Journal of Statistical Physics, Vol. 25, No. 4, 1981

Causal Green's Function Formalism in Statistical Mechanics of Composite Particles

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Received August 5, 1980; revised November 26, 1980

A causal Green's function formalism is established within the framework of statistical mechanics of composite particles. It is shown that it provides a systematic way for calculating shift and broadening of atomic levels in partially ionized plasmas.

KEY WORDS: Green functions; composite particles; line broadening; line shift.

1. INTRODUCTION

Statistical mechanics, and in particular the Green's function method, is solidly established in cases of systems of particles which behave as if "elementary," i.e., maintain their identities and internal structure in the course of their interactions. But the standard approaches encounter grave difficulties in regimes where processes of decomposition, recombination, and rearrangement are important or even dominant; a typical case of such situations is the partially ionized plasma.

This is the reason why a general approach to the statistical mechanics of composite particles has been developed in recent years.(1-8) A detailed review of the various approaches is going to be published;(9) however, let us draw the common main feature of these approaches from an example: the hydrogenic plasma. The system is correctly described by using the Fock space:

$$\mathcal{F} = \bigoplus_{i,j=0}^{\infty} \left(\mathcal{F}_i^{(P)} \otimes \mathcal{F}_j^{(e)} \right) \tag{1.1}$$

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where $\mathscr{F}_i^{(p)}$ and $\mathscr{F}_j^{(e)}$ are, respectively, the i-proton and j-electron Fock subspaces. However, we can obtain a better representation of the system by using the Fock space:

$$\underline{\mathscr{F}} = \bigoplus_{i,j,k=0}^{\infty} \left(\mathscr{F}_i^{(p)} \otimes \mathscr{F}_j^{(e)} \otimes \mathscr{F}_k^{(a)}\right) \tag{1.2}$$

which is the Fock space of three types of particles: protons, electrons, and atoms; within this formulation we can apply the various tools of statistical mechanics (Wigner function and Green's function formalisms, etc. . . .). We see that the system is described by any subspace $\underline{\mathscr{F}}'$ of $\underline{\mathscr{F}}$ isometric to $\mathscr{F}$. The first task in the composite particle theory is to choose a subspace $\underline{\mathscr{F}}'$ in such a way that atomic states are described in terms of the additional atomic state spaces $\mathscr{F}_k^{(a)}$ "as well as possible"; the task is complicated by the fact that the unitary transformation U (explicitly exhibited in the method of Ref. 5 and implicitly defined in the other methods) which maps $\mathscr{F}$ onto $\underline{\mathscr{F}}'$ preserves the antisymmetry with respect to atomic and free proton (electron) exchange. The transformed Hamiltonian has the desired properties; i.e., it involves terms describing the free propagation of free protons, free electrons and atoms and terms describing interactions among which we find ionization and recombination terms; the first terms of the Girardeau Hamiltonian are explicitly given at the beginning of Section 3.

Up to now, some applications of these formulations have been published (an extensive review of all applications will be found in Ref. 9) but none of them is concerned with plasma physics. The aim of this paper is to develop a causal Green's function formalism within the frame of the formulation of Girardeau (5) in order to set up a systematic method leading to shift and broadening of atomic levels in partially ionized plasmas.

In Section 2 we present our causal Green's function method within the framework of the many-electron quantum theory developed by Balescu(10,11) which is particularly convenient when dealing with plasmas (the classical limits of the Wigner functions are the classical distribution functions). The relation between our method and the well-known Feynman method is discussed.

In Section 3 we give the one-atom causal Green's function calculated by means of the method presented in Section 2. This Green's function is obtained from the composite particle Hamiltonian of Girardeau(5); the calculation is limited to electron–atom weak coupling approximation and some complicated exchange contributions are neglected.

In Section 4, we show that a rough approximation of the profile of state $\{4,0,0\}$ of hydrogen can be obtained analytically.

In Section 5, we discuss briefly the rough result obtained in Section 4 and we comment on the advantages of our method; in particular we show that it provides a systematic way for calculating shift and broadening of atomic levels in more general cases (unstable plasma, strongly correlated plasma, quantum plasma, etc. . . .).

2. GREEN'S FUNCTION EQUATION OF MOTION METHOD FOR THE USUAL MANY-ELECTRON PROBLEM

Let us consider the many-electron problem treated by means of the formalism developed by Balescu.(11) We define the causal retarded one-electron Green's function as

$$\begin{aligned} \mathcal{G}(\mathbf{k}\tau t) &= \hbar^{-3}\mathrm{Tr}\left[a(\hbar\mathbf{k},\tau)a^+(\hbar\mathbf{k})\rho(t)\right], \qquad \tau > 0 \\ &= \hbar^{-3}\mathrm{Tr}\left[a(\hbar\mathbf{k},t+\tau)a^+(\hbar\mathbf{k},t)\rho(0)\right], \qquad \tau > 0 \\ &= 0, \qquad \tau < 0 \end{aligned} \tag{2.1}$$

where $a(\hbar\mathbf{k},\tau)$ obeys the evolution equation

$$\begin{aligned} \frac{d}{d\tau}a(\hbar\mathbf{k},\tau) &= \frac{d}{d\tau}\left\{\exp\left(\frac{i}{\hbar}H\tau\right)a(\hbar\mathbf{k})\exp\left(-\frac{i}{\hbar}H\tau\right)\right\} \\ &= \frac{i}{\hbar}\exp\left(\frac{i}{\hbar}H\tau\right)\left\{H, a(\hbar\mathbf{k})\right\}\exp\left(-\frac{i}{\hbar}H\tau\right) \end{aligned} \tag{2.2}$$

in which H is the usual many-electron Hamiltonian.(11)

If we Laplace transform $\mathcal{G}(\mathbf{k}\tau t)$ with respect to τ we find in the noninteracting case

$$\mathcal{G}(\mathbf{k}zt) = i\left(\frac{\hbar k^2}{2m} - z\right)^{-1}\mathcal{G}(\mathbf{k}0t)$$

In the general case, the pole of $\mathcal{G}(\mathbf{k}zt)$ gives $\hbar^{-1}$ times the energy of a dressed electron of wave vector **k**.

Let us consider functions

$$\begin{aligned} \mathcal{S}_s(\mathbf{k}_2\mathbf{p}_2\cdots\mathbf{k}_s\mathbf{p}_s\mathbf{k}_1\tau\mathbf{k}_1't) = \hbar^{-3s}\mathrm{Tr}\Big[&a^+(\mathbf{p}_2-\tfrac{1}{2}\hbar\mathbf{k}_2,\tau)\cdots a^+(\mathbf{p}_s-\tfrac{1}{2}\hbar\mathbf{k}_2,\tau) \\ &\times a(\mathbf{p}_s+\tfrac{1}{2}\hbar\mathbf{k}_s,\tau)\cdots a(\mathbf{p}_2+\tfrac{1}{2}\hbar\mathbf{k}_2,\tau) \\ &\times a(\hbar\mathbf{k}_1,\tau)a^+(\hbar\mathbf{k}_1')\rho(t)\Big] \end{aligned} \tag{2.3}$$

$$\begin{aligned} \mathcal{F}_s(\mathbf{k}_1\mathbf{p}_1\cdots\mathbf{k}_s\mathbf{p}_s\tau t) = \hbar^{-3s}\mathrm{Tr}\Big[&a^+(\mathbf{p}_1-\tfrac{1}{2}\hbar\mathbf{k}_1,\tau)\cdots a^+(\mathbf{p}_s-\tfrac{1}{2}\hbar\mathbf{k}_s,\tau) \\ &\times a(\mathbf{p}_s+\tfrac{1}{2}\hbar\mathbf{k}_s,\tau)\cdots a(\mathbf{p}_1+\tfrac{1}{2}\hbar\mathbf{k}_1,\tau)\rho(t)\Big]. \end{aligned} \tag{2.4}$$

We notice that

$$\mathcal{S}_1(\mathbf{k}\tau\mathbf{k}t) = \mathcal{G}(\mathbf{k}\tau t) \tag{2.5}$$

$$\mathcal{F}_s(\mathbf{k}_1\mathbf{p}_1 \cdots \mathbf{k}_s\mathbf{p}_s 0 t) = f_s(\mathbf{k}_1\mathbf{p}_1 \cdots \mathbf{k}_s\mathbf{p}_s t) \tag{2.6}$$

where $f_s(\cdots)$ is the usual S-electron reduced Wigner function introduced in Ref. 11. By means of (2.2) we find the following hierarchies:

$$\begin{aligned}\frac{\partial}{\partial\tau}\mathcal{S}_1(\mathbf{k}_1\tau\mathbf{k}_1't) &= -i\frac{\hbar k_1^2}{2m}\mathcal{S}_1(\mathbf{k}_1\tau\mathbf{k}_1't)\\ &\quad - \frac{i}{\hbar}\int d\mathbf{p}_2\,d\mathbf{l}\,V_l\exp\left(\frac{\hbar}{2}\mathbf{l}\cdot\boldsymbol{\partial}_2\right)\mathcal{S}_2(\mathbf{l},\mathbf{p}_2,\mathbf{k}_1-\mathbf{l},\tau,\mathbf{k}_1',t)\end{aligned} \tag{2.7}$$

