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ON QUANTUM-MECHANICAL UNIFIED THEORIES OF COLLISIONAL SPECTRAL LINE BROADENING

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Abstract—We compare the Baranger-type unified theory of line broadening with a quantum version of the binary-collision approach. For the simple model system of a two-state atom, where both treatments are well-defined, the binary-collision theory results only from the exact formalism after an inversion of an integration variable in an integral equation. On the other hand, the binary-collision theory is applicable to more general systems. In the limiting cases of the impact and the quasistatic theories, the two treatments yield identical results.

1. INTRODUCTION

Unified theories of spectral-line broadening by collisions are designed to describe the entire frequency range of the line, including the quasistatic wing, the impact core and the intermediate region, at least for a defined range of perturber densities. Two types of unified theories have appeared in the literature in recent years, based on different approximations and with a slightly different range of applicability. One theory introduces a one-perturber correlation function in terms of stationary scattering states. It has been originally applied by Baranger[1] in the impact limit, and it has been further exploited by Szudy and Baylis[2] for the entire profile. The other theory is based on a binary-collision approximation and leads to an expression for the line profile in terms of a frequency-dependent collision operator that is proportional to the perturber density. The first result of this type was obtained in a fully quantum-mechanical form by Fano.[3] Later derivations, mainly based on classical-path treatments, utilised projection-operator techniques[4,5] or a BBGKY hierarchy.[6] A general discussion of the binary-collision theory of line broadening has been given by Ben-Reuven.[7]

Here, we point out the main difference between the two types of unified theories. This is best done for the simple model system of a non-moving two-state atom, where both theories apply.

2. THE N-PERTURBER TIME EVOLUTION OPERATOR

According to general line-broadening theory,[8] the normalised line profile of a two-state atom is given by

$$P(\omega) = (1/\pi)\,\mathrm{Re}\int_0^\infty \mathrm{d}t\, \mathrm{e}^{\mathrm{i}(\omega-\omega_0)t}\, Tr_A p\langle \hat{U}_N(t)\rangle p\dagger, \tag{1}$$

where we introduce the atomic lowering and raising operators

$$p = |g\rangle\langle e|\; p\dagger = |e\rangle\langle g|, \tag{2}$$

in terms of the atomic ground state $|g\rangle$ and excited state $|e\rangle$. The trace in Eq. 1 extends over the atomic states only and ω_0 designates the atomic transition frequency. The average N-perturber evolution operator $\langle \hat{U}_N\rangle$ acts only on density matrices σ of the active atom. When inelastic

collisions and perturber-perturber interactions are ignored, this operator is defined by

$$\langle \hat{U}_N(t)\rangle\sigma = Tr_p \exp\left(-i \sum_{i=1}^{N} \hat{H}_i t\right)\rho_p\sigma, \tag{3}$$

with ρ_p the equilibrium density matrix of the perturbers and $\hat{H}_i$ the Liouvillian for the ith perturber, including its interaction with the atom. Superoperators acting in operator space will be denoted by symbols with a caret.

In binary-collision theories of line broadening, the average evolution operator is represented by[9]

$$\langle \hat{U}_N(t)\rangle = 1 - \int_0^t \mathrm{d}s\hat{h}(t-s)\langle \hat{U}_N(s)\rangle, \tag{4}$$

where $\hat{h}$ is an operator averaged over the density matrix ρ_1 of one perturber only and

$$\hat{h}(t)\sigma = NTr_1 \exp(-i\hat{H}_1 t)i\hat{H}_1\rho_1\sigma. \tag{5}$$

An integral equation of the type (4) also holds for the evolution of an atom with two levels that may be composed of several degenerate or nearly degenerate substates. The derivation of Eq. (4) requires explicit use of the binary-collision assumption that the duration of a collision is small compared with the time between collisions, so that simultaneous interactions of the active atom with more than one perturber may be ignored.

In contrast, the Baranger approach constitutes an exact representation of the operator $\langle \hat{U}_N\rangle$, provided that the perturber density matrix ρ_p reduces to a product of N one-perturber density matrices. Then the evolution operator $\langle \hat{U}_N\rangle$ may also be factored into a product of one-perturber averages, where each factor deviates from unity only by an amount of the order of a^3/Ω, and a is the range of the atom-perturber interaction while Ω is the volume of the system. In the thermodynamic limit $N\to\infty$, $\Omega\to\infty$, $N/\Omega\to n$, which is fully justified for a macroscopic system, we can write

$$\langle \hat{U}_N(t)\rangle = \exp[-\hat{\phi}(t)], \tag{6}$$

with $\hat{\phi}$ an operator on the atomic states, defined as an average over the states of one perturber according to

$$\hat{\phi}(t)\sigma = N[\sigma - Tr_1 \exp(-i\hat{H}_1 t)\rho_1\sigma]. \tag{7}$$

Differentiation and reintegration of Eq. (6) yields the integral equation

$$\langle \hat{U}_N(t)\rangle = 1 - \int_0^t \mathrm{d}s\hat{h}(s)\langle \hat{U}_N(s)\rangle, \tag{8}$$

where $\hat{h}(t) = \mathrm{d}\hat{\phi}/\mathrm{d}t$ is given in Eq. (5). The derivation of Eq. (8) required explicitly that the Liouvillians $\hat{H}_i$ for different perturbers commute, which is only correct for the simple system of a non-moving atom with two non-degenerate states. For this single system Eq. (8) has a more general validity than Eq. (4). On the other hand, within the binary-collision approximation, Eq. (4) remains valid for more complicated systems.

