A Toy Model For Electron Transfer

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I. INTRODUCTION

When two atomes or molecules collide with each other, electrones might be transfered from one to another. Sometimes the electron transfer means the electronic state changes from one Potential Energy Surface(PES) to another, as shown in fig.1. If initially the electron comes from the nucleus with higher binding energy, after the collision, there should be some probability for the electron to be transfered to another nucleus, as long as the kinetic energy permits. In this situation, non-adiabatic effect plays an important role. Because within the adiabatic approximation, the system will always stay on one PES, no electron transfer will happen.

The whole problem is too complicated to solve exactly. There are quite a few approximation methods proposed, which are computationally affordable. The key points are how to separate the system in to a classical part and a quantum part, and how these two subsystems interact with each other. Usually, the actions of the classical nuclei on the electrons are simple, while how the electrons act on the nuclei are not clear. In this project, two methods are investigated. In the *Ehrenfest* method, the nuclei evolve under an single effective potential. In the *Surface Hopping* method, a stochastic method is used to describe the nuclear motion.

To compare these approximate methods, we proposed a very simple model, and treat the nuclei by exact quantum mechanics. Then the problem becomes solving a time-independent Schrodinger equation. The scattering state we get will give the electron transfer probability. We can compare the results with various approximate methods.

II. DESCRIPTION OF THE MODEL

This toy model is trying to find the electron transfer probability during a collision, as shown in the figure2. In this model, there are two nuclei, they are identifiable. The spin is completely ignored. Initially, the electron is coming with one nucleus, after the collision, there is a possibility for the electron to be transfered to the other nucleus. Assuming the potential between the electron and nuclei are V_1 and V_2 , the potential between the two nuclei is U_1 , the Hamiltonian can be written as :

$$H = \frac{p^2}{2m} + \frac{P_1^2}{2M_1} + \frac{P_2^2}{2M_2} + V_1(r - R_1) + V_2(r - R_2) + U(R_1 + R_2). \tag{1}$$

The potentials V_1 and V_2 are chosen so that only one bound state is relevant. Their bound states can be written as ϕ_1 and ϕ_2:

$$\left(\frac{p^2}{2m} + \frac{P_1^2}{2M_1} + V_1(r - R_1)\right)\phi_1(r - R_1) = E_1\phi(r - R_1), \tag{2}$$

$$\left(\frac{p^2}{2m} + \frac{P_2^2}{2M_2} + V_2(r - R_2)\right)\phi_2(r - R_2) = E_2\phi(r - R_2). \tag{3}$$

To simplify the problem, the initial kinetic energy of the system is small enough, so that electron must bind to one or the other nucleus. That is, there is not enough kinetic energy to ionize the system. Assuming that the electron comes with the left nucleus, after the collision, there are two possibilities: the electron can either go to the right, or go to the left, if the kinetic energy permits. There are a few parameters we can change: the initial kinetic energy, the repulsion distance between the two nuclei, and the binding potential of the electron.

III. COMPUTATIONAL METHODS

A. Full Quantum Mechanical Method

We only want to calculate the scattering eigenstate for this Hamiltonian. The scattering state should have only one incoming component and two outgoing components. The asymptotic form for the scattering solution of the