$$\begin{aligned}\frac{\partial}{\partial\tau}\mathcal{S}_2(\mathbf{k}_2\mathbf{p}_2\mathbf{k}_1\tau\mathbf{k}_1't) &= -i\left(\frac{\hbar k_1^2}{2m} + \mathbf{k}_2\cdot\frac{\mathbf{p}_2}{m}\right)\mathcal{S}_2(\mathbf{k}_2\mathbf{p}_2\mathbf{k}_1\tau\mathbf{k}_1't)\\ &\quad - \frac{i}{\hbar}\int d\mathbf{l}\,V_l\exp\left(\frac{\hbar}{2}\mathbf{l}\cdot\boldsymbol{\partial}_2\right)\mathcal{S}_2(\mathbf{k}_2+\mathbf{l},\mathbf{p}_2,\mathbf{k}_1-\mathbf{l},\tau,\mathbf{k}_1',t)\\ &\quad + \frac{i}{\hbar}\int d\mathbf{p}_3\,d\mathbf{l}\,V_l\left\{\exp\left(\frac{\hbar}{2}\mathbf{l}\cdot\boldsymbol{\partial}_{23}\right) - \exp\left(-\frac{\hbar}{2}\mathbf{l}\cdot\boldsymbol{\partial}_{23}\right)\right\}\\ &\quad \times\mathcal{S}_3(\mathbf{k}_2-\mathbf{l},\mathbf{p}_2,\mathbf{l},\mathbf{p}_3,\mathbf{k}_1,\tau,\mathbf{k}_1',t)\\ &\quad - \frac{i}{\hbar}\int d\mathbf{p}_3\,d\mathbf{l}\,V_l\exp\left(\frac{\hbar}{2}\mathbf{l}\cdot\boldsymbol{\partial}_3\right)\mathcal{S}_3(\mathbf{k}_2,\mathbf{p}_2,\mathbf{l},\mathbf{p}_3,\mathbf{k}_1-\mathbf{l},\tau,\mathbf{k}_1',t)\end{aligned} \tag{2.8}$$

$$\begin{aligned}\frac{\partial}{\partial\tau}\mathcal{S}_3(\mathbf{k}_2\mathbf{p}_2\mathbf{k}_3\mathbf{p}_3\mathbf{k}_1\tau\mathbf{k}_1't) &= -i\left(\frac{\hbar k_1^2}{2m} + \mathbf{k}_2\cdot\frac{\mathbf{p}_2}{m} + \mathbf{k}_3\cdot\frac{\mathbf{p}_3}{m}\right)\\ &\quad \times\mathcal{S}_3(\mathbf{k}_2\mathbf{p}_2\mathbf{k}_3\mathbf{p}_3\mathbf{k}_1\tau\mathbf{k}_1't) + \cdots\end{aligned} \tag{2.9}$$

$$\begin{aligned}\frac{\partial}{\partial\tau}\mathcal{F}_1(\mathbf{k}_1\mathbf{p}_1\tau t) &= -i\mathbf{k}_1\cdot\frac{\mathbf{p}_1}{m}\mathcal{F}_1(\mathbf{k}_1\mathbf{p}_1\tau t)\\ &\quad + \frac{i}{\hbar}\int d\mathbf{p}_2\,d\mathbf{l}\,V_l\left\{\exp\left(\frac{\hbar}{2}\mathbf{l}\cdot\boldsymbol{\partial}_{12}\right) - \exp\left(-\frac{\hbar}{2}\mathbf{l}\cdot\boldsymbol{\partial}_{12}\right)\right\}\\ &\quad \times\mathcal{F}_2(\mathbf{k}_1-\mathbf{l},\mathbf{p}_1,\mathbf{l},\mathbf{p}_2,\tau,t)\end{aligned} \tag{2.10}$$

$$\frac{\partial}{\partial\tau}\mathcal{F}_2(\mathbf{k}_1\mathbf{p}_1\mathbf{k}_2\mathbf{p}_2\tau t) = -i\left(\mathbf{k}_1\cdot\frac{\mathbf{p}_1}{m} + \mathbf{k}_2\cdot\frac{\mathbf{p}_2}{m}\right)\mathcal{F}_2(\mathbf{k}_1\mathbf{p}_1\mathbf{k}_2\mathbf{p}_2\tau t) + \cdots \tag{2.11}$$

where $\boldsymbol{\partial}_i$ stands for $\partial/\partial\mathbf{p}_i$ and $\boldsymbol{\partial}_{ij}$ for $\partial/\partial\mathbf{p}_i - \partial/\partial\mathbf{p}_j$. We also need the following quantum cluster expansions:

$$\begin{aligned}\mathcal{F}_2(\mathbf{k}_1\mathbf{p}_1\mathbf{k}_2\mathbf{p}_2\tau t) &= P(1\,|\,2)\mathcal{F}_1(\mathbf{k}_1\mathbf{p}_1\tau t)\mathcal{F}_1(\mathbf{k}_2\mathbf{p}_2\tau t)\\ &\quad + \mathcal{G}_2(\mathbf{k}_1\mathbf{p}_1\mathbf{k}_2\mathbf{p}_2\tau t)\end{aligned} \tag{2.12}$$

where the symmetry operator $P(1\,|\,2)$ is defined in Ref. 11, and

$$\begin{aligned}\mathcal{S}_2(\mathbf{k}_2\mathbf{p}_2\mathbf{k}_1\tau\mathbf{k}_1't) &= Q(1\,|\,2)\mathcal{F}_1(\mathbf{k}_2\mathbf{p}_2\tau t)\mathcal{S}_1(\mathbf{k}_1\tau\mathbf{k}_1't)\\ &\quad+\mathcal{C}_2(\mathbf{k}_2\mathbf{p}_2\mathbf{k}_1\tau\mathbf{k}_1't) \qquad (2.13)\\ \mathcal{S}_3(\mathbf{k}_2\mathbf{p}_2\mathbf{k}_3\mathbf{p}_3\mathbf{k}_1\tau\mathbf{k}_1't) &= Q(1\,|\,2\,|\,3)\mathcal{F}_1(\mathbf{k}_2\mathbf{p}_2\tau t)\mathcal{F}_1(\mathbf{k}_3\mathbf{p}_3\tau t)\mathcal{S}_1(\mathbf{k}_1\tau\mathbf{k}_1't)\\ &\quad+\text{six }\mathcal{F}_1(\cdots)\mathcal{C}_2(\cdots)\text{ terms}\\ &\quad+\text{three }\mathcal{G}_2(\cdots)\mathcal{S}_1(\cdots)\text{ terms}\\ &\quad+\mathcal{C}_3(\mathbf{k}_2\mathbf{p}_2\mathbf{k}_3\mathbf{p}_3\mathbf{k}_1\tau\mathbf{k}_1't) \qquad (2.14)\end{aligned}$$

where $Q(1\,|\,2)\{Q(1\,|\,2\,|\,3)\}$ is the symmetry operator corresponding to $P(1\,|\,2)\{P(1\,|\,2\,|\,3)\}$; for example

$$\begin{aligned}Q(1\,|\,2)\mathcal{F}_1(\mathbf{k}_2\mathbf{p}_2\tau t)\mathcal{S}_1(\mathbf{k}_1\tau\mathbf{k}_1't) &= \mathcal{F}_1(\mathbf{k}_2\mathbf{p}_2\tau t)\mathcal{S}_1(\mathbf{k}_1\tau\mathbf{k}_1't)\\ &\quad+\Theta\mathcal{F}_1\Big(\mathbf{k}_1+\frac{1}{2}\mathbf{k}_2-\frac{1}{\hbar}\mathbf{p}_2,\\ &\qquad\frac{1}{2}\mathbf{p}_2+\frac{\hbar}{2}\mathbf{k}_1-\frac{\hbar}{4}\mathbf{k}_2,\tau,t\Big)\\ &\quad\times\mathcal{S}_1\Big(\frac{1}{2}\mathbf{k}_2+\frac{1}{\hbar}\mathbf{p}_2,\tau,\mathbf{k}_1',t\Big) \qquad (2.15)\end{aligned}$$

Here, Θ is the statistical factor ($\Theta=-1$ for electrons; however, Θ is conserved because we will have to set $\Theta=0$ in this formalism, see Ref. 11, in order to get the classical limit).

Although our method holds out of equilibrium, we restrict the following developments to the equilibrium state. So, the $\mathcal{S}_s(\cdots)$ and $\mathcal{F}_s(\cdots)$ functions become independent on t; moreover the $\mathcal{F}_s(\cdots)$ functions become independent on τ; as a matter of fact

$$\begin{aligned}&\mathcal{F}_s(\mathbf{k}_1\mathbf{p}_1\cdots\mathbf{k}_s\mathbf{p}_s\tau)\\ &\quad=\hbar^{-3s}\mathrm{Tr}\Big[\exp\Big(\frac{i}{\hbar}H\tau\Big)a^+\Big(\mathbf{p}_1-\frac{\hbar}{2}\mathbf{k}_1\Big)\cdots a^+\Big(\mathbf{p}_s-\frac{\hbar}{2}\mathbf{k}_s\Big)\\ &\qquad\times a\Big(\mathbf{p}_s+\frac{\hbar}{2}\mathbf{k}_s\Big)\cdots a\Big(\mathbf{p}_1+\frac{\hbar}{2}\mathbf{k}_1\Big)\exp\Big(-\frac{i}{\hbar}H\tau\Big)\rho^{\mathrm{eq}}\Big]\\ &\quad=\hbar^{-3s}\mathrm{Tr}\Big[a^+\Big(\mathbf{p}_1-\frac{\hbar}{2}\mathbf{k}_1\Big)\cdots a^+\Big(\mathbf{p}_s-\frac{\hbar}{2}\mathbf{k}_s\Big)\\ &\qquad\times a\Big(\mathbf{p}_s+\frac{\hbar}{2}\mathbf{k}_s\Big)\cdots a\Big(\mathbf{p}_1+\frac{\hbar}{2}\mathbf{k}_1\Big)\rho^{\mathrm{eq}}\Big]\end{aligned}$$

because

$$\exp\Big(-\frac{i}{\hbar}H\tau\Big)\rho^{\mathrm{eq}}\exp\Big(\frac{i}{\hbar}H\tau\Big)=\rho^{\mathrm{eq}}$$

