PHYSICAL REVIEW A VOLUME 21, NUMBER 1 JANUARY 1980

Exchange and polarization effects in the elementary excitation spectrum of a hydrogen atom immersed in a hot plasma

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(Received 14 November 1978; revised manuscript received 22 August 1979)

The one-particle hydrogenic Green's function has been calculated for a partially ionized plasma consisting of hydrogen atoms, electrons, and protons at high temperatures. The theoretical method extends a previous publication and involves an evaluation of the mass operator in the Dyson equation to include proper self-energy parts to "all orders" in the screened interaction. This mass operator characterizes the effective micropotential felt by the atom in the plasma and determines all of the one-particle properties and some two-particle properties associated with the atomic subsystem. The first-order mass operator is nonzero only for exchange scattering, which leads to a frequency-independent exchange shift. This temperature- and density-dependent theory of the exchange shift replaces the usual semiphenomenological schemes based on the Slater-Kohn-Sham type of theory. The exchange-shifted Green's functions are used in evaluating the higher-order contributions. Computer calculations and the resolution of the poles of the Green's function lead to level shifts, widths, and spectral functions. These are calculated within both the second-order and the all-order theory. The second-order theory, which may be valid at sufficiently high densities and in turbulent plasmas, overemphasises the atom-plasmon coupling and shows new structures. The inclusion of contributions beyond second order removes these structures and produces a more "conventional" spectral-intensity function. The effects of center-of-mass motion on the level shifts and level profiles are investigated and the onset of plasma instabilities touched upon. These calculations make contact with the work on "plasma-polarization shifts" and provide an approach to q,ω-dependent plasma microfields.

I. INTRODUCTION

A partially ionized high-temperature hydrogenic plasma contains two essential subsystems in interaction, viz., the plasma subsystem containing electrons and ions and the atomic subsystem containing nuclei still containing one bound electron. Even though the atomic subsystem, having a negligible particle density, has virtually no effect on the plasma subsystem, the latter greatly affects the atoms by shifting and broadening the *levels*,[1] changing the ionization potential, optical spectrum, level populations, etc. The properties of such atoms can be used to probe the system of electrons and ions. The electrons and ions in the plasma subsystem interact with each other via the Coulomb interaction, and here too renormalization of particle energies, lifetimes, and distribution functions comes into being. For the plasma subsystem at high temperature, at least the ions can be fairly well treated by methods of classical statistical mechanics using Bogoliubov-Born-Green-Kirkwood-Yvon-type (BBGKY) approaches, direct numerical methods of trajectory dynamics,[2] or even Debye-Hükel-type approaches when only static properties are needed.

However, the study of a plasma consisting of atoms, ions, and electrons is strictly a quantum-statistical many-body problem. In fact, the techniques of modern quantum many-body theory are now well known[3-5] and versatile enough that it may be easier to carry through the quantum treatment, which is possibly more flexible than the analogous classical theory. However, most of the literature (e.g., Ref. 6) is formal, directed to the two-particle Green's function, and has not proved to be computationally tractable. In the present paper we study the one-particle excitations via the one-particle Green's function, using a quantum many-body approach given by one of the authors.[7-9]

The calculation of the shifts and widths of the levels of an atom immersed in a plasma is in fact formally analogous to the theory of the modification of core energy levels of atoms in a metal due to the band electrons,[10] or even to the problem of the calculation of the Lamb shift, where the vacuum polarization shifts could be reviewed as being due to the effect of the particles in the Dirac sea (quite appropriately the name "plasma-polarization shift," analogous to "vacuum-polarization shift," has actually been applied[11] to the shift of energy levels of atoms immersed in plasmas).

The spectroscopically observable polarization shift is a *line* shift and not a level shift. However, all the present theories of plasma-polarization shifts[11,12] calculate the *line*-polarization shift as a difference of *level*-polarization shifts and ignore the cross terms that arise in constructing a two-body shift operator out of one-body operators. Thus we could say that the existing theories of plasma-polarization shifts are really theories of *level* shifts. Since we are also interested in level shifts, widths, and one-particle densities of states, the existing theories of polarization shifts are of some interest to us, in so far as they are primarily level-shift theories. The extent to which two-particle-propagators could be constructed from one-particle propagators is relevant here, and we comment on this later. [See after Eq. (5.1).]

The intuitive arguments used in Griem's original discussion of polarization-level shifts proceed by pointing out that a charge inhomogeneity occurs around the atom owing to the atomic nucleus polarizing the plasma medium. But the subsequent development[12] attempts to construct quantitative theories out of unphysical assumptions involving excessively simplified models where all ion-atom and perturber-perturber interactions, exchange, etc. are ignored and the plasma electrons are merely assumed to "fill" the "space" between the nucleus and the Bohr orbit of the atomic electron in question, thus screening it from the nucleus and causing a level shift. The more sophisticated approaches available[13,14] to date involve a mixture of semiclassical assumptions and could be considered as stemming from the early work of Planck[15] and leading to the study of the eigenvalues of the hydrogen atom in a Debye-shielded potential.[16] The Debye-shielded nuclear model is unphysical, especially for a neutral atom. Even in the case of an ion the bound electrons will relate to a frequency component of the field associated with the level frequency and not necessarily to a static potential. The work of Theimer and Kepple[13] departs from the naive Debye model and attempts to calculate the level shifts using a mixture of quantum mechanics and classical electrostatics to obtain the discrete states of the atom in the plasma. Rozsnyai[14] uses similar methods involving a mixture of Thomas-Fermi theory and atomic self-consistent-field theory involving a phenomenological form of Slater-type exchange corrections to extract a level shift. These methods, valid in certain limits, do not have the clarity of first-principles approaches and are inherently incapable of including lifetime effects, particle dynamics, and plasma instability effects.

The work of Nakayama and DeWitt[17] contains an attempt to use a fluctuating potential within a quantum-statistical framework. The thermodynamic potential is written as a linked cluster expansion, and their method involves the solution of a "pseudo-Schrödinger" equation which contains the complex potential $Z/r\tilde{\epsilon}(k,\omega)$, where $\tilde{\epsilon}(k\omega)$ is the random-phase-approximation (RPA) dielectric function. The complex eigenvalue is interpreted to give a shifted energy and a damping for the *level* in question. The methods we use are faintly similar to those of Nakayama and DeWitt and reflect the state of the art in present day many-body Green's function theory.[3] Instead of solving a non-Hermitian Schrödinger equation, we essentially solve the integral equation (Heisenberg representation)

$$\left(i\frac{\partial}{\partial t} - h(xt)\right)G(xt,x't') = \delta(xx')\delta(tt') + \int M(xt,x't')G(x''t'',x't')dx''\,dt'', \tag{1.1}$$

where $h(xt)$ is the one-body term in the Hamiltonian and $M(xt,x't')$ is the mass operator (or self-energy operator) which defines a non-Hermitian nonlocal time-dependent many-body potential felt by the propagating particle. This is also the potential which would determine the effective microfield felt by the atom. This theoretical approach, though not too often used in plasma theory, is a well established basic method of quantum field theory, contemporary solid-state theory, and related disciplines. A good review of the crucial role played by $M(xt,x't')$ in determining many system properties is given, in that context, by Hedin and Lundqvist.[3]

The main burden of the calculation falls on the determination of this mass operator in some approximation, thus determining the Green's function. The complex poles of this Green's function define the shifted and broadened one-particle excitations in the system. We use the temperature-dependent double-time retarded functions[4] and the methods already used in Ref. 7. This provides a rigorous approach where infinite-order summations are achieved via a Dyson equation. The plasma electron (or proton) Green's function turns out to be essentially those of a fully ionized plasma, since the atoms have little effect on the plasma subsystem. Thus the main thrust of the present study is toward the atomic Green's functions which yield the shifted and broadened hydrogenic levels[18] in a plasma. Owing to the complexity of the final expressions we resort to extensive numerical work to obtain computational results for the roots of the equations defining the quasiparticles, and also study the dependence on center-of-mass motion which cannot be ignored in ion-atom collisions.

The developments reported in this paper should be regarded as a preliminary step toward the larger objective of putting into operation a set of computer programs based on a systematic many-body approach to the theory of plasma-atom interactions. The properties of the elementary excitation spectrum obtained here will be of direct interest in constructing realistic plasma microfields, calculating of two-body Green's functions, etc. In the H-atom problem treated here the correlation (or direct) part of the first-order mass operator is zero, but there is an exchange shift which has been ignored in the level-shift literature.

The correlation effects arising from the strong atom-ion interaction do not admit a low-order perturbation treatment unless, say, $T/\rho^{2/3}$ is much larger than the ion mass. Even for electrons, low-order theory is applicable only for sufficiently weak scattering processes. This is a difficulty which has beleaguered plasma theory for many years and the standard escape route involves the use of rather *ad hoc* cutoff procedures and model microfields of various sorts. Although Dufty[19] has given a formal construction to introduce microfield descriptions, the existing approaches cannot be extracted from a first-principles quantum theory. On the other hand, any given experimental data could perhaps be shown to agree with "theory," owing to the considerable freedom available in the choice of cutoffs and microfields.

Plasma-polarization shifts are believed to be small ($\Delta\omega \simeq 0$), and hence the relevant interactions involve effects over large time periods ($\Delta\tau \simeq 1/\Delta\omega$) within which atomic and ionic motions are non-negligible. This is just the sort of situation where existing microfields are useless, since they imply a static (or stochastic static) model which ignores energy and momentum conservation in each collision event. These negative considerations, as well as the doubtful physical contents of available modelizations, are sufficient to rule out microfield methods from the present study, even if they have proven useful in other contexts.

In the present study we treat the atom-perturber interaction exactly to second order and evaluate the higher-order contributions via the approximate solution of an integral equation to the Green's function contained in the mass operator. This introduces natural cutoffs in q and ω and corresponds to an all-order theory where a certain class of terms (or diagrams) is summed to infinite order.

II. FORMULATION OF PROBLEM

The total Hamiltonian of the system can be written as ($\hbar = e = 1$)

$$H = H_a + H_f + H_I + H_r , \tag{2.1}$$

where

$$H_a = H_a^0 + H_{a\text{-}a} , \tag{2.2a}$$

$$H_a^0 = \sum_a \left(\frac{p_a^2}{2M} + H_a^{\text{el}} \right) \tag{2.2b}$$

is the Hamiltonian of the atomic subsystem; $p_a^2/2M$ represents the center-of-mass (c.m.) motion of the atom labeled a, while H_a^{el} is the "electronic Hamiltonian" of the atom referred to the center of mass. The atomic and ionic kinetic-energy terms are neglected in the usual quasistatic theories; this is partly the origin of one aspect of the current problem of incorporating effects of ion-dynamics into plasma microfields. The last term, $H_{a\text{-}a}$, is the interaction between two atoms and is given in Eq. (2.12) of Ref. 7.

In the present problem $H_{a\text{-}a}$ represents the interaction between two neutral hydrogen atoms, and this is entirely negligible owing to the extremely small number density of neutral atoms in a high-temperature plasma of the type considered here and also to the screening of the interactions by the free-particle subsystem. The latter is described by the Hamiltonian

$$H_f = H_f^0 + H_{f\text{-}f} , \tag{2.3a}$$

$$H_f = \sum_{i\tau} \frac{p_{i\tau}^2}{2M_\tau} + \tfrac{1}{2} \sum_{i_1 i_2} \sum_{\tau_1 \tau_2} \frac{Z_{\tau_1} Z_{\tau_2}}{|r_{i_1\tau_1} - r_{i_2\tau_2}|} , \tag{2.3b}$$

where the index τ ($=e$ or p) refers to electrons or protons and i sums over particles of each type, Z_τ being the charge on particle type τ ($Z_e = -1$, $Z_p = 1$) specified by the position vector $\vec{r}_{i\tau}$. The plasma is taken to have overall charge neutrality.