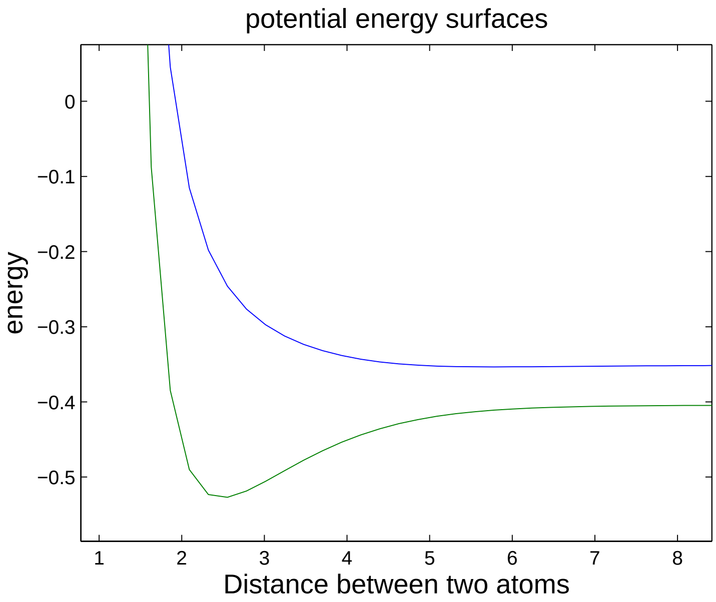

FIG. 1: The schematic potential energy surfaces of the collision process. The lower curve is the bound state. The upper curve is the antibonding state. The two nuclei have slightly different binding energies. At large separation, the adiabatic states are localized atomic orbitals. Thus, electron transfer means change of the potential energy surface.

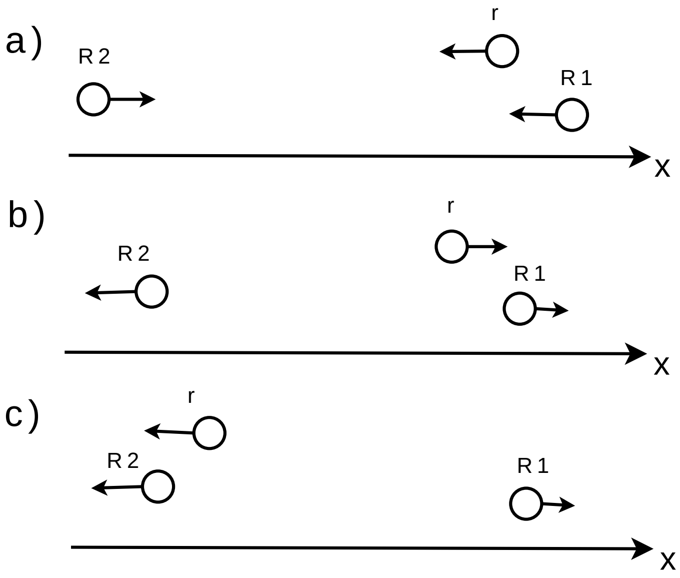

FIG. 2: Schematic illustration of the collision process. (a) For the initial state, an electron comes with the nucleus from the right. (b) For one component of the final state, the electron is reflected. (c) For the other component of the final state, the electron is transferred to the other nucleus.

Hamiltonian(eq.1) at $R1 - R2 \to \infty$ is :

$$\psi = \psi_1 + r(E) \cdot \psi_2 + t(E) \cdot \psi_3. \tag{4}$$

The asymptotic form ($R1 - R2 \to \infty$) for the incoming and outgoing components are

$$\psi_1 = \phi_1(r - R_1) \;\; \exp\left[-ik\frac{mr + M_1R_1}{m + M_1}\right] \exp\left[ikR_2\right], \tag{5}$$

$$\psi_2 = \phi_1(r - R_1) \;\; \exp\left[ik\frac{mr + M_1R_1}{m + M_1}\right] \exp\left[-ikR_2\right], \tag{6}$$

$$\psi_3 = \phi_2(r - R_2) \;\; \exp\left[ik'R_1\right] \exp\left[-ik'\frac{mr + M_2R_2}{m + M_2}\right]. \tag{7}$$

Here

$$\hbar k = \sqrt{(E - E_1) \Big/ \left(\frac{1}{2(m + M_1)} + \frac{1}{2M_2}\right)}, \tag{8}$$

$$\hbar k' = \sqrt{(E - E_2) \Big/ \left(\frac{1}{2(m + M_2)} + \frac{1}{2M_1}\right)}. \tag{9}$$

The coefficients $r(E)$ and $t(E)$ are for reflection and transmission. According to the definition of the probability flux (note: this is the definition of single particle probability flux, in our case, there are three particles)

$$j = \frac{\hbar}{2mi}\left(\psi^* \Delta\psi - \psi\Delta\psi^*\right). \tag{10}$$

The reflection and transmisson probabilities $R(E)$ and $T(E)$, and conservation of probability flux relation, are

$$R(E) = |r(E)|^2, \tag{11}$$

$$T(E) = |t(E)|^2 \cdot \frac{k\,'}{k}, \tag{12}$$

$$R(E) + T(E) = 1, \tag{13}$$

respectively.

