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## AN ANALYSIS OF THE UNIFIED AND SCALAR ADDITIVITY THEORIES OF SPECTRAL LINE BROADENING\*

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**Abstract**—A new derivation of both unified and scalar additivity theories is given. This derivation concentrates on their regions of validity and certain key differences are analyzed in detail.

### 1. INTRODUCTION

IN RECENT years there has been much activity in the development of unified theories for spectral line broadening (VOSLAMBER,<sup>(1)</sup> BEZZERIDES,<sup>(2)</sup> SMITH *et al.*<sup>(3)</sup>). Basically these theories permit a description of both static and dynamic aspects of a radiator perturber interaction; the unified theories reduce to the familiar impact theory of Baranger and Griem in the line center and the “one-perturber” or nearest neighbor static theory<sup>(4,5)</sup> in the line wings. This type of behavior was sought by ANDERSON and TALMAN<sup>(6)</sup> (see also ANDERSON,<sup>(7)</sup> and Section 20 of CHEN and TAKEO<sup>(8)</sup>) when they developed their scalar additivity theory which reduces to the Lindholm–Foley or scalar impact theory in the line center and the statistical theory of Margenau in the wings.<sup>(8)</sup> The essential difference between the unified and scalar theories lies in their treatment of overlapping strong collisions. The unified theories assume that strong collisions do not overlap in time hence the radiator is perturbed by a random sequence of binary collisions. The scalar theories do not use this approximation and they contain some effects of three-body and higher order collision complexes but these results are achieved by assuming that all radiator-perturber interactions can be approximated as scalar operators (i.e. spherical tensor operators of rank zero). The primary purpose of the present paper is to discuss and compare the details of these approximations and to discuss the regions of validity for the scalar and unified theories. The need to distinguish between these two theories is made particularly important by the fact that some recently published “unified theories” are actually scalar theories (FUTRELLE,<sup>(9)</sup> BOTTCHE<sup>(10)</sup>) and their lack of agreement with other unified theories has caused a great deal of confusion.

In this paper we also provide a new derivation of the unified theory which does not employ the elaborate projection operator, BBGKY or Green function techniques found

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in previous papers. We hope this simpler derivation will serve to clarify some misgivings concerning a crucial factorization in the unified theory (BOTTCHEER,<sup>(10)</sup> LEE<sup>(11)</sup>). In addition we compare the unified theory with Fano's relaxation theory<sup>(12)</sup> and in particular we show that the unified theory is identical to Fano's results if his relaxation operator  $\langle M_c(\omega) \rangle$  is expanded to first order in the gas density.

## 2. THE UNIFIED THEORY

The starting point for most line-shape theories is an expression which equates the line shape  $I(\omega)$  to the Fourier transform of the dipole autocorrelation function

$$I(\omega) = (1/\pi) \operatorname{Re} \int_0^{\infty} \exp(i\omega t) C(t) dt \quad (1)$$

$$C(t) = \sum_{a,b} \mathbf{d}_{ab} \cdot \mathbf{d}_{ba}(t) \rho_a \exp(-i\omega_{ab}t), \quad (2)$$

$$\mathbf{d}(t) = \langle U_N^\dagger(t, 0) \mathbf{d} U_N(t, 0) \rangle, \quad (3)$$

where  $\mathbf{d}$  is the dipole operator for the radiating (or absorbing) particle and  $U_N(t, 0)$  is the time development operator for a system consisting of one radiating particle and  $N$  other particles which perturb the radiator through the interaction

$$V_N(t) = \sum_j V(j, t) \quad (4)$$

and where  $V(j, t)$  denotes the interaction between the radiator and the  $j$ th perturber. The states  $|a\rangle$ ,  $|b\rangle$ , etc. are eigenstates of the unperturbed radiator Hamiltonian  $H_0$ ,  $\rho_a$  denotes the probability of finding the radiator in state  $|a\rangle$  and  $\langle \dots \rangle$  denotes an average over positions and velocities of the  $N$  perturbers. Initial correlations of the radiator and perturbers have been excluded by writing the probability as  $\rho_a$ , however, these are not important for frequency separations from the allowed line center less than  $\sim kT/\hbar$  where  $T$  is the temperature of the system.<sup>(13)</sup> For simplicity, Doppler effects have been excluded by taking  $\mathbf{d}$  as the simple dipole operator.<sup>(14)</sup> Also, for simplicity, we will neglect lower state interaction so that  $U_N^\dagger \mathbf{d} U_N$  becomes simply  $\mathbf{d} U_N$  (this means we only have simple matrix elements rather than more complicated tetradic operators) and we need only consider  $\langle U_N(t, 0) \rangle$ .

We will henceforth assume that the  $N$  perturbers are statistically independent and may therefore be averaged separately. This is a common approximation (see MARGENAU<sup>(15)</sup>) however, it neglects two-body and higher order correlations which are of order  $n^2$  and higher ( $n$  being the perturber density). For Stark broadening this approximation can be fulfilled by considering a gas of shielded quasi-particles as perturbers, in which the shielding accounts for most of the plasma correlations.

The time development operator  $U_N(t, 0)$  can be written in the form ( $\hbar = 1$ )

$$\begin{aligned} U_N(t, 0) &= 1 + \sum_{r=1}^{\infty} (-i)^r \int_0^t dt_r \int_0^{t_r} dt_{r-1} \dots \int_0^{t_2} dt_1 \tilde{V}_N(t_r) \tilde{V}_N(t_{r-1}) \dots \tilde{V}_N(t_1) \\ &= \mathcal{O} \exp \left\{ -i \int_0^t \tilde{V}_N(s) ds \right\} \end{aligned} \quad (5)$$

with

$$\tilde{V}_N(s) \equiv \exp(isH_0)V_N(s)\exp(-isH_0), \tag{6}$$

where we have written  $U_N(t, 0)$  in the exponential form by using the Dyson time ordering operator  $\mathcal{O}$ .<sup>(16)</sup> It should be emphasized that in general the iterated integrals of equation (5) *cannot* be reduced to a *simple* (nonordered) exponential since  $\tilde{V}_N(s)$  does not commute with itself at different times.

The function  $U_N(t, 0)$  may also be written (BARANGER<sup>(17)</sup> equation 18) in the form

$$U_N(t, 0) = \mathcal{O}\Pi_j U(j; t, 0), \tag{7}$$

$$U(j; t, 0) = \mathcal{O} \exp \left\{ -i \int_0^t \tilde{V}(j, s) ds \right\}, \tag{8}$$

where  $U(j; t, 0)$  is the time development operator for the encounter between the radiator and the  $j$ th perturber.

