toward the longer wavelengths. In an experimental study of this line,⁹ a shift of about 0.2 \AA was observed. Although the observed shift is somewhat larger, it does provide an indication that the theoretical shift is at least qualitatively correct.

In conclusion it may be said that the correction of the relaxation theory for electron correlations has altered the Lyman- α profile in a wholly predictable way; the dip in the center of previous ideal-gas profiles has been removed and a closer agreement with the impact theo-

ry has been obtained. While the impact and relaxation theories agree rather well over most of the Lyman- α profile, apart from asymmetries,¹ there is a significant difference in intensity at the line center. This disparity should be decreased considerably in other neutral-hydrogen lines although the relaxation theory may give a slightly lower intensity at the center of these lines.

*This research was supported in part by the Research Corporation, New York, New York, and the National Aeronautics and Space Administration.

¹E. W. Smith and C. F. Hooper, Jr., Phys. Rev. (to be published).

²R. Zwanzig, J. Chem. Phys. **33**, 1338 (1960); in

Lectures in Theoretical Physics, edited by W. E. Downs and J. Down (Interscience Publishers, Inc., New York, 1961), Vol. III, p. 106.

³U. Fano, Phys. Rev. **131**, 259 (1963); Rev. Mod. Phys. **29**, 74 (1957).

⁴C. F. Hooper, Jr., to be published; B. Mozer and M. Baranger, Phys. Rev. **115**, 521 (1959).

⁵J. Drummond, Plasma Physics (McGraw-Hill Book Company, New York, 1961).

⁶M. Lewis, Phys. Rev. **121**, 501 (1960).

⁷H. R. Griem, private communication.

⁸H. R. Griem, A. C. Kolb, and H. Y. Shen, Phys. Rev. **116**, 4 (1960); U. S. Naval Research Laboratory Report No. 5455, 1960 (unpublished).

⁹R. C. Elton and H. R. Griem, Phys. Rev. **135**, A1550 (1964).

¹⁰W. L. Wiese, D. R. Paquette, and J. E. Solariski, Phys. Rev. **129**, 1225 (1963).

LOW-TEMPERATURE ANOMALY OF ELECTRON-SPIN RESONANCE IN DILUTE ALLOYS*

H. J. Spencer and S. Doniach

Physics Department, Imperial College, London, England

(Received 6 February 1967; revised manuscript received 5 May 1967)

The electron-spin-resonance g factor for a spin- $\frac{1}{2}$ impurity in a dilute alloy is predicted to be logarithmically divergent at low temperatures.

Recently a number of authors working both with a localized-impurity model¹ and with the Anderson model² have shown that the Curie-like susceptibility for a dilute alloy in the limit of low concentration of magnetic impurities contains a logarithmically divergent factor of the type found by Kondo in his theory³ of the resistance-minimum phenomenon. In this Letter we show for a spin- $\frac{1}{2}$ localized-impurity model that this logarithmic divergence is closely related to a logarithmic shift of the electron-spin-resonance frequency, i.e., of the g factor for the impurity, and discuss the possibility of observation of this g shift in dilute alloys.

The result is derived using a drone-fermion representation⁴ for the spin- $\frac{1}{2}$ operators S for the localized impurity:

$$\begin{aligned} S_+ &= c^\dagger \varphi, \\ S_z &= c^\dagger c - \frac{1}{2}, \\ \varphi &= d + d^\dagger, \end{aligned} \quad (1)$$

in which both the spin deviation "c-on" operators and the drone "d-on" operators mutual-

ly anticommute, $\{c, c^\dagger\} = 1$, $\{d, d^\dagger\} = 1$ and $\{c, d\} = 0$, etc. (1) provides a double representation of the spin- $\frac{1}{2}$ commutation rules based on the orthogonal pair of spin-down states $|\downarrow\rangle = |0\rangle$ and $|\downarrow\rangle = d^\dagger |0\rangle$; however, thermodynamic averages may be calculated by taking a trace over both sets of states without the complications which arise with other fermion representations.⁵ Using this representation, Wick's theorem for fermions applies in its usual form to time- or temperature-ordered products of spin- $\frac{1}{2}$ operators. We use it to investigate the frequency-dependent susceptibility of a system of randomly spaced local moment bearing impurities coupled to the conduction electrons in a metal.

It is shown below that in practical cases, coupling between impurities is important even in very dilute alloys. However, we first give the results for the local-moment transverse susceptibility:

$$\chi^{-+}(t) = i\sigma(t)\langle[S_-(t), S_+(0)]\rangle \quad (2)$$

for a single localized impurity (i.e., in the dilute limit) in external magnetic field \mathcal{H} interacting with conduction electrons, creation op-