

# Collisional Frequency Shifts of Absorption Lines in an Atomic Hydrogen Gas

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## Abstract

We consider the effect of interactions on the line shape of the two-photon  $1s-2s$  transition in a (doubly) spin-polarized atomic hydrogen gas in terms of the interatomic interaction potentials. We show that the frequency-weighted sum rule for the intensity of the line is not given simply in terms of the pseudopotentials that describe the interactions between low-energy atoms. The origin of the departures from the simple pseudopotential result for the frequency-weighted sum rule is traced to what we refer to as incoherent contributions to the spectral weight. These arise from more complicated final states of the many-body system than the ones usually considered. In particular, we show how the relevant response function may be treated in a manner similar to the density-density response function for Fermi liquids, and express it as a coherent part coming from single particle-hole pairs, and an incoherent part coming from other excitations. We argue that in experiments only the coherent part of the response of the system is observed, and its contribution to the frequency-weighted sum rule is shown to be given correctly by the pseudopotential approximation. Finally we calculate the width of the coherent part of the line due to collisional damping.

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## I. INTRODUCTION

After two decades of concentrated effort Fried *et al.* recently succeeded in realizing Bose-Einstein condensation in spin-polarized atomic hydrogen in a magnetic trap [1]. In this experiment a key role is played by collisional frequency shifts, since the density of the atomic hydrogen cloud is monitored by observing the frequency shift of the Doppler-free peak in the two-photon  $1s - 2s$  absorption spectrum [2]. Previously, collisional frequency shifts have also been observed in hydrogen masers [3] and in atomic fountains [4], where they lead to a serious limitation on the stability of these devices. A thorough understanding of such shifts is therefore central to the interpretation of various experimental results with atomic quantum gases.

In the theory of line shifts that is currently standard [5], one considers only the normal state of the gas and uses a Boltzmann equation to determine the effect of collisions on the absorption profile. The line shift is then found to be proportional to the difference of the  $1s - 2s$  scattering length,  $a_{1s-2s}$ , and the  $1s - 1s$  one,  $a_{1s-1s}$ . Recently two papers have appeared on the theory of the line shifts, one employing the random phase approximation [6], and the other using sum-rule arguments [7]. One striking prediction of these calculations is that the line shift in a dilute, fully Bose-Einstein condensed gas should be one half that for an uncondensed gas of the same density. These papers have in common the assumption that the interaction between atoms may be assumed to be of the usual contact pseudopotential form, and that the interactions may be taken into account in a mean-field approach. In this paper we investigate the problem allowing for a more general interaction. We demonstrate that the frequency-weighted sum rule is given in terms of the *bare* interaction potential, not the pseudopotential. By using microscopic many-body theory we trace the origin of the discrepancy between the true frequency-weighted sum rule and the one calculated using the pseudopotential to *incoherent* contributions to the atomic propagators, which arise when a  $1s$  atom is excited close to another such atom. The latter processes, while relatively infrequent in a low-density gas, give contributions to the spectral weight at frequencies very different from those for excitation of an atom far away from any other atom. However, as we demonstrate in this paper, the shift of the *coherent* contribution to the response, which corresponds physically to excitation of an atom when it is relatively far away from other atoms, is given by the pseudopotential result.

We have organized the paper as follows. In Sec. II we first derive an exact sum rule for the frequency-weighted spectral weight, and will show that this is not given correctly by the pseudopotential result. In Sec. III we then study the problem from a microscopic point of view, and indicate how the absorption spectrum can be separated into coherent and incoherent parts. We also argue that the coherent part of the response is of greatest interest experimentally. In Sec. IV we determine the collisional broadening of the coherent absorption peak and we end in Sec. V with our conclusions.

## II. SUM RULE APPROACH

Let us begin by considering a system of hydrogen atoms in the  $1s$  ground state. The effect of applying the laser radiation is to excite some hydrogen atoms to the metastable  $2s$  state, which has a radiative lifetime  $1/\Gamma_{2s}$  of the order of one second. Experimentally, the hydrogen

clouds investigated are inhomogeneous, but since the length scale for density variations is large compared with the microscopic lengths in the problem, it is an excellent approximation to take the effects of inhomogeneity into account in the local density approximation, and consequently in our calculations we consider a spatially uniform system. If the radiation field is spatially uniform, its interaction with the hydrogen gas may be represented by a perturbing Hamiltonian

$$H_1 = \frac{\hbar\Omega}{2} \int d\mathbf{x} \left[ e^{-i\omega t} \psi_{2s}^\dagger(\mathbf{x}) \psi_{1s}(\mathbf{x}) + e^{i\omega t} \psi_{1s}^\dagger(\mathbf{x}) \psi_{2s}(\mathbf{x}) \right], \quad (1)$$

where  $\omega$  is the angular frequency of the pair of photons, the operators  $\psi_\alpha^\dagger(\mathbf{x})$  and  $\psi_\alpha(\mathbf{x})$  create and destroy atoms in the state  $|\alpha\rangle$ , and  $\Omega$  is the effective Rabi frequency determined by the strength of the laser field and atomic matrix elements.