The time ordering operator in equations (5), (7) and (8) keeps the collisions in chronological order and also entangles various collisions. To show this we consider the fourth order (in  $\tilde{V}(j, t)$ ) term in the series expansion of  $U_N(t, 0)$ . Using equation (4), the fourth order term in equation (5) is

$$\sum_{ijkl} \int_0^t dt_4 \int_0^{t_4} dt_3 \int_0^{t_3} dt_2 \int_0^{t_2} dt_1 \tilde{V}(i, t_4) \tilde{V}(j, t_3) \tilde{V}(k, t_2) \tilde{V}(l, t_1). \tag{9}$$

Various terms occur according to the values of  $i, j, k$  and  $l$ . For example, if  $i = j = k = l$ , the average of equation (9) would be

$$N \int_0^t dt_4 \int_0^{t_4} dt_3 \int_0^{t_3} dt_2 \int_0^{t_2} dt_1 \langle \tilde{V}(t_4) \tilde{V}(t_3) \tilde{V}(t_2) \tilde{V}(t_1) \rangle_1, \tag{10}$$

where  $\langle \dots \rangle_1$  denotes a single particle average; we have used the fact that there are  $N$  different values of  $i$  for which  $i = j = k = l$  and we dropped this particle index in writing equation (10) since all particles are equivalent under the average and this index is then redundant.

If the  $i, j, k, l$  etc. refer to two different particles (say 1 and 2), the following possibilities arise :

$$\begin{aligned} &\tilde{V}(2, t_4) \tilde{V}(2, t_3) \tilde{V}(1, t_2) \tilde{V}(1, t_1), \\ &\tilde{V}(2, t_4) \tilde{V}(1, t_3) \tilde{V}(2, t_2) \tilde{V}(1, t_1), \\ &\tilde{V}(2, t_4) \tilde{V}(1, t_3) \tilde{V}(1, t_2) \tilde{V}(2, t_1), \\ &\tilde{V}(1, t_4) \tilde{V}(1, t_3) \tilde{V}(2, t_2) \tilde{V}(2, t_1), \\ &\tilde{V}(1, t_4) \tilde{V}(2, t_3) \tilde{V}(1, t_2) \tilde{V}(2, t_1), \\ &\tilde{V}(1, t_4) \tilde{V}(2, t_3) \tilde{V}(2, t_2) \tilde{V}(1, t_1). \end{aligned} \tag{11}$$

If, as is often the case, the average interaction is zero (i.e.  $\langle V(t) \rangle_1 = 0$ ), terms like  $\tilde{V}(2, t_4)\tilde{V}(2, t_3)\tilde{V}(2, t_2)\tilde{V}(1, t_1)$  etc. will vanish for statistically independent perturbers. For the same reason, terms involving three or four different particles will average to zero. Thus, the terms of equation (11) are the only ones we need to consider in addition to the term of equation (10).

Since the time integrals in equation (11) are ordered such that  $t_4 \geq t_3 \geq t_2 \geq t_1$ , the first term in equation (11) corresponds to the case where the radiator collides with particle 1 before particle 2, the fourth term corresponds to a collision with particle 2 before particle 1; the four remaining terms are overlap terms which are nonzero *only* if the collisions with particles 1 and 2 overlap in time. Since only two particles are involved, we obtain only terms of order  $N^2$  from equation (11) on performing the average, i.e.

$$N(N-1)\langle \tilde{V}(2, t_4)\tilde{V}(2, t_3) \rangle_1 \langle \tilde{V}(1, t_2)\tilde{V}(1, t_1) \rangle_1, \quad (12)$$

$$N(N-1)\langle \tilde{V}(1, t_4)\tilde{V}(2, t_3)\tilde{V}(2, t_2) \rangle_1 \tilde{V}(1, t_1) \rangle_1, \quad (13)$$

$$N(N-1)\langle \langle \tilde{V}(1, t_4)\tilde{V}(2, t_3)\tilde{V}(1, t_2)\tilde{V}(2, t_1) \rangle_1 \rangle_1. \quad (14)$$

It was necessary to retain the particle index in equations (13) and (14) because the single particle averages over particles 1 and 2 are entangled. This is not necessary for equation (12) and that term could equally well be written  $\langle \tilde{V}(t_4)\tilde{V}(t_3) \rangle_1 \langle \tilde{V}(t_2)\tilde{V}(t_1) \rangle_1$ . We can now see that, if strong collisions (those for which an expansion to second order in  $\tilde{V}$  is insufficient) are separated in time, the entangled terms (equations 13 and 14) must vanish and the unentangled term (equation 12) is the only one which remains. The hypothesis that strong collisions do not overlap in time is the impact approximation, the heart of both the impact and unified theories. With this approximation there remain only unconnected terms (such as  $\langle \tilde{V}\tilde{V}\tilde{V}\tilde{V} \rangle \langle \tilde{V}\tilde{V} \rangle$  etc.) and there are no entangled terms due to overlapping collisions (of type  $\langle \tilde{V}\tilde{V}\tilde{V}\langle \tilde{V}\tilde{V} \rangle \tilde{V} \rangle$  etc.). This disentanglement could not easily be achieved without some form of impact hypothesis, and it indicates why the unified theory goes over to the usual impact theory of line broadening in the line center.<sup>(4,17,18)</sup>

It is not possible to treat the entangled terms in all generality, but the overlap terms of equations (13) and (14) are treated in an approximate manner in the scalar theory: in that theory the time ordering is simply ignored, the entangled terms of equations (13) and (14) are factored into simple products and added to the contribution of equation (12).

It should be emphasized that the treatment of the entangled terms (i.e. the time ordering) is the essential difference between the unified and scalar additivity theories. The entangled terms (equations 13 and 14) are rigorously zero when strong collisions do not overlap so the validity criterion for the unified theory is clear; the validity of the scalar theory will be discussed in Section 4.

We now return to the derivation of the unified theory results. The average of  $U_N(t, 0)$  may be obtained from equation (7) in the form

$$\begin{aligned} \langle U_N(t, 0) \rangle &= \langle \mathcal{O} \Pi_j U(j; t, 0) \rangle \\ &= \mathcal{O} \langle U(t, 0) \rangle_1^N \\ &= \mathcal{O} \{ 1 + \langle U(t, 0) - 1 \rangle_1 \}^N \\ &= \mathcal{O} \exp \{ N \langle U(t, 0) - 1 \rangle_1 \}. \end{aligned} \quad (15)$$

In the second line we set the average of the product of one body operators equal to the product of one body averages (statistical independence assumption) and we dropped the particle index  $j$  since all particles are equivalent under the average. In the last line we used the fact that the number of perturbers  $N$  is very large. Next, using the identity (MESSIAH,<sup>(19)</sup> equation XVII.7)

$$U(t, 0) - 1 = -i \int_0^t U(t, s) \tilde{V}(s) ds, \quad (16)$$

equation (15) becomes

$$\begin{aligned} \langle U_M(t, 0) \rangle &= \mathcal{O} \exp \left\{ -i \int_0^t N \langle U(t, s) \tilde{V}(s) \rangle_1 ds \right\} \\ &= 1 + \sum_{r=1}^{\infty} \frac{(-i)^r N^r}{r!} \int_0^t dt_r \int_0^{t_r} dt_{r-1} \cdots \int_0^{t_2} dt_1 \\ &\quad \cdot \mathcal{O} \langle U(t, t_r) \tilde{V}(t_r) \rangle_1 \cdots \langle U(t, t_2) \tilde{V}(t_2) \rangle_1 \langle U(t, t_1) \tilde{V}(t_1) \rangle_1. \end{aligned} \quad (17)$$