The interaction Hamiltonian H_I is given by

$$H_I = \sum_{a, i, \tau} \frac{Z_a Z_\tau}{|\vec{R}_a - \vec{r}_{i\tau}|} + \frac{Z_e Z_r}{|\vec{R}_a + \vec{r}_a - \vec{r}_{i\tau}|} , \tag{2.4}$$

where Z_a ($=Z = 1$) is the charge on the atomic nucleus having a position vector $\vec{R}_a$, while $\vec{r}_a$ is the coordinate of the atomic electron with respect to the nucleus (this is taken to be the effective c.m. of the atom). The last term on the right-hand side of (2.1), H_r, is the Hamiltonian of the radiation field and its interaction. In Ref. 7 we showed how H_r could be systematically treated. In the present calculation we neglect H_r, since the radiation-reaction effects are many orders smaller than the collisional effects in a plasma, if intense fields (e.g., laser radiation) are absent. We note that in the usual theories of plasma spectroscopy the term $H_{f\text{-}f}$ is entirely neglected or nominally accounted for by replacing H_I by the Debye-screened form. We will see from Eq. (3.12) that this is valid only at exact resonance for collisions involving limitingly small momentum transfers. Further, in the present approach it is not necessary to approximate (2.4) by a dipole or low-order multipole truncation.

This Hamiltonian (2.1) is usually[6] cast into an occupation-number formalism by using plane waves for free particles and atomic eigenfunctions for bound states. This traditional procedure is analogous to the use of plane waves for valence electrons and atomic states for core electrons in solid-state physics and formally leads to an overcomplete basis. As emphasized in §2 of Ref. 7, such a basis leads to complicated communication rules which may have to be considered at some stage of the theory. Here, as is customary, we introduce the basis functions

$$\phi_{nl\,ms}(\vec{k}) = \Omega^{-1\;2} e^{i\vec{k}\cdot\vec{R}} \phi_{nl\,ms}(\vec{r}_e) = \phi_{\nu k}(r_p r_e)\,, \qquad (2.5a)$$

$$\phi_{\tau s}(\vec{k}) = \Omega^{-1\;2} e^{i\vec{k}\cdot\vec{R}} e_{\sigma_s} = \phi_{\tau k}(r_\tau) \qquad (2.5b)$$

where $\vec{R}$ is the atom center-of-mass coordinate, with a c.m. momentum $\vec{k}$. Integration over $\vec{R}$ and $\vec{r}$ in constructing matrix elements leads to $\vec{k}$- and *nlm*-dependent second quantization operators $A_{nlm}(k), A^\dagger_{nlm}(k)$ for atomic operators. These operators act on electronic bound states defined by the atomic center. We write $\nu \equiv n,\ l,\ m$ and $k \equiv \vec{k},\ s$ and suppress vector notation unless it becomes necessary to prevent confusion. The charged-particle creation and annihilation operators corresponding to (2.5b) are denoted by $C^\dagger_\tau(k)$, $C_\tau(k)$; these are Fermi operators. As in Appendix B of Ref. 20, $A(k)$ operators also can be shown to be Fermi-like to an excellent approximation under conditions where the nuclear exchange can be neglected. Owing to the overcompleteness of the basis the commutation relations between the A and C operators come out to be[21]

$$[A_\nu(k), C^\dagger_{\tau q}]_+ = \langle \phi_\nu(\vec{k}) \,|\, \phi_{\tau s}(\vec{q})\rangle \delta_{\tau e}$$

$$= \delta_{\tau e} \int \phi_{\nu k}(\vec{r}_p, \vec{r}_e)\phi_{ek}(\vec{r}_e) d\vec{r}_e\,. \qquad (2.5c)$$

In traditional treatments[6] this overlap term is neglected and A, $C^\dagger_q$ operators are taken to commute or anticommute. We retain its effects in the first-order mass operator and neglect them in higher orders, after having renormalized the propagators to take account of the correction arising from the effect of (2.5c).

The Hamiltonian in the second quantized representation is given by

$$H_a = H^0_a = \sum_{\nu, k} \epsilon^0_\nu(k) A^\dagger_\nu(k) A_\nu(k)\,, \qquad (2.6a)$$

$$H_f = \sum_{\tau, k} \epsilon_\tau(k) C^\dagger_\tau(k) C_\tau(k) + \tfrac{1}{2} \sum_{\substack{\tau_1\tau_2 \\ k_1k_2q}} Z_{\tau_1} Z_{\tau_2} V_q$$

$$\times C^\dagger_{\tau_1}(k_1) C^\dagger_{\tau_2}(k_2+q) C_{\tau_2}(k_2) C_{\tau_1}(k_1+q)\,, \qquad (2.6b)$$

$$H_I = \sum Z_\tau \langle \tau\vec{k}_1, \nu_1(\vec{I}_1) \,|V|\, \nu_2(\vec{I}_2), \tau\vec{k}_2\rangle$$

$$\times C^\dagger_{\tau k_1} A^\dagger_{\nu_1}(\vec{I}_1) A_{\nu_2}(\vec{I}_2) C_{\tau k_2}\,. \qquad (2.6c)$$

For direct scattering this reduces to

$$H_I = \sum_{\substack{\tau\nu_1\nu_2 \\ k_1k_2q}} Z_\tau V_{\nu_1\nu_2}(q) C^\dagger_\tau(k_1) A^\dagger_{\nu_1}(k_2+q)$$

$$\times A_{\nu_2}(k_2) C_\tau(k_1+q) \qquad (2.6d)$$

and has been treated in Ref. 22. The reduction of the exchange-scattering term will be shown in discussing the exchange contributions to the first-order mass operator [see Eq. (3.5b)].

In the above,

$$\epsilon^0_\nu(k) = -Z^2_a/2n^2 + k^2/2M - \mu_a\,, \quad \nu \equiv n,\ l,\ m\,, \qquad (2.7a)$$

$$\epsilon_\tau(k) = k^2/2M\tau - \mu_\tau\,, \qquad (2.7b)$$

$$V_q = (1/\Omega)(4\pi/q^2)\,, \quad q \neq 0\,; \quad V_q = 0\,, \quad q = 0 \qquad (2.7c)$$

and

$$V_{\nu_1\nu_2}(q) = V_q(Z_a\delta_{\nu_1\nu_2} - \langle \nu_1 | e^{-i\vec{q}\cdot\vec{r}} | \nu_2\rangle)\,, \qquad (2.7d)$$

with

$$\langle \nu_1 | e^{-i\vec{q}\cdot\vec{r}} | \nu_2\rangle$$

$$= \int \phi^*_{n_1 l_1 m_1}(\vec{r}) e^{-i\vec{q}\cdot\vec{r}} \phi_{n_2 l_2 m_2}(\vec{r}) d\vec{r}\,.$$

In (2.7a) and (2.7b), μ_a and μ_τ are the chemical potentials of the atomic species and charges species τ; μ_a is known in terms of μ_τ, since we assume that the system is in thermal equilibrium (or quasiequilibrium at some effective temperature). We have

$$H = H^+ + e^-\,, \quad \mu_a = \mu_p + \mu_e\,, \qquad (2.7e)$$

where μ_e and μ_p are effectively the unperturbed electron and proton chemical potentials (since the equilibrium number of atoms is so low that the atomic subsystem has little or no effect on the free-particle subsystem). It is clear that the effect of ionizing collisions on the mass operator for low-lying states would be negligible, owing to their low frequency at the temperatures and densities considered, compared to elastic- and bound-bound processes involving smaller energy changes. It is possible to estimate the effects of these thermal bound-free processes even within the present formalism by taking the final hydrogenic states [say ν_1 in (2.7)] to be continuum Coulomb functions. This question was examined in the numerical studies reported in Ref. 22. In the present study we neglect the contribution from such transitions, since these earlier studies (see Table III) justify such a procedure, at least for the low-lying states.

The matrix element (2.7d) incorporates the dynamics of the atom-perturber collision via the momentum transfer $\vec{q}$ and is a generalized[23] oscillator strength for the transition $\nu_1 \rightarrow \nu_2$. The form (2.7d) results from (2.4) when matrix elements are calculated using the basis (2.5) and has already been given in Eq. (2.13a) of Ref. 7.

We write the final Hamiltonian to be used as

$$H = H_a^0 + H_f^0 + H_{f\text{-}f} + H_I \;; \tag{2.8}$$

one of our principal problems is to evaluate the effect of H_f^0, $H_{f\text{-}f}$, and H_I on the eigenstates (levels) of H_a^0. We do this by calculating suitable single-particle Green's functions for the Hamiltonian (2.8), where the screening effects arising from $H_{f\text{-}f}$ are treated within an approximation which reduces to RPA for weak atom-perturber collisions. This modified RPA (MRPA) includes the changes in screening arising from the effects of atom-perturber multiple collisions. As we shall show in detail, if only second-order atom-perturber theory is used, then the screening is in RPA with the screening frequency $\tilde{\omega}$ depending on the atom c.m. momentum $\vec{k}$, electronic state 2, and the momentum transfer $\vec{q}$. In the all-order atom-perturber theory, $\tilde{\omega}$ depends in addition on the atom-perturber interaction. This has the effect of cutting off the screening for large $\vec{q}$ values and for resonant ω values. In effect, we may write our Hamiltonian schematically as

$$H = H_a^0 + H_f^{\mathrm{MRPA}} + H_I^{\mathrm{sc}} \tag{2.9}$$

and describe the method by stating that all interactions to second order are treated explicitly, while higher-order effects are included by partial summations to all orders. The main physical approximation is this partial summation where only a selected class of terms is retained. As will be indicated later, simplifying approximations are needed in the numerical reduction of the expressions bringing in the higher-order contributions. Aside of such defects the potentials used are exact and no quasistatic or microfield approximations are used, while such formal matters as causality (time-ordering) and energy and momentum conservation are built into the Green's-function methods used and would be preserved if reasonable care were taken in the approximations.

III. GREEN'S FUNCTIONS

The calculation of level shifts and widths involves the determination of the elementary (here one-particle) excitation spectrum of the Hamiltonian (2.8). In the present approach, suited to low-lying excitations and associated with the theory in Ref. 7 and as distinct from the theory in Ref. 20, we recognize three kinds of excitations, viz., those of bound (i.e., atomic) electrons, free electrons, and free protons, given by the poles of the corresponding one-particle Green's functions.

