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THE SCATTERING MATRIX ELEMENT OF THE THREE BODY REACTIVE COLLISION *

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ABSTRACT

The optical model approximation has been applied to the previously derived [1,2] set of coupled equations representing the dynamics of the three-body reactive scattering. The Schrödinger equation obtained describing the scattering problem has then been solved by inserting the effective mass approximation. The asymptotic requirements for both the entrance and exit channels, respectively, have been supplied to give the scattering matrix element of the reactive collision.

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Introduction

In view of the increasing importance of the so-called ab-initio calculation of the reaction rate constant of the chemical interactions, we proceed to study the three-body-molecular dynamics. In previous publications [1,2] , the classical Lagrangian of this scattering problem has been derived and then quantized.

In the present article, the previously obtained set of coupled channel equations has been decoupled by using the optical model approximation. Such a procedure yields an analytical solution that considerably saves the efforts necessary for the numerical integration that has been undertaken until now [4,5] .

Theory

The reactive scattering of three particles has been found to be represented by the following set of coupled equations [2]:

$$\left\{\left[-\frac{\hbar^2}{2\mu(u)}\left(\frac{\delta^2}{\delta u^2}-\tilde{\delta}_u\frac{\delta}{\delta u}\right)+V(u,0)+\xi_n(u)-E\right]\delta_{mn}+U_{mn}(u)\right\}F_n(u)=0\,;^{1} \tag{1}$$

where

$$U_{mn}(u) = L_{mn} + \frac{\hbar^2}{2\mu(u)}\left[M_{mn}\left(\tilde{\delta}_u-\frac{\delta}{\delta u}\right)-N_{mn}\right] . \tag{2}$$

Until now, the above equation has been solved by means of the numerical integration techniques [4,5] that evidently consume considerable efforts.

Alternatively, one may decouple such set of equations by employing the optical model approximation [3]. To accomplish this, let us write the above set of coupled equations symbolically as

$$(H - E) \mid F_m \rangle = -\sum_{n=0}^{\infty} U_{mn} \mid F_n \rangle \tag{3}$$

which by virtue of the following transformation:

$$| F_m \rangle = - \lim_{\sigma \to 0} \frac{1}{H-E+i\sigma} V_m | F_0 \rangle \tag{4}$$

becomes

$$V_m | F_0 \rangle = - \sum_{n=0}^{\infty} \lim_{\sigma \to 0} U_{mn} \frac{1}{H-E+i\sigma} V_n | F_0 \rangle \ . \tag{5}$$

This last expression can be written in the form

$$V_m = - \lim_{\sigma \to 0} \sum_{n=0}^{\infty} U_{mn} \frac{1}{H-E+i\sigma} V_n = - \Big[U_{m0} \lim_{\sigma \to 0} \frac{1}{H-E+i\sigma} V_0 + \sum_{n \neq 0}^{\infty} \lim_{\sigma \to 0} U_{mn} \frac{1}{H-E+i\sigma} V_n \Big] \ . \tag{6}$$

However, Eq. (4) implies that for $m = 0$, the first term of this last equation reduces simply to U_{m0}, and therefore one might rewrite this expression as follows:

$$V_m = - \Big[U_{m0} + \sum_{n \neq 0}^{\infty} U_{mn} \lim_{\sigma \to 0} \frac{1}{H-E+i\sigma} V_n \Big] \ . \tag{7}$$

Now, let us specify Eq. (3) for the channel $m = 0$, then by virtue of Eq. (4) one gets

$$(H - E) | F_0 \rangle = - \sum_{n=0}^{\infty} U_{0n} \frac{1}{H-E} V_n | F_0 \rangle \ , \tag{8}$$

which again by virtue of Eq. (7) becomes

$$(H-E) | F_0 \rangle = - \Big[\sum U_{0n} \lim_{\sigma \to 0} \frac{1}{H-E+i\sigma} U_{mn} + \sum_{n} \sum_{n'} \lim_{\sigma \to 0} U_{0n} \frac{1}{H-E+i\sigma} U_{mn} \frac{1}{H-E+i\sigma} U_{mn} + \dots E \Big] | F_0 \rangle = 0 \ . \tag{9}$$

It is to be noted here that the right-hand side of this last equation contains inverses of differential operators, which are complex and non-local.