In general the effect of the ordering operator  $\mathcal{O}$  is to entangle the various interactions; that is,  $U(t, t_r)$  is defined by the Dyson expansion, equation (5), and the effect of  $\mathcal{O}$  in equation (17) is to entangle the interactions in  $\langle U(t, t_2) \tilde{V}(t_2) \rangle_1$  with those in  $\langle U(t, t_1) \tilde{V}(t_1) \rangle_1$  etc. By analogy with the fourth order term (equations 12–14), we regard  $\langle U(t, t_1) \tilde{V}(t_1) \rangle_1$  and  $\langle U(t, t_2) \tilde{V}(t_2) \rangle_1$  as referring to two different interactions; thus, when collisions do not overlap, we write

$$\begin{aligned} \langle U(t, t_2) \tilde{V}(t_2) \rangle_1 \langle U(t, t_1) \tilde{V}(t_1) \rangle_1 &= \langle U(2; t, t_2) \tilde{V}(2, t_2) \rangle_1 \langle U(1; t, t_2) \tilde{V}(1, t_1) \rangle_1 \\ &= \langle U(2; t_3, t_2) \tilde{V}(2, t_2) \rangle_1 \langle U(1; t_2, t_1) \tilde{V}(1, t_1) \rangle_1 \\ &= \langle U(t_3, t_2) \tilde{V}(t_2) \rangle_1 \langle U(t_2, t_1) \tilde{V}(t_1) \rangle_1. \end{aligned} \quad (18)$$

The results of (18) are obtained because whenever  $\tilde{V}(2, t_2)$  is not equal to zero,  $\tilde{V}(1, t_1) \equiv 0$  by the impact hypothesis, thus  $U(1; t, t_1) = U(1; t, t_2)U(1; t_2, t_1) = U(1; t_2, t_1)$  since  $U(1; t, t_2) = 1$  when  $\tilde{V}(1, t_2) = 0$ . Therefore, if we make the impact approximation by removing the overlap of collisions in equation (17) we obtain

$$\begin{aligned} \langle U_M(t, 0) \rangle &= 1 + \sum_{r=1}^{\infty} \frac{(-i)^r N^r}{r!} \int_0^t dt_r \int_0^{t_r} dt_{r-1} \cdots \int_0^{t_2} dt_1 \\ &\quad \cdot \langle U(t, t_r) \tilde{V}(t_r) \rangle_1 \cdots \langle U(t_3, t_2) \tilde{V}(t_2) \rangle_1 \langle U(t_2, t_1) \tilde{V}(t_1) \rangle_1. \end{aligned} \quad (19)$$

The integrals in equation (19) are ordered thus keeping the sequence but the entangling effect of  $\mathcal{O}$  has been eliminated (a more complete and rigorous derivation of equation (19) is given in Appendix A). If we define

$$K(t, t') \equiv N \langle U(t, t') \tilde{V}(t') \rangle_1, \quad (20)$$

equation (19) becomes

$$\langle U_M(t, 0) \rangle = 1 + \sum_{r=1}^{\infty} \frac{(-i)^r}{r!} \int_0^t dt_r \int_0^{t_r} dt_{r-1} \cdots \int_0^{t_2} dt_1 K(t, t_r) \cdots K(t_3, t_2) K(t_2, t_1) \quad (21)$$

and differentiation with respect to  $t$  gives [note  $K(t, t) = 0$  since  $\langle V(t) \rangle_1 = 0$ ]

$$\begin{aligned} i \frac{d}{dt} \langle U_N(t, 0) \rangle &= \int_0^t ds \frac{d}{dt} K(t, s) \langle U_N(s, 0) \rangle \\ &= \int_0^t ds G(t, s) \langle U_N(s, 0) \rangle, \end{aligned} \quad (22)$$

where

$$G(t, s) = -iN \langle \tilde{V}(t) U(t, s) \tilde{V}(s) \rangle_1, \quad (23)$$

which is the basic expression used by the unified theory.

To get the Fourier transform of  $\langle U_N(t, 0) \rangle$ , we first use the time translation invariance (see Appendix A of SMITH *et al.*<sup>(3)</sup>)

$$\begin{aligned} \langle V(t_1) \cdots V(t_N) \rangle_1 &= \langle V(t_1 + \tau) \cdots V(t_N + \tau) \rangle_1, \\ \langle \tilde{V}(t_1) \cdots \tilde{V}(t_N) \rangle_1 &= \exp(-i\tau H_0) \langle \tilde{V}(t_1 + \tau) \cdots \tilde{V}(t_N + \tau) \rangle_1 \exp(i\tau H_0) \end{aligned} \quad (24)$$

to obtain

$$G(t, s) = -iN \exp(isH_0) \langle \tilde{V}(t-s) U(t-s, 0) V(0) \rangle_1 \exp(-isH_0) \quad (25)$$

and equation (22) is then readily solved by Fourier transform to yield the familiar result

$$\int_0^\infty dt e^{i(\omega - H_0)t} \langle U_N(t, 0) \rangle = i[\omega - H_0 - \mathcal{L}(\omega)]^{-1}, \quad (26)$$

$$\mathcal{L}(\omega) = -iN \int_0^\infty dt e^{i(\omega - H_0)t} \langle \tilde{V}(t) U(t, 0) V(0) \rangle_1, \quad (27)$$

where  $\mathcal{L}(\omega)$  is again calculated in terms of a single particle average and, as seen in Section 3, it is simply related to Fano's  $\langle M^{(1)}(\omega) \rangle$ . It has been shown<sup>(3)</sup> that the unified theory goes to the usual impact results in terms of  $S$ -matrix elements in the line center ( $\Delta\omega \rightarrow 0$  limit) and the single perturber (nearest neighbor) results in the line wings; if strong collisions are separated in time, this will also according to the following argument be a true representation of the profile in the intermediate region between line center and line wings. Since  $U(t, 0) = \mathcal{O} \exp\{-i \int_0^t \tilde{V}(t) dt\}$ , we can say that a collision will be strong (i.e. second order theory in  $\tilde{V}$  will not be sufficient) when  $\int_0^t \tilde{V}(t) dt > 1$ . However,  $\int_0^t \tilde{V}(t) dt$  is at most equal to the integral  $\int_{-\infty}^\infty V(t) dt$  (which will be applicable in the line center or  $S$ -matrix limit) so the condition  $\int_{-\infty}^\infty V(t) dt \simeq 1$  is usually used to establish the so-called strong collision radius  $\rho_0$ , from which one obtains the customary validity condition  $(\rho_0/v) < (1/nv\rho_0^2\pi)$ ; namely the time between strong collisions must exceed their duration (see SMITH *et al.*<sup>(3)(13)</sup>). Further into the line wings, when a collision cannot be completed in the time of interest, strong collisions (defined by  $\int_0^t V(t) dt \simeq 1$ ) will only occur for radii

smaller than  $\rho_0$  (since  $\int_0^t V(t) dt \lesssim \int_{-\infty}^{\infty} V(t) dt$ ) and the frequency of strong collisions is correspondingly smaller. Thus, *if this validity criterion is satisfied near line center, it will be even more so in the line wings.* We also know that far enough in the line wings only very close collisions are important and the nearest neighbor theory always becomes valid.