The unperturbed part  $H_0$  of the Hamiltonian is given by the sum of the intrinsic atomic energies of isolated atoms at rest, the kinetic energy associated with the translation of atoms, and terms that take into account interactions between atoms. To an excellent approximation the interaction energy is given in terms of local two-body potentials dependent only on the distance  $r$  between atoms, and we denote the potential for two atoms in the  $1s$  state by  $V_{1s-1s}(r)$  and that for one atom in the  $1s$  state and the other in the  $2s$  state by  $V_{1s-2s}(r)$ . Since we consider the case of weak excitation, we shall not need to specify the interaction between two excited-state atoms. In detail we thus have

$$\begin{aligned} H_0 = & \int d\mathbf{x} \psi_{1s}^\dagger(\mathbf{x}) \left( -\frac{\hbar^2 \nabla^2}{2m} + \epsilon_{1s} \right) \psi_{1s}(\mathbf{x}) + \int d\mathbf{x} \psi_{2s}^\dagger(\mathbf{x}) \left( -\frac{\hbar^2 \nabla^2}{2m} + \epsilon_{2s} \right) \psi_{2s}(\mathbf{x}) \\ & + \frac{1}{2} \int d\mathbf{x} \int d\mathbf{x}' \psi_{1s}^\dagger(\mathbf{x}) \psi_{1s}^\dagger(\mathbf{x}') V_{1s-1s}(\mathbf{x} - \mathbf{x}') \psi_{1s}(\mathbf{x}') \psi_{1s}(\mathbf{x}) \\ & + \int d\mathbf{x} \int d\mathbf{x}' \psi_{1s}^\dagger(\mathbf{x}) \psi_{2s}^\dagger(\mathbf{x}') V_{1s-2s}(\mathbf{x} - \mathbf{x}') \psi_{2s}(\mathbf{x}') \psi_{1s}(\mathbf{x}), \end{aligned} \quad (2)$$

where  $m$  is the mass of an atom and  $\epsilon_\alpha$  denotes the energy of the atomic state  $\alpha$ . Note that for clarity we have in the first instance neglected the effect of the finite lifetime of the excited atom. In Sec. III, however, we show how it can be easily incorporated into the theory.

The net rate of transitions may now be calculated from Fermi's Golden Rule, and is given by

$$I(\omega) = \frac{2\pi}{\hbar} \sum_{m,n} |\langle m|H_1|n\rangle|^2 \delta(\hbar\omega + E_n - E_m) (p_n - p_m). \quad (3)$$

Here  $p_n$  is the initial probability for occurrence of the many-body state  $|n\rangle$ , which is an eigenstate of the Hamiltonian  $H_0$  and therefore obeys  $H_0|n\rangle = E_n|n\rangle$ . We note that for the situations of interest in the Bose-Einstein condensation experiments, initial states containing  $2s$  atoms play essentially no role, since the probability of  $2s$  atoms being present is very small because the energy difference between a  $2s$  atom and a ground-state one is much larger than the thermal energy  $k_B T$ . From Eq. (3) we thus find that the rate of absorption of energy is

$$\hbar\omega I(\omega) = \frac{2\pi}{\hbar} \sum_{m,n} (E_m - E_n) |\langle m|H_1|n\rangle|^2 \delta(\hbar\omega - E_m + E_n) p_n, \quad (4)$$

and the average frequency of the line is given by

$$\bar{\omega} = \frac{\int d\omega \omega I(\omega)}{\int d\omega I(\omega)} = \frac{\sum_{m,n} (E_m - E_n) |\langle m|H_1|n\rangle|^2 p_n}{\hbar \sum_{m,n} |\langle m|H_1|n\rangle|^2 p_n}. \quad (5)$$

To evaluate the average frequency we, following the procedure adopted by Ohtel *et al.* [7], again make use of  $H_0|n\rangle = E_n|n\rangle$ , and consider the thermal average of  $H_1[H_0, H_1]$ , or equivalently the double commutator  $[H_1, [H_0, H_1]]$ . In contrast to Ref. [7], we however do not assume that the interaction may be represented by a pseudopotential. The average frequency is then given by

$$\bar{\omega} = \frac{\langle H_1[H_0, H_1] \rangle}{\hbar \langle H_1^2 \rangle}. \quad (6)$$

The physical content of this equation is that the average frequency shift is given by the difference in energies of the expectation value of the energy in the initial state and that in the state created by operating with  $H_1$  on the initial state. Evaluating the expectation value of the commutator expression above directly, we find for the frequency shift relative to its value for an isolated atom the result

$$\overline{\Delta\omega} = \frac{n}{\hbar} \int d\mathbf{r} [V_{1s-2s}(r) - V_{1s-1s}(r)] g_2(\mathbf{r}), \quad (7)$$

where  $n$  is the density of the gas and

$$g_2(\mathbf{r}) = \frac{1}{n^2} \langle \psi_{1s}^\dagger(\mathbf{r}) \psi_{1s}^\dagger(\mathbf{0}) \psi_{1s}(\mathbf{0}) \psi_{1s}(\mathbf{r}) \rangle \quad (8)$$

is the pair distribution function for ground state atoms in the initial state of the system. In arriving at this expression we have again neglected the possibility of 2s atoms being present in the initial state. This result is simple to understand, since the operator  $H_1$  converts a single ground-state atom in the initial state into an excited state one with an amplitude that does not depend on position. The average energy difference between the initial state and the one created by the laser is therefore the energy required to convert a 1s atom into a 2s one. Since the masses of the atoms in the two states are the same, there is no contribution from the kinetic energy, and the sole contribution, apart from the energy difference for an isolated atom, comes from interactions. This situation should be contrasted with that of an isotopic impurity, like a  $^3\text{He}$  atom in liquid  $^4\text{He}$ , which is just the opposite, in that the masses are different, while the interaction potentials are the same. The sum rule derived here is analogous to sum rules for spin response of condensed matter systems, and for spin, isospin, and spin-isospin response of nuclei. In these cases the basic origin of the shifts is terms in the interaction that are not invariant under rotations in spin, and/or isospin space, or, in the present problem, rotations in the pseudospin space corresponding to conversion of a 1s atom into a 2s one.

The long-wavelength assumption is appropriate for the two-photon transition when the two photons that are absorbed have equal and opposite momenta. When the total momentum  $\mathbf{q}$  of the absorbed photons is non-zero, the perturbing Hamiltonian depends on space and we need to generalize the sum rule to spatially varying interactions. This is straightforward and we find that the average frequency shift is given by adding the recoil energy  $\hbar^2 \mathbf{q}^2 / 2m$  to the spatially homogeneous result for  $\mathbf{q} = \mathbf{0}$ .

