GENERAL SOLUTION OF VARIATIONAL S-MATRIX EXPRESSION

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Keywords: S-matrix, Time-dependent, General solution

The quantum mechanic expression of reaction probability is the square of the modulus of the S-matrix elements. One can prove using the method in Ref.[1] that for $t_1 \leq t \leq t_2$

$$S_{fi} = \langle \Psi_0^-(t) | \Psi_0^+(t) \rangle + \frac{i}{\hbar} \int_{t_1}^t \langle \Psi_0^-(t') | \left(i\hbar \frac{\partial}{\partial t'} - H \right) | \Psi_0^+(t') \rangle dt' \\ + \frac{i}{\hbar} \int_t^{t_2} \langle \Psi_0^+(t') | \left(i\hbar \frac{\partial}{\partial t'} - H \right) | \Psi_0^-(t') \rangle^* dt' \quad (1)$$

is a time-dependent variational expression of the S-matrix elements, where $\Psi_0^+(t)$ and $\Psi_0^-(t)$ are trial functions of the exact $\Psi^+(t)$ and $\Psi^-(t)$ respectively and satisfy the following initial conditions,

$$\langle \Psi_0^+(t_1) | \Psi_0^+(t_1) \rangle = 1, \quad \Psi_0^+(t_1) = \Psi^+(t_1), \quad \delta \Psi_0^+(t_1) = 0 \\ \langle \Psi_0^-(t_2) | \Psi_0^-(t_2) \rangle = 1, \quad \Psi_0^-(t_2) = \Psi^-(t_2), \quad \delta \Psi_0^-(t_2) = 0 \quad (2)$$

By taking $t = t_2$, one gets the expression in Ref.[1],

$$S_{fi} = \langle \Psi_0^-(t_2) | \Psi_0^+(t_2) \rangle + \frac{i}{\hbar} \int_{t_1}^{t_2} \langle \Psi_0^-(t) | \left(i\hbar \frac{\partial}{\partial t} - H \right) | \Psi_0^+(t) \rangle dt \quad (3)$$

and by taking $t = t_1$, one gets

$$S_{fi} = \langle \Psi_0^-(t_1) | \Psi_0^+(t_1) \rangle + \frac{i}{\hbar} \int_{t_1}^{t_2} \langle \Psi_0^+(t) | \left(i\hbar \frac{\partial}{\partial t} - H \right) | \Psi_0^-(t) \rangle^* dt \quad (4)$$

or, one can take more symmetric form

$$S_{fi} = \frac{1}{2} \{ \langle \Psi_0^-(t_1) | \Psi_0^+(t_1) \rangle + \langle \Psi_0^-(t_2) | \Psi_0^+(t_2) \rangle + \frac{i}{\hbar} \int_{t_1}^{t_2} \langle \Psi_0^-(t) | \left(i\hbar \frac{\partial}{\partial t} - H \right) | \Psi_0^+(t) \rangle dt \\ + \frac{i}{\hbar} \int_{t_1}^{t_2} \langle \Psi_0^+(t) | \left(i\hbar \frac{\partial}{\partial t} - H \right) | \Psi_0^-(t) \rangle^* dt \} \quad (5)$$

In this communication, we provide a general solution to these variational expres-

sions. We will show that all these expressions can be arranged into the form

$$S_{fi} = M_0 - M_1 M^{-1} M_2 \quad (6)$$

where M_0 , M_1 , M , and M_2 are certain matrices of the operator $(i\hbar\partial/\partial t - H)$ with respect to properly chosen basis sets.