### 3. FANO'S RELAXATION THEORY

In order to shed more light on the results of the unified theories, we next consider the quantum mechanical relaxation theory developed by FANO.<sup>(12)</sup> Fano's theory was designed to describe the relaxation of a subsystem through its interaction with a thermal bath; this theory included long time Markovian relaxation as well as the non-Markovian relaxation which occurs over times shorter than a collision duration (or correlation time). Since this approach is somewhat different from the unified theories, it is interesting to note that when Fano's relaxation operator  $\langle M_c(\omega) \rangle$  is approximated to first order in perturber density, Fano's results are identical to the results of the unified theories. To show this, we combine Fano's equations (20), (41) and (42) to obtain

$$\langle M_c(\omega) \rangle = n \langle M^{(1)}(\omega) \rangle + \dots, \tag{28}$$

where the first order term is given by

$$\begin{aligned} \langle M^{(1)}(\omega) \rangle &= \langle [1 - L_1(\omega - L_0)^{-1}]^{-1} L \rangle \\ &= \langle (\omega - L_0)(\omega - L_0 - L_1)^{-1} L_1 \rangle \\ &= i \langle (\omega - L_0) \int_0^{\infty} dt \exp[-i(\omega - L_0 - L_1)t] L_1 \rangle \\ &= i \langle (\omega - L_0) \int_0^{\infty} dt \exp[-i(\omega - L_0)t] U(t, 0) L_1 \rangle \\ &= -i \int_0^t dt \exp[-i(\omega - L_0)t] \langle \tilde{L}_1(t) U(t, 0) L_1 \rangle \end{aligned} \tag{29}$$

and where

$$\tilde{L}_1(t) = \exp(itL_0) L_1 \exp(-itL_0). \tag{30}$$

Comparing equation (29) with (27) we see that the results are identical (note however that Fano's results employ tetrads whereas our results in Section 2 employ matrices since we neglected lower state interactions).

In Appendix B we verify the now rather obvious result that Fano's  $O(n^2)$  term, namely  $\langle M_c^{(2)}(\omega) \rangle$ , is an overlap term which vanishes if strong collisions do not overlap.

### 4. THE SCALAR ADDITIVITY THEORY

The scalar additivity theory proposed by ANDERSON<sup>(7)</sup> and ANDERSON and TALMAN<sup>(6)</sup> (see also Section 20 of CHEN and TAKEO<sup>(8)</sup>) was designed to provide a theory which would

cover the entire line profile from the line center to the line wings. This theory uses the statistical independence approximation discussed in connection with equation (15), but the key approximation which sets the scalar theory apart from the unified theory, is the neglect of all time ordering in the scalar theory. In the scalar theory, equation (15) is approximated by dropping  $\mathcal{O}$  with the result

$$\langle U_N(t, 0) \rangle = \exp\{N\langle U(t, 0) - 1 \rangle_1\}, \quad (31)$$

$$U(t, 0) = \exp\left\{-i \int_0^t \tilde{V}(s) ds\right\}. \quad (32)$$

In addition to the approximations stated in equations (31) and (32), the matrix elements of  $\langle U_N \rangle$  are sometimes incorrectly evaluated; we emphasize that equation (31) is to be regarded as an operator equality so that the matrix elements of  $\langle U_N \rangle$  are the matrix elements of the exponential *not* the exponential of the matrix elements of  $N\langle U - 1 \rangle_1$ .

In order to determine the region of validity for equation (31) we will derive a rigorous expression which contains (31) plus correction terms and then examine the circumstances under which the correction terms are negligible. To do this, we start from equation (15), viz.

$$\begin{aligned} \langle U_N(t, 0) \rangle &= \mathcal{O} \exp\{N\langle U(t, 0) - 1 \rangle_1\} \\ &= \mathcal{O}\{1 + N\langle U(t, 0) - 1 \rangle_1 + (N^2/2)\langle U(t, 0) - 1 \rangle_1^2 + \dots\} \\ &= 1 + N\langle U(t, 0) - 1 \rangle_1 + (N^2/2!)\mathcal{O}\langle U(t, 0) - 1 \rangle_1^2 + \dots \end{aligned} \quad (33)$$

and we set this equal to

$$\begin{aligned} \langle U_N(t, 0) \rangle &= \exp\{NA_1 + (N^2/2)A_2 + \dots\} \\ &= 1 + NA_1 + (N^2/2)(A_1^2 + A_2) + \dots \end{aligned} \quad (34)$$

Equating powers of  $N$  we solve for  $A_1$ ,  $A_2$ , etc. and obtain

$$\langle U_N(t, 0) \rangle = \exp\{N\langle U(t, 0) - 1 \rangle_1 + (N^2/2)[\langle U(t, 0) - 1 \rangle_1^2 - \mathcal{O}\langle U(t, 0) - 1 \rangle_1^2] + \dots\}. \quad (35)$$

The lead term in this expression gives the result of the scalar additivity theory if we neglect time ordering in  $U(t, 0)$  [see equation (32)]; the terms of  $\mathcal{O}(N^2)$  and higher give corrections due to overlap effects.

We first consider the effect of time ordering in the binary collision operator  $U(t, 0)$ . The effect of this ordering has been studied by two methods; one method obtains corrections to the unordered result by means of the Magnus expansion<sup>(20,21)</sup>

$$U(t, 0) = \exp\left\{-i \int_0^t \tilde{V}(s) ds - \frac{1}{2} \int_0^t ds \int_0^s ds' [\tilde{V}(s), \tilde{V}(s')] + \dots\right\} \quad (36)$$

and the other method solves the set of coupled Schrödinger equations<sup>(22-24)</sup>

$$i \frac{\partial}{\partial t} \langle a|U(t, 0)|b \rangle = \sum_c \langle a|\tilde{V}(t)|c \rangle \langle c|U(t, 0)|b \rangle. \quad (37)$$

At the present time, there is no simple validity criterion which can be given for neglecting time ordering but thus far its effect on spectral line profiles has been found to be the order



of 10–15 per cent or less.<sup>(22,23)</sup> It should be noted that most unified theory calculations have neglected this time ordering but recent developments in the Stark broadening of hydrogen lines<sup>(21,24–26)</sup> should permit a detailed study of its effect for these lines.