2.1. First-Order Approximation (Hartree–Fock Approximation)

We insert (2.13) into (2.7) and we neglect the $\mathcal{C}_2(\cdots)$ term; we find

$$\frac{\partial}{\partial \tau}\mathcal{S}_1(\mathbf{k}_1\tau\mathbf{k}_1') = -i\frac{\hbar k_1^2}{2m}\mathcal{S}_1(\mathbf{k}_1\tau\mathbf{k}_1') - \frac{\Theta i}{\hbar}8\pi^3 n_e\hbar^3\int d\mathbf{l}\,V_l\varphi(\hbar\mathbf{k}_1 - \hbar\mathbf{l})\mathcal{S}_1(\mathbf{k}_1\tau\mathbf{k}_1') \tag{2.16}$$

where $\varphi(\cdots)$ is the Fermi distribution function and where we have used the homogeneity condition:

$$\mathcal{F}_1(\mathbf{k}_1\mathbf{p}_1\tau) = f_1(\mathbf{k}_1\mathbf{p}_1) = 8\pi^3 n_e\delta(\mathbf{k}_1)\varphi(\mathbf{p}_1) \tag{2.17}$$

and disregarded the V_0 term, exactly compensated by the continuous positive background effect. Then, we Laplace-transform (2.16) and we find

$$i\left(\frac{\hbar k_1^2}{2m} - z\right)\mathcal{G}(\mathbf{k}z) = \mathcal{G}(\mathbf{k}0) - \frac{\Theta i}{\hbar}8\pi^3 n_e\hbar^3\int d\mathbf{l}\,V_l\varphi(\hbar\mathbf{k} - \hbar\mathbf{l})\mathcal{G}(\mathbf{k}z) \tag{2.18}$$

which can be diagrammatically represented by

$$\mathcal{G}(\mathbf{k}z) = \rule[0.5ex]{4em}{2pt}\,\mathcal{G}(\mathbf{k}0) + \rule[0.5ex]{4em}{2pt}\!\bullet\,\mathcal{G}(\mathbf{k}z) \tag{2.19}$$

So, we find

$$\mathcal{G}(\mathbf{k}z) = \left[i\left(\frac{\hbar k^2}{2m} + \frac{\Delta_{HF}}{\hbar} - z\right)\right]^{-1}\mathcal{G}(\mathbf{k}0) \tag{2.20}$$

where

$$\Delta_{\mathrm{HF}} = \Theta n_e h^3\int d\mathbf{l}\,V_l\varphi(\hbar\mathbf{k} - \hbar\mathbf{l}) \tag{2.21}$$

If we insert the momentum Fermi distribution function in (2.21), we find for $\hbar^2k^2/2m + \Delta_{\mathrm{HF}}$ the well-known Hartree–Fock quasiparticle energy (see Raimes [12], p. 172). So, our point diagram corresponds to the open oyster Feynman diagram (see Mattuck,$^{(13)}$ p. 79).

2.2. Second-Order Approximation (Leading to the Random Phase Approximation)

We insert (2.13) into (2.7); we find

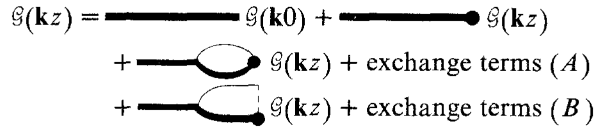
$$i\left(\frac{\hbar k^2}{2m} - z\right)\mathcal{G}(\mathbf{k}z) = \mathcal{G}(\mathbf{k}0) - \frac{i\Theta}{\hbar}8\pi^3 n_e\hbar^3\int d\mathbf{l}\,V_l\varphi(\hbar\mathbf{k} - \hbar\mathbf{l})\mathcal{G}(\mathbf{k}z)$$
$$- \frac{i}{\hbar}\int d\mathbf{p}_2\,d\mathbf{l}\,V_l\exp\left(\frac{\hbar}{2}\mathbf{l}\cdot\partial_2\right)\mathcal{C}_2(\mathbf{l},\mathbf{p}_2,\mathbf{k}-\mathbf{l},z,\mathbf{k}) \tag{2.22}$$

Then, owing to (2.7), (2.8), and (2.10), we write the evolution equation for $\mathcal{C}_2(\cdots)$. In the right-hand side of this equation, we insert the first term of the cluster expansions (2.12), (2.13), and (2.14), we make use of the homogeneity condition (2.17), and we only take into account the terms involving $\mathbb{S}_1(\mathbf{k}\tau\mathbf{k})$. At last we Laplace-transform the resulting equation in which we neglect the initial value $\mathcal{C}_2(\mathbf{l}, \mathbf{p}_2, \mathbf{k}-\mathbf{l}, 0, \mathbf{k})$. So, we obtain $\mathcal{C}_2(\mathbf{l}, \mathbf{p}_2, \mathbf{k}-\mathbf{l}, z, \mathbf{k})$ as a functional of $\mathbb{S}_1(\mathbf{k}z\mathbf{k})$ and $\varphi(\cdots)$, we insert it in (2.22), and we find

$$\begin{aligned}
\mathcal{G}(\mathbf{k}z) = {} & \left[i\left(\frac{\hbar k^2}{2m} - z\right)\right]^{-1} \mathcal{G}(\mathbf{k}0) + \left[i\left(\frac{\hbar k^2}{2m} - z\right)\right]^{-1} \frac{-i\Theta}{\hbar} 8\pi^3 n_e \hbar^3 \\
& \times \int d\mathbf{l}\, V_l \varphi(\hbar\mathbf{k} - \hbar\mathbf{l}) \mathcal{G}(\mathbf{k}z) + \left[i\left(\frac{\hbar k^2}{2m} - z\right)\right]^{-1} \frac{-i}{\hbar} \\
& \times \int d\mathbf{p}\, d\mathbf{l}\, V_l \left\{ i\left[\frac{\hbar(\mathbf{k}-\mathbf{l})^2}{2m} + \mathbf{l}\cdot\frac{\mathbf{p}}{m} - z\right]\right\}^{-1} \frac{-i8\pi^3 n_e}{\hbar} V_l \varphi\left(\mathbf{p} - \frac{\hbar}{2}\mathbf{l}\right) \\
& \times \left[1 + \Theta h^3 n_e \varphi\left(\mathbf{p} + \frac{\hbar}{2}\mathbf{l}\right)\right] \mathcal{G}(\mathbf{k}z) + \text{exchange terms } (A) \\
& + \left[i\left(\frac{\hbar k^2}{2m} - z\right)\right]^{-1} \frac{-i}{\hbar} \int d\mathbf{p}\, d\mathbf{l}\, V_l \left\{ i\left[\frac{\hbar(\mathbf{k}-\mathbf{l})^2}{2m} + \mathbf{l}\cdot\frac{\mathbf{p}}{m} - z\right]\right\}^{-1} \\
& \times \frac{i\Theta(8\pi^3 n_e)^2}{\hbar} V_l \left[\varphi\left(\mathbf{p} + \frac{\hbar}{2}\mathbf{l}\right) - \varphi\left(\mathbf{p} - \frac{\hbar}{2}\mathbf{l}\right)\right] \varphi(\hbar\mathbf{k} - \hbar\mathbf{l}) \mathcal{G}(\mathbf{k}z) \\
& + \text{exchange terms } (B)
\end{aligned} \tag{2.23}$$

The derivation of this result is rather lengthy, but straightforward. Equation (2.23) for $\mathcal{G}(\mathbf{k}z)$ is equivalent to the momentum distribution function evolution equation (18.7.7) of Ref. 11, which has been derived by using the splitting of the Wigner function vector into its vacuum and correlation components. A similar splitting of the $\mathbb{S}_s(\cdots)$ function vector can be introduced in the present case by using (2.13)- and (2.14)-like cluster expansions.

Equation (2.23) can be diagrammatically written:



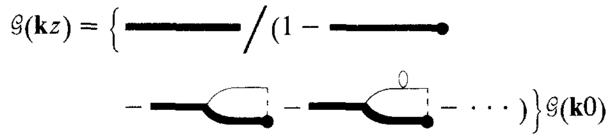
(2.24)

The above diagrammatic representation arises logically from the first Balescu diagram method.$^{(10)}$ Systematic graphical representation of any term in the general equation for $\mathcal{G}(\mathbf{k}z)$ can be introduced, but this task is beyond the scope of the present work. We only notice that the contribution of both cycle diagrams of equation (2.24) is that of the Feynman ring diagram; exchange terms (A) and (B) are the contribution of the two other second-order Feynman diagrams.