To simplify this equation, let us introduce the optical model approximation [3]. In this course, one might replace the brackets on the right-hand side of Eq. (9) by a non-local complex interaction $U(u,u')$. The last equation could then be rewritten as

$$(H-E) | F_0(u) \rangle = - \int_{-\infty}^{\infty} du' \, U(u,u') \, F_0(u') \ . \tag{10}$$

Now, spelling out the explicit form of H [2], one gets

$$\Big[-\frac{\hbar^2}{2\mu(u)} \Big(\frac{\delta^2}{\delta u^2} - \tilde{\delta}_{\mu} \frac{\delta}{\delta u} \Big) + V(u,0) + \xi_m(u) - E \Big] F_0(u) = - \int du \, U(u,u') \, F_0 \ . \tag{11}$$

Of course, this criterion has a certain similarity to that used previously and which is known as the adiabatic approximation [6] in spite of the fact that the present treatment is more transparent.

Asymptotically, as $u \to \pm\infty$, the non-local interaction vanishes while the static potential, $V(u,0)$, the vibrational energy $\xi_n(u)$ and the varying reduced mass, $\mu(u)$ approach constant values V^-, ξ_n^-, μ^- and V^+, ξ_n^+, μ^+ respectively that are corresponding to the entrance and exit channels respectively.

We are now in a position to solve the scattering equation given by Eq. (11) which involves a non-local potential that may be complex. This can be accomplished by converting the above integro-differential equation into an asymptotically equivalent differential equation by employing the moment expansion for non-local potential operators.

More precisely, we expand the scattering wave function, $F_0(u')$, in Taylor's series around u as:

$$F_0(u') = \sum_{k}^{\infty} \frac{(u'-u)^k}{k!} \quad \frac{\delta^k}{\delta u^k} \; F_0(u) \quad . \qquad (12)$$

The right-hand side of Eq. (11) then becomes

$$\int_{-\infty}^{\infty} du' \; U(u,u') \; F_0(u') = \sum_{k=0}^{\infty} U_k(u) \frac{\delta^k}{\delta u^k} \; F_0(u) \quad , \qquad (13)$$

where $U_k(u)$ stands for the abbreviation

$$U_k(u) = \frac{1}{k!} \quad du' \; U(u,u') \; (u'-u)^k \quad . \qquad (14)$$

Let us now assume that the non-locality of the interaction is not so strong such that the term of order higher than two in the above series can be neglected.

Substituting from expression (12),after being truncated into Eq. (11), yields a second order differential equation with a local potential, namely

$$\left\{ -\left(\frac{\hbar^2}{2\mu(u)} - U_2(u) \right) \frac{\partial^2}{\delta u^2} + \left(\frac{\hbar^2}{2\mu(v)} \tilde{\delta}(u) + U_1(u) \right) \frac{\partial}{\partial u} + U_0(u) + V(u,0) + \mathcal{E}_m(u) - E \right\} F_0(u) = 0 \quad . \qquad (15)$$

Moreover, the first order differential operator can be eliminated by inserting the substitution

$$F_0(u) = \Omega(u) \; \phi(u) \qquad (16)$$

into Eq. (15) one obtains

$$\left\{ -\left(\frac{\hbar^2}{2\mu(u)} - U_2(u) \right) \frac{\delta^2}{\delta u^2} + \left[\frac{\hbar^2}{2\mu(u)} \tilde{\delta}_u + U_1 - 2\left(\frac{\hbar^2}{2\mu(u)} - U_2(u) \right) \frac{\Omega'(u)}{\Omega(u)} \right] \frac{\delta}{\delta(u)} + \left(\frac{\hbar^2}{2\mu(u)} \tilde{\delta}_u + U_1(u) \right) \frac{\Omega'(u)}{\Omega(u)} - \left(\frac{\hbar^2}{2\mu(u)} - U_2(u) \right) \frac{\Omega''(u)}{\Omega(u)} + U_0 + V(u,0) + \mathcal{E}_m(u) - E \right\} \phi(u) = 0 \quad . \qquad (17)$$

If the term containing $\frac{\delta}{\delta u}$ is assumed to vanish, then it is necessary that this function $\Omega(u)$ must satisfy the following first order differential equation i.e.

$$\Omega'(u) = \frac{\tilde{\delta}_u \; \hbar^2/2\mu(u) + U_1(u)}{2\left(\hbar^2/2\mu(u) - U_2(u) \right)} \; \Omega(u) \quad . \qquad (18)$$