We next consider the terms of order  $N^2$  and higher in equation (35) which represent corrections due to overlapping collisions (recall that the scalar theory contains some, but not all, overlap effects). One case where these terms are negligible is when  $t \rightarrow 0$  in the far line wings because they are higher order in  $t$ . One often sees the statement that the scalar theory is “exact” in the line wings because it agrees with the static theory of Margenau to all orders in the gas density. In fact one must be very careful about this because some  $\mathcal{O}(N^2)$  correlation effects have been ignored in our derivation of equations (15) and (33) and these  $\mathcal{O}(N^2)$  terms are also ignored by Margenau. These correlations were neglected when we assumed that  $\langle U_N \rangle$  could be replaced by  $\langle U \rangle^N$  (see equation 15 of this paper and equation (1) of MARGENAU);<sup>(15)</sup> this approximation assumes that the perturbers are statistically independent and thereby neglects two-body and higher order correlations which are of order  $n^2$  and higher. While it is possible to approximate some correlations by using shielded interaction potentials (e.g. Debye shielding), such approximations do not contain all correlations and the results are certainly not valid to  $O(n^2)$ . A detailed discussion of  $O(n^2)$  correlation terms in the static limit is given by BARANGER and MOZER<sup>(27)</sup> and by HOOPER.<sup>(28)</sup> Their  $O(n)$  term is called  $h_1$  and the  $O(n^2)$  term is  $h_2$  (see equation (23) of BARANGER and MOZER<sup>(27)</sup> or equation (21) of HOOPER<sup>(28)</sup>); the  $h_2$  term is proportional to the two-body correlation function  $g_2$ . The line wing intensity is proportional to an exponential of  $(nh_1 + n^2h_2/2 + \dots)$  hence the  $O(n^2)$  term in the intensity is  $(h_1^2 + h_2)$ . Comparison with Margenau shows that his results contain only  $h_1$ ; thus we may say that Margenau’s static theory and the wings of the scalar theory are valid to  $O(n^2)$  only if two-body correlation effects are negligible (i.e. if  $h_2 \ll h_1^2$ ). It is therefore clear that the scalar theory is valid in the far line wings (because the  $\mathcal{O}(N^2)$  corrections in equation (35) are negligible) but its validity to  $\mathcal{O}(N^2)$  hinges on the importance of two-body correlation effects. These correlations have been found to be very important for Stark broadening by ions in plasmas where the long range nature of Coulomb forces enhances such effects.<sup>(27,28)</sup> For neutral gases, it is not clear what effect these correlations will have on a line profile; however, if  $\mathcal{O}(N^2)$  terms make a significant contribution to the line wing, we would not expect to be able to ignore the correlation terms since, when two perturbers are simultaneously perturbing the radiating atom, they will usually be strongly affected by their own mutual interaction at the same time.

Another case where the correction terms in equation (35) vanish is for isolated non-degenerate energy levels (by “isolated” we mean that the frequency spacing between spectral lines arising from two adjacent energy levels is much greater than their line widths). For such systems the interaction operator  $V(t)$  is a diagonal matrix on  $H_0$  eigenstates (off diagonal “quenching” terms would be negligible). Consequently  $U(t, 0)$  would be represented by a diagonal matrix, the commutators in equation (36) would vanish, all time ordering would vanish, and the scalar theory would be *exact*. This model is extremely popular because it results in exactly soluble equations and it is often used to test other theories because of these exact solutions.<sup>(29)</sup> We must therefore emphasize that these exact solutions apply only to a mathematical model which might not represent any physically realizable system;<sup>(30)</sup> for example, almost all atoms and molecules have  $(2j+1)$  degenerate  $m$  states and may not be represented by diagonal  $V$  matrices (an exception

arises in large magnetic fields). In an attempt to use the scalar model one often replaces the matrix  $\langle jm|V|jm'\rangle$  by the scalar  $V(j) = \sum_m \langle jm|V|jm'\rangle / (2j+1)$  (or with a  $V$ -effective replacing  $V$ ). In fact, it should be emphasized that this replacement of  $V$  by a scalar  $V$ -effective may be achieved by evaluating the time development operator (or  $S$ -matrix) in the adiabatic approximation (see CALLOWAY and BAUER<sup>(31)</sup>). Thus, *the scalar additivity and adiabatic approximations are closely linked* (and are essentially exact if one is dealing with nondegenerate  $s$ -states). This so-called "Lindholm-Foley theory" (see CHEN and TAKEO<sup>(8)</sup> Section II.B.2) results in an  $S$ -matrix (or  $U(t)$  operator) whose "matrix elements" are completely unlike those of the true  $S$ -matrix resulting from  $\langle jm|V|jm'\rangle$ . STACEY and COOPER<sup>(32)</sup> have shown that this difference may be unimportant for some line broadening problems; on the other hand, LEWIS and co-workers<sup>(33,34)</sup> have shown that it is inadequate for an analysis of some cross-section and line shape data. A model similar to the Lindholm-Foley theory has been proposed by BRUECKNER.<sup>(35)</sup> He allows the interaction potentials to commute to obtain an  $S$ -matrix essentially as an unordered exponential

$$S = \exp \left\{ -i \int_{-\infty}^{\infty} V dt \right\}.$$

He is careful, however, to evaluate fully the matrix elements of the exponential, rather than the Lindholm-Foley procedure which essentially just replaces the exponent with an averaged interaction. Under some circumstances, Brueckner shows that his results are close to Lindholm-Foley results. At the present time one can only say that this approximation is very dangerous since it obviously produces an incorrect  $S$ -matrix and the extent of its validity has not been fully investigated as yet.