Let us now compare our result in Eq. (7) with that of earlier work. If the interaction potentials are weak, the correlation function will vary little over the ranges of the potentials, and we may replace the pair distribution function by its value for zero separation. We then obtain

$$(\overline{\Delta\omega})_{\text{B}} = \frac{n}{\hbar} g_2(\mathbf{0}) \int d\mathbf{r} [V_{1s-2s}(r) - V_{1s-1s}(r)] . \quad (9)$$

This is equivalent to the result of Levitov *et al.* [7], since for weak potentials the Born approximation may be applied, and thus the scattering lengths  $a$  are related to the interaction potentials by  $4\pi\hbar^2 a/m = \int d\mathbf{r} V(r)$ .

The interaction potentials for hydrogen atoms are not weak, and the Born approximation is not valid. Therefore it is important to explore how the pair distribution function behaves at short distances. On length scales larger than the range of the atomic interactions, correlations should be well described in terms of mean fields. However, for strong potentials it is not permissible to assume that the correlation function for small separations varies slowly on distances of the order of the range of the potential. Rather one expects that the many-body wave function for small particle separations will behave as that for a pair of atoms interacting via the  $1s - 1s$  interaction, since the effects of other atoms will then be negligible at low densities. Hence, provided the energies of elementary excitations of the system are small compared with the typical energy scale over which the two-atom relative wave function changes significantly, it will be a good approximation to assume that the pair distribution function scales as the square of the scattering wave function at zero energy, i.e.,  $|\Psi_{\text{rel}}(r)|^2$ . We therefore write

$$g_2(\mathbf{r}) \simeq |\Psi_{\text{rel}}(r)|^2 g_2^{\text{MF}}(\mathbf{0}) , \quad (10)$$

where the mean-field correlation function  $g_2^{\text{MF}}(\mathbf{0})$  is the pair correlation function on length scales that are greater than the range of the interaction but small compared with other lengths in the problem, such as the thermal de Broglie wavelength, the particle separation, and, when a condensate is present, the coherence length. We have chosen the normalization of the wave function such that at distances large compared with the range of the  $1s - 1s$  potential it behaves as  $\Psi_{\text{rel}}(r) \simeq 1 - a_{1s-1s}/r$ . Note that the above procedure is equivalent to assuming a wave function of the Jastrow form to describe the correlations at short distances, the Jastrow factor being taken to be of the form of the relative wave function of two atoms at zero energy [8].

The final result for the shift is thus

$$\overline{\Delta\omega} = \frac{n}{\hbar} g_2^{\text{MF}}(\mathbf{0}) \int d\mathbf{r} [V_{1s-2s}(r) - V_{1s-1s}(r)] |\Psi_{\text{rel}}(r)|^2 . \quad (11)$$

This expression cannot be simply rewritten in terms of scattering lengths. A simple example that demonstrates this is a  $1s - 1s$  interaction with a hard core at a radius  $r_c$ . The expression for the frequency shift does not depend on the  $1s - 2s$  potential at distances less than  $r_c$ , since the relative wave function for two atoms in the  $|1s\rangle$  state vanishes there. However, the  $1s - 2s$  scattering length is sensitive to the behavior of the  $1s - 2s$  potential at distances less than  $r_c$ , and therefore this is incompatible with the frequency shift being expressible solely in terms of scattering lengths. We expect the Jastrow form of the wave function to

be accurate irrespective of whether or not the gas is Bose condensed, and consequently in a completely Bose-condensed gas the shifts are predicted to be a factor of 2 smaller than in a gas of the same density with no condensate, reflecting the usual  $2!$  reduction factor for two-body processes [9].

The result of this calculation is that the frequency-weighted sum rule is quite different from what one predicts if one uses the pseudopotential. To understand the origin of these differences it is convenient to explore the problem from a microscopic viewpoint.

### III. MICROSCOPIC APPROACH

To understand the sum-rule result, it is helpful to think about the nature of the final states that can be created from the initial state by the operator of interest, which in this case converts a  $1s$  atom into a  $2s$  one. Relative to the initial state, the simplest excited states have an extra  $2s$  quasiparticle and an extra  $1s$  quasihole, and will be referred to as single quasiparticle-quasihole pair excitations. In the random phase approximation these are the only states taken into account. The physics of the process may be understood by regarding the degree of freedom associated with converting a  $1s$  atom into a  $2s$  one as a pseudospin. If the commutator of the pseudospin-raising operator with the unperturbed Hamiltonian is zero, there is a unique frequency for all transitions. Because the interaction between a  $1s$  atom and a  $2s$  atom differs from that between two  $1s$  atoms, however, the Hamiltonian is not invariant under rotations in pseudospin space, and its commutator with the pseudospin-raising operator is not zero. Consequently there can be transitions to states with a range of energies. It is perhaps helpful to consider a spin system in an applied magnetic field. If the interaction between the particles commutes with the spin-raising operator, the raising operator will couple only to states whose energy differs from that of the original state by  $\hbar$  times the Larmor frequency. However, if the interaction is not invariant under spin rotations, other excited states with different energies can be created. In Fermi-liquid theory the first sort of transitions correspond to the creation of a single quasiparticle-quasihole pair, while the more complicated excitations correspond to creation of many pairs. For the problem under study here, an  $n$ -pair excitation has one extra  $2s$  quasiparticle,  $n$  extra  $1s$  quasiparticles, and  $n + 1$  extra  $1s$  quasiholes. The difference between the results for the frequency-weighted sum rule calculated with the pseudopotential and the actual potential is due to the multipair excitations. For Fermi liquids an analysis of the density response in terms of single-pair and multipair states may be found in Ref. [10]. A formulation of the problem for more general sorts of response was presented in terms of microscopic theory by Leggett [11], and the results were discussed in terms of Fermi-liquid theory in Ref. [12].