Eq. (17) might then be simplified to the form

$$\left[-\left(\frac{\hbar^2}{2\mu(u)} - U_2(u) \right) \frac{\delta^2}{\delta^2 u} + V(u,0) + \mathcal{E}_m(u) + U_m(u) - E \right] \phi(u) = 0 \quad , \qquad (19)$$

where

$$U_m(u) = U_0 + \frac{1}{4} \frac{\left(\frac{\hbar^2}{2\mu} \tilde{\delta}_u + U_1(u) \right)^2}{\left(\frac{\hbar^2}{2\mu} - U_2(u) \right)} - \frac{1}{2} \left(\frac{\hbar^2}{2\mu} - U_2 \right) \frac{\delta}{\delta u} \frac{\left(\frac{\hbar^2 \tilde{\delta}}{2\mu} + U_2(u) \right)}{\left(\frac{\hbar^2}{2\mu} - U_2(u) \right)} \quad . \qquad (20)$$

Finally, Eq. (19) can be expressed simply as

$$\left[-\frac{\hbar^2}{2\tilde{\mu}(u)} \; \frac{\delta^2}{\delta u^2} + \tilde{U}_n(u) - E \right] \phi(u) = 0 \quad , \qquad (21)$$

where $\tilde{\mu}(u)$ the effective reduced mass, ERM, and U_n, the effective potential barrier, EPB, explicitly read

$$\tilde{\mu}(u) = \frac{\mu(u)}{1 - \frac{2\mu(u)}{\hbar^2} U_2(u)} \qquad (22)$$

and

$$\tilde{U}_n(u) = V(u,0) + \xi_n(u) + U_n(u) \quad . \qquad (23)$$

The asymptotic behaviour of these quantities can now be expressed as

$$\lim_{u \to \pm\infty} \tilde{\mu}(u) = \mu^{\pm}$$

and

$$\lim_{u \to \pm\infty} \tilde{U}_n(u) = U^{\pm} \quad . \qquad (24)$$

The corresponding dimensional scattering equation in the asymptotic regions therefore becomes

$$\left[- \frac{\hbar^2}{2\mu^{\pm}} \frac{\partial^2}{\partial u^2} + U(u) - E \right] \phi_0(u) = 0 \quad . \qquad (25)$$

Evidently, it is to be noted that the effect of the interchannel interaction is contained in both the EPB $\tilde{U}_n(u)$ and ERM $\tilde{\mu}(u)$ which, in general, are complex valued in view of the fact that the kernel $U(u,u')$ is assumed to be a complex optical potential.

Furthermore, the interaction moments $U_n(u)$ vanish as $u \to \pm\infty$ and consequently the EPB also vanishes, while the ERM becomes constant.

Asymptoticaly, for $u \to \pm\infty$, Eq. (25) can be expressed as a linear combination of incoming and outgoing plane waves. More precisely, the asymptotic solution corresponding to the entrance channel is

$$\lim_{u \to -\infty} \phi_0 = a_r^+ \exp\left(ik_n^+ u\right) + a_r^- \exp\left(-ik_n^- u\right) \quad , \qquad (26)$$

while in the exit channel these are only outgoing waves, that is to say

$$\lim_{u \to \infty} \phi_0 = a_p^+ \exp\left(i k_n u\right) \quad , \qquad (27)$$

where $k_n^{\pm}$ denotes the channel wave number

$$k_n^{\pm} = \sqrt{\frac{2\mu^{\pm}}{\hbar^2} \left(E - \xi_n^{\pm} - V^{\pm} \right)} \quad . \qquad (28)$$

It is to be noted at this point, that the penetrability through the EPB $U_n(u)$ is simply the ration of the transmitted flux to the incident one, namely, the modulus square of the scattering matrix element, i.e.

$$P(E) = |S|^2 = \frac{k_n^+}{k_n^-} \left| \frac{a_p^+}{a_p^-} \right|^2 \quad . \qquad (29)$$

This last expression will be very useful in calculating the penetrability factor with the eventual purpose of evaluating the reaction rate constant.

Concluding Remarks

It has been shown here that by employing the optical model approximation [3], it is possible to decouple the channel coupled equation into an integro-differential equation. Such an equation could be further reduced to an equivalent differential equation in the frame of the effective mass approximation.

This equivalent differential equation has been provided with an effective potential energy barrier and an effective reduced mass that may be complex.

Further, and more important, the penetrability factor through the effective potential barrier has been identified as the modulus square of the scattering matrix element.

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