One often sees the statement that the scalar theory is valid in the line center because it reduces to the results of the adiabatic impact theory. Actually this is true only for the nondegenerate or Lindholm-Foley model discussed above (sometimes called the scalar impact theory). The scalar theory definitely does not reduce to the modern impact theories of Baranger and Griem both because it contains  $O(n^2)$  contributions to the half width which are not present in their theories and because, if the Lindholm-Foley approximation is used, the scalar theory gives *only an approximation* (often adiabatic) to the  $S$ -matrix elements required by the full impact theory. In the case where the Lindholm-Foley method is used, the validity of the scalar theory hangs on the validity of that approximation. If the Lindholm-Foley method is not used, the validity of the scalar theory is determined by the relative importance of the  $O(n^2)$  terms which it retains. To show this we first note that the impact and unified theories are valid in the line center when strong collisions do not overlap. We also know that the "relaxation" operator which gives rise to the half width (called  $\mathcal{L}(\omega)$  in equation 26),  $\Phi_{ab}$  by GRIEM<sup>(36)</sup> and  $\mathcal{H}$  by BARANGER<sup>(4)</sup>) is linear in gas density. From the discussion of equations (12)–(14) it is clear that the scalar theory contains  $O(n^2)$  terms which are not present in the impact and unified theories; from the previous discussion it is also clear that the scalar theory neglects some  $O(n^2)$  terms. If the  $O(n^2)$  terms retained are small, the scalar theory will be valid in line center (e.g. for the nondegenerate model they vanish identically); however, if they are large terms which should have been cancelled out by the neglected  $O(n^2)$  terms, the scalar theory could be in error in the line center. An easy way to check this would be to look for an  $n^2$  dependence in the half width in a pressure region where the impact approximation is known to be

valid. This would not verify the scalar theory in the high pressure regime but it would certainly clarify the role of the  $O(n^2)$  terms.

### 5. CONCLUSIONS

From the above discussions we see that the Unified Theory is valid throughout the entire line profile when strong collisions do not overlap in time. (Actually, for Stark broadening, where the interaction is long range, the cumulative effects of weak collisions must be considered,<sup>(39)</sup> for electron perturbers there is no problem, but for ion perturbers the validity regime may be slightly more restricted). On the other hand, by ignoring time ordering the scalar additivity theories are seen to include to some extent the effects of overlap of collisions, however, they do not give correct  $S$ -matrices (but some adiabatic approximation) in the impact limit, nor is their validity simply ascertained. Experiments at pressures where  $O(n^2)$  terms are important will help to clarify the approximations used in these theories.

### APPENDIX A DERIVATION OF UNIFIED THEORY

Using the approximation that the perturbers are statistically independent, the average of some arbitrary function  $F$  takes the form

$$\langle F \rangle = \int \cdots \int dx_1 dv_1 \cdots dx_N dv_N P(\mathbf{x}_1)W(\mathbf{v}_1) \cdots P(\mathbf{x}_N)W(\mathbf{v}_N)F(\mathbf{x}_1\mathbf{v}_1 \cdots \mathbf{x}_N\mathbf{v}_N), \quad (A-1)$$

where  $P$  and  $W$  are the single particle position and velocity distribution functions.  $W$  can be taken to be the Maxwellian velocity distribution and, with spatial homogeneity,  $P$  is taken to be

$$P(\mathbf{x}) = 1/\mathcal{V} = n/N, \quad (A-2)$$

where  $n$  is the perturber density and  $\mathcal{V}$  is the volume of the system. We are interested in the limit  $N \rightarrow \infty$ ,  $\mathcal{V} \rightarrow \infty$  in such a way that  $n = N/\mathcal{V}$  remains fixed.

The average of the time development operator for the  $N$ -body system can be written in the general form (see equations 4 and 5)

$$\begin{aligned} \langle U_N(t, 0) \rangle &= 1 + \sum_{r=1}^{\infty} (-i)^r \int_0^t dt_r \int_0^{t_r} dt_{r-1} \cdots \int_0^{t_2} dt_1 \langle \tilde{V}_N(t_r) \cdots \tilde{V}_N(t_1) \rangle \\ &= 1 + \sum_{r=1}^{\infty} (-i)^r \int_0^t dt_r \int_0^{t_r} dt_{r-1} \cdots \int_0^{t_2} dt_1 \sum_{j_1 j_2 \cdots j_r} \langle \tilde{V}(j_r, t_r) \cdots \tilde{V}(j_1, t_1) \rangle. \end{aligned} \quad (A-3)$$

Thus the  $r$ th term of the sum in equation (A-3) consists of a product of  $r$  interactions  $\tilde{V}(j, t)$  in exactly the same way that the fourth order term in equation (9) consists of four interactions. In examining the fourth order term we had to consider all the possible ways in which the  $N$  perturbers could occur in the various interactions. In addition, with the impact hypothesis of the unified theory we are only interested in combinations that have no overlap, i.e. disentangled averages. We saw, for the fourth order term, that there were  $N$  terms in which all perturbers were the same in the single particle average, and that there were  $N(N-1)$  terms with two ordered single particle averages as given in equation (12) (we get  $N(N-1)$  rather than  $N(N-1)/2$ , which is the number of ways of choosing two

perturbors, since the perturber index  $j$  is irrelevant under average; that is,  $\langle \tilde{V}(2, t_4) \tilde{V}(2, t_3) \rangle_1 \cdot \langle \tilde{V}(1, t_2) \tilde{V}(1, t_1) \rangle_1$  is the same as  $\langle \tilde{V}(1, t_4) \tilde{V}(1, t_3) \rangle_1 \langle \tilde{V}(2, t_2) \tilde{V}(2, t_1) \rangle_1$ .

These ideas may be simply extended to the  $r$ th term of equation (A-3) counting only those combinations for which the collisions do not overlap in time we have

$$\begin{aligned} & \sum_{j_1 j_2 \dots j_r} \langle \tilde{V}(j_r, t_r) \dots \tilde{V}(j_1, t_1) \rangle \\ &= N \langle \tilde{V}(t_r) \dots \tilde{V}(t_1) \rangle_1 + N(N-1) \sum_{\substack{m_1, m_2 = 1 \\ m_1 + m_2 = r}}^r \langle \tilde{V}(t_{m_1+m_2}) \dots \tilde{V}(t_{m_1+1}) \rangle_1 \langle \tilde{V}(t_{m_1}) \dots \tilde{V}(t_1) \rangle_1 \\ &+ N(N-1)(N-2) \sum_{\substack{m_1, m_2, m_3 = 1 \\ m_1 + m_2 + m_3 = r}}^r \langle \tilde{V}(t_{m_1+m_2+m_3}) \dots \tilde{V}(t_{m_1+m_2+1}) \rangle_1 \langle \tilde{V}(t_{m_1+m_2}) \dots \\ &\cdot \tilde{V}(t_{m_1+1}) \rangle_1 \langle \tilde{V}(t_{m_1}) \dots \tilde{V}(t_1) \rangle_1 + \text{etc.} \end{aligned} \tag{A-4}$$