B. Ehrenfest Method

We prefer to call this method "the average classical trajectory method." We assume that a single Newtonian trajectory $R(T)$ describes the nuclei. The classical nuclei move on a single effective potential. The effective potential is a self-consistently weighted average of different adiabatic potential energy surfaces. This approach has limitations, especially when the adiabatic potential surfaces are very different. Then the nuclear motion can never be described by a single trajectory. But still it might provide some useful results.

Here is a simplified derivation. The classical nuclear coordinate is R. The total Hamiltonian is

$$H = T_N + H_0(r, R). \tag{14}$$

T_N is the kinetic energy of nuclei. H_0 contains all the electronic part H_{el} and the nuclear potential energy $U_N(R)$. The nuclei evolve as a single trajectory $R(t)$ on an effective potential H_0.

First we construct the electronic wave function. Suppose we have an adiabatic basis $\{\psi_j(r; R)\}$, and H_0 is diagonal on this basis. We assume the existence of an electronic wavefunction $\psi(r; R)$. In full generality, it can be expanded as

$$\psi(r, R(t), t) = \sum c_i(t) \cdot \psi_j(r; R(t)). \tag{15}$$

Put it into $i\hbar\frac{\partial}{\partial t}\psi = H_0\psi$, and project onto ψ_k. We get

$$i\hbar\; \dot{c}_k + i\hbar\sum_j c_j \left\langle \psi_k \left| \frac{\partial}{\partial t} \right| \psi_j \right\rangle = \sum_j c_j \left\langle \psi_k \left| H_0 \right| \psi_j \right\rangle. \tag{16}$$

After making the substitutions:

$$\left\langle \psi_k \left| \frac{\partial}{\partial t} \right| \psi_j \right\rangle = \left\langle \psi_k \left| \frac{\partial}{\partial R} \right| \psi_j \right\rangle \cdot \dot{R} = d_{kj} \cdot \dot{R} \tag{17}$$

$$\langle \psi_k \left| H_0 \right| \psi_j \rangle = V_{kj}, \tag{18}$$

we get

$$i\hbar \, \dot{c}_k = \sum_j \left(V_{kj} - i\hbar \dot{R} \cdot d_{kj} \right) c_j. \tag{19}$$

Note that in the adiabatic representation $\{\psi_j(r;R)\}$, the matrix element $V_{kj}(R)$ is diagonal, and non-adiabatic coupling $d_{kj}(R)$ is anti-symmetric. The "Coupling" matrix d_{kj} plays the role of the leading term in the non-adiabatic coupling. The second order term, which involves the second derivative of R, does not appear here. Usually this is enough.

The trajectory $R(t)$ is still unknown. To calculate the nuclear trajectory, one way is to use the weighted "effective" potential:

$$\overline{V}(R) = \langle \psi_{el} \left| H_0 \right| \psi_{el} \rangle . \tag{20}$$

In the adiabatic representation,

$$\overline{V}(R) = \sum_j |c_j|^2 \cdot E_j(R). \tag{21}$$

Then, Newtonian evolution is used,

$$\ddot{R} = \frac{1}{M_{\text{eff}}} \left(-\frac{\partial \overline{V}}{\partial R} \right). \tag{22}$$

The equations(19)(22) can be integrated together, giving the time dependence of the probabilities $|c_j(t)|^2$ on different surfaces.