2.2.1. The Random Phase Approximation (RPA). We select the most divergent contributions which are proportional to any power of $e^2 n_e$ in the general equation for $\mathcal{G}(\mathbf{k}z)$; so, we are led to

(2.25)

where the contribution of the loop vertex has been established in Ref. 11. Equation (2.25) leads to



$$= \left[i\left(\frac{\hbar k^2}{2m} + \frac{\Delta_{\mathrm{RPA}}}{\hbar} - z \right) \right]^{-1} \mathcal{G}(\mathbf{k}0) \tag{2.26}$$

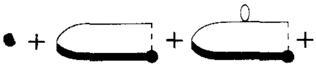
We first notice that

$$= -\frac{i\Theta}{\hbar} n_e h^3 \int d\mathbf{l}\, V_l \varphi(\hbar\mathbf{k} - \hbar\mathbf{l})\alpha_{\mathrm{RPA}}\left[\mathbf{l}, z - \frac{\hbar(\mathbf{k}-\mathbf{l})^2}{2m}\right]$$

where

$$\alpha_{\mathrm{RPA}}(\mathbf{l}, z) = \frac{8\pi^3 n_e}{\hbar} V_l \int d\mathbf{p}\left(\mathbf{l}\cdot\frac{\mathbf{p}}{m} - z\right)^{-1}\left[\varphi\left(\mathbf{p} + \frac{\hbar}{2}\mathbf{l}\right) - \varphi\left(\mathbf{p} - \frac{\hbar}{2}\mathbf{l}\right)\right] \tag{2.27}$$

At last, we get



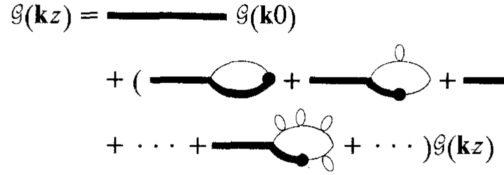
$$= -\frac{i\Theta}{\hbar} n_e h^3 \int d\mathbf{l}\, V_l \varphi(\hbar\mathbf{k} - \hbar\mathbf{l})$$
$$\times \left\{ 1 + \alpha_{\mathrm{RPA}}\left[\mathbf{l}, z - \frac{\hbar(\mathbf{k}-\mathbf{l})^2}{2m}\right] + \alpha^2_{\mathrm{RPA}}\left(\mathbf{l}, z - \frac{\hbar(\mathbf{k}-\mathbf{l})^2}{2m}\right) + \cdots \right\}$$
$$= -\frac{i\Theta}{\hbar} n_e h^3 \int d\mathbf{l} \frac{V_l}{\epsilon_{\mathrm{RPA}}\left(\mathbf{l}, z - \hbar(\mathbf{k}-\mathbf{l})^2/2m\right)} \varphi(\hbar\mathbf{k} - \hbar\mathbf{l}) \tag{2.28}$$

where

$$\epsilon_{\mathrm{RPA}}(\mathbf{l}, z) = \frac{1}{1 - \alpha_{\mathrm{RPA}}(\mathbf{l}, z)} \tag{2.29}$$

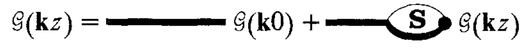
is the dielectric constant in the RPA. So, we recover Δ_{RPA} (see Mattuck,(13) p. 163), i.e., Δ_{HF} in which the Coulomb potential is replaced by the dynamically screened potential. Although $\epsilon_{\mathrm{RPA}}(\cdots)$ has a classical limit, we see that both Δ_{HF} and Δ_{RPA} vanish in the classical limit (for which we have to set $\Theta = 0$).

2.2.2. The Classical Limit for Plasmas. We select the most divergent contributions which are proportional to $(e^2 n_e)^n e^2$, $n = 1, 2, \ldots,$ in the general equation for $\mathcal{G}(\mathbf{k}z)$; so, we are led to the equation



(2.30)

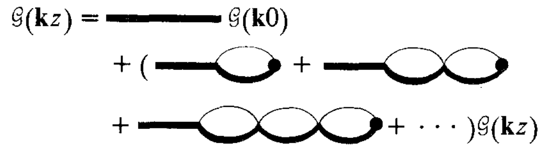
The summation of the rings appearing in the above equation is beyond the scope of the present work; however, we can expect to obtain a very rough approximation to (2.30) by using the equation



(2.31)

where the contribution of the S cycle is that of the closed cycle of Eq. (2.24) in which the Coulomb potential is replaced by the Debye potential. As can be seen in Eq. (2.24), this S cycle has a nonvanishing limit in the classical case (in which we have to set $\Theta = 0$).

2.2.3. The Boltzmann Approximation for Low Density Neutral Gases. If we select in the general equation for $\mathcal{G}(\mathbf{k}z)$ the contributions proportional to $(e^2 n_e)e^{2n}$, $n = 1, 2, \ldots,$ we are led to the equation



(2.32)

2.3. Discussion

Our equation of motion method has some advantages with respect to the usual Feynman diagram method:

(a) It holds for nonequilibrium systems; in particular it can be useful when dealing with systems in stationary nonequilibrium state forced by external stationary constraints.

(b) It allows us to take into account effects arising from initial correlations (it has been already noticed(14) that the usual Feynman diagram method cannot take into account these effects). A typical example of such contributions, which has been disregarded when deriving Eq. (2.23), is

$$\left[i\left(\frac{\hbar k^2}{2m}-z\right)\right]^{-1}\frac{-i}{\hbar}\int d\mathbf{p}_2\,d\mathbf{l}\,V_l\left[i\left(\frac{\hbar(\mathbf{k}-\mathbf{l})^2}{2m}+\mathbf{l}\cdot\frac{\mathbf{p}_2}{m}-z\right)\right]^{-1}$$
$$\times\frac{-i8\pi^3 n_e^2}{\hbar}\int d\mathbf{p}_3\,V_l\eta(\mathbf{l}\mathbf{p}_2\mathbf{p}_3)\mathcal{G}(\mathbf{k}z)$$

where we have used the homogeneity condition

$$\mathcal{G}_2(\mathbf{l}\mathbf{p}\mathbf{l}'\mathbf{p}')=8\pi^3 n_e^2\delta(\mathbf{l}+\mathbf{l}')\eta(\mathbf{l}\mathbf{p}\mathbf{p}')$$

This term arises from one of the $\mathcal{G}_2(\cdots)\mathcal{S}_1(\cdots)$ terms of cluster expansion (2.14) when this cluster expansion is introduced into the evolution equation for $\mathcal{C}_2(\cdots)$, see the derivation of Eq. (2.23). Far from equilibrium, such contributions can become important when dealing with systems for which initial correlations are known to play a fundamental role.

(c) The classical limit can be taken as in the Wigner function formalism for which this limit results from$^{(10,11)}$ (1) setting

$$\Theta=0 \tag{2.33}$$

into the cluster expansions, and (2) taking the limit

$$\lim_{\hbar\to 0}\frac{i}{\hbar}\left[\exp\left(\frac{\hbar}{2}\mathbf{l}\cdot\boldsymbol{\partial}\right)-\exp\left(-\frac{\hbar}{2}\mathbf{l}\cdot\boldsymbol{\partial}\right)\right]=i\mathbf{l}\cdot\boldsymbol{\partial} \tag{2.34}$$

into the vertex contributions; this limit causes $\hbar$ to disappear.

In our method, we first introduce (2.33) into the cluster expansions and take limit (2.34) into the vertex contributions when possible. But we have to pay attention when taking the classical limit of the contributions of the remaining vertices; let us consider for example equation (2.24): We find easily that the open cycle contribution vanishes but we cannot take limit (2.34) into the closed cycle contribution; we only can use the following approximation:

$$\frac{\hbar l}{2}\text{ negligible with respect to }p \tag{2.35}$$

So, $\hbar$ does not disappear in the classical limit; we can understand this feature in the following way:

(1) When we are dealing with two-time functions as

$$\mathrm{Tr}\left[a^+(\cdots\tau)a(\cdots\tau)a^+(\cdots\tau')a(\cdots\tau')\rho\right] \tag{2.36}$$

in which the number of creation operators at time τ (τ') is equal to the number of annihilation operators at time τ (τ'), we find that $\hbar$ disappears when we introduce the classical limit (2.33) and (2.34) into the equations of motion.$^{(10,11)}$ This feature results from the fact that (2.36)-like functions represent two time correlation functions corresponding to two physical observables, and thus, have a classical limit (which can be calculated within the framework of classical statistical mechanics).

(2) On the other hand, we see that definition (2.1) has not a corresponding classical definition; as a matter of fact, (2.1)-like functions, in which the number of creation operators at time τ (τ') is different from the number of annihilation operators at time τ (τ'), are no longer two-time correlation functions corresponding to some two physical observables; they are two-time correlation functions associated to two states [usual interpretation of $\mathcal{G}(\mathbf{k}\tau)$, see Nozières,(15) p. 51]. Even if the system can be treated classically (the transport coefficients are related to (2.36)-like functions, and thus have a classical limit), the Green's function $\mathcal{G}(\mathbf{k}\tau)$ appears to be essentially a pure quantum concept; as a matter of fact, $\mathcal{G}(\mathbf{k}z)$ is the Green's function of the Schrödinger equation of a dressed electron; let us introduce

$$\mathcal{G}'(\mathbf{k}z) = \frac{i}{\hbar}\,\frac{\mathcal{G}(\mathbf{k}z)}{\mathcal{G}(\mathbf{k}0)} \tag{2.37}$$

Eq. (2.31) becomes

$$\left[\frac{\hbar^2k^2}{2m} + V(\mathbf{k},\hbar z) - \hbar z\right]\mathcal{G}'(\mathbf{k}z) = 0 \tag{2.38}$$

where

$$V(\mathbf{k},\hbar z) = i\hbar \tag{2.39}$$

We see that (2.38) is the Green's function equation corresponding to the Schrödinger equation:

$$\left[\frac{\hbar^2k^2}{2m} - \tilde{V}(\mathbf{k},\mathcal{E})\right]\psi(\mathbf{k}) = \mathcal{E}\psi(\mathbf{k}) \tag{2.40}$$

or

$$-\frac{\hbar^2}{2m}\Delta_{\mathbf{x}}\psi(\mathbf{x}) + \int \tilde{V}(\mathbf{x}-\mathbf{x}',\mathcal{E})\psi(\mathbf{x}')d\mathbf{x}' = \mathcal{E}\psi(\mathbf{x}) \tag{2.41}$$

for the wave function $\psi(\mathbf{x})$ of an electron interacting with the medium by means of some nonlocal potential $\tilde{V}(\mathbf{x}-\mathbf{x}',\mathcal{E})$, which is the analytical continuation of $V(\mathbf{x}-\mathbf{x}',\mathcal{E})$ defined with $\mathcal{E}$ in the upper half complex plane.