The first term in equation (A-4), of order  $N$ , represents the case where all the  $V$  refer to the same particle (i.e. the case where  $j_1 = j_2 = \dots = j_r$ : cf. equation 10), the second term, of order  $N(N-1)$ , represents the two particle case ( $j_1 = j_2 = \dots = j_{m_1}$  and  $j_{m_1+1} = \dots = j_{m_1+m_2}$  where  $m_1 + m_2 = r$  and  $j_1 \neq j_{m_1+1}$ ), the third term represents three particles and so on. The indices  $m_i$  denote the number of particles in each group; for example, in the case  $r = 4$ , the two particle term is  $\langle V \rangle \langle VVV \rangle + \langle VV \rangle \langle VV \rangle + \langle VVV \rangle \langle V \rangle$  and the sum over  $m_1, m_2$  produces these three terms. The restriction  $m_1 + m_2 = r$  ties  $m_1$  and  $m_2$  together so that, while there are  $m_1$  particles under the first average and  $m_2$  under the second, the total number of  $\tilde{V}$  operators is always  $r$ . Equation (A-4) may be written in the general form

$$\begin{aligned} & \sum_{j_1 \dots j_r} \langle \tilde{V}(j_r, t_r) \dots \tilde{V}(j_1, t_1) \rangle \\ &= \sum_{q=1}^r N(N-1) \dots (N-q+1) \sum_{\substack{m_1, m_2 \dots m_q = 1 \\ (\sum m_i = r)}}^r \langle \tilde{V}(t_{m_1+m_2 \dots m_q}) \dots \rangle_1 \dots \langle \tilde{V}(t_{m_1+m_2}) \dots \\ &\cdot \tilde{V}(t_{m_1+1}) \rangle_1 \langle \tilde{V}(t_{m_1}) \dots \tilde{V}(t_1) \rangle_1 \\ &= \sum_{q=1}^r N^q \sum_{\substack{m_1, m_2 \dots m_q = 1 \\ (\sum m_i = r)}}^r \langle \tilde{V}(t_{m_1+m_2 \dots m_q}) \dots \rangle_1 \dots \langle \tilde{V}(t_{m_1+m_2}) \dots \\ &\cdot \tilde{V}(t_{m_1+1}) \rangle_1 \langle \tilde{V}(t_{m_1}) \dots \tilde{V}(t_1) \rangle_1, \end{aligned} \tag{A-5}$$

where we have used fact that  $N \rightarrow \infty$  to write  $N^q$ . Notice that in the  $r$ th term there are  $r$  single particle averages, so each average is multiplied by a factor  $N$ , this finally leads to a result proportional to  $n$  since  $P(x) = n/N$  (from equation A-2). Substituting back into equation (A-3) gives

$$\begin{aligned} \langle U_n(t, 0) \rangle &= 1 \\ &+ \sum_{r=1}^{\infty} (-i)^r \sum_{q=1}^r N^q \sum_{\substack{m_1, m_2 \dots m_q = 1 \\ (\sum m_i = r)}}^r \int_0^t dt_r \int_0^{t_r} dt_{r-1} \dots \int_0^{t_2} dt_1 \langle \tilde{V}(t_r) \dots \rangle_1 \dots \langle \tilde{V}(t_{m_1}) \dots \tilde{V}(t_1) \rangle_1. \end{aligned} \tag{A-6}$$

To proceed further, we work out the useful identity

$$\begin{aligned}
 & \int_0^t ds_m \int_0^{s_m} ds_{m-1} \cdots \int_0^{s_2} ds_1 \langle \tilde{V}(s_m) \cdots \tilde{V}(s_1) \rangle_1 f(s_1) \\
 &= \int_0^t ds_1 \int_{s_1}^t ds_2 \cdots \int_{s_{m-1}}^t ds_m \langle \tilde{V}(s_m) \cdots \tilde{V}(s_1) \rangle_1 f(s_1) \tag{A-7} \\
 &= \int_0^t ds_1 F_m(t, s_1) f(s_1),
 \end{aligned}$$

where

$$\begin{aligned}
 F_m(t, s_1) &\equiv \int_{s_1}^t ds_2 \int_{s_2}^t ds_3 \cdots \int_{s_{m-1}}^t ds_m \langle \tilde{V}(s_m) \cdots \tilde{V}(s_1) \rangle_1 \\
 &= \int_{s_1}^t ds_m \int_{s_1}^{s_m} ds_{m-1} \cdots \int_{s_1}^{s_3} ds_2 \langle \tilde{V}(s_m) \cdots \tilde{V}(s_1) \rangle_1. \tag{A-8}
 \end{aligned}$$

We inverted the order of integration in equations (A-7) and (A-8) by repeated application of the Dirichlet integral theorem<sup>(37)</sup>

$$\int_a^b dx \int_a^x dy f(x, y) = \int_a^b dy \int_y^b dx f(x, y). \tag{A-9}$$

The identity expressed in equation (A-7) holds for any function  $f$  and any number of integrals  $m$ . Applying this identity to the first  $m_1$  integrals in equation (A-6) gives

$$\int_0^{t_{m_1+1}} dt_{m_1} \int_0^{t_{m_1}} dt_{m_1-1} \cdots \int_0^{t_2} dt_1 \langle \tilde{V}(t_{m_1}) \cdots \tilde{V}(t_1) \rangle = \int_0^{t_{m_1+1}} dt_1 F_{m_1}(t_{m_1+1}, t_1); \tag{A-10}$$

application to the next  $m_2$  integrals yields

$$\begin{aligned}
 & \int_0^{t_{m_1+m_2+1}} \cdots \int_0^{t_{m_1+2}} dt_{m_1+1} \langle \tilde{V}(t_{m_1+m_2}) \cdots \tilde{V}(t_{m_1+1}) \rangle \int_0^{t_{m_1+1}} dt_1 F_{m_1}(t_{m_1+1}, t_1) \\
 &= \int_0^{t_{m_1+m_2+1}} dt_{m_1+1} F_{m_2}(t_{m_1+m_2+1}, t_{m_1+1}) \int_0^{t_{m_1+1}} dt_1 F_{m_1}(t_{m_1+1}, t_1) \tag{A-11}
 \end{aligned}$$

and, in general,

$$\begin{aligned} \langle U_N(t, 0) \rangle &= 1 + \sum_{r=1}^{\infty} \sum_{q=1}^r N^q \sum_{\substack{m_1, m_2, \dots, m_q=1 \\ \{\sum m_i=r\}}}^r (-i)^{m_1 + \dots + m_q} \int_0^t d\tau_q F_{m_r}(t, \tau_r) \\ &\quad \dots \int_0^{\tau_3} d\tau_2 F_{m_2}(\tau_3, \tau_2) \int_0^{\tau_2} d\tau_1 F_{m_1}(\tau_2, \tau_1). \end{aligned} \tag{A-12}$$

We next use

$$\sum_{r=1}^{\infty} \sum_{q=1}^r = \sum_{q=1}^{\infty} \sum_{r=q}^{\infty} \tag{A-13}$$

$$\sum_{r=q}^{\infty} \sum_{\substack{m_1, m_2, \dots, m_q=1 \\ \{\sum m_i=r\}}}^r = \sum_{m_1=1}^{\infty} \sum_{m_2=1}^{\infty} \dots \sum_{m_q=1}^{\infty} . \tag{A-14}$$