To be explicit, we take unimolecular dissociation as an example, where $t_1 = 0$ and $t_2 \rightarrow \infty$. We consider Eqn (3) as example. One expands $\Psi_0^+(t)$ and $\Psi_0^-(t)$ as,

$$\Psi_0^+(t) = \Phi_i(t) + \sum_{l=1}^N a_l u_l(t), \quad \Psi_0^-(t) = \Phi_f(t) + \sum_{l=1}^N b_l w_l(t) \quad (7)$$

where $\Phi_i(t)$ and $\Phi_f(t)$ satisfy the initial conditions (2), and also

$$\Phi_i(t \rightarrow \infty) \rightarrow 0, \quad \Phi_f(0) = 0 \quad (8)$$

$$\left(i\hbar \frac{\partial}{\partial t} - H\right) u_l(t \rightarrow \infty) \rightarrow 0, \quad u_l(0) = 0, \quad w_l(t \rightarrow \infty) \rightarrow 0; \quad l = 1, 2, \dots, N$$

$\{u_l\}$ and $\{w_l\}$ are quadratic integrable, not necessarily orthonormal basis sets, and $\{a_l\}$ and $\{b_l\}$ are variational parameters to be optimized. By solving

$$\frac{\partial S_{fi}}{\partial a_l} = 0, \quad \frac{\partial S_{fi}}{\partial b_l} = 0; \quad l = 1, 2, \dots, N \quad (9)$$

the best $\{a_l\}$ and $\{b_l\}$ can be found.

In order for the formulation to be concise, we take the matrix notation,

$$\Psi_0^+ = \Phi_i + UA$$

$$\Psi_0^- = \Phi_f + WB \quad (10)$$

Substituting Eqn (10) into Eqn (3), one gets

$$S_{fi} = \langle \Phi_f | U \rangle_\infty A + \frac{i}{\hbar} \int_0^\infty \left[\langle \Phi_f | + B^+ \langle W | \right] \left(i\hbar \frac{\partial}{\partial t} - H \right) \left[|U\rangle A + |\Phi_i\rangle \right] dt \quad (11)$$

where $\langle \Phi_f | U \rangle_\infty$ stands for that the values are taken at the limit $t \rightarrow \infty$.

Defining

$$\frac{i}{\hbar} \int_0^\infty \langle \chi | \left(i\hbar \frac{\partial}{\partial t} - H \right) | \Phi \rangle dt = \langle \chi | Q | \Phi \rangle \quad (12)$$

Eqn (11) is rewritten as

$$S_{fi} = \langle \Phi_f | U \rangle_\infty A + \langle \Phi_f | Q | U \rangle A + \langle \Phi_f | Q | \Phi_i \rangle + B^+ \langle W | Q | U \rangle A + B^+ \langle W | Q | \Phi_i \rangle \quad (13)$$

To optimize Eqn (13), we take

$$\frac{\partial S_{fi}}{\partial A} = \langle \Phi_f | U \rangle_\infty + \langle \Phi_f | Q | U \rangle + B^+ \langle W | Q | U \rangle = 0$$

$$\frac{\partial S_{fi}}{\partial B^+} = \langle W | Q | U \rangle A + \langle W | Q | \Phi_i \rangle = 0 \quad (14)$$

From Eqn (14), we have

$$B^+ = -[\langle \Phi_f | U \rangle_\infty + \langle \Phi_f | Q | U \rangle] \langle W | Q | U \rangle^{-1}$$

$$A = -\langle W | Q | U \rangle^{-1} \langle W | Q | \Phi_i \rangle \quad (15)$$

Plugging Eqn (15) into Eqn (13), it is found that

$$S_{fi} = \langle \Phi_f | Q | \Phi_i \rangle - [\langle \Phi_f | U \rangle_\infty + \langle \Phi_f | Q | U \rangle] \langle W | Q | U \rangle^{-1} \langle W | Q | \Phi_i \rangle \quad (16)$$

We would like to point out that Eqn (16) has very similar structure and thus property as the counterpart in the time-independent version^[2]. Especially, the problem of scattering becomes a standard matrix manipulation. Numerical tests via model system are in progress.

References

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含时变分S矩阵解的一般形式

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摘要 推导出含时S散射矩阵变分表达式经基函数展开并优化后的解的一般形式。

关键词: S散射矩阵 含时变分 求解