C. Surface Hopping Method

The surface hopping method has a few variants, here we only considered the *Fewest Switches* Algorithm proposed by Tully[1]. The argument is that, it is too expensive to treat the nuclei quantum mechanically, but it is over simplified to just considered a single effective potential. SInce the dynamics of the nuclei on different potential energy surfaces may be very different, they need to be treated accordingly. The energy and momentum for each branch must be conserved separately, not just the total energy and momentum.

The surface hopping method achieves this requirement by considering a swarm of trajectories instead of only one trajectory. In this method, the trajectory evolves on only one PES at any particular time, interrupted by random switches to another PES. It is essentially a stochastic method. The nuclear wave function is replaced by a distribution of trajectories; the phase of the nuclear wave function is completely ignored. This might cause some problemes when the coherence of nuclei is important. Surface hopping method should provide better results than the Ehrenfest method. But, it is very expensive, since a large number of trajectories are calculated instead of only one; and turns out not to be always better.

For each trajectory, the electronic wave functions are treated the same way as in the Ehrenfest method. But the nuclear motions are governed by only one PES at a each time. For each time step Δt, the trajectory has a certain probability g_{kj} to hop from its current PES k to another PES j. The g_{kj} must ensure that, for a large number of trajectories, the state population of nuclei approximates the correct one. For the fewest switches algorithm,

$$g_{kj} = \frac{\Delta t b_{jk}}{a_{kk}}, \tag{23}$$

$$\text{where } b_{kj} = \frac{2}{\hbar} \text{Im} \left(a^*_{kj} \cdot V_{kj} \right) - 2\text{Re} \left(a^*_{kj} \dot{R} \cdot d_{kj} \right), \tag{24}$$

$$\text{and } a_{kj} = c_k \cdot c^*_j. \tag{25}$$

In the numerical calculation, at each time step, a random number generator is used to decide if a surface hopping will happen. And if the hopping happened, the kinetic energy of the nuclei is adjusted to conserve the energy and momentum. Thus, in this algorithm, for each branch, the energy and momentum are guaranteed to be conserved.

After running a lot of trajectories, the transfer probability is given by counting how many trajectories are on the excited potential energy surface.

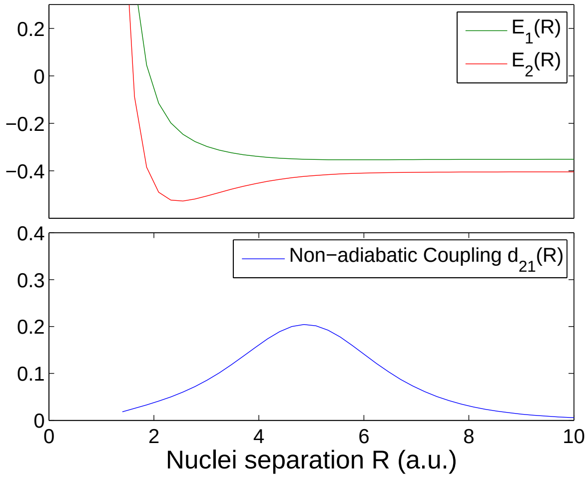

FIG. 3: The calculated Born-Oppenheimer energies and non-adiabaic coupling term. The binding potential for the nuclei are $V_1 = -0.9e^{-|x|}$ and $V_2 = -1.0e^{-|x|}$. The binding energies are -0.3513, -0.4043a.u., respectively. The repulsion between these two nuclei is $1\big/(R/R_0)^6$, with the repulsion parameter $R_0 = 1.5$a.u.. the mass of the nuclei is chosen to be 30 electron masses. The coupling is the strongest around $R = 5a.u.$.

IV. NUMERICAL RESULTS AND DISCUSSION

A. The Approximate Adiabatic Representation

To proceed, we must first calculate the PES and relevant non-adiabatic coupling term. The ideal way is to solve the 1d Schrodinger equation exactly. However, for large nuclear separation, it is hard to solve exactly. Also, it is even harder to calculate the non-adiabatic coupling term, because it involves the derivative of the nuclei coordinates.

