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COMMENT

The density operator approach to scattering theory

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Abstract. The equations obeyed by the density operator in a scattering problem are derived. In Liouville space notation, these resemble the Lippmann–Schwinger equations. Expressions for the transition rate for one- and two-potential scatterings are also derived.

1. Introduction

The conventional approach to scattering theory is in terms of the wavefunction and the equation obeyed by it, namely the Lippmann–Schwinger equation. An approach to scattering theory in terms of the density operator is interesting in view of the fact that the density operator is a more physically meaningful quantity than the wavefunction. It is also of interest in problems involving scattering from systems which are in contact with a heat bath (Mukamel and Nitzan 1977, Metiu 1978). Although the expression for the transition rate has been given in terms of the tetradic T -matrix (Ben-Reuven 1975, Ben-Reuven and Mukamel 1975), the equations obeyed by the density operator for a scattering problem do not seem to have been derived. It is the purpose of this paper to report the equations obeyed by the density operator and to derive the expression for transition rate in a very simple fashion. The equations obeyed by the density operator are particularly pleasing in that they are very similar to the Lippmann–Schwinger equations. We also give expressions for the rate in the case of a two-potential scattering problem. Application of the equations to the scattering of atoms from surfaces will form the subject of a later publication.

2. The Fano–Ben-Reuven–Mukamel equations

A natural framework for the density operator approach to scattering theory is provided by the Liouville space approach. We refer the reader to papers by Fano (1963) and Ben-Reuven (1975) for details. We shall denote the density operator by W . If we wish to stress the fact that W is an element of the Liouville space, we shall enclose it within the ket $| \rangle\rangle$. This often has the advantage of making the equations look like those of the usual scattering theory. For the purpose of formulating and discussing the equations, we make use of the simplest possible case, namely, the scattering of a single particle by a potential V . The formalism is the most natural one to use, if the scattering occurs from a system which is in a mixed state.

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We write the Hamiltonian as

$$H = H_0 + V \quad (1)$$

where H_0 is the free part of the Hamiltonian. Assuming the system to be in a mixed stationary state of H_0 , W_{in} , at $t = -\infty$, one can write the exact density operator as

$$W^+ = \lim_{t \rightarrow -\infty} e^{iHt} e^{-iH_0 t} W_{\text{in}} e^{iH_0 t} e^{-iHt}. \quad (2)$$

As W_{in} is stationary with respect to H_0 , (i.e. $[H_0, W_{\text{in}}] = 0$), we obtain

$$W^+ = \lim_{t \rightarrow -\infty} e^{iHt} W_{\text{in}} e^{-iHt}. \quad (3)$$

The superscript '+' on W indicates that it will satisfy an 'incoming plane wave' boundary condition.

In Liouville space notation, equation (3) becomes

$$|W^+\rangle\rangle = \lim_{t \rightarrow -\infty} e^{i\mathcal{H}t} |W_{\text{in}}\rangle\rangle. \quad (4)$$

\mathcal{H} is the Liouvillian corresponding to H and is defined by (Ben-Reuven 1975)

$$\mathcal{H}X = [H, X] \quad (5)$$

for any X belonging to the Liouville space. Interpreting the limit in (4) as

$$\lim_{t \rightarrow -\infty} f(t) = \lim_{\eta \rightarrow +0} \eta \int_{-\infty}^0 e^{\eta t} f(t) dt,$$

we obtain

$$|W^+\rangle\rangle = \frac{i\eta}{(i\eta - \mathcal{H})} |W_{\text{in}}\rangle\rangle, \quad \eta = +0. \quad (6)$$

Let \mathcal{H}_0 and \mathcal{V} be the Liouvillians corresponding to H_0 and V . Then equation (6) could be rearranged to give

$$|W^+\rangle\rangle = |W_{\text{in}}\rangle\rangle + \mathcal{G}(+i0)\mathcal{V}|W_{\text{in}}\rangle\rangle \quad (7)$$

or

$$|W^+\rangle\rangle = |W_{\text{in}}\rangle\rangle + \mathcal{G}_0(+i0)\mathcal{V}|W^+\rangle\rangle \quad (8)$$

where

$$\mathcal{G}(\omega) = (\omega - \mathcal{H})^{-1}$$

and

$$\mathcal{G}_0(\omega) = (\omega - \mathcal{H}_0)^{-1} \quad (9)$$

are tetradic Green functions (Ben-Reuven 1975). Equations (7) and (8) are the analogues of the Lipmann–Schwinger equations for the density operator approach. We shall call them the Fano–Ben-Reuven–Mukamel (FBM) equations as these are direct extensions of the work of these authors. One can also define $|W^-\rangle\rangle$, which will satisfy the outgoing plane wave boundary condition and show that it obeys the equation

$$|W^-\rangle\rangle = (-i\eta - \mathcal{H})^{-1}(-i\eta)|W_{\text{out}}\rangle\rangle$$

in an exactly similar fashion.