Using the double-time statistical Green's functions in Refs. 4 and 7, we define the one-particle propagators

$$G_\nu(k\omega) = \langle\langle a_\nu(k), a_\nu^\dagger(k)\rangle\rangle \,, \tag{3.1}$$

$$G_\tau(k\omega) = \langle\langle C_\tau(k), C_\tau^\dagger(k)\rangle\rangle \,, \tag{3.2}$$

where the Fourier component of $\langle\langle X(t)X^\dagger(t')\rangle\rangle$ is implied. More explicitly,

$$\begin{aligned}\langle\langle X(t), X^\dagger(t')\rangle\rangle &\\ &= -i\theta(t-t')\langle[X(t), X^\dagger(t')]_+\rangle_{\mathrm{av}}\\ &= \frac{l}{2\pi}\int_{-\infty}^{+\infty}\langle\langle X, X^\dagger\rangle\rangle e^{-i\omega(t-t')}\,d\omega \end{aligned}\tag{3.3a}$$

defines the retarded function and its Fourier component. The mean values $\langle\;\rangle_{\mathrm{av}}$ are taken with respect to the grand canonical ensemble and $\theta(t-t')$ is the Heaviside step function. The Fourier transforms of the retarded ($\mathrm{Im}\omega > 0$) and advanced functions ($\mathrm{Im}\omega < 0$) form one analytic function in the complex ω plane with a discontinuity along the real axis. The equations of motion of $\langle\langle X, Y\rangle\rangle$ can be written as

$$\omega\langle\langle X, Y\rangle\rangle = \langle[X, Y]_+\rangle_{t=t'} + \langle\langle[X, H]_-, Y\rangle\rangle \,, \tag{3.3b}$$

$$\omega\langle\langle X, Y\rangle\rangle = \langle[X, Y]_+\rangle_{t=t'} - \langle\langle X, [Y, H]_-\rangle\rangle \tag{3.3c}$$

by differentiating with respect to t or t' in $\langle\langle X(t), Y(t')\rangle\rangle$ and then taking the Fourier components defined by (3.3a). The Green's functions (3.1) and (3.2) have the form $\langle\langle X, X^\dagger\rangle\rangle$, and we can show that, as in Ref. 8 (see also Tyablikov and Bonch-Bruevich[5]), the Dyson equation

$$G(k\omega) = G^0(k\omega) + G^0(k\omega)M(k\omega)G(k\omega) \tag{3.4a}$$

leads to a mass operator given by

$$M(k\omega) = (G^0)^{-1}\langle\langle U, X^\dagger\rangle\rangle / [C_{XX} + \langle\langle U, X^\dagger\rangle\rangle] \,, \tag{3.4b}$$

where

$$U = [X, H_I]_- \,,$$

$$C_{XX} = \langle[X, X^\dagger]_+\rangle_{t\to t'} \;;$$

C_{XX} is 1 since $X = C_\tau(k)$ or $a_\nu(k)$. Also,

$$[X, H^0]_- = (\omega_X^0)X \,,$$

with

$$G^0 = C_{XX}/(\omega - \omega_X^0) \,.$$

The denominator in (3.4b) serves to remove the "unlinked clusters" or improper terms in the numerator, and we can in fact write

$$M(k\omega)=(G^0)^{-1}\langle\langle U, X^\dagger\rangle\rangle_{\text{proper}}\,.$$

Since

$$\langle\langle U, X^\dagger\rangle\rangle=\langle\langle U, X^\dagger\rangle\rangle+G^0\langle\langle U, U^\dagger\rangle\rangle\,,$$

$$\begin{aligned}M(k\omega)&=(G^0)^{-1}\langle\langle U, X^\dagger\rangle\rangle^0+\langle\langle U, U^\dagger\rangle\rangle_{\text{proper}}\\&=m_1(k\omega)+m_{\text{higher}}(k\omega)\,.\end{aligned}\tag{3.4c}$$

We also note that we can develop (3.4b) in a perturbation series[5] and write the mass operator up to second order as

$$\begin{aligned}m_1(k\omega)&=(G^0)^{-1}\langle\langle U, X^\dagger\rangle\rangle^0\,,\\m_2(k\omega)&=\langle\langle U, U^\dagger\rangle\rangle^0-(\langle\langle U, X^\dagger\rangle\rangle^0)^2\\&=\langle\langle U, U^\dagger\rangle\rangle^0_{\text{proper}}\,.\end{aligned}\tag{3.4d}$$

Here we see how the denominator has brought in the term $(\langle\langle U, X^\dagger\rangle\rangle^0)^2$, which is $G^0 m_1(k\omega)^2$, to cancel the unlinked term in which two first-order parts are held together by a single G^0 line.

Finally we note that an all-order calculation of $M(k\omega)$ involves

$$m_{\text{higher}}(k\omega)=\langle\langle U, U^\dagger\rangle\rangle_{\text{proper}}\,.\tag{3.4e}$$

So far the theory is exact, and the approximations arise in calculating (3.4e).

In Eqs. (3.4a)–(3.4e) the superscript zero indicates that the corresponding quantities are only needed in zeroth order.[5] In the second-order mass operator (3.4d), the interaction potential occurs twice via the presence of two $[X, H_I]$ terms. In the actual calculation we show how an all-order theory is developed, leading to screened interactions inclusive of atom-perturber scattering effects, as in the scheme of Eq. (2.9). The screening effects embody simultaneous multiple collisions of a relatively weak nature, while the calculation of $\langle\langle U, U^\dagger\rangle\rangle$ to be presented incorporates effects arising from stronger collision processes.

At this point the question of achieving a self-consistent calculation should be raised. Since the calculation of $M(k\omega)$ depends on G^0, and since $G=G^0/(1-MG^0)$, once an initial mass operator is calculated, this calculation should be used to define a new, renormalized propagator, and hence a new M, until consistency is reached. We have renormalized our propagators using the Hartree-Fock shift (first-order mass operator), but no attempt has been made to do a higher-order self-consistent calculation. To put the magnitude of the task in perspective, we may note that even in the simpler many-body problem on which the maximum of theoretical effort has been spent, viz., the problem of the electron gas (the one-component plasma), the mass operator has been evaluated only to first order in the screened interaction (RPA), and *without* any effort at self-consistency. "Plasmaron" side peaks (similar to our second-order results) appear in the RPA electron-gas calculation, and these are probably an artifact of the low-order approximation (see Refs. 3 and 24). The all-order calculation of the type given here has only recently[25] been achieved for the self-energy, while there are recent calculations for the t matrix, limited to the on-the-energy-shell case (e.g., Bedell and Brown[26]). None of these calculations are self-consistent. In our problem, unlike in the electron gas, we have complicated atomic matrix elements, angular-momentum and wave-vector sums, complicated frequency, and level-dependent screening functions. Thus a full self-consistent calculation is unlikely to be available within the immediate future.

A. Atom Green's function

The zero-order atom Green's function $G^0_\nu(k,\omega)$ is given by

$$G^0_\nu(k\omega)=1/[\omega-\epsilon^0_\nu(k)]\,.\tag{3.5a}$$

A word of clarification may be relevant here. If an electron-proton Green's function is set up using free-particle states and the multiple scattering of the pair is included to all orders, then the resulting function will have poles corresponding to the spectrum of a hydrogen atom and will be diagonal in the hydrogenic basis. The diagonal element corresponding to the state ν is (3.5a). In effect, (3.5a) provides us with a convenient representation of the electron-proton Green's function which does not appear explicitly in the present theory. (3.5a) follows directly from (3.1) and the form of the Hamiltonian used.

From (3.4c), the first-order mass operator $m_1(k,\omega)$ requires an evaluation of $\langle\langle[X, H_I]_-, X^\dagger\rangle\rangle^0$, where H_I is given by (2.6c). In reducing the commutator $[X, H_I]_-$, we obtain an exchange term and a direct term. Thus, using (2.6c) for H_I and $a_\nu(k)$ for X, we have

$$\begin{aligned}&[a_\nu, c^\dagger_{\tau_1}a^\dagger_1 a_2 c_{\tau_2}]_-\\&\quad=\langle\nu\,|\,k_{\tau_1}\rangle\delta_{\tau_1 e}a^\dagger_1 a_2 c_2-\delta_{\nu_1}c^\dagger_{\tau_1}a_2 c_{\tau_2}\,.\end{aligned}\tag{3.5b}$$

Each of these terms has to be treated in calculating the first-order mass operator.

1. *First-order mass operator*

From (3.4c) and (3.5b) we write

$$\begin{aligned}m^\nu_1(k\omega)&=\langle\langle[a_\nu(k), H_I]_-, a^\dagger_\nu\rangle\rangle^0[\omega-\epsilon^0_\nu(k)]\\&=m^\nu_1(k\omega)_{\text{ex}}+m^\nu_1(k\omega)_d\,.\end{aligned}\tag{3.6a}$$

Using (2.6b) and (3.3c), we easily reduce the direct term to give

$$m_1^\nu(k\omega)_d = G_\nu^I(k\omega)_d[\omega - \epsilon_\nu^0(k)], \tag{3.6b}$$

in which

$$G_\nu^I(k\omega)_d = \sum Z_\tau V_{\nu\nu}(q)\langle C_\tau^\dagger(k_1+q)C_\tau(k_1)\rangle^0$$

$$\times \delta_{k,k+q}/[\omega - \epsilon_\nu(k)]$$

$$= V_{\nu\nu}(0)\sum Z_\tau \bar{\rho}_{\tau k_1}/[\omega - \epsilon_\nu^0(k)],$$

where

$$\bar{\rho}_{\tau k_1} = \langle \rho_\tau(k_1)\rangle^0, \quad \rho_\tau(k) = C_\tau^\dagger(k_1)C_\tau(k_1).$$

For a neutral plasma, $\sum_{\tau k_1} Z_\tau \rho_{\tau k_1} = 0$, and also $V_{\nu\nu}$ is zero, as in Eqs. (2.7c)–(2.7d). Hence we have

$$m_1^\nu(k\omega)_d = 0. \tag{3.6c}$$

The exchange term [first term on the right-hand side (RHS) of (3.5b)] appears only for electrons, since we neglect nuclear exchange. The reduction of the mass operator proceeds by noting that, for example,

$$\sum_{k_1}\langle \nu(k)\,|\,k_1\rangle\langle k_1\nu_1(K_1)\,|\,V\,|\,\nu_2(K_2)k_2\rangle$$

$$= \langle \nu(k_1)\nu_1(K_1)\,|\,V\,|\,\nu_2(K_2)k_2\rangle$$

and

$$a_1^\dagger = \sum_{k_1}\langle k_1\,|\,\nu_1(K_1)\rangle C_{k_1}^\dagger,$$

since $|k_1\rangle$ is a complete set. We proceed as follows:

$$m_1^\nu(k\omega)_{\text{ex}} = \sum Z_e\langle k_1\nu_1\,|\,V\,|\,\nu_2k_2\rangle\langle\nu\,|\,k_1\rangle$$

$$\times\langle\langle a_1^\dagger a_2 c_{k_2}, a_\nu^\dagger(k)\rangle\rangle^0[\omega - \epsilon_\nu(k)]$$

$$= \sum Z_e\langle \nu k_1\,|\,V\,|\,\nu_2 k_2\rangle$$

$$\times\langle\langle c_{k_1}^\dagger a_2 C_{k_2}, a_\nu^\dagger(k)\rangle\rangle^0[\omega - \epsilon_\nu(k)]$$

$$= -\sum Z_e\langle \nu k_1\,|\,V\,|\,\nu k_1\rangle\bar{\rho}_{ek_1} \tag{3.7a}$$

$$= +\tfrac{1}{2}\sum_{\vec{q}\vec{k}_1} V_q\langle\nu\,|\,e^{i\vec{q}\cdot\vec{r}}\,|\,k_1\rangle$$

$$\times(Z\langle k_1\,|\,\nu\rangle - \langle k_1\,|\,e^{-i\vec{q}\cdot\vec{r}}\,|\,\nu\rangle)\bar{\rho}_{ek_1} \tag{3.7b}$$

$$= m_{\text{ex}}^\nu.$$

We have suppressed the center-of-mass momenta k, K_1, and K_2 up to Eq. (3.7a), since the same result (independent of the c.m. momentum) is obtained by correctly carrying through all the momenta and reducing the integrals.

Also, in evaluating $\langle\langle c_{k_1}^\dagger a_2 c_{k_2}, a_\nu^\dagger(k)\rangle\rangle^0$, we can either decouple $\langle c_{k_1}^\dagger c_{k_2}\rangle$ as $\bar{\rho}_{k_1}\delta_{k_1k_2}$ or calculate the anticommutator $\langle[c^\dagger ac, a^\dagger]\rangle^0$, keeping in mind that the commutation rule to be used is (2.5c), owing to the overlap between atomic and plane-wave functions. Both methods lead to the form given in (3.7a). Its computational form is given below [Eq. (4.2)].

The energy shift defined by (3.7a) is independent of the frequency parameter ω and the c.m. motion of the atom, at least in this approximation. We may call it a mean-field exchange shift. Noting that the first-order mass operator m_1^ν is simply equal to the exchange shift (which is independent of k and ω), we rewrite the zero-order Hamiltonian (2.6a) in the form

$$H_a^{(0)} = \sum_{\nu,k}\epsilon_\nu(k)a_\nu^\dagger(k)a_\nu(k),$$

where

$$\epsilon_\nu(k) = \epsilon_\nu^0(k) + m_1^\nu. \tag{3.7c}$$

We also replace (3.5a) by the renormalized propagator

$$G_\nu^{(0)}(k) = 1/[\omega - \epsilon_\nu^0(k) - m_1^\nu]. \tag{3.7d}$$

Having carried out such a "renormalization," we ignore exchange effects in all higher-order processes, i.e., in evaluating contributions to the mass operators in higher order.