Let us begin by expressing the result for the transition rate in terms of the response function for the operator

$$O = \frac{1}{V} \int d\mathbf{x} \left( e^{-i\omega t} \psi_{2s}^\dagger(\mathbf{x}) \psi_{1s}(\mathbf{x}) + e^{i\omega t} \psi_{1s}^\dagger(\mathbf{x}) \psi_{2s}(\mathbf{x}) \right), \quad (12)$$

where  $V$  is the volume of the system. The response function is defined in the usual way as the temporal Fourier transform of the retarded commutator, and is given by

$$\chi(\omega) = -\frac{1}{V} \int d\mathbf{x} \int_0^\infty dt e^{i\omega t} \langle [\psi_{1s}^\dagger(\mathbf{x}, t) \psi_{2s}(\mathbf{x}, t), \psi_{2s}^\dagger(\mathbf{0}, 0) \psi_{1s}(\mathbf{0}, 0)] \rangle$$

$$= \sum_{m,n} \frac{|\langle m|\mathcal{O}|n\rangle|^2 p_n}{\hbar\omega + i0 + E_n - E_m}, \quad (13)$$

where  $p_n$  is again the probability of the state  $n$  being occupied and we neglected the occupancy of the final state compared with that of the initial one. The transition rate in Eq. (3) is therefore given by

$$I(\omega) = -\frac{2}{\hbar} \Im [\Pi(\omega)], \quad (14)$$

where

$$\Pi(\omega) = \left(\frac{\hbar\Omega}{2}\right)^2 \chi(\omega) \quad (15)$$

is the polarizability of the gas. This is the desired result, because it explicitly shows that the transition rate is related to the polarizability of the gas, which is easily accessible with equilibrium many-body techniques. Indeed, in that language  $\hbar\Pi(\omega)$  is equal to the (retarded) self energy for the “effective photon” causing the  $1s - 2s$  transition and the imaginary part therefore determines its finite lifetime, which physically is due to absorption by  $1s$  atoms in the gas. We are thus left with the task of calculating the polarizability, which theoretically implies that we have to evaluate the diagram in Fig. 1. We begin by considering two simple calculations, the Hartree-Fock approximation and the random phase approximation, before discussing the more general formulation.

### A. The Hartree-Fock and Random Phase Approximations

In this section we consider a number of examples where only coherent contributions to the response are taken into account. These calculations lead to results identical with those of Ohtel and Levitov [6]. To familiarize ourselves with the present formulation, let us first consider the ideal Bose gas. Then Eq. (13) becomes

$$\chi(\omega) = -\frac{1}{V} \int d\mathbf{x} \int_0^\infty dt e^{i\omega t} \langle \psi_{1s}^\dagger(\mathbf{x}, t) \psi_{1s}(\mathbf{0}, 0) \rangle \langle \psi_{2s}(\mathbf{x}, t) \psi_{2s}^\dagger(\mathbf{0}, 0) \rangle. \quad (16)$$

Moreover, the single-particle propagator is given by

$$\langle \psi_{1s}^\dagger(\mathbf{x}, t) \psi_{1s}(\mathbf{0}, 0) \rangle = \frac{1}{V} \sum_{\mathbf{k}} N_{\mathbf{k}} e^{-i\mathbf{k}\cdot\mathbf{x} + i(\epsilon_{\mathbf{k}} + \epsilon_{1s} - \mu)t/\hbar}, \quad (17)$$

where  $\epsilon_{\mathbf{k}} = \hbar^2 \mathbf{k}^2 / 2m$  is the kinetic energy of a  $1s$  atom,  $\mu$  is the chemical potential for  $1s$  atoms, and  $N_{\mathbf{k}} = 1/(e^{\beta(\epsilon_{\mathbf{k}} - \mu)} - 1)$  is the Bose distribution function with  $\beta = 1/k_B T$ . Similarly we have, including now the finite atomic lifetime of the  $2s$  atom,

$$\langle \psi_{2s}(\mathbf{x}, t) \psi_{2s}^\dagger(\mathbf{0}, 0) \rangle = \frac{1}{V} \sum_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{x} - i(\epsilon_{\mathbf{k}} + \epsilon_{2s} - i\hbar\Gamma_{2s}/2 - \mu)t/\hbar}. \quad (18)$$

Substituting the last two results, we find for the polarizability in Eq. (15) the expression

$$\begin{aligned}\Pi(\omega) &= -i \frac{nV\hbar\Omega^2}{8} \int_0^\infty dt e^{i\omega t} e^{i(\epsilon_{1s} - \epsilon_{2s} + i\hbar\Gamma_{2s}/2)t/\hbar} \\ &= \frac{nV(\hbar\Omega)^2}{8} \frac{1}{\hbar\omega + \epsilon_{1s} - \epsilon_{2s} + i\hbar\Gamma_{2s}/2} .\end{aligned}\tag{19}$$

Therefore, we conclude that the absorption line of the gas has a profile given by

$$I(\omega) = N \frac{(\hbar\Omega)^2}{8} \frac{\Gamma_{2s}}{(\hbar\omega - (\epsilon_{2s} - \epsilon_{1s}))^2 + (\hbar\Gamma_{2s}/2)^2} ,\tag{20}$$

which is just the number of atoms  $N = nV$  times the atomic line profile and exactly centered at the atomic resonance in this case. Note that diagrammatically we have now calculated the lowest order contribution to the polarizability in Fig. 1, in which the exact  $1s$  and  $2s$  propagators are replaced by the ideal gas ones and there are no vertex corrections.