3. ATOMIC GREEN'S FUNCTION FOR PARTIALLY IONIZED HYDROGENIC PLASMA IN THE WEAK COUPLING LIMIT

After our Green's function method has been developed in the previous section within the framework of the usual many-electron problem we only summarize the results when dealing with partially ionized plasma.

We use the Hamiltonian for composite particle systems established by Girardeau(5) by means of a general Tani transformation: We only consider the following low-density terms:

$$\begin{aligned} H = {} & \int d\mathbf{X}\varphi^{+}(\mathbf{X})\frac{-\hbar^2}{2M}\Delta_{\mathbf{X}}\varphi(\mathbf{X}) + \int d\mathbf{x}\,\varphi^{+}(\mathbf{x})\frac{-\hbar^2}{2m}\Delta_{\mathbf{x}}\varphi(\mathbf{x}) \\ & + \sum_n \int d\mathbf{R}\,a^{+}(\mathbf{R}n)\left[-\frac{\hbar^2}{2(M+m)}\Delta_{\mathbf{R}} + E_n\right]a(\mathbf{R}n) \\ & + \sum_n \int d\mathbf{R}\,d\mathbf{X}\,d\mathbf{x}\,d\mathbf{x}'\,d\mathbf{x}''\,\varphi^{+}(\mathbf{X})\varphi^{+}(\mathbf{x})\varphi^{+}(\mathbf{x}') \\ & \qquad \times (\mathbf{X}\mathbf{x}\mathbf{x}'|H|\mathbf{R}n\mathbf{x}'')\varphi(\mathbf{x}'')a(\mathbf{R}n) + \mathrm{H.c.} \\ & + \sum_{nn'} \int d\mathbf{R}\,d\mathbf{R}'\,d\mathbf{x}\,d\mathbf{x}'\,a^{+}(Rn)\varphi^{+}(\mathbf{x})(\mathbf{R}n\mathbf{x}|H|\mathbf{R}'n'\mathbf{x}')\varphi(\mathbf{x}')a(\mathbf{R}'n') \end{aligned} \tag{3.1}$$

in which

$$(\mathbf{X}\mathbf{x}\mathbf{x}'|H|\mathbf{R}n\mathbf{x}'') = -\delta(\mathbf{x}'-\mathbf{x}'')\left[V^{pe}(\mathbf{X}\mathbf{x}') + V^{ee}(\mathbf{x}\mathbf{x}')\right](\mathbf{X}\mathbf{x}\,|\,\mathbf{R}n)$$

$$\begin{aligned} & (\mathbf{R}n\mathbf{x}|H|\mathbf{R}'n'\mathbf{x}') \\ & \quad = \delta(\mathbf{x}-\mathbf{x}')\int d\mathbf{Y}\,d\mathbf{y}\,(\mathbf{R}n\,|\,\mathbf{Y}\mathbf{y})\left[V^{pe}(\mathbf{Y}\mathbf{x}) + V^{ee}(\mathbf{y}\mathbf{x})\right](\mathbf{Y}\mathbf{y}\,|\,\mathbf{R}'n') \end{aligned}$$

$$(\mathbf{X}\mathbf{x}\,|\,\mathbf{R}n) = \delta(\mathbf{R}-\Lambda\mathbf{X}-\lambda\mathbf{x})\varphi_n(\mathbf{x}-\mathbf{X}), \qquad \Lambda = \frac{M}{M+m}, \qquad \lambda = \frac{m}{M+m}$$

[the $\varphi_n(\cdots)$ are the hydrogenic wave functions, n is the set of usual quantum numbers]. In (3.1) we find successively the proton, electron, and atomic free propagation terms, the electron–atom ionization and recombination terms, and the electron–atom scattering term. Then we introduce

$$\varphi^{+}(\hbar\mathbf{K}) = (8\pi^3)^{-1/2}\int d\mathbf{X}\exp(i\mathbf{K}\cdot\mathbf{X})\varphi^{+}(\mathbf{X}), \qquad \varphi^{+}(\hbar\mathbf{k}) = \cdots \tag{3.2}$$

$$a^{+}(\hbar\mathbf{L}n) = (8\pi^3)^{-1/2}\int d\mathbf{R}\exp(i\mathbf{L}\cdot\mathbf{R})a^{+}(\mathbf{R}n) \tag{3.3}$$

$$\varphi_n(\mathbf{l}) = (8\pi^3)^{-1/2}\int d\mathbf{r}\exp(-i\mathbf{l}\cdot\mathbf{r})\varphi_n(\mathbf{r}) \tag{3.4}$$

$$V^{ee}(\mathbf{l}) = (8\pi^3)^{-1}\int d\mathbf{r}\exp(-i\mathbf{l}\cdot\mathbf{r})V^{ee}(\mathbf{r}) = \frac{e^2}{8\pi^3\epsilon_0 l^2} = -V^{pe}(\mathbf{l}) \tag{3.5}$$

and we define

$$\mathcal{S}_1(\mathbf{L}n\tau\mathbf{L}'n't) = \hbar^{-3}\mathrm{Tr}\left[a(\hbar\mathbf{L}n\tau)a^+(\hbar\mathbf{L}'n')\rho(t)\right] \tag{3.6}$$

$$\begin{aligned}&\mathcal{S}_2(\mathbf{lpL}n\tau\mathbf{L}'n't)\\ &\quad= \hbar^{-6}\mathrm{Tr}\left[\varphi^+\left(\mathbf{p}-\frac{\hbar}{2}\mathbf{l},\tau\right)\varphi\left(\mathbf{p}+\frac{\hbar}{2}\mathbf{l},\tau\right)a(\hbar\mathbf{L}n\tau)a^+(\hbar\mathbf{L}'n)\rho(t)\right]\end{aligned} \tag{3.7}$$

We also need to define

$$\mathcal{S}_1'(\mathbf{Kk}\tau\mathbf{L}'n't) = \hbar^{-3}\mathrm{Tr}\left[\varphi(\hbar\mathbf{K}\tau)\varphi(\hbar\mathbf{k}\tau)a^+(\hbar\mathbf{L}'\mathbf{n}')\rho(t)\right] \tag{3.8}$$

$$\begin{aligned}&\mathcal{S}_2'(\mathbf{lpKk}\tau\mathbf{L}'n't)\\ &\quad= \hbar^{-6}\mathrm{Tr}\left[\varphi^+\left(\mathbf{p}-\frac{\hbar}{2}\mathbf{l},\tau\right)\varphi\left(\mathbf{p}+\frac{\hbar}{2}\mathbf{l},\tau\right)\varphi(\hbar\mathbf{K}\tau)\varphi(\hbar\mathbf{k}\tau)a^+(\hbar\mathbf{L}'n')\rho(t)\right]\end{aligned} \tag{3.9}$$

$$\mathcal{F}_1(\mathbf{lp}\tau t) = \hbar^{-3}\mathrm{Tr}\left[\varphi^+\left(\mathbf{p}-\frac{\hbar}{2}\mathbf{l},\tau\right)\varphi\left(\mathbf{p}+\frac{\hbar}{2}\mathbf{l},\tau\right)\rho(t)\right] \tag{3.10}$$

and introduce the cluster expansions

$$\mathcal{S}_2(\mathbf{lpL}n\tau\mathbf{L}'n't) = \mathcal{F}_1(\mathbf{lp}\tau t)\mathcal{S}_1(\mathbf{L}n\tau\mathbf{L}'n't) + \mathcal{C}_2(\mathbf{lpL}n\tau\mathbf{L}'n't) \tag{3.11}$$

$$\begin{aligned}\mathcal{S}_2'(\mathbf{lpKk}\tau\mathbf{L}'n't) &= \mathcal{F}_1(\mathbf{lp}\tau t)\mathcal{S}_1'(\mathbf{Kk}\tau\mathbf{L}'n't)\\ &\quad+ \Theta\mathcal{F}_1\left(\mathbf{k}+\frac{1}{2}\mathbf{l}-\frac{1}{\hbar}\mathbf{p},\frac{1}{2}\mathbf{p}+\frac{\hbar}{2}\mathbf{k}-\frac{\hbar}{4}\mathbf{l},\tau,t\right)\\ &\quad\times\mathcal{S}_1'\left(\mathbf{K},\frac{1}{\hbar}\mathbf{p}+\frac{1}{2}\mathbf{l},\tau,\mathbf{L}',n',t\right) + \mathcal{C}_2'(\mathbf{lpKk}\tau\mathbf{L}'n't)\end{aligned} \tag{3.12}$$

Owing to the usual interpretation (see Nozières,$^{(15)}$ p. 51), we notice that $\mathcal{S}_1'(\mathbf{Kk}\tau\mathbf{L}'n't)$ is the probability amplitude for an atom (center of mass momentum $\hbar\mathbf{L}$, internal quantum number n) added to the system at time t, to become dissociated into a proton (momentum $\hbar\mathbf{K}$) and an electron (momentum $\hbar\mathbf{k}$) at time $t+\tau$. So, $\mathcal{S}_1'^*\mathcal{S}_1'(\cdots)$ increases from 0 to n_e/n_a when t increases from 0 to ∞ (n_e electronic density, n_a atomic density), and

$$\lim_{\tau\to 0}\frac{d}{d\tau}\mathcal{S}_1'^*(\cdots\tau)\mathcal{S}_1'(\cdots\tau)$$

is the ionization rate of an atom [state $|\hbar\mathbf{L},n)$] into a proton–electron pair [state $|\hbar\mathbf{K}\hbar\mathbf{k})$]. In this way, the Green's function method provides a rigorous definition of the various ionization, recombination, and transition rates.