Note that since m_1^ν, i.e., m_{ex}^ν, is *independent* of frequency, the *line* shift for the transition $\nu_1 \to \nu_2$ would be the difference between the *level* shifts, viz., $m_{\text{ex}}^{\nu_2} - m_{\text{ex}}^{\nu_1}$ at this level of approximation. Numerical values of $m_1^\nu/\bar{\rho}_e$ are presented in Table I.

2. *Screened first-order mass operator*

For regimes of high plasma density it is necessary to consider screening effects arising from the Coulomb interactions among the charged particles. The method of evaluation of the Green's function to obtain a full Coulomb treatment in RPA will be given in detail with respect to the second-order mass operator. In first order it turns out that the potentials V_q occurring in the frequency-independent expressions (3.7) get replaced by $V_q/[\bar{\epsilon}(q, 0)]$, where $\bar{\epsilon}(q, 0)$ is the static RPA dielectric function. In order to simplify numerical work, we adopted for $\bar{\epsilon}$ the form $1 + k_D^2/q^2$, where k_D is the Debye momentum at the given density and temperature. Numerical results are given in Table II. The effects of static screening are found to be negligible at the densities and temperatures of interest to us.

3. *Screened second-order mass operator*

The second-order mass operator involves the Green's function

$$G_\nu^{\rm II}(\omega)=\langle\langle[a_\nu(k),H_I]_-,[a_\nu(k),H_I]_-^\dagger\rangle\rangle^0$$

$$=\sum Z_\tau Z_{\tau'}V_{\nu\nu_1}(q_1)V^*_{\nu\nu'_1}(q'_1)$$

$$\times\langle\langle\rho_\tau(k_1q_1)a_{\nu_1}(k-q_1),\ a^\dagger_{\nu'_1}(k-q'_1)\rho^\dagger_{\tau'}(k'_1q'_1)\rangle\rangle^0$$

$$=\sum V_x(q_1)V^*_{x'}(q'_1)\langle\langle Q_x,Q^\dagger_{x'}\rangle\rangle^0\,,\qquad(3.8a)$$

where we have introduced the definitions

$$\rho_\tau(k_1q_1)=C^\dagger_\tau(k_1)C_\tau(k_1+q_1)\,,\qquad(3.8b)$$

$$Q_{\tau\nu_1}(kk_1q_1)=Q_x=Z_\tau\rho_\tau(k_1q_1)a_{\nu_1}(k-q_1)\,,$$

$$x\equiv\tau,\nu_1,k_1,q_1\,.\qquad(3.8c)$$

The Green's function $\langle\langle Q_x, Q^\dagger_{x'}\rangle\rangle$ of Eq. (3.8a) has the same structure as the Green's function (3.42) of Ref. 3 and contains the operators $\rho_\tau(k_1q)$ corresponding to charged-particle density fluctuations. Thus $\langle\langle Q_x, Q^\dagger_{x'}\rangle\rangle^0$ should be calculated so as to pick up the screening effects which are brought about by such charge-density fluctuations. This implies that $\langle\langle Q_x, Q^\dagger_{x'}\rangle\rangle$ should be calculated inclusive of $H_{f\text{-}f}$, at least in the random-phase approximation. That is, we define

$$\hat{Q}_{xx'}=\langle\langle Q_x,Q^\dagger_{x'}\rangle\rangle\qquad(3.9a)$$

and write its equation of motion

$$\hat{Q}_{xx'}=\langle[Q_x,Q^\dagger_{x'}]_-\rangle^0D_x^{-1}+\langle\langle[Q_x,H_{f\text{-}f}]_-,Q^\dagger_{x'}\rangle\rangle D_x^{-1}\,,\qquad(3.9b)$$

$$D_x=\omega-\epsilon_{\nu_1}(k-q_1)+\epsilon_\tau(k_1)-\epsilon_\tau(k_1+q_1)\qquad(3.9c)$$

and evaluate the last Green's function on the RHS by RPA decoupling to give (see p. 2740 of Ref. 7)

$$\hat{Q}_{xx'}=\langle\langle Z_\tau\rho_\tau(k_1q_1)a_{\nu_1}(k-q_1),\ Z_{\tau'}\rho^\dagger_{\tau'}(k'_1q'_1)\,a^\dagger_{\nu_1}(k-q'_1)\rangle\rangle$$

$$=\frac{C^0_{xx'}}{D_x}+V_{q_1}Z_\tau^2\left(\frac{\bar\rho_{\tau k_1}-\bar\rho_{\tau,k_1+q_1}}{D_x}\right)$$

$$\times\sum_{k_2T_1}\langle\langle a_{\nu_1}(k-q_1)\rho_{\tau_1}(k_2q_2)Z_{\tau_1},Q^\dagger_{x'}\rangle\rangle\,,\qquad(3.10a)$$

where

$$C^0_{xx'}=\langle[Q_x,Q^\dagger_{x'}]_-\rangle_{t=t'}\,.\qquad(3.10b)$$

Summing over τ, k_1 and identifying the Green's functions on the LHS and RHS to be the same, we have

$$\left[1-V_{q_1}\sum_{\tau,k_1}Z_\tau^2\left(\frac{\bar\rho_{\tau,k_1}-\bar\rho_{\tau,k_1+q_1}}{D_x}\right)\right]\left\langle\left\langle\sum_{\tau,k_1}a_{\nu_1}(k-q_1)\rho_\tau(k_1q_1)Z_\tau,\ Z_{\tau'}\rho^\dagger_{\tau'}(k'_1q'_1)a^\dagger_{\nu_1}(k-q'_1)\right\rangle\right\rangle=\sum_{\tau,k_1}C_{xx'}/D_x\,.\qquad(3.11a)$$

The term in large round parentheses on the LHS is the RPA response function with its frequency shifted to $\omega-\epsilon_{\nu_1}(k-q_1)$. Thus we define the dielectric function

$$\tilde\epsilon(q,\tilde\omega)=1-V_qL(q\tilde\omega)\,,\qquad(3.12a)$$

where the response function $L(q_1\tilde\omega)$ is given by

$$L(q,\tilde\omega)=\sum_{\tau k}\frac{Z_\tau^2(\bar\rho_{\tau,k}-\bar\rho_{\tau,k+q})}{[\tilde\omega+\epsilon_\tau(k)-\epsilon_\tau(k+q)]}\,,\qquad(3.12b)$$

$$\tilde\omega=\tilde\omega_x=\omega-\epsilon_\nu(k-q)\,.$$

The particle distribution functions $\bar\rho_{\tau,k}$ have already been defined in (3.6d) and are merely the Fermi distribution functions for particles of species τ and momentum k, that is,

$$\bar\rho_{\tau,k}=[1+\exp(k^2/2m_\tau-\mu_\tau)\beta]^{-1}\,.\qquad(3.12c)$$

For the high-temperature situations in which we are interested, (3.12c) can be replaced by the Boltzmann distribution and (3.12b) can be expressed in terms of the Dawson function[27] [see Eq. (3.27)].

We complete the evaluation of $G_\nu^{\rm II}(k\omega)$ by summing over τ', k'_1 occurring in (3.11a) and by multiplying by V_x, V^*_x, as indicated in (3.8a), to obtain

$$G_\nu^{\rm II}(k\omega)=\sum_{\substack{q_1q_1\\ \nu_1,\nu'_1}}V_{\nu\nu_1}(q_1)V^*_{\nu\nu'_1}(q'_1)\sum_{\substack{\tau,\tau'\\ k_1,k'_1}}\frac{C^0_{xx'}}{\tilde\epsilon(q_1\tilde\omega)D_x}\,,\qquad(3.13a)$$

where the mean value $C^0_{xx'}$ must be evaluated. We have

$$C^0_{xx'}=\langle[Z_\tau a_{\nu_1}(k-q_1)\rho_\tau(k_1q_1),$$

$$Z_{\tau'}\rho^\dagger_{\tau'}(k'_1q'_1)a^\dagger_{\nu'_1}(k-q'_1)]_+\rangle^0\,,\qquad(3.13b)$$

which we can simplify using the commutation rules of the operators to get

$$C^0_{xx'}=Z_\tau^2\{\bar\rho_\tau(k_1)[1-\bar\rho_\tau(k_1+q_1)]-\bar n_{\nu_1}(k-q_1)$$

$$\times[\bar\rho_\tau(k_1)-\bar\rho_\tau(k_1+q_1)]\}\delta_{k_1k'_1}\delta_{q_1q'_1}\delta_{\tau\tau'}\delta_{\nu_1\nu'_1}$$

$$\simeq Z_\tau^2\bar\rho_\tau(k_1)\delta_{11'}\delta_{\tau\tau'}$$

when

$$m_1(k\omega)=\sum_{\tau\nu_1q_1k_1}\frac{Z_\tau^2|V_{\nu\nu_1}(q_1)|^2\{\bar\rho_\tau(k_1)[1-\bar\rho_\tau(k_1+q_1)]-\bar n_{\nu_1}(k-q_1)[\bar\rho_\tau(k_1)-\bar\rho_\tau(k_1+q_1)]\}}{\tilde\epsilon\{q_1\tilde\omega[\tilde\omega+\epsilon_\tau(k_1)-\epsilon_\tau(k_1+q_1)]\}}$$

$$=\sum_{\nu_1q_1}\frac{|V_{\nu\nu_1}(q_1)|^2[L'(q_1\tilde\omega)-\bar n_\nu(k-q_1)L(q_1,\tilde\omega)]}{\tilde\epsilon(q_1,\tilde\omega)}\,,\qquad(3.14)$$

where

$$\tilde{\omega} = \omega - \epsilon_{\nu_1}(\vec{k} - \vec{q}_1) . \tag{3.15a}$$

$$\bar{n}_\nu(k - q_1) = \langle A_\nu^\dagger(k - q_1) A_\nu(k - q_1) \rangle^0 \tag{3.15b}$$

is the mean number of atoms in the electronic state ν and c.m. momentum state $\vec{k} - \vec{q}_1$. The $L'(q_1\tilde{\omega})$ function is closely analogous to the Lindhard function and is given by

$$L'(q_1\tilde{\omega}) = \sum_{\tau, k_1} \frac{Z_\tau^2 \rho_\tau(k_1)[1 - \rho_\tau(k_1 + q_1)]}{\tilde{\omega} + \epsilon_\tau(k_1) - \epsilon_\tau(k_1 + q_1)} . \tag{3.15c}$$

Thus we can write the atomic Green's function $G_\nu(k\omega)$ in terms of the second-order mass operator and the exchange-shifted energy levels $\epsilon_\nu(k)$ as

$$\begin{aligned} G_\nu(k\omega) &= G^{(0)}(k\omega)/[1 - M_\nu(k\omega)]G^{(0)}(k\omega) \\ &= 1/[\omega - \epsilon_\nu(k) - m_2(k\omega)], \end{aligned} \tag{3.16}$$

where $m_2(k\omega)$ is explicitly given by (3.14) and $G^{(0)}$ is the normalized zero-order function of Eq. (3.7c). This result corresponds to the RPA self-energy of electron-gas theory, and it is, in a sense, a useful point of reference.

B. "All-order" theory of mass operator

The results given so far provide an explicit evaluation of the mass operator taken to second order in the dynamically screened atom-plasma interaction. We can at this stage introduce an effective quasiparticle Hamiltonian of the form

$$H_{\mathrm{ef}} = \sum \epsilon_\nu(k, \omega) A_\nu^\dagger(k) A_\nu(k) , \tag{3.17a}$$

where

$$\epsilon_\nu(k\omega) = \epsilon_\nu(k) + m_\nu(k, \omega)_2 .$$

This is a valid description of the system in the sense that (3.17a) gives $G_\nu(k\omega)$ correct to second order.