At the next level of approximation we dress the  $1s$  and  $2s$  propagators by including the effect of atom-atom ladder diagrams as shown in Fig 2. This corresponds to a Hartree-Fock approximation, in which the effective interaction is taken to be the  $T$  matrix for two-body scattering. For a gas with no condensate, the effect of dressing the propagators in the above calculation is to replace  $\epsilon_\alpha$  by  $\epsilon_\alpha + \hbar\Sigma_\alpha$ , where to lowest order in the  $T$  matrix

$$\hbar\Sigma_{1s} = \frac{8\pi a_{1s-1s}\hbar^2 n}{m} ,\tag{21}$$

and

$$\hbar\Sigma_{2s} = \frac{4\pi a_{1s-2s}\hbar^2 n}{m} .\tag{22}$$

The factor-of-two difference between the numerical factors in Eqs. (21) and (22) reflects the fact that both the Hartree and Fock terms contribute to the energy of a  $1s$  atom, but only the Hartree term contributes for a pair of unlike atoms. Because these interaction corrections to the atomic energies are purely real, the absorption line is of the same shape as in Eq. (20), but is now centered at a frequency shifted from the single-atom resonance by an amount

$$(\Delta\omega)_{\text{HF}} = \frac{4\pi\hbar n}{m} (a_{1s-2s} - 2a_{1s-1s}) .\tag{23}$$

This is the “naive” Hartree-Fock result for the collisional frequency shift due to the mean-field interaction that a  $1s$  and a  $2s$  atom experience from the surrounding gas of  $1s$  atoms. Most important for our purposes is that if we repeat the above calculation for a fully Bose condensed gas of  $1s$  atoms, we find that now

$$(\Delta\omega)_{\text{HF}} = \frac{4\pi\hbar n}{m} (a_{1s-2s} - a_{1s-1s}) ,\tag{24}$$

which shows that only the contribution from the  $1s - 1s$  mean-field interaction is reduced by a factor of 2, in agreement with the fact that  $1s$  and  $2s$  atoms are distinguishable.

We have called the above Hartree-Fock approximation naive, because it is well known that for an approximation to satisfy the conservation laws, it is necessary to include vertex



corrections in addition to the self energy corrections discussed above. For this problem this amounts to including the effects of the mean field self-consistently. Formally, these two kinds of corrections are related by the condition that the vertex correction must be the functional derivative of the self energy corrections with respect to the applied field [13]. In our case this implies that we also have to calculate the “maximally crossed” diagrams shown in Fig. 3. These correspond to the chains of particle-hole bubble diagrams calculated in the random phase approximation and in Fermi liquid theory. This is easily achieved since it corresponds to summing the geometric series

$$\frac{1}{\hbar\omega - (\Delta\omega)_{\text{HF}} + \epsilon_{1s} - \epsilon_{2s} + i\hbar\Gamma_{2s}/2} + \frac{1}{\hbar\omega - (\Delta\omega)_{\text{HF}} + \epsilon_{1s} - \epsilon_{2s} + i\hbar\Gamma_{2s}/2} \frac{4\pi a_{1s-2s}\hbar^2 n}{m} \frac{1}{\hbar\omega - (\Delta\omega)_{\text{HF}} + \epsilon_{1s} - \epsilon_{2s} + i\hbar\Gamma_{2s}/2} + \dots$$

In the end we thus find that

$$I(\omega) = N \frac{(\hbar\Omega)^2}{8} \frac{\Gamma_{2s}}{(\hbar\omega - (\Delta\omega)_{\text{RPA}} - (\epsilon_{2s} - \epsilon_{1s}))^2 + (\hbar\Gamma_{2s}/2)^2}, \quad (25)$$

with

$$(\Delta\omega)_{\text{RPA}} = (\Delta\omega)_{\text{HF}} + \frac{4\pi a_{1s-2s}\hbar n}{m} = \frac{8\pi\hbar n}{m} (a_{1s-2s} - a_{1s-1s}). \quad (26)$$

Moreover, in the fully Bose-Einstein condensed case the vertex corrections are absent and we recover the Hartree-Fock result,

$$(\Delta\omega)_{\text{RPA}} = (\Delta\omega)_{\text{HF}} = \frac{4\pi\hbar n}{m} (a_{1s-2s} - a_{1s-1s}). \quad (27)$$

We therefore conclude that for a fully condensed Bose gas the collisional frequency shift is indeed reduced by an overall factor of 2, in agreement with our sum-rule result in Sec. II and the work of Ref. [6].

## B. Coherent and Incoherent Contributions to Response Functions

To explore the physics in greater detail, it is convenient to adopt an approach exploited in the context of Fermi-liquid theory [11]. We first express the single-particle propagator in a many-body system as the sum of a coherent part coming from an intermediate state with a single quasiparticle excitation, and an incoherent part coming from more complicated excitations. Mathematically this implies that

$$G^{(2)}(\mathbf{p}, \epsilon) = G_{\text{coh}}^{(2)}(\mathbf{p}, \epsilon) + G_{\text{inc}}^{(2)}(\mathbf{p}, \epsilon), \quad (28)$$

where  $\mathbf{p}$  is the momentum, and  $\epsilon$  is the energy. The coherent part, which corresponds to the quasiparticle, is given by

$$G_{\text{coh}}^{(2)}(\mathbf{p}, \epsilon) = \frac{Z(\mathbf{p})}{\epsilon - \epsilon(\mathbf{p})}, \quad (29)$$

where  $Z(\mathbf{p})$  is the renormalization factor or quasiparticle residue, and  $\epsilon(\mathbf{p})$  is the quasiparticle energy. Both of these quantities depend on the atomic species considered. The incoherent contribution to the propagator corresponds to transient effects due to the dressing of a free atom to make it into a quasiparticle. Likewise the two-particle propagator  $G^{(4)}(\mathbf{p}, \epsilon; \mathbf{p}', \epsilon')$  for a pseudospin fluctuation may be expressed in terms of a coherent part, corresponding to a single quasiparticle-quasihole pair, plus an incoherent part coming from multipair excitations, i.e.,

$$G^{(4)}(\mathbf{p}, \epsilon; \mathbf{p}', \epsilon') = \frac{Z_{1s}(\mathbf{p})}{(\epsilon - \epsilon_{1s}(\mathbf{p}))} \frac{Z_{2s}(\mathbf{p}')}{(\epsilon' - \epsilon_{2s}(\mathbf{p}'))} + G_{\text{inc}}^{(4)}(\mathbf{p}, \epsilon; \mathbf{p}', \epsilon'). \quad (30)$$