Equation (A-13) is just equation (A-9) in summation form and (A-14) may be obtained from ABRAMOWITZ and STEGUN<sup>(38)</sup> (Section 24.1.2) (noting that  $F_{m_r} \dots F_{m_1}$  is not invariant under permutation). Applying these identities to equation (A-12) gives

$$\begin{aligned} \langle U_N(t, 0) \rangle &= 1 + \sum_{q=1}^{\infty} N^q \int_0^t dt_q \int_0^{t_q} \dots \int_0^{t_2} dt_1 \sum_{m_q=1}^{\infty} (-i)^{m_q} F_{m_q}(t, t_q) \sum \dots \sum_{m_1=1}^{\infty} (-i)^{m_1} F_{m_1}(t_2, t_1) \\ &= 1 + \sum_{q=1}^{\infty} (-i)^q \int_0^t dt_q \int_0^{t_q} \dots \int_0^{t_2} dt_1 K(t, t_q) \dots K(t_3, t_2) K(t_2, t_1), \end{aligned} \tag{A-15}$$

where we have used

$$\begin{aligned} \sum_{m=1}^{\infty} (-i)^m F_m(t, s_1) &= \sum_{m=1}^{\infty} (-i)^m \int_{s_1}^t ds_m \int_{s_1}^{s_m} \dots \int_{s_1}^{s_3} ds_2 \langle \tilde{V}(s_m) \dots \tilde{V}(s_1) \rangle_1 \\ &= -i \langle U(t, s_1) V(s_1) \rangle = -i K(t, s_1) / N, \end{aligned} \tag{A-16}$$

and the definition of  $K(t, t')$  given in equation (20). Comparing equation (A-15) with (21) we see that these equations are identical.

### APPENDIX B FANO'S SECOND ORDER TERM

Averaging Fano's equation (42a) gives for ( $i = 1$ )

$$\begin{aligned} \langle M^{(1)} \rangle &= \left\langle \frac{1}{[1 - L_1(\omega - L_0)^{-1}] L_1} \right\rangle \\ &= \left\langle (\omega - L_0) \frac{1}{(\omega - L_0 - L_1)} L_1 \right\rangle \\ &= \sum_{n=0}^{\infty} \left\langle L_1 \left\{ \frac{1}{\omega - L_1} L_1 \right\}^n \right\rangle. \end{aligned} \tag{B-1}$$

Similarly, equation (42b) gives (for  $i, j = 1, 2$ )

$$\begin{aligned} \langle M^{(2)} \rangle + 2\langle M^{(1)} \rangle &= \left\langle \sum_{n=0}^{\infty} (L_1 + L_2) \left\{ \frac{1}{\omega - L_0} (L_1 + L_2) \right\}^n \right\rangle \\ &= \left\langle \sum_{n=0}^{\infty} \sum_{p=0}^n \left[ L_1 \left\{ \frac{1}{\omega - L_0} L_1 \right\}^p \left\{ \frac{1}{\omega - L_0} L_2 \right\}^{n-p} \right. \right. \\ &\quad \left. \left. + L_2 \left\{ \frac{1}{\omega - L_0} L_2 \right\}^p \left\{ \frac{1}{\omega - L_0} L_1 \right\}^{n-p} \right] \right\rangle + C, \end{aligned} \tag{B-2}$$

where  $C$  denotes a sum of entangled terms of fourth and higher order in the interaction; for example,

$$\begin{aligned} C(\text{4th order}) &= \left\langle L_1 \frac{1}{\omega - L_0} L_2 \frac{1}{\omega - L_0} L_1 \frac{1}{\omega - L_0} L_2 \right\rangle + \left\langle L_1 \frac{1}{\omega - L_0} L_2 \frac{1}{\omega - L_0} L_2 \frac{1}{\omega - L_0} L_1 \right\rangle \\ &\quad + \left\langle L_2 \frac{1}{\omega - L_0} L_1 \frac{1}{\omega - L_0} L_2 \frac{1}{\omega - L_0} L_1 \right\rangle \\ &\quad + \left\langle L_2 \frac{1}{\omega - L_0} L_1 \frac{1}{\omega - L_0} L_1 \frac{1}{\omega - L_0} L_2 \right\rangle. \end{aligned} \tag{B-3}$$

Since 1 and 2 are dummy indices under an average, we have, averaging 1 and 2 independently,

$$\langle M^{(2)} \rangle + 2\langle M^{(1)} \rangle = 2 \sum_{n=0}^{\infty} \sum_{p=0}^n \left\langle L_1 \left\{ \frac{1}{\omega - L_0} L_1 \right\}^p \right\rangle \left\langle \left\{ \frac{1}{\omega - L_0} L_2 \right\}^q \right\rangle + C. \tag{B-4}$$

Using the following identity for an iterated double sum,

$$\sum_{n=0}^{\infty} \sum_{p=0}^n f(n, p) = \sum_{p=0}^{\infty} \sum_{q=0}^{\infty} f(p+q, p), \tag{B-5}$$

we have

$$\begin{aligned} \langle M^{(2)} \rangle + 2\langle M^{(1)} \rangle &= 2 \sum_{p=0}^{\infty} \sum_{q=0}^{\infty} \left\langle L_1 \left\{ \frac{1}{\omega - L_0} L_1 \right\}^p \right\rangle \left\langle \left\{ \frac{1}{\omega - L_0} L_2 \right\}^q \right\rangle + C \\ &= 2\langle M^{(1)} \rangle \left\langle 1 + \sum_{q=0}^{\infty} \frac{1}{\omega - L_0} L_1 \left\{ \frac{1}{\omega - L_0} L_1 \right\}^q \right\rangle + C \\ &= 2\langle M^{(1)} \rangle \left[ 1 + \frac{1}{\omega - L_0} \sum_{q=0}^{\infty} \left\langle L_1 \left\{ \frac{1}{\omega - L_0} L_1 \right\}^q \right\rangle \right] + C \\ &= 2\langle M^{(1)} \rangle \left[ 1 + \frac{1}{\omega - L_0} \langle M^{(1)} \rangle \right] + C \end{aligned} \tag{B-6}$$

or

$$\langle M^{(2)} \rangle = 2\langle M^{(1)} \rangle \frac{1}{\omega - L_0} \langle M^{(1)} \rangle + C. \tag{B-7}$$

Following Fano's equation (41), we may write

$$\langle M_c \rangle = n \langle M_c^{(1)} \rangle + \frac{n^2}{2} \langle M_c^{(2)} \rangle + \dots \quad (\text{B-8})$$

Using Fano's equation (20) then gives

$$\begin{aligned} \langle M_c^{(2)} \rangle &= \frac{1}{2} \langle M^{(2)} \rangle - \langle M^{(1)} \rangle \frac{1}{\omega - L_0} \langle M^{(1)} \rangle \\ &= C \\ &= \text{entangled terms of fourth and higher order.} \end{aligned} \quad (\text{B-9})$$

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