Thus, we contruct the approximate adiabatic eigenstates by the linear combination of the atomic eigenstates. In this project, the mass of the nuclei is chosen to be 30 electron masses. The binding potential for the nuclei are $V_1 = -0.9e^{-|x|}$ and $V_2 = -1.0e^{-|x|}$. The binding energies are -0.3513, -0.4043a.u., respectively. The repulsion between these two nuclei is $\frac{1}{(R/R_0)^6}$. The calculated electronic Hamiltonian matrix elements and the non-adiabatic coupling term are shown in fig.3.

To evaluate the accuracy of this approximation, the exact eigenstates are calculated at $R = 2.0a.u.$ for $H_{el} = T_{el} + V_{el}$ (the nuclear repulsion potential $U_N(R)$ is excluded). The exact eigenenergy for ground and excited states are -0.653 and -0.255, the approximate energies are -0.639 and -0.243, the error is about 2% and 5%, respectively. The projection $\langle\psi_{\text{exact}}|\psi_{\text{approxi}}\rangle = 0.99$. For most calculations in this project, the area of interest is $R > 2.0a.u.$, so it is an acceptable approximation. The only problem is that, I don't know the accuracy of the non-adiabatic coupling term. In fig.3, the coupling term is small for very small nuclear separation, I don't know if this is due to the approximation or if it is the correct behavior.

For the Ehrenfest and surface hopping method, only the matrix elements and coupling terms are needed. Details of the electronic wave function are unimportant.

B. Full Quantum Mechanical Method

If two nuclei have different binding potential, as long as the kinetic energy permits, the electron will be transfered, even if the final state has higher energy than the initial state. In the following, we study the case where the electron starts from the lower PES.

A typical exact scattering solution is shown in fig.4. The exact solution correctly reproduced the planewave behavior of each components: electron coming in, reflected, and transferred, as shown in equation(5) to (7). The electron transfer probabilities are calculated for different repulsion parameters(fig.6), and different initial kinetic energies(fig.5). These results are used to compare the various approximate method.