We next analyse the diagrams for the response function  $\chi$  by separating the single particle propagators into their coherent and incoherent contributions, as was done by Leggett in the context of Fermi systems. We then divide these diagrams into two classes. The first class contains those diagrams which are reducible with respect to the coherent contributions of two (one  $1s$  and one  $2s$ ) single-particle propagators. We refer to these as the coherent contribution. The second class contains all diagrams which are not reducible in this sense and we call this the incoherent contribution. We remark that since the operator  $\mathcal{O}$  does not change the total particle number, the two coherent particle lines must have their arrows in opposite directions, and therefore correspond to a quasiparticle-quasihole pair.

Expressed in a formal matrix notation the response function may be written as

$$\chi = \text{Tr}[G^{(4)}(1 - \Gamma^{(4)}G^{(4)})^{-1}], \quad (31)$$

where  $\Gamma^{(4)}$  is the two-particle vertex function that is irreducible with respect to two particle lines with oppositely directed arrows, i.e., it is irreducible in the particle-hole channel. Separating out the terms that contain only incoherent contributions to  $G^{(4)}$  from the others, we find

$$\chi = \chi_{\text{inc}} + \chi_{\text{coh}}, \quad (32)$$

where

$$\chi_{\text{inc}} = \text{Tr}[G_{\text{inc}}^{(4)}(1 - \Gamma^{(4)}G_{\text{inc}}^{(4)})^{-1}] \quad (33)$$

and

$$\chi_{\text{coh}} = \text{Tr}[(1 - \Gamma^{(4)}G_{\text{inc}}^{(4)})^{-1}G_{\text{coh}}^{(4)}(1 - \Gamma_{\text{coh}}^{(4)}G_{\text{coh}}^{(4)})^{-1}(1 - \Gamma^{(4)}G_{\text{inc}}^{(4)})^{-1}]. \quad (34)$$

The factor  $(1 - \Gamma^{(4)}G_{\text{inc}}^{(4)})^{-1}$  corresponds to a vertex renormalization and the quantity

$$\Gamma_{\text{coh}}^{(4)} = \Gamma^{(4)}(1 - G_{\text{inc}}^{(4)}\Gamma^{(4)})^{-1} \quad (35)$$

is a renormalization of the interactions between the coherent parts of a particle-hole excitations due to intermediate states with incoherent particle-hole pairs. For the present problem, an important feature of this result is the existence of the incoherent contribution to  $\chi$ , since this is what is responsible for the difference between the sum rule evaluated with the pseudopotential and the true sum rule.

We turn now to the coherent contribution to the response function. The coherent part of  $G^{(4)}$  has the same form as for two particles with energies modified by the medium, apart from the renormalization factors  $Z$ . However, if one multiplies the matrix element for coupling of the two photons to the excitations by a factor  $(1 - \Gamma^{(4)}G_{\text{inc}}^{(4)})^{-1}(Z_{2s}Z_{1s})^{1/2}$  and uses for the effective interaction between a quasiparticle and a quasihole the quantity  $Z_{1s}Z_{2s}\Gamma^{(4)}$ , the coherent contribution to the response has precisely the same form as in the random phase approximation calculation above. This modified interaction plays a role analogous to that of the quasiparticle-quasiparticle interaction introduced in Fermi-liquid theory by Landau.

Let us now analyse the consequences of the above for a low density gas. In that case the renormalization factors tend to unity, and the two-particle vertex reduces to the T matrix. The quasiparticle energies reduce to the Hartree-Fock ones, and the mean-field interaction is also just the T matrix. Thus the coherent contribution to the response has precisely the form predicted by the mean-field theory calculation in Sec. III A. Observe that in calculating the average frequency associated with the coherent part of the response, the renormalization factor for the effective two-photon matrix element cancels out. What implications does our calculation have for experiment? In addition to a sharp peak in the absorption due to the excitation of a single quasiparticle-quasihole pair, the calculation predicts a broad background due to creation of more complicated final states. However, because the background is expected to be a rather smoothly-varying function of frequency that extends over a large frequency range, it is difficult to detect. Consequently, the part of the absorption spectrum that is investigated experimentally is only that due to the coherent contribution to the response function.

#### IV. COLLISIONAL BROADENING

We now consider how collisions broaden the coherent part of the line. One effect is that the self energy of the atoms acquires an imaginary part, and the coherent parts of the propagators become

$$G_{\text{coh}}^{(2)}(\mathbf{p}, \epsilon) = \frac{Z(\mathbf{p})}{\epsilon - \epsilon(\mathbf{p}) + i\hbar\Sigma''(\mathbf{p}, \epsilon(\mathbf{p}))}, \quad (36)$$

where  $\Sigma''(\mathbf{p}, \epsilon)$  is the imaginary part of the self energy. Another effect is that there are vertex corrections analogous to those responsible for the contributions to the line shift beyond what is predicted by the Hartree-Fock approximation. The total width is most easily calculated by observing that the propagation of a  $2s$  atom and a  $1s$  hole is determined by the difference between the  $1s - 2s$  interaction and the  $1s - 1s$  interaction. For definiteness, let us consider a gas with no condensate. In the absence of the  $1s - 2s$  interaction, the only contribution to the width comes from the imaginary part of the self energy of the  $1s$  atom, which is given in the dilute limit by [14]

