Time-dependent wave packet study of non-adiabatic transitions in a A+BC type reaction

The non-adiabatic dynamics of the present system is studied using wave packet methods. The time-dependent Schrödinger equation is written as

$$i\hbar\frac{d\Psi}{dt} = \hat{H}\Psi. \tag{1}$$

$$= -\frac{\hbar^2}{2\mu}\frac{d^2\Psi}{dx^2} + \hat{V}\Psi. \tag{2}$$

Here $\hat{H}$ is the Hamiltonian operator $(\hat{T} + \hat{V})$ for the system. V is the potential matrix in the diabatic representation and is given as

$$V = \begin{pmatrix} V_{11} & V_{12} \\ V_{21} & V_{22} \end{pmatrix}. \tag{3}$$

μ is the reduced mass of the system and is equal to 3474.057. The solution of the equation 2 can be written as

$$\Psi(t) = exp(-i\hat{H}t/\hbar)\ \Psi(t=0), \tag{4}$$

where $\Psi(t=0)$ is the initial wave packet vector. Ψ is written as

$$\Psi = \begin{pmatrix} \psi_1(x;t) \\ \psi_2(x;t) \end{pmatrix}.$$

ψ_1 and ψ_2 correspond to the wave packets in the ground and excited states, respectively.

A. Initial wave packet

The initial wave packet is a normalised Gaussian

$$\psi_{[1,2]}(x;0) = \left(\frac{1}{2\pi\sigma^2}\right)^{1/4} e^{(-\beta(x-x_0)^2)} \times e^{(ip_0\ (x-x_0))},\ p_0 = -\sqrt{2\mu\ (0.029 - V_{11})}. \tag{5}$$

In this case, the wave packet is located in the state 1. Hence, $\psi_{[2,1]}(x;0) = 0$. An equidistant grid of 2048 points ranging from -45 to 45 is to be used. The other Gaussian parameters are σ =0.3, $\beta = 1/(4.0\sigma^2)$ and $x_0 = 9.0$.

B. Potentials and Coupling

The potentials (V_{11} and V_{22}) are calculated from $V_1^{ad}(x)$ and $V_2^{ad}(x)$.

$$V_1^{ad}(x) = \frac{V_1\ e^{\beta_1\ (x-x_1)}}{(1+e^{\beta_1\ (x-x_1)})^2} + \frac{V_2\ e^{\beta_1\ (x-x_1)}}{(1+e^{\beta_1\ (x-x_1)})}. \tag{6}$$

Here V_1 = 4.0167971782296 $\times$ 10^{-2}, β_1 = 5.5, x_1 = -4.364721325998 $\times$ 10^{-2}, and V_2 = 4.79833373 $\times$ 10^{-3}.

The potential function for the excited state adiabatic curve is of the form

$$V_2^{ad}(x) = V_{asym} - \frac{V_3\ e^{\beta_2\ (x-x_2)}}{(1+e^{\beta_2\ (x-x_2)})^2} - \frac{V_4\ e^{\beta_2\ (x-x_2)}}{(1+e^{\beta_2\ (x-x_2)})} - \frac{V_5\ e^{\beta_3\ (x-x_3)}}{(1+e^{\beta_3\ (x-x_3)})^2} - V_{lower} \tag{7}$$

Here V_{asym} = 3.61196179 $\times$ 10^{-1}, V_3 = 9.8998917754 $\times$ 10^{-1}, β_2 = 4.9818195151, x_2 = 5.0012635420 $\times$ 10^{-2}, V_4 = 1.122019 $\times$ 10^{-2}, V_5 = 7.9781762366 $\times$ 10^{-1}, β_3 = 2.3471780470, V_{lower} = 0.0 and x_3 = -7.6042693477 $\times$ 10^{-1}.
The corresponding diabatic potential energy curves are given by

$$V_{11}(x) = (1-f)V_1^{ad} + fV_2^{ad} \tag{8}$$

and

$$V_{22}(x) = fV_1^{ad} + (1-f)V_2^{ad}. \tag{9}$$

The diabatic coupling is modeled by the following function,

$$V_{12}(x) = -\sqrt{f(1-f)}\left(V_2^{ad} - V_1^{ad}\right) \tag{10}$$

where

$$f(x) = \frac{1}{2}\left[1 - tanh(\beta_4(x-x_4))\right] \tag{11}$$

Here β_4 = 1.0487590725 and x_4 = 8.1790045179 $\times$ 10^{-1}.