By means of the equation of motion method we have developed in the previous section, we find that, at equilibrium, the Laplace transform of the atomic Green's function

$$\mathcal{G}(\mathbf{L}_1 n_1 \tau) = \mathcal{S}_1(\mathbf{L}_1 n_1 \tau \mathbf{L}_1 n_1) \tag{3.13}$$

obeys

$$\begin{aligned}
\mathcal{G}(\mathbf{L}_1 n_1 z) = {} & \left\{ i\left[\frac{\hbar L_1^2}{2(M+m)} + \frac{E_{n_1}}{\hbar} - z \right] \right\}^{-1} \mathcal{G}(\mathbf{L}_1 n_1 0) \\
& + \left\{ i\left[\frac{\hbar L_1^2}{2(M+m)} + \frac{E_{n_1}}{\hbar} - z \right] \right\}^{-1} \\
& \times \left\{ O_i(\mathbf{L}_1 n_1 z) + O_{i,\mathrm{ex}}(\mathbf{L}_1 n_1 z) + O_{\mathrm{sc}}(\mathbf{L}_1 n_1 z) \right\} \mathcal{G}(\mathbf{L}_1 n_1 z)
\end{aligned} \tag{3.14}$$

with

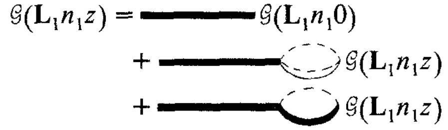
$$\begin{aligned}
O_i(\mathbf{L}_1 n_1 z) = {} & -\frac{1}{\hbar^2} \frac{e^4 n_e}{8\pi^3 \epsilon_0^2} \int d\mathbf{L}\, d\mathbf{l}\, d\mathbf{p} \\
& \times \frac{1}{l^2} \left[\varphi_{n_1}^*\left(\mathbf{L} + \Lambda \mathbf{L}_1 - \frac{\mathbf{l}}{2} \right) - \varphi_{n_1}^*\left(\mathbf{L} + \Lambda \mathbf{L}_1 + \frac{\mathbf{l}}{2} \right) \right] \\
& \times \left\{ i\left[\frac{\hbar}{2M} \left(\mathbf{L} + \frac{\mathbf{l}}{2} \right)^2 + \frac{\hbar}{2m} \left(\mathbf{L}_1 + \mathbf{L} - \frac{\mathbf{l}}{2} \right)^2 + \mathbf{l} \cdot \frac{\mathbf{p}}{m} - z \right] \right\}^{-1} \\
& \times \frac{1}{l^2} \left[\varphi_{n_1}\left(\mathbf{L} + \Lambda \mathbf{L}_1 - \frac{\mathbf{l}}{2} \right) - \varphi_{n_1}\left(\mathbf{L} + \Lambda \mathbf{L}_1 + \frac{\mathbf{l}}{2} \right) \right] \varphi\left(\mathbf{p} - \frac{\hbar}{2} \mathbf{l} \right)
\end{aligned} \tag{3.15}$$

$$\begin{aligned}
O_{i,\mathrm{ex}}(\mathbf{L}_1 n_1 z) = {} & \cdots \left(\mathbf{L}_1 + \mathbf{L} - \frac{\mathbf{p}}{\hbar} \right)^{-2} \left[\varphi_{n_1}\left(\frac{\mathbf{p}}{\hbar} + \frac{\mathbf{l}}{2} - \lambda \mathbf{L}_1 \right) \right. \\
& \left. - \varphi_{n_1}\left(\mathbf{L} + \Lambda \mathbf{L}_1 + \frac{\mathbf{l}}{2} \right) \right] \varphi\left(\mathbf{p} - \frac{\hbar}{2} \mathbf{l} \right)
\end{aligned} \tag{3.16}$$

$$\begin{aligned}
O_{\mathrm{sc}}(\mathbf{L}_1 n_1 z) = {} & -\frac{1}{\hbar^2} \frac{e^4 n_e}{8\pi^3 \epsilon_0^2} \sum_n \int d\mathbf{L}\, d\mathbf{L}'\, d\mathbf{l}\, d\mathbf{p}\, \varphi_{n_1}^*\left(\mathbf{L} + \Lambda \mathbf{l} - \frac{\mathbf{l}}{2} \right) \\
& \times \frac{1}{l^2} \left[\varphi_n\left(\mathbf{L} - \frac{\mathbf{l}}{2} \right) - \varphi_n\left(\mathbf{L} + \frac{\mathbf{l}}{2} \right) \right] \\
& \times \left\{ i\left[\frac{\hbar(\mathbf{L}_1 - \mathbf{l})^2}{2(M+m)} + \frac{E_n}{\hbar} + \mathbf{l} \cdot \frac{\mathbf{p}}{m} - z \right] \right\}^{-1} \\
& \times \varphi_n^*\left(\mathbf{L}' - \Lambda \mathbf{l} + \frac{\mathbf{l}}{2} \right) \frac{1}{l^2} \left\{ \varphi_{n_1}\left(\mathbf{L}' + \frac{\mathbf{l}}{2} \right) - \varphi_{n_1}\left(\mathbf{L}' - \frac{\mathbf{l}}{2} \right) \right\} \\
& \times \varphi\left(\mathbf{p} - \frac{\hbar \mathbf{l}}{2} \right)
\end{aligned} \tag{3.17}$$

$O_i(\cdots)$ represents the weak coupling (second-order) scattering in which the atomic proton–electron pair is dissociated in the intermediate state; $O_{i,\mathrm{ex}}(\cdots)$ represents an additional contribution to $O_i(\cdots)$ arising from exchange effects between the incident electron and the atomic electron; $O_{\mathrm{sc}}(\cdots)$ represents the weak coupling (second-order) scattering in which the atom suffers a transition in the intermediate state (the $n = n_1$ term in the summation represents the weak coupling elastic scattering). $O_{\mathrm{sc,ex}}(\cdots)$, which represents exchange contributions to $O_{\mathrm{sc}}(\cdots)$ does not appear in Eq. (3.14). $O_{\mathrm{sc,ex}}(\cdots)$ and exact $O_{i,\mathrm{ex}}(\cdots)$ can be found by inserting in Hamiltonian (3.1) all the electron–atom ionization, recombination, and scattering exchange terms (see Ref. 5). We should find two type of terms in $O_{i,\mathrm{ex}}(\cdots)$ and $O_{\mathrm{sc,ex}}(\cdots)$: those arising from exchange effects between the incident electron and the atomic electron and those arising from exchange effects between the incident electron and the other electrons of the plasma.

Equation (3.14) has been derived in a rather lengthy, but straightforward way as Eq. (2.23) was; in particular $O_{i,\mathrm{ex}}(\cdots)$ is approximated. Because an exact calculation with Hamiltonian (3.1) cannot lead to exact $O_{i,\mathrm{ex}}(\cdots)$ (as we explained just above), we disregard $O_{i,\mathrm{ex}}(\cdots)$ in the following. We also notice that (3.14) can be represented diagrammatically in the following way:



(3.18)