The densities and temperatures considered in the present study are such that the second-order theory provides an *inadequate* picture of the effect of the plasma (especially the ions) on the atom. In effect, an all-order partial summation of a selected class of perturbation terms is necessary, and we shall examine several possibilities in this section.

From Eq. (3.8a) we see that the basic quantity to be calculated is

$$M_\nu(k, \omega) = \sum_{1,1'} V_{\nu\nu_1}(q_1) \langle\langle Q_1, Q_{1'}^\dagger \rangle\rangle V_{\nu_1'\nu}(q_1') , \tag{3.18}$$

where

$$Q_1 = Q_x = a_{\nu_1}(k - q_1) C_\tau^\dagger(k_1) C_\tau(k_1 + q_1) .$$

The second-order calculation of Sec. IIIA3 used $\langle\langle Q_1, Q_1^\dagger \rangle\rangle^0$ evaluated to zero order in H_I. To proceed further we need its full equation of motion, which is schematically illustrated in Fig. 1. It is

$$\begin{aligned} &D_x \langle\langle Q_x, Q_{x'}^\dagger \rangle\rangle = C_{xx'} + \langle\langle [Q_x, H_I]_-, Q_{x'}^\dagger \rangle\rangle , \\ &C_{xx'} = \langle [Q_x, Q_{x'}^\dagger]_- \rangle . \end{aligned} \tag{3.19a}$$

To simplify the discussion, we leave out the $H_{f\text{-}f}$ term, which produces screening effects, as this can be treated later, as in Sec. IIIA3.

Denoting ν_1 by 1, ν_1' by 1′, etc., we can write Eq. (3.19a) more explicitly as

$$\begin{aligned} D_x &\langle\langle A_1(k - q_1) C_\tau^\dagger(k_1) C_\tau(k_1 + q_1), Q_{1'}^\dagger \rangle\rangle \\ &= C_{11'} + \sum_{2, q_2} Z_\tau V_{12}(-q_1) \\ &\quad \times \langle\langle A_2(k - q_1 + q_2) C_\tau^\dagger(k_1) C_\tau(k_1 + q_1 - q_2), Q_{1'}^\dagger \rangle\rangle + \mathcal{T} , \end{aligned}$$

where $\mathcal{T}$ stands for terms involving 8 or more field operators.

Some of the effects of these 8-field-operator terms can be incorporated into the screening function by a procedure similar to that of Eqs. (3.1)–(3.10). Equation (3.19a) can thus be approximated as

$$D_1 \langle\langle Q_1, Q_{1'}^\dagger \rangle\rangle = C_{11'} + \sum V_{12}^\tau(-q_2) \langle\langle Q_2, Q_{1'}^\dagger \rangle\rangle . \tag{3.19b}$$

Different methods of treating (3.19b) to extract an "all-order" solution correspond to the selective summation of different classes of diagrams in perturbation theory. For instance, we can introduce the center-of-mass momentum coordinates of the pair of particles undergoing multiple interactions by setting

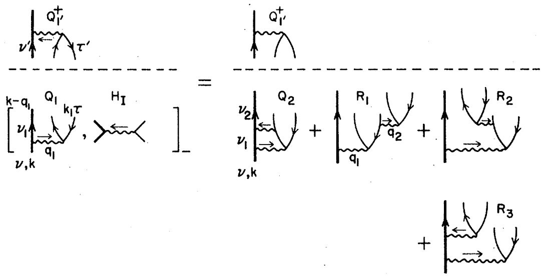

FIG. 1. Generation of higher-order terms from the commutation of Q_1 with H_I in the equation of motion (3.19a). Thick lines, atom propagators; thin lines, type-τ free-particle propagators; wavy line, atom-perturber interaction (2.7d) with dynamic screening. Terms like Q_2 are retained for further propagation, while R_1, R_2, and R_3 are included via their contribution to screening effects.

$$\xi_1 = (k - q_1) + (k_1 + q_1),$$
$$2\lambda_1 = (k - q_1) - (k_1 + q_1),$$
$$2\lambda_2 = (k - q_1 + q_2) - (k_1 + q_1 - q_2), \quad \text{etc.}$$

The (3.19b) can be written as an integral equation, as in the case of usual treatment of the Bethe-Salpeter equation. This leads to the equation

$$\phi_1^\tau(\lambda_1) = C_{11'} + \sum_{\lambda_2 \nu_2} V_{12}^\tau(\lambda_1 - \lambda_2)\phi_2^\tau(\lambda_2)/D_2^\tau(\lambda_2), \tag{3.20a}$$

where

$$\phi_1^\tau(\lambda_1) = D_1^\tau(\lambda_1)\langle\langle Q_1, Q_{1'}^\dagger\rangle\rangle,$$
$$D_1^\tau(\lambda_1) = \omega - \epsilon_1(\xi_1 + \lambda_1) - \epsilon_\tau(\xi_1 - \lambda_1) + \epsilon_\tau(2\xi_1 - k), \tag{3.20b}$$
$$Q_1 = A_{\nu_1}(\xi_1 + \lambda_1)C_\tau^\dagger(2\xi_1 - k)C_\tau(\xi_1 - \lambda_1).$$

An approximate solution of this integral equation can be achieved if, say, the same momentum is assumed to be exchanged back and forth between the scattering pair, while only one intermediate-atomic-state index (besides ν_1) is retained in the summations. Detailed numerical calculations based on such an approach showed that these contributions are negligible at the densities and temperatures of interest to us.

Another class of terms can be treated by considering a Dyson development for the Green's function of Eq. (3.18). Here again several alternatives are possible, corresponding to slightly different rearrangements of the perturbation series. One approach would be to proceed as follows: Let

$$F^\dagger = \sum_{1' q_1'} Q_{1'}^\dagger V_{1'\nu}(q')$$
$$= \sum_{\tau' \nu_1' q_1'} C_{\tau'}^\dagger(k_1' + q_1')C_{\tau'}(k_1')V_{\nu'\nu}^{\tau'}(q_1'),$$
$$\hat{R}_{1F} = \langle\langle Q_1, F^\dagger\rangle\rangle.$$

Then, as in (3.19b),

$$D_1\langle\langle Q_1, F^\dagger\rangle\rangle = C_{1F} + \sum_{2, q_2} V_{12}^\tau(-q_2)\langle\langle Q_2, F^\dagger\rangle\rangle,$$
$$\langle\langle Q_2, Q_1'\rangle\rangle D_1' = C_{12}' + \sum_{\tau'} V_{1'2'}(-q_2')\langle\langle Q_2, Q_2^{\dagger\prime}\rangle\rangle.$$

Hence, we have

$$\langle\langle Q_1, F^\dagger\rangle\rangle = C_{1F}D_1^{-1} + D_1^{-1}\sum_{2, q_2} V_{12}^\tau(-q_2)\sum_{1' q_1'} V_{1'\nu}^{\tau'}(q_1') \times\left(\frac{C_{21}'}{D_1'} + \frac{1}{D_1'}\sum_{2' q_1'} V_{1'2'}(-q_2')\langle\langle Q_2, Q_2^{\dagger\prime}\rangle\rangle^0\right). \tag{3.21}$$

This can, as usual, be cast into the form of a Dyson equation with a kernel $\hat{K}_{1F}$ such that

$$R_{1F} = \hat{R}_{1F}^0 + \hat{R}_{1F}^0\hat{K}_{1F}\hat{R}_{1F},$$

where the first-order evaluation of $\hat{K}_{1F}$ gives

$$\hat{K}_{1F}^{(\mathrm{i})} = \left(\sum_{\substack{2, q_2 \\ 1', q_1', \tau'}} \frac{V_{12}^\tau(-q_2)V_{1'\nu}^{\tau'}(q_1')C_{21'}}{D_1'}\right)\Big/ C_{1F}\hat{R}_{1F}^0, \tag{3.22}$$

with

$$\hat{R}_{1F}^0 = \bar{\rho}_k V_{1\nu}^\tau(q_1)/[\omega - \epsilon_1(k - q_1) + \epsilon_{k_1} - \epsilon_{k_1+q_1}],$$
$$C_{21'} = \delta_{21'}\delta_{q_2, q_1 - q_1'}\delta_{k_1 k_1'}\bar{\rho}_{k_1'}\delta_{\tau\tau'},$$
$$D_1' = \omega - \epsilon_{1'}(k - q_1') + \epsilon_{k_1} - \epsilon_{k_1+q_1}$$

$\hat{K}_{1F}^{(\mathrm{i})}$ can finally be reduced to the form

$$\hat{K}_{1F}^{(\mathrm{i})} = \sum_{1' q_1'} V_{11'}^\tau \frac{(q_1 - q_1')\hat{R}_{1'F}^0}{D_{1F}(\hat{R}_{1F}^0)^2}. \tag{3.23}$$

Hence to first order,

$$\hat{R}_{1F}^{(\mathrm{i})} = V_{1\nu}^\tau(q_1)\bar{\rho}_{k_1}\Big/ \left(\omega - \epsilon_{\nu_1}(k - q) + \epsilon_{k_1+q_1} - \sum_{1' q_1'} V_{11'}^\tau(q_1 - q_1')\frac{\hat{R}_{1'F}^0}{\hat{R}_{1F}^0}\right).$$

The second-order contribution arising from the $\langle\langle Q_2, Q_2^\dagger\rangle\rangle^0$ term in (3.21) can be similarly reduced and shown to be of the form

$$K_{1F}^{(\mathrm{ii})} = \frac{1}{D_1 R_{1F}^0}\sum_{2, 1'} \frac{V_{12}^\tau(-q_1)V_{21'}(-q_1)}{D_2}\frac{\hat{R}_{1'F}^0}{\hat{R}_{1F}^0}\bar{\rho}_{k_1},$$

where D_2 is as in (3.20b). The final mass operator $M_\nu(k, \omega)$ is then given by

$$M_\nu(k\omega) = \sum_{\tau, \nu_1 k_1 q_1}\left\{|V_{\nu\nu_1}^\tau(q_1)|^2\bar{\rho}_{k_1}\Big/\left[D_1^\tau - \sum_{1' q_1'}\left(V_{11'}^\tau(q_1 - q_1') + \sum_2 \frac{V_{12}^\tau(-q_1)V_{21}(-q_1)\bar{\rho}_{k_1}}{D_2}\right)\frac{\hat{R}_{1'F}^0}{\hat{R}_{1F}^0}\right]\right\}. \tag{3.24}$$

As it stands, this expression is computationally very uneconomical. Some fairly straightforward simplifications can be achieved by noting that, for instance, the terms arising from $\hat{K}_{1F}^{(\mathrm{ii})}$ have more or less the effect of replacing the bare lines in the mass operator with propagators containing second-order self-energy insertions. (This could also be thought of as a second-order dynamical Stark splitting.) The ratio

$\alpha_{11'} = \hat{R}^0_{1'F}/\hat{R}^0_{1F}$ can be computed approximately by averaging over q'_1 and k_1 and using the mean value for the type of particles concerned. Hence we write

$$M_\nu(k\omega) \simeq \sum_{\tau\nu_1 q_1 k_1} \left[|V^\tau_{\nu\nu_1}(q_1)|^2 \bar{\rho}_{k_1} \Big/ \left(D^\tau_1 - \sum_{1'q'_1} [\bar{V}^\tau_{11'}(q_1 - q'_1) + m_{\nu_1}(k, \omega)_2] \alpha_{11'} \right) \right] . \tag{3.25}$$