The validity of the Eq. (4) can be understood in a more direct fashion by considering two complementary limiting cases. In the large-time limit, we may replace $\hat{h}(s)$ in Eq. (8) by its stationary limit

$$\hat{h}_0 = \lim_{t\to\infty} \hat{h}(t); \tag{9}$$

the solution of Eq. (8) is then

$$\langle \hat{U}_N(t)\rangle = \exp(-\hat{h}_o t). \tag{10}$$

Since the quantity $\hat{h}$ refers to a single collision, one expects this large-time limit to be justified for times that are large compared to the duration of a collision. This limit yields the impact limit of line broadening. In the short-time limit $\langle \hat{U}_N(t) \rangle$ has had no chance to deviate appreciably from unity and Eq. (8) may be solved by iterating once, viz.

$$\langle \hat{U}_N(t) \rangle = 1 - \int_0^t \mathrm{d}s \hat{h}(s) = 1 - \hat{\phi}(t). \tag{11}$$

The corresponding result for the spectrum is the quasistatic single-perturber approximation. This limit is expected to be valid for times small compared with the duration of a collision τ_c. It will be obvious that, in both limiting cases, Eqs. (4) and (8) are equivalent, since each limiting case corresponds to the assumption that one of the two factors in Eqs. (4) or (8) is practically constant. In the intermediate region, i.e., for times comparable with τ_c, the binary-collision approximation must be expected to deviate markedly from the value of Eq. (6) which is exact for the simple model system. This deviation can be traced back to the time ordering of different collisions that is implied in the binary-collision approximation. Corrections to this simple model due to correlations between perturbers have been discussed by Royer[10].

3. THE LINE PROFILE

Introducing the Laplace-transformed quantity

$$\hat{G}_N(z) = \int_0^\infty \mathrm{d}t \, \mathrm{e}^{-zt} \langle \hat{U}_N(t) \rangle, \tag{12}$$

we can write Eq. (1) in the form

$$P(\omega) = (1/\pi) Re Tr_A p \hat{G}_N(z) p\dagger, \qquad z = -i(\omega - \omega_0). \tag{13}$$

In the binary-collision approximation, it follows from Eq. (4) that $\hat{G}_N(z)$ may be expressed as

$$\hat{G}_N(z) = 1/[z + \hat{\Phi}(z)], \tag{14}$$

where $\hat{\Phi}(z)$ is the collision operator given by

$$\hat{\Phi}(z) = z\hat{g}(z) \tag{15}$$

with $\hat{g}(z)$ the Laplace transform of $\hat{h}(t)$, i.e.,

$$\hat{g}(z) = \int_0^\infty \mathrm{d}t \, \mathrm{e}^{-zt} \hat{h}(t). \tag{16}$$

By using Eq. (5), we see that the collision operator is

$$\hat{\Phi}(z) = zNTr_1 \frac{1}{z + i\hat{H}_1} i\hat{H}_1 \rho_1. \tag{17}$$

Equation (13) shows that we only need to consider the action of the various operators on the raising operator $p\dagger$. It is convenient to introduce the outgoing stationary translational scattering states $|\boldsymbol{k}\rangle_g$ and $|\boldsymbol{k}\rangle_e$[11], which are eigenstates for the perturber motion in the ground-state and the excited-state interaction potential, as illustrated by the relations

$$H_g|\boldsymbol{k}\rangle_g = E_k|\boldsymbol{k}\rangle_g \qquad H_e|\boldsymbol{k}\rangle_e = E_k|\boldsymbol{k}\rangle_e. \tag{18}$$

Here,

$$H_g = T + V_g, \quad H_e = T + V_e, \tag{19}$$

with T the kinetic Hamiltonian of the perturber and V_g and V_e the familiar adiabatic interaction potentials. The Hamiltonian H_1, acting on the complete set of perturber and atom states, obeys the relation

$$H_1 = |g\rangle H_g \langle g| + |e\rangle H_e \langle e|. \tag{20}$$

The one-perturber density matrix ρ_1 may be expressed in terms of the stationary scattering states; thus,

$$\rho_1 = \sum_k |\boldsymbol{k}\rangle_g f_{k\,g} \langle \boldsymbol{k}|, \tag{21}$$

where f_k denotes a Maxwell–Boltzmann distribution. The effect of the ground-state potential V_g has been incorporated in the Boltzmann distribution. Applying Eq. (20), we find

$$\hat{H}_1 \rho_1 p\dagger = (H_e \rho_1 - \rho_1 H_g) p\dagger. \tag{22}$$

From Eq. (17), we then find that $p\dagger$ is an eigenvector of the collision operator $\hat{\Phi}$, with the eigenvalue relation

$$\hat{\Phi}(z) p\dagger = \Phi(z) p\dagger, \tag{23}$$

where $\Phi(z)$ is a scalar function given by

$$\Phi(z) = izN \sum_k f_{k\,g} \langle \boldsymbol{k}| \frac{1}{z + iH_e - iE_k} \Delta V |\boldsymbol{k}\rangle_g \tag{24}$$

and $\Delta V = H_e - H_g = V_e - V_g$ is the commonly known difference potential. The final general expression for the profile follows from Eqs. (13), (14) and (23), yielding

$$P(\omega) = (1/\pi)\, Re\{1/[z + \Phi(z)\}, \quad z = -i(\omega - \omega_0). \tag{25}$$