At last, owing to (3.14), we find that the Laplace transform of

$$\mathcal{G}'(\mathbf{L}_1 n_1 \tau) = \frac{i}{\hbar}\,\frac{\mathcal{G}(\mathbf{L}_1 n_1 z)}{\mathcal{G}(\mathbf{L}_1 n_1 0)} \tag{3.19}$$

obeys

$$\left\{ \frac{\hbar^2 L_1^2}{2(M+m)} + E_{n_1} + i\hbar\left[O_i(\mathbf{L}_1 n_1 z) + O_{\mathrm{sc}}(\mathbf{L}_1 n_1 z)\right] - \hbar z \right\} \mathcal{G}'(\mathbf{L}_1 n_1 z) = 1 \tag{3.20}$$

which is the definition equation for the Green's function of the Schrödinger equation:

$$\left[\frac{\hbar^2 L_1^2}{2(M+m)} + E_{n_1} + \tilde{V}_i(\mathbf{L}_1 n_1 \mathcal{E}) + \tilde{V}_{\mathrm{sc}}(\mathbf{L}_1 n_1 \mathcal{E}) \right] \psi(\mathbf{L}_1 n_1) = \mathcal{E}\, \psi(\mathbf{L}_1 n_1) \tag{3.21}$$

in which $\tilde{V}_i(\cdots\mathcal{E})$ and $\tilde{V}_{\mathrm{sc}}(\cdots\mathcal{E})$ are the $z=\mathcal{E}/\hbar$ value of the analytical continuation of $i\hbar O_i(\cdots z)$ and $i\hbar O_{\mathrm{sc}}(\cdots z)$ defined by (3.15) and (3.17) with z in the upper half complex plane. Equation (3.21) is a Schrödinger equation written in a mixed representation (momentum representation for the atomic center-of-mass motion, internal quantum number representation for the proton–electron relative motion). It can be easily interpreted if we write it in momentum representation:

$$\int d\mathbf{L}\,d\mathbf{l}\,\langle\mathbf{L}_1\mathbf{l}_1|\mathcal{H}_0+\tilde{\mathcal{V}}(\mathcal{E})|\mathbf{L}\mathbf{l}\rangle\psi(\mathbf{L}\mathbf{l})=\mathcal{E}\psi(\mathbf{L}_1\mathbf{l}_1) \tag{3.22}$$

with

$$\langle\mathbf{L}_1\mathbf{l}_1|\mathcal{H}_0|\mathbf{L}\mathbf{l}\rangle=\sum_n\delta(\mathbf{L}_1-\mathbf{L})\varphi_n^*(\mathbf{l}_1)\left[\frac{\hbar^2L_1^2}{2(M+m)}+E_n\right]\varphi_n(\mathbf{l}) \tag{3.23}$$

$$\langle\mathbf{L}_1\mathbf{l}_1|\tilde{\mathcal{V}}(\mathcal{E})|\mathbf{L}\mathbf{l}\rangle=\sum_n\delta(\mathbf{L}_1-\mathbf{L})\varphi_n^*(\mathbf{l}_1)\left[\tilde{V}_i(\mathbf{L}_1n\mathcal{E})+V_{\mathrm{sc}}(\mathbf{L}_1n\mathcal{E})\right]\varphi_n(\mathbf{l}) \tag{3.24}$$

$$\psi(\mathbf{L}_1\mathbf{l}_1)=\sum_{n_1}\varphi_{n_1}(\mathbf{l}_1)\psi(\mathbf{L}_1n_1)$$

So, (3.22) is the Schrödinger equation describing an atom perturbed by the free electrons of the plasma; their effect is taken into account by the additional dressing potential $\tilde{\mathcal{V}}(\mathcal{E})$. This equation has the following properties:

(α) It is a self-consistent eigenvalue equation.

(β) Its perturbative potential $\tilde{\mathcal{V}}(\mathcal{E})$ is diagonal with respect to the eigenfunctions of the unperturbed Hamiltonian $\mathcal{H}_0$, which are

$$\psi_{\mathbf{L}_1n_1}(\mathbf{L}\mathbf{l})=\delta(\mathbf{L}_1-\mathbf{L})\varphi_{n_1}(\mathbf{l}) \tag{3.25}$$

So, the corresponding eigenvalues $\mathcal{E}_{\mathbf{L}_1n_1}$ are the solutions of the algebraic equation

$$\mathcal{E}_{\mathbf{L}_1n_1}=\frac{\hbar^2L_1^2}{2(M+m)}+E_{n_1}+\tilde{V}_i(\mathbf{L}_1n_1\mathcal{E}_{\mathbf{L}_1n_1})+\tilde{V}_{\mathrm{sc}}(\mathbf{L}_1n_1\mathcal{E}_{\mathbf{L}_1n_1}) \tag{3.26}$$

The fact that unperturbed atomic wave function (3.25) is eigenfunction of the perturbed Schrödinger equation (3.22) with eigenvalue $\mathcal{E}_{\mathbf{L}_1n_1}$ such that $\operatorname{Im}\mathcal{E}_{\mathbf{L}_1n_1}<0$[2] means that a proton–electron state, whose wave function is (3.25) at a given time, suffers a decay resulting from its interaction with the surrounding medium; proton–electron states which could be interpreted as atomic states in the plasma have clearly distorted wave functions with respect to that of isolated atomic states; in this sense, our method gives, at present stage, a low-density approximation.

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[2] This property of the Green's function poles is pointed out in the various textbooks; see for example Refs. 15 and 17.

(γ) Its total Hamiltonian does not allow any more the separation between the center-of-mass motion and the relative motion: this method does not allow the splitting of $\Delta E_{\mathbf{L}_1 n_1} = \mathcal{E}_{\mathbf{L}_1 n_1} - \hbar^2 L_1^2/2(M+m) - E_{n_1}$ into a correction to center-of-mass energy and a correction to the internal energy.

4. PROFILE OF THE $\{4,0,0\}$ LEVEL OF HYDROGEN

As an application of our method, we calculate in this section the profile of the state $n_1 = \{4,0,0\}$ of hydrogen; this level has been chosen because the radiative transition $\{4,0,0\} \to \{2,1,0\}$ is one of the components of the H_β line.

We choose $L_1 = 0$ and we introduce the following approximations:

$$m \ll M \approx M + m \Leftrightarrow \Lambda \approx 1, \lambda \approx 0 \tag{4.1}$$

$$l \ll L \tag{4.2}$$

Approximation (4.2) allows the use of expansion in powers of l/L; it means that we only take into account long-range (with respect to the atomic radius) electron–atom interaction; so, it appears to be consistent with the weak coupling approximation which led to Eq. (3.14); within this approximation, the electron–atom interaction is reduced to the dipolar interaction, as can be seen in the following equations. Using (4.1) and (4.2), (3.15) and (3.17) lead to

$$\tilde{\mathcal{V}}_i(0n_1\mathcal{E}) = -\frac{e^4 n_e}{8\pi^3\epsilon_0^2}\int d\mathbf{L}\,d\mathbf{l}\,d\mathbf{p}\,\frac{1}{l^4}\,\frac{|\mathbf{l}\cdot\partial_{\mathbf{L}}\varphi_{n_1}(\mathbf{L})|^2}{\hbar^2L^2/2m + (\hbar/m)\mathbf{l}\cdot\mathbf{p} - \mathcal{E}}\,\varphi\left(\mathbf{p} - \frac{\hbar}{2}\mathbf{l}\right) \tag{4.3}$$

$$\begin{aligned}\tilde{\mathcal{V}}_{\mathrm{sc}}(0n_1\mathcal{E}) &= -\frac{e^4 n_e}{8\pi^3\epsilon_0^2}\sum_n\int d\mathbf{L}\,d\mathbf{L}'\,d\mathbf{l}\,d\mathbf{p}\,\frac{1}{l^4}\\ &\quad\times\frac{\left[\varphi_{n_1}^*(\mathbf{L})\mathbf{l}\cdot\partial_{\mathbf{L}}\varphi(\mathbf{L})\right]\left[\varphi_n^*(\mathbf{L}')\mathbf{l}\cdot\partial_{\mathbf{L}'}\varphi_{n_1}(\mathbf{L}')\right]}{(\hbar^2l^2/2M) + (\hbar/m)\mathbf{l}\cdot\mathbf{p} + E_n - \mathcal{E}}\,\varphi\left(\mathbf{p} - \frac{\hbar}{2}l\right)\\ &= -\frac{e^4 n_e}{8\pi^3\epsilon_0^2}\sum_n\int d\mathbf{l}\,d\mathbf{p}\,\frac{1}{l^2}\,\frac{|\langle n_1|\mathbf{l}\cdot\mathbf{r}/l|n\rangle|^2}{(\hbar^2l^2/2M) + (\hbar/m)\mathbf{l}\cdot\mathbf{p} + E_n - \mathcal{E}}\\ &\quad\times\varphi\left(\mathbf{p} - \frac{\hbar}{2}\mathbf{l}\right)\end{aligned} \tag{4.4}$$

where $\langle n_1|\mathbf{l}\cdot\mathbf{r}/l|n\rangle$ is the usual dipolar matrix element with respect to the $\mathbf{l}/l$ axis. A rough evaluation shows that the main contribution to the dressing potential arises from the $n = \{\nu, l, m\}$ terms of $\mathcal{V}_{\mathrm{sc}}(0n_1\mathcal{E})$ in which

$\nu = 4$; so, we are led to calculate

$$\tilde{\mathcal{V}}_{\mathrm{sc}}(0n_1\mathcal{E}) = -\frac{e^4 n_e}{8\pi^3\epsilon_0^2}\int d\mathbf{l}\, d\mathbf{p}\, \frac{1}{l^2}\, \frac{Q_{400}(\mathbf{l}/l)}{(\hbar^2 l^2/2m) + (\hbar/m)\mathbf{l}\cdot\mathbf{p} + E_4 - \mathcal{E}}\, \varphi(\mathbf{p}) \tag{4.5}$$

where

$$Q_{400}\left(\frac{\mathbf{l}}{l}\right) = \sum_{lm} \delta_{4-4} |\langle 400| \frac{\mathbf{l}}{l}\cdot\mathbf{r}|4lm\rangle|^2 \tag{4.6}$$

The meaning of this approximation is the following: the main contribution to the dressing potential arises from collisions in which the intermediate state [see interpretation of $O_{\mathrm{sc}}(L_1 n_1 z)$ in Section 3] has the same energy (has almost the same energy if fine and hyperfine structure are taken into account) as the unperturbed state: a nondegenerate and well-separated atomic state would suffer a negligible dressing potential.