This form of the all-order mass operator includes the already calculated second-order mass operator in the energy denominator, together with a term linear in the potential. The bar symbol over $V^\tau_{11'}(q_1 - q'_1)$ indicates that the $\hat{R}^0_{1'F}/\hat{R}^0_{1F}$ term was treated in an approximate manner, by decoupling it out and averaging over all intermediate variables. In practice, we found that the results were quite insensitive to the exact form of $\alpha_{11'}$. Writing

$$\hat{\omega}_\gamma = \tilde{\omega} - \mathrm{Re}\left(\sum V^\tau_{11'}(q_1 - q'_1) + m_{\nu_1}(k, \omega)_2 \right) \alpha_{11'} ,$$

$$\hat{\omega}_i = \mathrm{Im}\left(\sum V^\tau_{11'}(q_1 - q'_1) + m_{\nu_1}(k, \omega)_2 \right) \alpha_{11'} ,$$

we can reduce Eq. (3.25) to the form

$$M_\nu(k\omega) = \sum_{k_1 q_1 \nu_1 \tau} |V^\tau_{\nu\nu_1}(q_1)|^2 \tilde{G}^\tau(q, \hat{\omega}^-_\tau)/\tilde{\epsilon}(q, \hat{\omega}_\gamma) , \tag{3.26}$$

where

$$\hat{\omega}^-_\tau = \hat{\omega}_\gamma - q^2/2M_\tau , \quad \tilde{G}^\tau(q, \hat{\omega}^-_\tau) = f^\tau(\omega_\gamma, \omega_i) \alpha^\tau(q, x^-_\tau) ,$$

$$f^\tau(\omega_\gamma, \omega_i) = \exp[\hat{\omega}_i (\xi_\tau/q)^2 (\hat{\omega}_i + 2i\hat{\omega}^-_\tau)] ,$$

$$\alpha^\tau(q, x^-_\tau) = \bar{\rho}_\tau \frac{\xi_\tau}{q} \{2D(x^-_\tau) - i[(\sqrt{\pi}\, e^{-(x^-_\tau)^2} + E(x^-_\tau, \hat{\omega}_i)]\} ,$$

$$\xi_\tau = (M_\tau/2T)^{1\ 2} , \quad x^-_\tau = \hat{\omega}^-_\tau (\xi_\tau/q) ,$$

$$D(t) = e^{-t^2} \int_0^t e^{y^2} \, dy , \tag{3.27}$$

$$E(t, u) = e^{-t^2} \int_t^{t-iu} e^{y^2} \, dy . \tag{3.28}$$

In general, since $\hat{\omega}_i$ is considered to be small, the integral $E(x^-_\tau, \hat{\omega}_i)$ was ignored in numerical work. Note that the dielectric function $\tilde{\epsilon}(q, \hat{\omega}_\gamma)$ screens with a displaced frequency $\hat{\omega}_\gamma$ and hence includes some modifications from multiple scattering effects.

IV. CALCULATION OF LEVEL SHIFTS, WIDTHS, AND PROFILES

The calculation of the level shifts and widths requires a complete evaluation of the mass operator [(3.7) and (3.26)] as a function of k and ω and the resolution of the equation

$$\omega - \epsilon_\nu(k) - M_\nu(k\omega) = 0 , \tag{4.1a}$$

which determines the shifted and broadened elementary excitations $E_\nu(k)$ of atomic electrons in the system. Equation (4.1a) defines elementary excitations with unperturbed quantum numbers $\nu = n$, l, m and center-of-mass momentum $\vec{k}$ (as well as any new modes). Then the level shift is defined by

$$\Delta\epsilon_\nu(k) = E_\nu(k) - \epsilon_\nu(k) . \tag{4.1b}$$

In practice, the mass operator should be averaged over all m values of the state ν. The results given in the tables involve such an averaging.[18]

The exchange shift, independent of $\vec{k}$ and ω, could be directly calculated from (3.7b), which can be reduced to the computational form

$$m^\nu_{\mathrm{ex}} = (A^\nu_1 - A^\nu_2 - A^\nu_3)(2\pi/T^3)^{1/2} \bar{\rho}_e , \tag{4.2}$$

where

$$A^\nu_1 = \delta_{m,0} \delta_{l,0} Z \int\int_0^\infty q^2 e^{-q^2/2T} U_{n0}(q) U^\dagger_{n0}(p) \, dp \, dq ,$$

$$A^\nu_2 = -\int\int_0^\infty (p^2 + q^2) e^{-(p^2+q^2)/2T} \frac{\sinh(pq/T)}{pq/T}$$

$$\times |U_{nl}(p)|^2 \, dp \, dq ,$$

$$A^\nu_3 = -2(2l+1)(-1)^{m^2} \sum_{L=0}^{l} \sum_{m_1=-1}^{+1} (2L+1)(-1)^{m_1}$$

$$\times \begin{bmatrix} 1 & 1 & L \\ 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} l & l & L \\ 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} l & l & L \\ -m & m & 0 \end{bmatrix} \begin{bmatrix} 1 & 1 & L \\ m_1 & -m_1 & 0 \end{bmatrix} X ,$$

$$X = \int\int_0^\infty e^{-(p^2+q^2)/2T}$$

$$\times T \left[\frac{\sinh(pq/T)}{pq/T} - \cosh\left(\frac{pq}{T}\right) \right] |U_{nl}(p)|^2 \, dp \, dq .$$

In (4.2) the m-averaged values of these quantities are used. The functions $U_{nl}(p)$ occurring in these expressions are the hydrogenic wave functions in the momentum representation and can be expressed in terms of Gegenbauer polynomials. Numerical results, presented in Tables I and II and Figs. 2 and 3, are considered in Sec. V.

The computation of the second-order screened mass operator has been discussed in detail in Ref. 22. The procedure for calculating the all-order mass operator given in Eq. (3.25) is similar, since (3.26) involves the same matrix elements and mathematical-function subroutines, upon neglecting (3.28). It was found that the level profile was quite insensitive to the quantity $\alpha_{11'}$ occurring in (3.25) for a wide range of possible approximate renderings of $\hat{R}^0_{1'F}/\hat{R}^0_{1F}$. The second-order mass operator $M_{\nu_1}(k, \omega)_2$ appearing in the denominator of (3.25) was interpolated from a precalculated table of values. The determination of the roots of the quasiparticle equation had to be carried out by a Newton-Raphson-like iterative procedure by looking for the intersection of the function

$$y = \mathrm{Re} M_\nu(k, x + \epsilon_\nu(k)) \tag{4.3a}$$

with the bisector

$$y = x\,, \quad x = \omega - \epsilon_\nu(k)\,. \tag{4.3b}$$

We shall often use the symbol $\Delta\omega$ for x and ω_0 for the frequency of the line center, where $x = 0$. If the theory were restricted to the second order, as in Ref. 22, each level profile would typically have two side peaks associated with the emission or absorption of a plasmon. [Similar results have been found in the RPA-type theory of the electron gas by Lundqvist (see review in Ref. 3).] The all-order theory, on the other hand, showed only a single peak (and a single root) very close to the unperturbed value. This simplified the numerical work of solving (4.3), although we ran into considerable difficulties with the level 3s, for which no level shifts are reported.

V. RESULTS AND DISCUSSION

The results of these calculations are given in Tables I–IV and exhibited in Figs. 2–9. Table I gives the exchange shift calculated by means of Eq. (4.2). These equations must be modified at higher densities to include the effects of screening. Such a calculation was performed and Table II shows that at the temperatures and densities of concern to us the effects of screening of the first-order mass operator are negligible. Figures 2 and 3 exhibit the data of Table I to show the temperature and level dependence of the exchange shift. It should be emphasized that the method, being only a first-order result, is essentially a many-body version of the Born approximation.

Note that the usual method of including exchange is to use the lowest-order result from the theory of the uniform electron gas, either via an energy calculation (Slater exchange) or via the Hohenberg-Kohn-Sham[28] density-functional theory (Dirac exchange). The latter can be shown to be equivalent to a first-order calculation of the self-energy or mass operator of the free-electron gas and gives the exchange potential

$$V_x(k) = -\sum_{k_1} V_{k-k_1}\theta(k_F - k_1)\,.$$

Application of this uniform-density formula (where k_F is the Fermi momentum) to atomic systems involves a local-density approximation and, usually, neglect of gradient corrections. In Ref. 14, where Slater exchange is used, a phenomenological interpolation formula is used to extend the theory to intermediate temperatures. In contrast, our formula [Eqs. (3.7) and (4.2)] does not need the uniform electron-gas local-density approximations, since it has the correct exchange-matrix element involving atomic wave functions and includes the temperature generalization by replacing the Fermi function $\theta(k_F - k_1)$ by the electron-density factor $\bar{\rho}_{ek_1}$. A more detailed discussion and extension of the theory of the exchange shift will be published elsewhere.

Contributions from terms in higher order (i.e., higher than first order) involve summations over a complete set of intermediate states. In actual numerical work only a finite basis of functions going up to the principal quantum number $n = n_{\max}$ was used. In Table III we have examined the

TABLE I. The quantity X given under each temperature below is such that the exchange shift $\Delta\epsilon_X$ in atomic units for a plasma of electron density $\bar{\rho}_e$ is given by $-X\bar{\rho}_e$; that is, $X = -\Delta\epsilon_x/\bar{\rho}_e$.

n,l \ T (eV)	2.0	4.0	10.0	50.0	100	1000.0
1,0	7.037	13.80	23.56	28.99	19.72	1.298
2,0	446.3	447.8	445.6	349.4	218.4	12.81
2,1	255.5	227.8	189.9	122.9	75.08	43.42
3,0	1566.0	1462.0	13.59	1085	683.9	40.13
3,1	634.9	585.1	531.6	390.3	242.0	14.04
3,2	475.5	407.4	339.4	236.1	145.8	8.436
4,0	3342.0	3314.0	3302.0	2679.0	1681.0	97.93
4,1	1313.0	1245.0	1176.0	905.1	564.6	32.79
4,2	900.1	815.0	731.2	545.6	339.5	19.69
4,3	720.2	616.2	530.8	390.3	242.6	14.06

TABLE II. $-\Delta\epsilon_x/\bar{\rho}_e$ for two densities and two temperatures when static screening effects are taken into account. Static screening effects seem to be negligible at the densities studied in this paper ($\bar{\rho}_e \approx 10^{-7}$ a.u., $T \approx 1-5$ eV).

	$\bar{\rho}_e = 0.5\times10^{-7}$ a.u.		$\bar{\rho}_e = 0.5\times10^{-4}$ a.u.	
n,l	4 eV	50 eV	4 eV	50 eV
1,0	12.15	28.98	7.694	28.76
2,0	441.2	349.4	419.4	348.9
2,1	226.9	122.9	206.4	122.5
3,0	1456.0	1085.0	1375.0	1084.0
3,1	583.7	390.3	543.2	389.6
3,2	406.4	236.1	368.8	239.6
4,0	3306.0	2679.0	3129.0	2677.0
4,1	1243.0	905.1	1170.0	904.1
4,2	813.8	545.6	753.9	544.9
4,3	615.0	390.3	562.5	389.8

sensitivity of the results to the size of the basis set and the effect of the continuum. (See Ref. 22, where extension of the discrete set to $n\rightarrow\infty$ by a Padé approximant procedure and other refinements have been considered. It is seen that, except in the case of 1s, where the level is virtually unchanged in any case, the other levels can be studied within a limited discrete basis set.) In evaluating the second-order mass operator of, say, a level with principal quantum number n, we used a discrete basis of all functions up to $n_{\max}=n+1$, i.e., $\frac{1}{2}(n+1)n$ functions. The all-order calculations were carried out for up to $n=3$ only and the basis was limited to six radial functions. Such limitation of the basis set is of course standard form in all atomic calculations. Also, it may be physically justifiable for atoms in a plasma, since many of the higher bound states are "lost" to the continuum by the shift and broadening effects of the plasma. In any case, as long as we are studying the low-lying levels, the use of a limited basis seems justifiable.