C. Propagation

Propagation will be carried out using the split-operator which you have used already in the previous home assignment. Use dt = 8 au. Propagate for 8000 au of total time, i.e. total

1000 steps. In the split-operator method, the exponential of the Hamiltonian operator is approximated as

$$exp\ (-i\hat{H}\Delta t/\hbar) = exp\ (-i\hat{V}\Delta t/2\hbar) exp\ (-i\hat{T}\Delta t/\hbar) exp\ (-i\hat{V}\Delta t/2\hbar). \tag{12}$$

The potential matrix in Eq. 3 can be re-written as

$$V = \begin{pmatrix} V_{11} & 0 \\ 0 & V_{22} \end{pmatrix} + V_{12} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}. \tag{13}$$

This leads to further splitting of the potential operator as,

$$e^{-i\hat{V}\Delta t/2\hbar} = e^{-i\begin{pmatrix} V_{11} & 0 \\ 0 & V_{22} \end{pmatrix}\Delta t/4\hbar} \times e^{-iV_{12}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\Delta t/2\hbar} \times e^{-i\begin{pmatrix} V_{11} & 0 \\ 0 & V_{22} \end{pmatrix}\Delta t/4\hbar}. \tag{14}$$

The exponential part containing the off-diagonal elements is further written as

$$e^{-iV_{12}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\Delta t/2\hbar} = \begin{pmatrix} cos(V_{12}\Delta t/2\hbar) & -i\ sin(V_{12}\Delta t/2\hbar) \\ -i\ sin(V_{12}\Delta t/2\hbar) & cos(V_{12}\Delta t/2\hbar) \end{pmatrix}. \tag{15}$$

Hence, the operations of the exponential containing the potential operator is carried out in three steps as shown in Eq. 14.

The action of radial kinetic energy operator is evaluated by Fourier transformation. We can use either discrete FT or fast FT. As we have seen, the discrete FT takes a lot longer. Hence, we will use the FFT in the present problem. At first the wave function is transformed into momentum space representation by doing forward FFT and multiplied with $e^{-ip^2\Delta t/2\mu\hbar}$. Then the wave function is transformed back to spatial representation by doing reverse FFT.

It is necessary to damp the wave packet after a certain distance in both the channels to avoid the unwanted reflection from the grid ending. For this purpose a sine damping function is multiplied with the wave function at each time step, which has the following form

$$D(X) = sin\left[\frac{\pi(X_{\text{mask}} + \Delta X_{\text{mask}} - X)}{2\Delta X_{\text{mask}}}\right] \qquad X \geq X_{\text{mask}}, \tag{16}$$

where $\Delta X_{\text{mask}} = (X_{\text{max}} - X_{\text{mask}})$ is the width of the damping region and X_{mask} is the starting point of the damping function. Use X_{mask} = 10 on the right side and X_{mask} = -30 on the left side.