$$\begin{aligned} \hbar\Sigma_{1s}''(\mathbf{p}, \epsilon_{\mathbf{p}}) &= -2\pi \left( \frac{4\pi a_{1s-1s}\hbar^2}{m} \right)^2 \frac{1}{V^2} \sum_{\mathbf{p}'\mathbf{p}''} \delta(\epsilon_{\mathbf{p}} + \epsilon_{\mathbf{p}'} - \epsilon_{\mathbf{p}+\mathbf{p}''} - \epsilon_{\mathbf{p}'-\mathbf{p}''}) \\ &\times [N_{\mathbf{p}'}(1 + N_{\mathbf{p}'-\mathbf{p}''})(1 + N_{\mathbf{p}+\mathbf{p}''}) - (1 + N_{\mathbf{p}'})N_{\mathbf{p}'-\mathbf{p}''}N_{\mathbf{p}+\mathbf{p}''}], \end{aligned} \quad (37)$$

the factor of two being the result of the Bose enhancement of the cross section, which is due to the exchange process. Since the imaginary part of the self energy is momentum dependent the absorption line of the gas is in principle not exactly Lorentzian. Nevertheless, the typical width of the line is determined by the average  $-(2/N)\sum_{\mathbf{p}}N_{\mathbf{p}}\Sigma''_{1s}(\mathbf{p},\epsilon_{\mathbf{p}})$  and thus equals

$$\begin{aligned}\Delta\Gamma_{2s} &= \frac{(4\pi\hbar)^3(a_{1s-1s})^2}{nm^2} \frac{1}{V^3} \sum_{\mathbf{p}\mathbf{p}'\mathbf{p}''} \delta(\epsilon_{\mathbf{p}} + \epsilon_{\mathbf{p}'} - \epsilon_{\mathbf{p}+\mathbf{p}''} - \epsilon_{\mathbf{p}'-\mathbf{p}''}) \\ &\times N_{\mathbf{p}}[N_{\mathbf{p}'}(1 + N_{\mathbf{p}'-\mathbf{p}''})(1 + N_{\mathbf{p}+\mathbf{p}''}) - (1 + N_{\mathbf{p}'})N_{\mathbf{p}'-\mathbf{p}''}N_{\mathbf{p}+\mathbf{p}''}].\end{aligned}\quad (38)$$

When the  $1s-2s$  interaction is included, the result is simply

$$\begin{aligned}\Delta\Gamma_{2s} &= \frac{(4\pi\hbar)^3(a_{1s-1s} - a_{1s-2s})^2}{nm^2} \frac{1}{V^3} \sum_{\mathbf{p}\mathbf{p}'\mathbf{p}''} \delta(\epsilon_{\mathbf{p}} + \epsilon_{\mathbf{p}'} - \epsilon_{\mathbf{p}+\mathbf{p}''} - \epsilon_{\mathbf{p}'-\mathbf{p}''}) \\ &\times N_{\mathbf{p}}[N_{\mathbf{p}'}(1 + N_{\mathbf{p}'-\mathbf{p}''})(1 + N_{\mathbf{p}+\mathbf{p}''}) - (1 + N_{\mathbf{p}'})N_{\mathbf{p}'-\mathbf{p}''}N_{\mathbf{p}+\mathbf{p}''}].\end{aligned}\quad (39)$$

In the classical limit, this reduces to

$$\Delta\Gamma_{2s} = 8\pi n(a_{1s-1s} - a_{1s-2s})^2 \langle v_{\text{rel}} \rangle, \quad (40)$$

where  $\langle v_{\text{rel}} \rangle = 4(kT/\pi m)^{1/2}$  is the average relative velocity between two  $1s$  atoms in the atomic hydrogen gas. The total width of the line is the sum of the natural width and the collisional contribution, and it is therefore equal to  $\Gamma_{2s} + \Delta\Gamma_{2s}$ . The width is of order  $(a_{1s-2s} - a_{1s-1s})/\lambda_T$  times the shift, where  $\lambda_T = \hbar/(2\pi mk_B T)^{1/2}$  is the thermal de Broglie wavelength. When a condensate is present, the above calculation can be easily generalized. In a first approximation we only need to take into account explicitly the macroscopic occupation of the zero-momentum state by substituting  $N_{\mathbf{p}} \rightarrow n_c V \delta_{\mathbf{p},0} + N_{\mathbf{p}}$ , with  $n_c$  the condensate density. At the next level of approximation we also need to incorporate the Bogoliubov coherence factors.

## V. CONCLUSIONS

In this paper we have considered the effect of interactions on the two-photon absorption line profile in spin-polarized atomic hydrogen by means of a frequency-weighted sum rule and by means of microscopic many-body theory. We have shown that the line profile consists of a narrow coherent peak on top of a broad incoherent background. For typical atomic potentials this background in principle has sufficient spectral weight that the pseudopotential approximation does not give an accurate estimate of the total contribution to the frequency-weighted sum rule. However, the frequency of the narrow peak, which is the feature most easily seen experimentally, may be expressed in terms of the low-energy pseudopotentials.

We have also shown that the collisional frequency shift of the absorption line is reduced by a factor of two if the gas is fully Bose condensed. We have pointed out that for this factor-of-two reduction it is crucial to take many-body correlation effects into account that go beyond the Hartree-Fock approximation commonly used for these dilute atomic gases. At this point it is worth mentioning that the Bose-Einstein condensation experiments by Fried *et al.* apparently do not see this effect. Their results seem to be consistent with the Hartree-Fock theory, which, due to the fact that  $a_{1s-1s} \ll |a_{1s-2s}|$  for atomic hydrogen, basically predicts no reduction at all [1]. At present we have no explanation for the cause of this discrepancy.