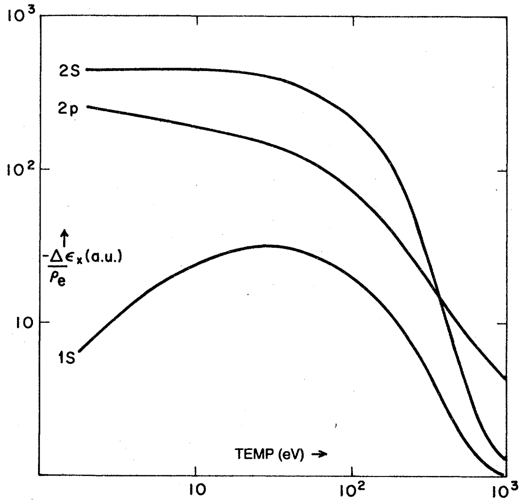

FIG. 2. Variation of the exchange shift per unit density as a function of temperature. Data, based on Table I, are without screening and depend linearly on the density.

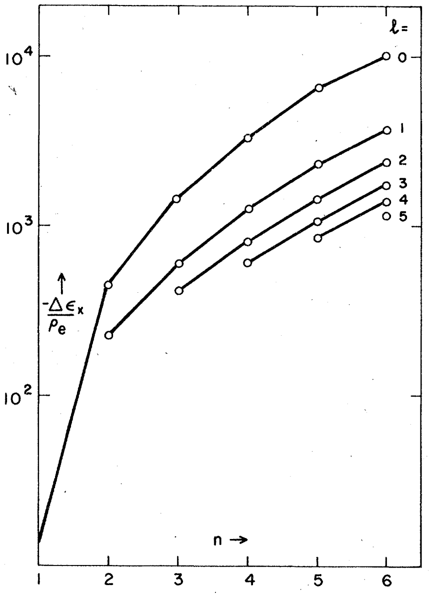

FIG. 3. Dependence of the exchange shift per unit density at $T=4$ eV on the quantum number.

Figure 4 shows how the ground state is modified by the plasma when the calculation is carried out to second-order. Such an approximation greatly exaggerates the effect of plasmon-atom coupling, and yet it is seen that the ground state remains quite sharp and unperturbed, as compared to, say, the second-order 2s curves given in Fig. 6. These studies merely confirm the well-known fact that the perturbation of the ground state is negligible at the temperatures and densities of interest to us. In Fig. 5 we study the behavior of the level shifts as a function of the atom center-of-mass momentum k. It is seen that the level shifts are not too sensitive to the c.m. motion until $k>\bar{k}$, where k is the mean thermal momentum $\sqrt{2MT}$. This is also found to be true for level profiles. When k exceeds $\bar{k}$, large values of $\Delta\epsilon$, as well as abrupt changes of sign, are observed. This can be interpreted in terms of the onset of instabilities and the spontaneous emission of plasmons. In effect, at this stage the present analysis loses its validity, since the plasma passes into a nonequilibrium turbulent phase. Although the data of Fig. 5 are obtained from a second-order calculation, limited tests show that the same qualitative behavior is valid for the more complete

TABLE III. Location of roots of Eq. (4.1a) with respect to ω_0(i.e., $\Delta\epsilon_{nl}$) as obtained from different basis sets, second-order theory, in units of the plasma frequency $\omega_p = 0.792\,88 \times 10^{-3}$ a.u. $= 1.7402\times 10^2$ cm^{-1}. For example, the values in the lower right corner are from calculations for the $3p$ level with a basis of all discrete functions up to and including principal quantum number 8 (i.e., $n_{\max} = n + 5$) together with the continuum functions. The original level is very slightly shifted and flanked by two new satellite excitations (for $n > 1$) having a greater spectral weight (as in Figs. 6 and 7) than the level center. Data are for $T = 4$ eV, $\bar{\rho}_e = 0.5\times 10^{-7}$ a.u. $\simeq 3.3\times 10^{17}$ e/cm^3 for atoms with a c.m. momentum $k = \bar{k}$ (= the thermal momentum). The satellites disappear in the all-order theory.

$n_{\max}$ / $\Delta\epsilon_{nl}$	Discrete basis		Discrete basis and continuum	
	$n+1$	$n+5$	$n+1$	$n+5$
$2s$	-1.36 2.38×10^{-3} 1.27	-1.39 2.18×10^{-3} 1.30	-1.40 3.58×10^{-3} 1.23	-1.41 3.96×10^{-3} 1.23
$2p$	-0.516 7.05×10^{-3} 0.407	-0.526 2.86×10^{-3} 0.396	-0.547 1.17×10^{-2} 0.397	-0.557 1.34×10^{-2} 0.416
$3s$	-4.19 1.49×10^{-3} 3.99	-4.21 1.78×10^{-3} 3.97	-4.26 2.31×10^{-3} 3.91	-4.29 2.56×10^{-3} 3.88
$3p$	-3.68 2.03×10^{-3} 3.43	-3.72 2.46×10^{-3} 3.41	-3.78 3.30×10^{-3} 3.36	-3.81 3.80×10^{-3} 3.30

all-order calculation.

The damping of the hydrogenic levels can be studied most transparently via the spectral weight function

$$J_\nu(k\omega) = -(1/\pi)(1 + e^{\omega/T})^{-1}\,\mathrm{Im}G_\nu(k\omega)\,, \qquad (5.1\mathrm{a})$$

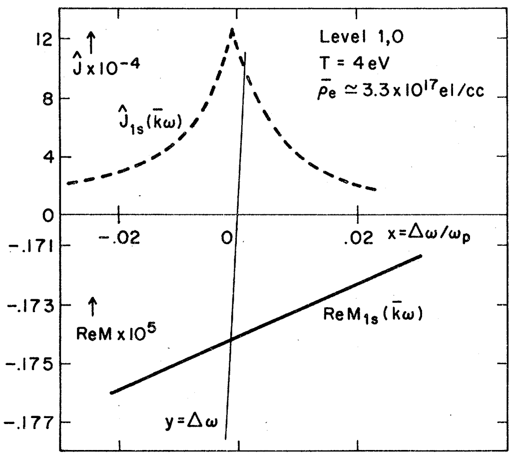

FIG. 4. Real part of the mass operator $\mathrm{Re}M_{1s}(k\omega)$ and the spectral weight function $\vec{J}_{1s}(\bar{k}\omega)$ in atomic units for a ground-state atom in a plasma at $T = 4$ eV. $\bar{\rho}_e = 0.5\times 10^{-7}$ a.u. ($= 3.3\times 10^{23}$ m^{-3}), with the atom center-of-mass momentum $k = \bar{k}$, the thermal momentum $(2MT)^{1/2}$. The frequency axis x is given by $x = \Delta\omega/\omega_p$, where ω_p is the plasma frequency, with $\omega_p = 0.7929\times 10^{-3}$ a.u.

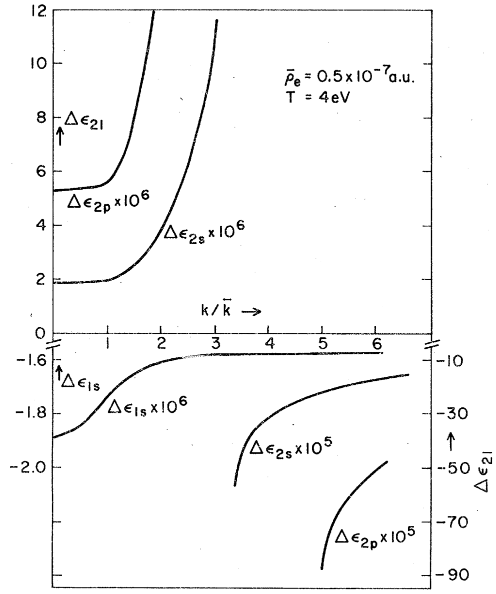

FIG. 5. The effect of atomic motion (c.m. momentum k) on the level shift $\Delta E_{nl}(k)$ for $n, l = 1s$, $2s$, and $2p$. The excited atomic states show a strong discontinuity and a change of sign for $k > 1$. This corresponds to the onset of instabilities. Note that different scales are used for different parts of the $2s, 2p$ curves. Data are based on a second-order calculation at $T = 4$ eV, $\bar{\rho}_e = 0.5\times 10^{-7}$ a.u.

which is the Fourier transform of the time-dependent level populations and becomes a δ function for the noninteracting system. The effects of the interactions are picked up by $\mathrm{Im}G_\nu(k\omega)$ and the sharp δ-function peaks become shape functions describing the broadened excitation. In Figs. 4, 6, 7, and 9 we plot the scaled spectral function defined by

$$\hat{J}_\nu(k\omega) = -e^{-\Delta\omega T}\,\mathrm{Im}G_\nu(k\omega)\,, \quad \Delta\omega = \omega - \omega_0\,, \tag{5.1b}$$

$$\tilde{J}_\nu = \hat{J}_\nu / \hat{J}_\nu^{\max} \tag{5.1c}$$

for the $1s$; $2s$, $2p$; and $3p$, $3d$ levels. The dramatic restoration of the multipeaked second-order profile to a more conventional form when multiple scattering effects are included (e.g., see Figs. 6 and 7) bears witness to their importance in determining the character of the excitation spectrum. In treating the atom-perturber interaction only to second order, together with a full plasmon description of the charged subsystem, the effect of atom-plasmon coupling is overemphasized. Such a picture would probably be valid for situations in which many plasmon modes are excited, as would be the case in certain nonequilibrium situation, and in high-density plasmas.

In Fig. 8 we show the spectral intensity function of the *level* $2p$ together with a Lyman-α *line* profile of Grützmacher and Wende.[29] The line profile is determined by the two-particle Green's function

$$\langle\langle a_{1s}^\dagger(\vec{k})a_2^\dagger a(\vec{k}+\vec{q}),\, a_2^\dagger a(\vec{k}+\vec{q})a_{1s}(\vec{k})\rangle\rangle\,,$$

where $\vec{k}$ is the c.m. momentum of the atom after emitting a photon of momentum $\vec{q}$. If the relevant elementary excitations could be considered to be weakly interacting, then the two-particle function could be written in terms of one-particle functions, neglecting various cross terms, exchange terms, etc. In the noninteracting case, or in any independent-particle model, the Ritz principle (line frequency = level frequency difference) is valid and is a manifestation of the separability of the two particle function into two one-particle functions. More complicated situations involving the construction of response functions within self-consistent one-body propagators have been discussed by, for example, Baym.[30] In the present study we do not attempt to construct a line profile but merely make the following *qualitative* observation. Since the $1s$ level has negligible broadening and since the $1s$, $2p$ energy difference is large, we may expect the spectral intensity function of the $2p$ *level* to be, on the whole, similar to the Lyman-α line profile. This property seems to be satisfied by the curves shown in Fig. 8.

The data in Table IV give an idea of the level shifts to be expected for the range of densities and temperatures considered in this paper. These

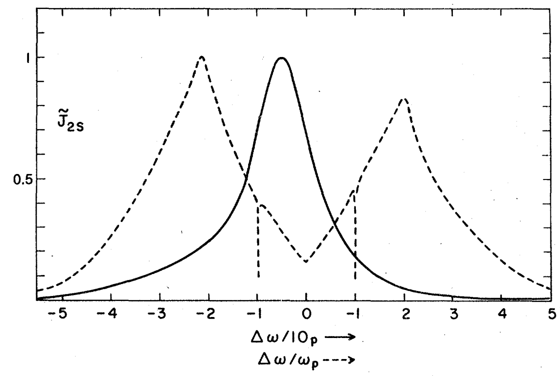

FIG. 6. Spectral intensity functions for the level $2s$ of an atom with c.m. momentum $k=\bar{k}$ in a plasma with $T=1.2$ eV, $\bar{\rho}_e = 0.6\times10^{-7}$ a.u., where dashed curve is the second-order calculation and solid curve is the all-order calculation. The second-order calculation emphasizes atom-plasmon coupling and leads to two side bands. These disappear on inclusion of multiple scattering, giving a much narrower profile (solid curve) with a single peak. Here $\omega_p = 0.8686\times10^{-3}$ a.u.