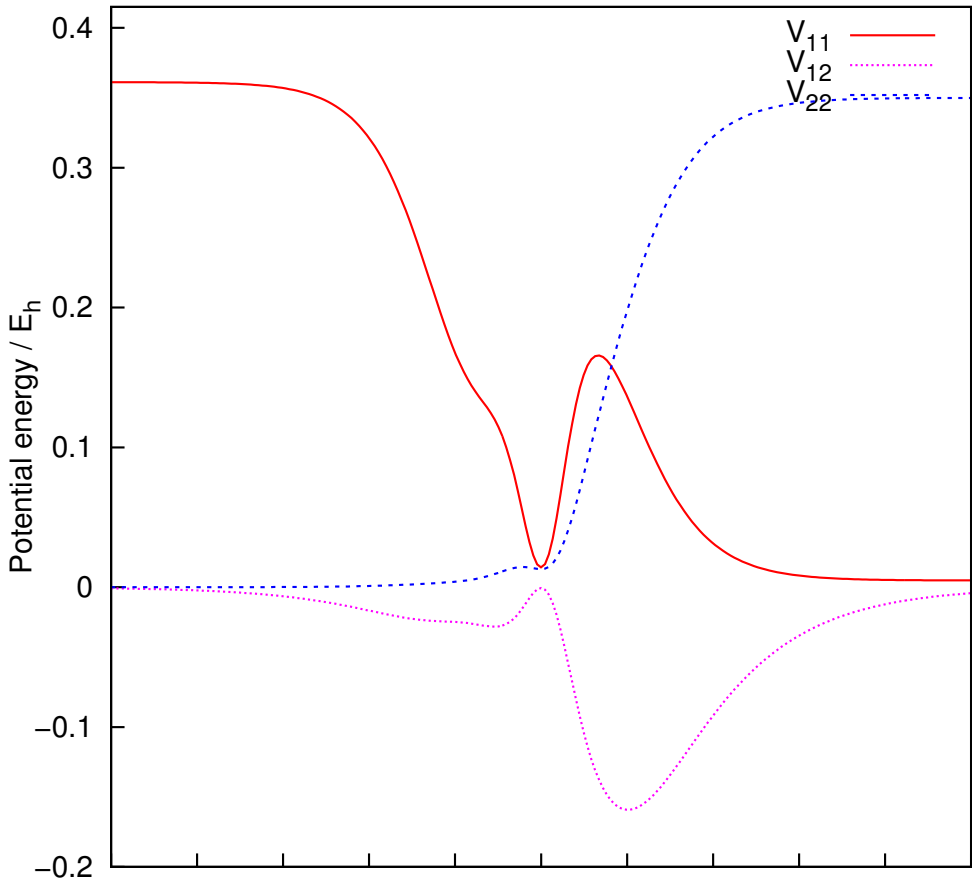

FIG. 1. The two potentials and the coupling.

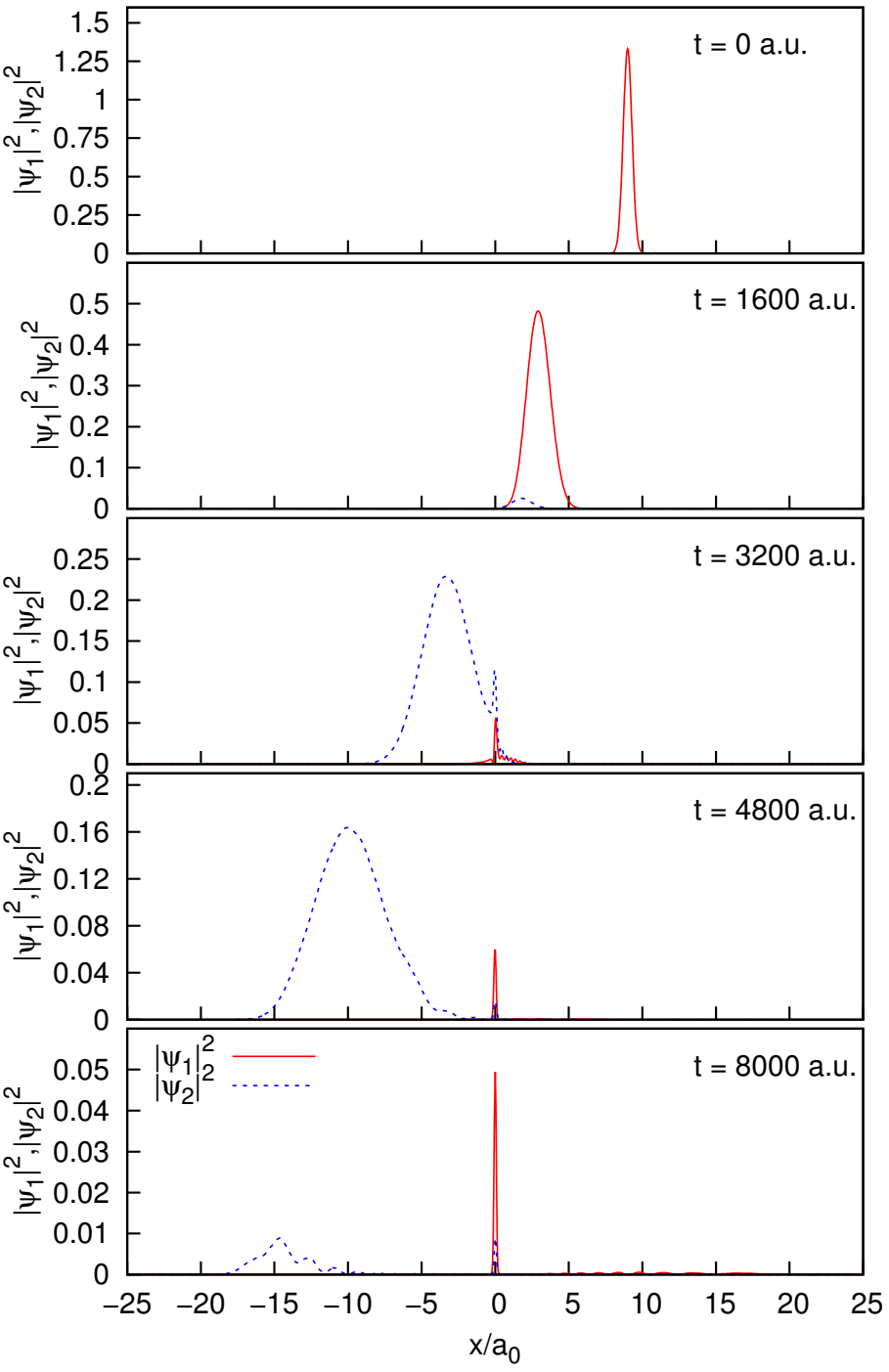

FIG. 2. Wavepackets are different time steps, on both the surfaces.