In Eq. (25) as in Eq. (13), z is supposed to include an infinitesimal positive real part.

It is illustrative to consider the two limiting cases discussed in Section 2. The large-time limit is obtained by evaluating the quantity

$$h_0 = \lim_{z \downarrow 0} z \int_0^\infty \mathrm{d}t\, \mathrm{e}^{-zt} h(t) = \Phi(0). \tag{26}$$

After using the alternative form

$$\Phi(z) = iN \sum_k f_{k\,g} \langle \boldsymbol{k}| \Delta V \left[1 + \frac{1}{iz - H_e + E_k} \Delta V \right] |\boldsymbol{k}\rangle_g \tag{27}$$

and the Lippmann-Schwinger equation[12] for outgoing scattering states

$$\lim_{z \downarrow 0} \left[1 + \frac{1}{iz - H_e + E_k} \Delta V \right] |\boldsymbol{k}\rangle_g = |\boldsymbol{k}\rangle_e, \tag{28}$$

we obtain

$$\Phi(0) = iN \sum_k f_{kg} \langle \boldsymbol{k}| \Delta V |\boldsymbol{k}\rangle_e. \tag{29}$$

If $\omega - \omega_0$ is small compared with the inverse duration of a collision, Eq. (26) determines the line

profile, which takes the Lorentzian form

$$P(\omega) = \gamma/\pi[\gamma^2 + (\omega - \omega_0 - \delta)^2], \tag{30}$$

with

$$\gamma + i\delta = \Phi(0). \tag{31}$$

This is the well-known result of Baranger.[1,8] The opposite small-time limit applies in the wing of the lines, where $\omega - \omega_0$ is large compared to the collision function Φ. We then find from Eq. (25) the approximate expression

$$P(\omega) = (1/\pi)\,\mathrm{Re}\{\Phi(-i(\omega - \omega_0))/(\omega - \omega_0)^2\}, \tag{32}$$

which can also be derived from Eq. (11). After insertion of a closure over the translational states $|\boldsymbol{k}\rangle_e$, we derive from Eq. (27).

$$Re\{\Phi(-i(\omega - \omega_0))\} = N\pi \sum_{\boldsymbol{k}} \sum_{\boldsymbol{k}'} f_k |{}_e\langle \boldsymbol{k}'|\Delta V|\boldsymbol{k}\rangle_g|^2 \delta(\omega - \omega_0 + E_k - E_{k'}). \tag{33}$$

The corresponding expression for the profile is

$$P(\omega) = N \sum_{\boldsymbol{k}} \sum_{\boldsymbol{k}'} f_k |{}_e\langle \boldsymbol{k}'|\boldsymbol{k}\rangle_g|^2 \delta(\omega - \omega_0 + E_k - E_{k'})$$

$$= N \sum_{\boldsymbol{k}} f_{kg} \langle \boldsymbol{k}|\delta(\omega - \omega_0 + E_k - H_e)|\boldsymbol{k}\rangle_g, \tag{34}$$

which is seen to represent a quantum version of the quasistatic single-perturber result.[8] Quasi-static contributions due to several perturbers in the near vicinity of the atom as studied by Royer[10] are also included in Eq. (6).

A direct calculation of the impact limit and the quasistatic limit with the quantum formalism of the Baranger type gives the same results.[11]

4. CONCLUSIONS

We have demonstrated the difference between the unified theory developed in the binary-collision approximation and the quantum formalism of the line profile in terms of overlap integrals between outgoing stationary scattering states. This difference is most clearly revealed by comparing the integral equations (4) and (8). In the quasistatic and the impact limit the two results become identical. The binary-collision theory is applicable to realistic atoms with degenerate substates, whereas the Baranger type approach is restricted to the simple case of a two-state atom. However, for this simple system, the latter formalism has more general validity. The central quantity in the Baranger type quantummechanical formalism is the eigenvalue $\phi(t)$, which corresponds to the operator (7) and determines the correlation function $\exp(-\phi(t))$ that has the profile as its Laplace transformation. An explicit expression for ϕ is

$$\phi(t) = N \sum_{\boldsymbol{k}} f_{k\,g} \langle \boldsymbol{k}|1 - \exp[i(H_e - E_k)t]|\boldsymbol{k}\rangle_g. \tag{35}$$

The same quantity occurs also in theories of more involved radiation processes of perturbed atoms, such as nonlinear absorption[13] and resonance fluorescence.[14]

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