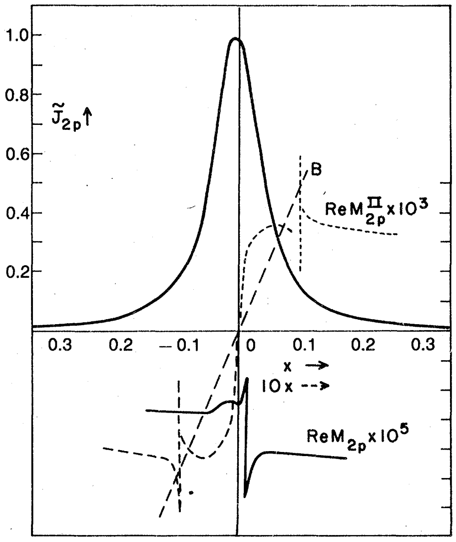

FIG. 7. Solid curve gives the spectral-intensity function $\tilde{J}_{2p}$ and the real part of the mass operator $\mathrm{Re}M_{2p}$ calculated in the all-order theory. Dotted curve is the real part calculated in second-order theory, together with the bisector B for the resolution of the roots. The second-order spectral function is similar to that of Fig. 6 and shows two spurious side bands. The all-order theory gives only a single root (the bisector is not shown, since it is ten times steeper than B) and a single peak. Here $x=\Delta\omega/\omega_p$. The second-order curve is plotted against $10x$ on the x axis, where $\omega_p = 0.8686\times10^{-3}$ a.u.

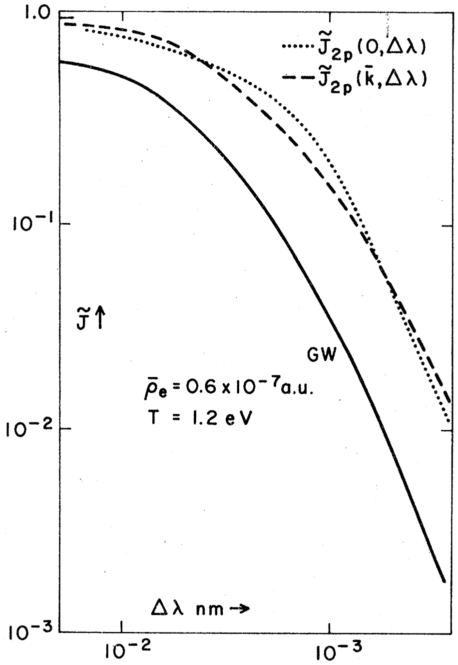

FIG. 8. Scaled spectral intensity functions $[\tilde{J}_\nu(k,\omega)$, see Eq. (5.1c)] for the $2p$ level at $T = 14\,000$ K, electron density $\bar{\rho}_e = 4 \times 10^{23}$ m^{-3}, and atom c.m. momenta $k = \bar{k}$ (dashed line) and $k = 0$ (dotted line) compared with experimental Lyman-α line profile of Grützmacher and Wende (Ref. 24). We compare a *level* profile with a *line* profile, although this cannot be justified in a quantitative way. The similarity of the form of the curves suggests that the mass operator has captured the correct microfield effects at $\Delta\omega = 0$.

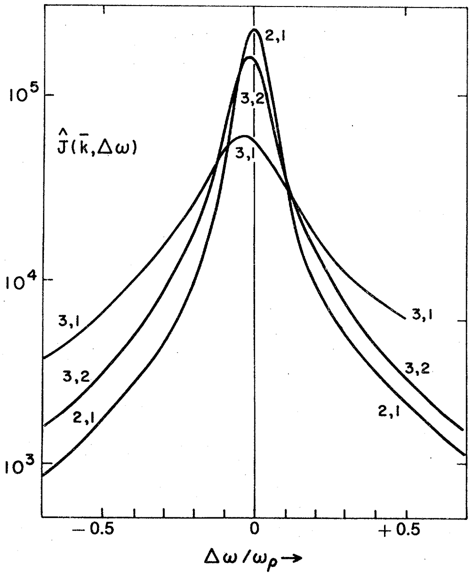

FIG. 9. Unnormalized spectral intensity functions [i.e., $\hat{J}_\nu(k,\omega)$, see Eq. (5.1b)] for $3d$, $3p$, and $2p$ levels of an atom with $k = \bar{k}$ in a plasma at $T = 1.2$ eV, $\bar{\rho}_e = 6 \times 10^{-7}$ a.u.

TABLE IV. Typical values (in atomic units) of the real and imaginary parts of the mass operator as calculated by the all-order theory at the shifted level center ω_s. Data are for a plasma at $T = 1.2$ eV, $\bar{\rho}_e = 0.6 \times 10^{-7}$ a.u. Results for n, l and atom center-of-mass momentum $k = \bar{k}$ or 0 are given, where $\text{Re}M_\nu(k, \omega_s)$ is the level shift. Values for $(n, l) = (3, 0)$ are not reported owing to numerical difficulties. The ground state is negligibly perturbed (See Fig. 4).

n, l	K	$\Delta\epsilon = \text{Re}M(k\omega_s)$	$\text{Im}M(k\omega_s)$
2,0	$\bar{k}$	-0.443×10^{-4}	-0.621×10^{-4}
2,1	0	-0.109×10^{-4}	-0.465×10^{-4}
2,1	$\bar{k}$	-0.511×10^{-5}	-0.416×10^{-4}
3,1	$\bar{k}$	-0.211×10^{-4}	-0.168×10^{-3}
3,2	$\bar{k}$	-0.559×10^{-5}	-0.607×10^{-4}

shifts depend nonlinearly on the density and have to be added to the exchange shifts of Table I. (The data of Table I must be multipled by the density and taken with the opposite sign.) The calculation of the level shift using the all-order theory is much more time consuming than the simpler second-order programs, and we have not attempted to calculate shifts for higher principal quantum numbers. The demands on computer time as well as the shortcomings of the method increase rapidly for high quantum numbers.

Some comments are necessary regarding the level shift and the question of the calculation of the perturbed chemical potential of hydrogen atoms in the plasma. Direct attempts to evaluate the atom partition function by an expression of the form[13,17]

$$Z = \sum_{\nu} \exp\{[\epsilon_\nu(k) + \Delta\epsilon_\nu(k)]/T\}, \quad \nu = n, l, m \tag{5.2}$$

or the chemical potential μ_a by

$$\sum_{\nu, k} \exp\{[\epsilon_\nu^0(k) + \Delta\epsilon_\nu(k) - \mu_a]/T\} = \bar{n}_a \tag{5.3}$$

$$\epsilon_\nu^0(k) = -1/2n^2 + k^2/2M$$

involve formal difficulties. Even if it is true that the shift $\Delta\epsilon_\nu$ on each level converts (5.2) to a finite sum and hence overcomes the classic problem of the divergence of the atomic partition function,[31] the perturbed energies at $E_\nu(k) = \epsilon_\nu(k) + \Delta\epsilon_\nu$ are *not* exact eigenstates of the total system. They correspond to the peaks of the one-particle spectral function of the system, the importance of these peaks being related to the quasiparticle strength $(1 - \partial M/\partial\omega)^{-1}$, where $\partial M/\partial\omega$ is a measure of the extent to which the bare particle is mixed into the other modes in the system. These difficulties can be avoided by using the full spectral function rather than just the peaks. The perturbed chemical potential is formally determined via an integration over the spectral function using the relations

$$\bar{n}_\nu(k,t)=\int_{-\infty}^{+\infty} J_\nu(k\omega)e^{-i\omega t}\,d\omega\,, \tag{5.4a}$$

$$\bar{n}_\nu(k)=\bar{n}_\nu(k,0)\,,\quad \bar{n}_\nu=\sum_{\nu,k}\bar{n}_\nu(k) \tag{5.4b}$$

for the level populations and the total number density of atoms. [Equation (5.4a) expresses the time-dependent level population $\bar{n}_\nu(k,t)$.] In practice, only a few levels above the ground state are needed in the sum (5.4b), taken over the bound states n, l, m, since $\bar{n}_\nu(k)$ rapidly decreases towards zero.

Within the context of the second-order theory the spectral functions $J_\nu(k\omega)$ are broad and have new structures. But within the all-order theory the profiles are narrow and only slightly shifted, and as such we have not taken up the numerical work involved in evaluating (3.4a)–(5.4b), since the shift in μ would most likely be within the numerical noise of the calculation. An alternative approach to the chemical potential, which correctly treats the upper bound states and lower continuum states, is being investigated. This is best done within a more complete scheme where the bound-free thermal processes ($H=H^++e^-$) are automatically incorporated. Such an approach has been given by, for example, Klimontovich,[32] where the theory is zero order in the pair interaction, and by Dharma-wardana,[20] where the interaction is treated explicitly to second order and then to all order via an approximation to the polarization operator.

VI. CONCLUSIONS

In the present paper we achieve several significant developments: (i) an actual numerical computation of the frequency, momentum, and level-dependent self-energy for an H atom in a hot plasma, noting that it has the potential of replacing the current concept of the plasma microfield by a rigorous quantum concept; (ii) the calculation of exchange shifts from the self-energy, since the latter, being an effective micropotential felt by the test atom, contains information on the exchange potential; and (iii) the calculation of polarization effects, as manifested in the self-energy. An important theoretical point here is the construction of an all-order theory inclusive of dynamic screening, which emerges naturally from the theory. The manipulation of the integral equation for summing to infinite order was the result of a number of numerical trials. The form finally used was that automatically selected by the Dyson development indicated in Eqs. (3.21)–(3.25). In terms of the language of diagrams, this is equivalent to introducing self-energy insertions and ladder corrections in the second-order mass operator to get an all-order mass operator. Any formal objections to overcomplete bases can be avoided if (as in Refs. 20 and 32) a complete discrete plus Coulomb continuum basis is used; this also has the advantage of treating interparticle interactions in a completely novel way. This leads to a nonzero first-order mass operator and clearly picks up (exchange and correlation) contributions which are approximated in the mass operator of the present theory. However, we feel that the present theory, where we have allowed for nonelementary commutation rules arising from overcompleteness, is quite satisfactory, especially in the case of hydrogen. We consider that this preliminary study has exposed the complexity of hydrogenic levels, especially near the level center (i.e., within a plasma frequency), and the competitive role played by atom-perturber and atom-plasmon processes in the elementary excitation spectrum of hydrogen in a plasma. Also, the real and imaginary parts of the mass operator (self-energy) were found to be valuable tools in the study of the onset of instabilities in the system, the former via its roots and singularities, the latter via its magnitude and functional behavior. We conclude by noting that the calculated mass operator $M(q,\omega)$ can, in principle, yield a plasma microfield $\vec{E}(\vec{q},\omega)$ which includes spatial and frequency-dispersion effects, and much more physics than the quasistatic fields which are currently used in plasma calculations.

ACKNOWLEDGMENTS

This work was started as a project supported by the CECAM workshop on plasma spectra held in the summer of 1976 in Orsay, France, where a detailed second-order calculation was completed.[25] Extension of the method to higher orders was carried out at the National Research Council of Canada, Ottawa, while the computations were done or Orsay and Limeil. We thank J. Bruaneau of Limeil for technical assistance and discussions and Dr. Carl Moser, Directeur, Centre européen de calcul atomique et moléculaire, for his interest in the work and for support of (M.W.C.D.) of the authors.

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[1] Level shifts, widths, and level intensity profiles are the main concern of this paper. *Line* shifts and *line* profiles require a calculation of the two-particle Green's function (except when an independent-particle approximation is reasonable).

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