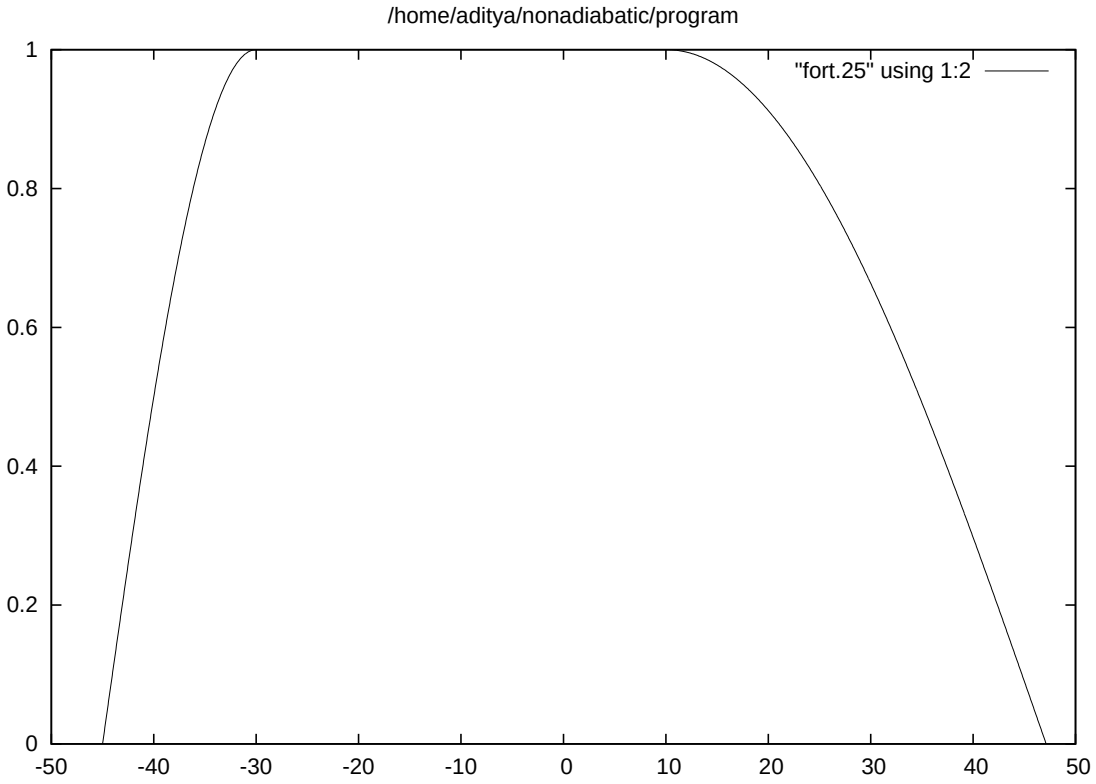

FIG. 3. Damping function.

Derivation of Equation 15

$$\sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \tag{17}$$

Power series expansion of exponential function (ϕ is a real number):

$$e^{i\phi\sigma_1} = \sum_{n=0}^{\infty} \frac{i\phi^n}{n!}\sigma_1^n \tag{18}$$

As it is known

$$\sigma_1^2 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}^2 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = \text{identity operator.} \tag{19}$$

Thus the following can be written,

$$\sigma_1^{2n} = 1 \text{ and } \sigma_1^{2n+1} = \sigma_1. \tag{20}$$

Hence, the following can be written by separating the even and odd terms,

$$e^{i\phi\sigma_1} = \sum_{n=0}^{\infty} \frac{i\phi^{2n}}{2n!}\sigma_1^{2n} + \sum_{n=0}^{\infty} \frac{i\phi^{2n+1}}{(2n+1)!}\sigma_1^{2n+1}. \tag{21}$$

$$e^{i\phi\sigma_1} = 1\sum_{n=0}^{\infty}(-1)^n\frac{\phi^{2n}}{2n!} + i\sigma_1\sum_{n=0}^{\infty}(-1)^n\frac{\phi^{2n+1}}{(2n+1)!} \tag{22}$$

$$= 1\ cos\ \phi + i\sigma_1 sin\ \phi \tag{23}$$

$$= \begin{pmatrix} cos\ \phi & 0 \\ 0 & cos\ \phi \end{pmatrix} + \begin{pmatrix} 0 & i\ sin\ \phi \\ i\ sin\ \phi & 0 \end{pmatrix} \tag{24}$$

$$= \begin{pmatrix} cos\ \phi & i\ sin\ \phi \\ i\ sin\ \phi & cos\ \phi \end{pmatrix} \tag{25}$$