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## REFERENCES

- [1] D. G. Fried, T. C. Killian, L. Willmann, D. Landhuis, S. C. Moss, D. Kleppner, and T. J. Greytak, *Phys. Rev. Lett.* **81**, 3811 (1998).
- [2] T. C. Killian, D. G. Fried, L. Willmann, D. Landhuis, S. C. Moss, T. J. Greytak, and D. Kleppner, *Phys. Rev. Lett.* **81**, 3807 (1998).
- [3] R. L. Walsworth, I. F. Silvera, E. M. Mattison, and R. F. Vessot, *Phys. Rev. A* **46**, 2495 (1992); M. E. Hayden, M. D. Hürlimann, and W. N. Hardy, *Phys. Rev. A* **53**, 1589 (1996).
- [4] K. Gibble and S. Chu, *Phys. Rev. Lett.* **70**, 1771 (1993).
- [5] P. L. Bender, *Phys. Rev.* **132**, 2154 (1963); L. C. Balling, R. J. Hanson, and F. M. Pipkin, *Phys. Rev.* **133**, A607 (1964); *Phys. Rev.* **135**, AB1 (1964); B. J. Verhaar, J. M. V. A. Koelman, H. T. C. Stoof, and O. J. Luiten, *Phys. Rev. A* **35**, 3825 (1988).
- [6] M. Ö. Oktel and L. Levitov, *Phys. Rev. Lett.* **83**, 6 (1999).
- [7] M. Ö. Oktel, T. C. Killian, D. Kleppner, and L. Levitov, e-print physics/9911020.
- [8] R. Jastrow, *Phys. Rev.* **98**, 1479 (1955).
- [9] H. T. C. Stoof, A. M. L. Janssen, J. M. V. A. Koelman, and B. J. Verhaar, *Phys. Rev. A* **39**, 3157 (1989).
- [10] D. Pines and P. Nozières, *The Theory of Quantum Liquids, Volume I*, (Benjamin, New York, 1966).
- [11] A. J. Leggett, *Ann. Phys.* **46**, 76 (1968).
- [12] G. Baym and C. Pethick, *Landau Fermi-Liquid Theory*, (Wiley, New York, 1991).
- [13] G. A. Baym, *Phys. Rev.* **127**, 1391 (1962).
- [14] H. T. C. Stoof, *Phys. Rev. Lett* **78**, 768 (1997).

FIGURES

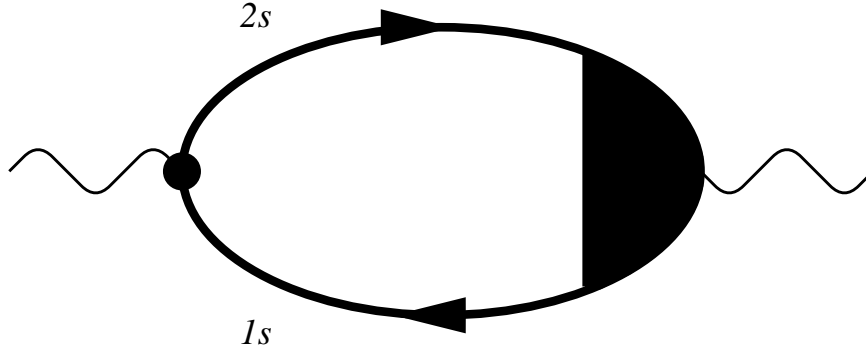


FIG. 1. The polarization diagram that determines the two-photon absorption line shape. The thick lines denote the exact  $1s$  and  $2s$  propagators, and the small and large black areas denotes the bare and exact vertex functions, respectively.

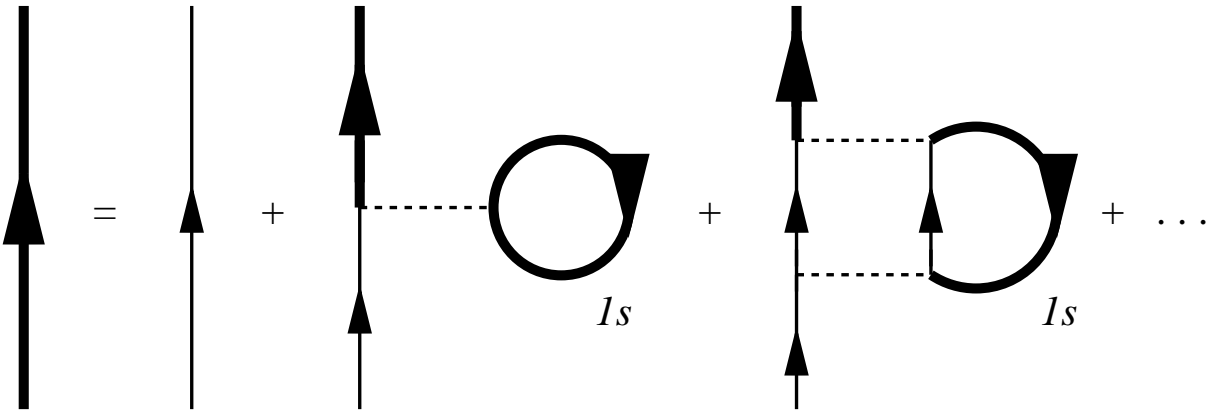


FIG. 2. The  $1s$  and  $2s$  propagators in the T-matrix approximation. The thin lines represent the bare propagators and the dashed lines the interactions.

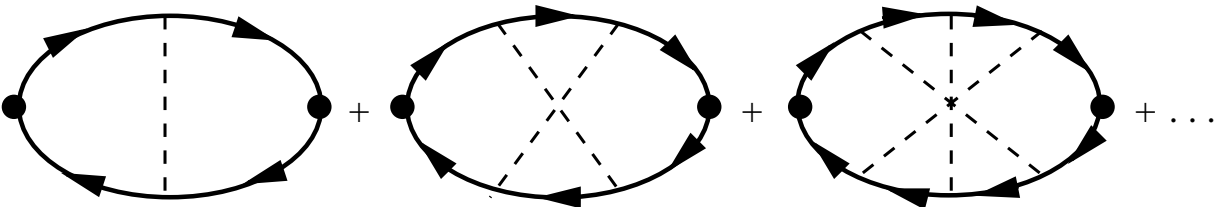


FIG. 3. The vertex corrections in the T-matrix approximation.