3. The transition rate

The rate of transitions into a final state $|\alpha\rangle$, which is an eigenfunction of H_0 , is given by

$$R_\alpha = \left(\frac{d}{dt} \langle \alpha | W^+(t) | \alpha \rangle \right)_{t=0}. \tag{10}$$

In Liouville space notation

$$R_\alpha = \left\langle\left\langle \alpha\alpha \left| \frac{d}{dt} W^+(t) \right. \right\rangle\right\rangle, \tag{11}$$

where

$$|\alpha\alpha\rangle \equiv |\alpha\rangle\langle\alpha| \tag{12}$$

and

$$|W^+(t)\rangle\rangle = e^{-i\mathcal{H}t} |W^+\rangle\rangle, \tag{13}$$

so

$$R_\alpha = -i\langle\langle \alpha\alpha | \mathcal{H} | W^+ \rangle\rangle = -i\langle\langle \alpha\alpha | \mathcal{H}_0 + \mathcal{V} | W^+ \rangle\rangle. \tag{14}$$

As $|\alpha\rangle$ is an eigenfunction of H_0 , the term involving \mathcal{H}_0 is zero and we obtain

$$R_\alpha = -i\langle\langle \alpha\alpha | \mathcal{V} | W^+ \rangle\rangle. \tag{15}$$

Using (7),

$$R_\alpha = -i\langle\langle \alpha\alpha | \mathcal{T}(+i0) | W_{in} \rangle\rangle \tag{16}$$

where

$$\mathcal{T}(\omega) = \mathcal{V} + \mathcal{V}\mathcal{G}(\omega)\mathcal{V} \tag{17}$$

is the tetradic T -matrix. Equation (16) was first given by Ben-Reuven and Mukamel (1975), though the manner in which it was arrived at is different.

4. Two-potential scattering

Now we consider the expression for transition rates for a case where the scattering is caused by two potentials U and V , with the tetradic analogues \mathcal{U} and \mathcal{V} . The Hamiltonian is

$$H = H_0 + U + V. \tag{18}$$

We assume U to be stronger than V . The rate of transition into $|\alpha\rangle$ is

$$R_\alpha = -i\langle\langle \alpha\alpha | \mathcal{U} + \mathcal{V} | W^+ \rangle\rangle. \tag{19}$$

Let us define

$$|X_\alpha^-\rangle\rangle = |\alpha\alpha\rangle\rangle + (-i0 - \mathcal{H}_0)^{-1}\mathcal{U}|X_\alpha^-\rangle\rangle \tag{20}$$

where $|X_\alpha^-\rangle\rangle$ is a stationary density operator of $H_0 + U$, and satisfies the outgoing plane

wave boundary condition. Then

$$\begin{aligned} R_\alpha &= -i[\langle\langle X_\alpha^- | \mathcal{U} + \mathcal{V} | W^+ \rangle\rangle - \langle\langle (-i0 - \mathcal{H}_0)^{-1} \mathcal{U} X_\alpha^- | \mathcal{U} + \mathcal{V} | W^+ \rangle\rangle] \\ &= -i[\langle\langle X_\alpha^- | \mathcal{U} + \mathcal{V} | W^+ \rangle\rangle - \langle\langle X_\alpha^- | \mathcal{U} (i0 - \mathcal{H}_0)^{-1} (\mathcal{U} + \mathcal{V}) | W^+ \rangle\rangle] \\ &= -i[\langle\langle X_\alpha^- | \mathcal{V} | W^+ \rangle\rangle + \langle\langle X_\alpha^- | \mathcal{U} | W_{in} \rangle\rangle]. \end{aligned} \quad (21)$$

We have made use of the fact that \mathcal{H}_0 and \mathcal{U} are Hermitian operators. The second term in (20) is the exact transition rate into the state $|\alpha\rangle$, if only the potential U were present. The first term thus gives the change in the rate due to the introduction of the potential V . If U is incapable of causing a transition to state $|\alpha\rangle$, then

$$R_\alpha = -i\langle\langle X_\alpha^- | \mathcal{V} | W^+ \rangle\rangle. \quad (22)$$

Finally, it is not immediately obvious that the solution of equations (7) and (8) would be identical with that obtained by direct, wavefunction approaches. Thus if

$$W_{in} = \sum_\alpha W_\alpha |\alpha\rangle \langle\alpha|, \quad (23)$$

the usual approach leads to

$$W^+ = \sum_\alpha W_\alpha |\alpha^+\rangle \langle\alpha^+| \quad (24)$$

where $|\alpha^+\rangle$ obeys

$$|\alpha^+\rangle = |\alpha\rangle + (E_\alpha + i0 - H)^{-1} V |\alpha\rangle, \quad (25)$$

E_α being defined by $H_0 |\alpha\rangle = E_\alpha |\alpha\rangle$. One can easily prove that a solution of equation (7) leads to a result identical with (23).

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