If the momentum distribution function $\varphi(\mathbf{p})$ is isotropic we find

$$\tilde{\mathcal{V}}(0n_1\mathcal{E}) = -\frac{e^4 n_e Q_{400}}{8\pi^3\epsilon_0^2}\int_0^\infty dl \int_{-\infty}^{+\infty} dp_\parallel \frac{\varphi_\parallel(p_\parallel)}{(\hbar^2 l^2/2m) + (\hbar/m) l p_\parallel + E_4 - \mathcal{E}} \tag{4.7}$$

where

$$\varphi_\parallel(p_\parallel) = \int d\mathbf{p}_\perp\, \varphi(\mathbf{p}), \qquad p_\parallel = \frac{\mathbf{l}}{l}\cdot\mathbf{p}, \qquad \mathbf{p}_\perp = \mathbf{p} - \frac{\mathbf{l}}{l} p_\parallel \tag{4.8}$$

$$Q_{400} = \sum_{lm} \delta_{4-4} \int_{|\mathbf{u}|=1} d\mathbf{u}\, |\langle 400|\mathbf{u}\cdot\mathbf{r}|4lm\rangle|^2 \tag{4.9}$$

Then, Q_{400} is evaluated by using the matrix elements $\langle n_1|x+iy|n\rangle$, $\langle n_1|x-iy|n\rangle$ and $\langle n_1|z|n\rangle$ tabulated in Ref. 16; we find

$$Q_{400} = 720.0\pi a_0^2 \tag{4.10}$$

where a_0 is the Bohr radius.

We use the normalized electron momentum distribution function

$$\varphi(\mathbf{p}) = \frac{4p_0^3}{\pi^2}\, \frac{1}{(p^2 + p_0^2)^3} \tag{4.11}$$

which is a rather good approximation for the Maxwellian distribution function; its advantage lies in the fact that it allows analytical calculations;(10) the temperature is given by

$$\frac{3}{2} k_B T = \frac{1}{2m}\int d\mathbf{p}\, p^2 \varphi(\mathbf{p}) = \frac{3p_0^2}{2m} \tag{4.12}$$

where k_B is the Boltzmann constant, and $\varphi_{\|}(p_{\|})$ is

$$\varphi_{\|}(p_{\|}) = \frac{2p_0^3}{\pi} \frac{1}{\left(p_{\|}^2 + p_0^2\right)} \tag{4.13}$$

Finally, the right-hand side of (4.7) is evaluated by the usual complex plane method:

Integral over $dp_{\|}$ is performed by closing the contour in the lower half plane [we have to keep in mind that the right-hand side of (4.7) is the analytical continuation of $i\hbar O_{\mathrm{sc}}(0n_1z)$ defined for z in the upper half complex plane!).

Before performing integration over dl, we insert factor $l^4/(l^2+\kappa^2)^2$ (κ is the Debye vector) in (4.7) in order to take into account the screening effects; moreover, we see that this factor avoids the long distance divergence (small l) for $\mathcal{E} = E_4$. We also notice that the short distance convergence (large l) has been deeply altered by the expansion into powers of l/L; in order to restore the initial convergence we introduce a cutoff $l_{\max} = 1/a$, where $a = 24a_0$ is the mean radius of the $\{4, 0, 0\}$ atomic state. Then we calculate

$$\int_0^{l_{\max}} dl \cdots = \int_0^{\infty} dl \cdots - \int_{l_{\max}}^{\infty} dl \cdots$$

by using the properties of the complex logarithmic function (the cut is chosen to be the positive real axis).

From (3.20) we find

$$\mathcal{G}'(0n_1z) = \left(E_{n_1} + i\hbar O_{\mathrm{sc}}(0n_1z) - \hbar z\right)^{-1} \tag{4.14}$$

so, the profile (or the density of states) of the perturbed level is given by the imaginary part of $\mathcal{G}'(0, \{4,0,0\}, \mathcal{E}/\hbar)$ for $\mathcal{E}$ real,(17) i.e.,

$$p(\mathcal{E}) = A\,\mathrm{Im}\left[\tilde{\mathcal{V}}_{\mathrm{sc}}(0, \{4,0,0\}, \mathcal{E}) + E_4 - \mathcal{E}\right]^{-1}, \qquad \mathcal{E} \in \mathbb{R} \tag{4.15}$$

instead of

$$\begin{aligned} p(\mathcal{E}) &= A\,\mathrm{Im}(E_4 - \mathcal{E})^{-1} = A\,\mathrm{Im}\left[\frac{P}{E_4 - \mathcal{E}} + i\pi\delta(E_4 - \mathcal{E})\right] \\ &= \pi A \delta(E_4 - \mathcal{E}), \qquad \mathcal{E} \in \mathbb{R} \end{aligned}$$

for the unperturbed atom (isolated atom); here P/z stands for the Cauchy principal part of $1/z$. Constant A can be evaluated by requiring the profile to be normalized to unity. Figure 1 shows the profile $p(\Delta\lambda)$ as a function of

$$\Delta\lambda = -\frac{(\mathcal{E} - E_4)\lambda_0^2}{hc} \tag{4.16}$$

where λ_0 is the wavelength of the H_β line.

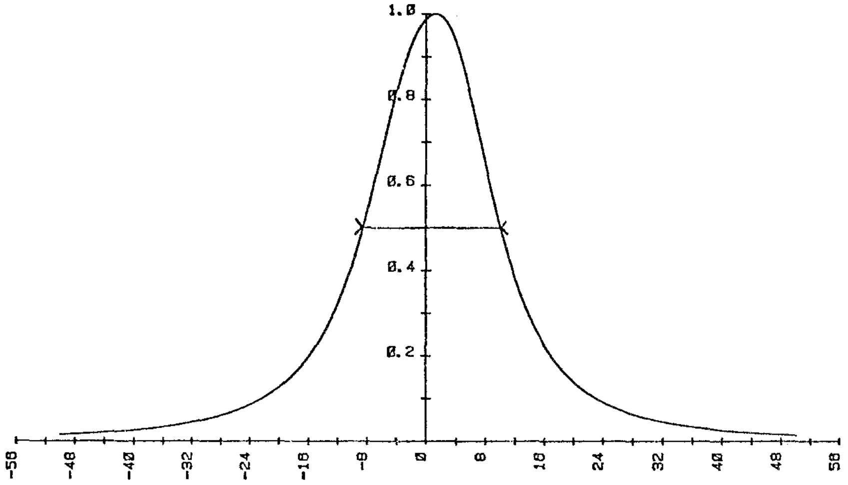

Fig. 1. Profile of the $n_1 = \{4, 0, 0\}$ state of hydrogen obtained analytically.

5. DISCUSSION

The profile we have obtained analytically is a very rough approximation to the true profile; in particular it leads to a broadening of the H_β line greater than the experimental value (half width 18.5 Å instead of 16 Å, when $n_e = 2 \times 10^{22}$ part./m^3 and $T = 13400$K).

We have introduced in (4.7) the Debye potential which is the *static approximation* of the true screened potential as Balescu has shown(10); it holds for long time evolution equations but it is not convenient for describing short time phenomena as electron–atom collisions leading to shift and broadening of atomic levels. The next task is thus the summation of the ring diagrams for electrons and ions in order to take correctly into account the collective effects.

Also, we notice that integrations over dl have been approximated when we have introduced the expansion in powers of l/L and limited the range of integration by means of the cutoff $l_{\max}$ (this cutoff also appears in the usual theories of line broadening). An exact calculation of this integral would avoid the necessity of the cutoff.

Moreover, we underline the fact that an improvement can be obtained by using the distorted wave functions for atomic states. The dressing potential (4.4) involves a summation over the intermediate states n; if terms corresponding to $E_n \neq E_{n_1}$ are not disregarded, then one can see that the corresponding profile $P(\mathfrak{E})$ of the perturbed state n_1 has a main bump around E_{n_1} but also has small bumps around E_n for $n \neq n_1$. The true atomic state n_1 has to be considered as some linear combination of atomic states:

$$\varphi_{n_1}^{\text{true}}(\mathbf{r}) = \sum_{n=1}^{\infty} C_{n_1 n}\varphi_n(\mathbf{r})$$

in which

$$|C_{n_1 n_1}| \gg |C_{n_1 n}|, \qquad \forall n \neq n_1$$

such that its corresponding profile has only a bump around E_{n_1} (no bump around E_n for $n \neq n_1$).

In this paper we have developed the foundations of a possible application of composite particle theories to the determination of shift and broadening of atomic lines in plasmas. This method appears to be promising because it is completely general:

It holds out of equilibrium; in particular it allows us to take into account collective effects (summation of ring diagrams) even in the unstable case.

It includes correlation contributions which can play an important role in turbulent situations.

It includes all the exchange effects: symmetry effects between atomic electrons and free electrons as well as symmetry effects between free electrons (high-density plasmas). The task lies in the choice of the classes of diagrams corresponding to the various phenomena we want to take into account.

Finally, we point out that we do not need to perform a Fourier transform as in the usual methods leading to shift and broadening of atomic lines; this is the reason why it has been possible to obtain analytically a meaningful approximate profile.

ACKNOWLEDGMENTS

We are indebted to Professors Girardeau, Balescu, and Grecos and Drs. Dewel, Blaizot, and Gaudin for stimulating and helpful discussions. Also, we thank Professor Prigogine for his kind hospitality in Brussels. We are thankful to Dr. Fleckinger for deep discussions during the course of this work. Support for this work has been provided by the Centre National de la Recherche Scientifique (A.I. 032586) and the Université Paul Sabatier (Tranche C, Projet "Physique de l'implosion laser").

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