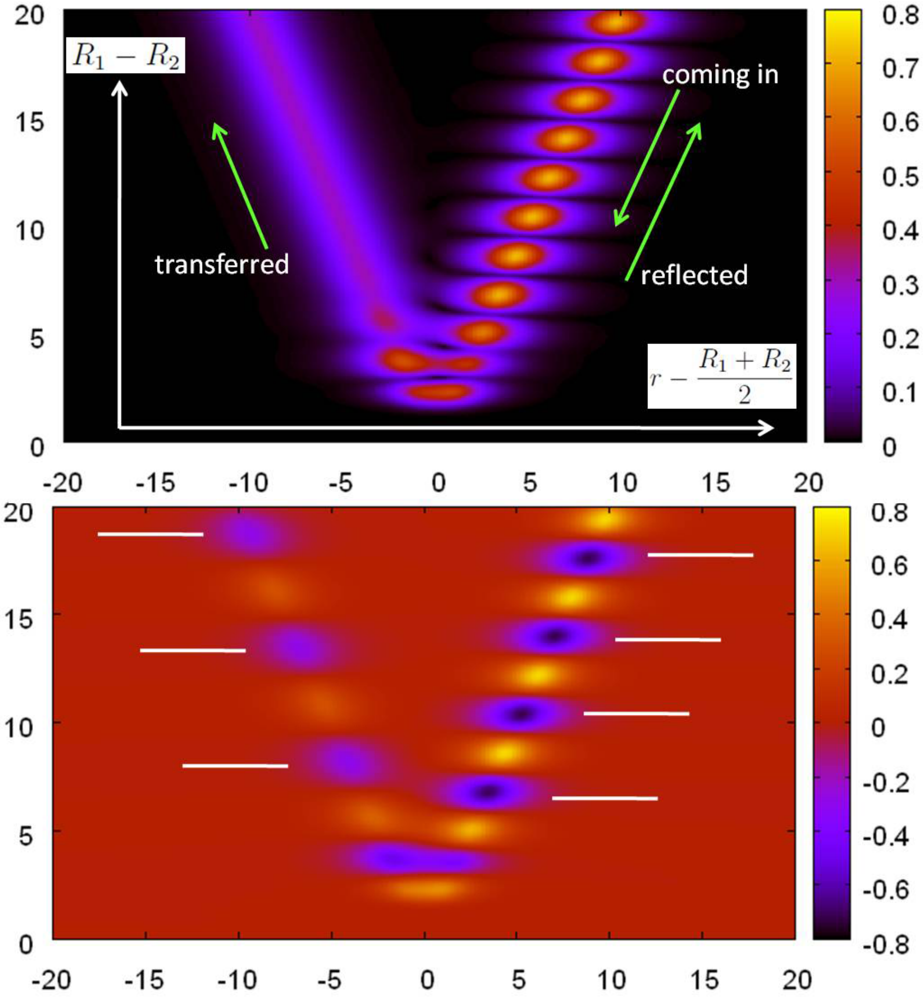

FIG. 4: The absolute value and the real part of an exact solution. The y-axis is the distance between these two nuclei. The x-axis is the distance from the electron to the center of these two nuclei. On the right side, the incoming and out going components interfere with each other, causing the oscillation of the of absolute value. Because these components have different kinetic energies, the periods of the left and right sides are different (illustrated as white lines in the second graph). The parameters here are the same as fig.3, except that the repulsion parameter $R_0 = 1.6a.u.$. The total initial kinetic energy T_0 is $0.10a.u.$, while the binding energies to these two nuclei are -0.3513, -0.4043a.u., respectively.

C. Ehrenfest Method

In the Ehrenfest Method, when integrating the equation, we can get the time dependence of the population distribution and the effective potential(fig.7). Nuclei evolve on this single effective potential. The two physically distinct branches are replaced by a single trajectory with a single value of nuclear kinetic energy which is an average of the actual kinetic energies of the two physical branches.

The comparison with the full quantum mechanical solution are shown in fig.5-6. Generally, it agrees well. But for small kinetic energy, it gives non-zero transfer probability, even when the transfer is forbidden by energy conservation. This is because it only conserves average energy and momentum.

The oscillation in fig.6 is shown in detail in fig.8. For smaller R_0, the system will spend more time in the strong coupling region, the population will oscillate between these two states in time.

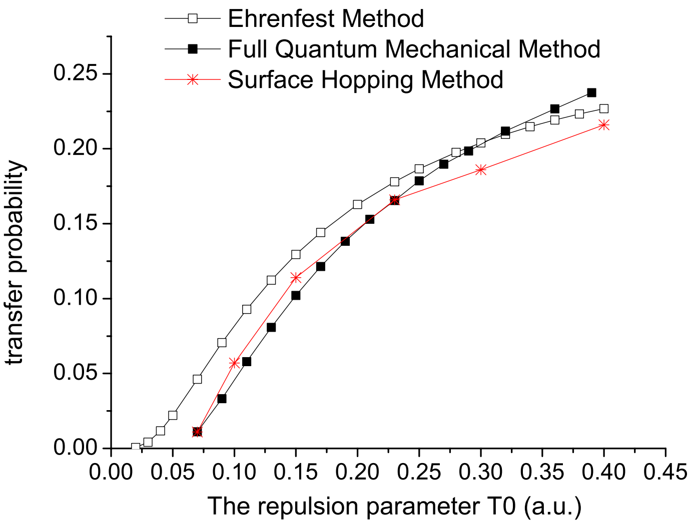

FIG. 5: The electron transfer probability as a function of initial kinetic energy T_0(a.u.). The repulsion parameter for this graph is $R_0 = 4.0(a.u.)$. Other parameters are the same as fig.3. Generally, both Ehrenfest and surface hopping method agree with the exact solution. Note the cutoff around $T_0 = 0.5(a.u.)$, which is the gap between the binding energies of these two nuclei. The Ehrenfest method gives non-zero transfer probability below this energy, where the transfer is forbidden by energy conservation.

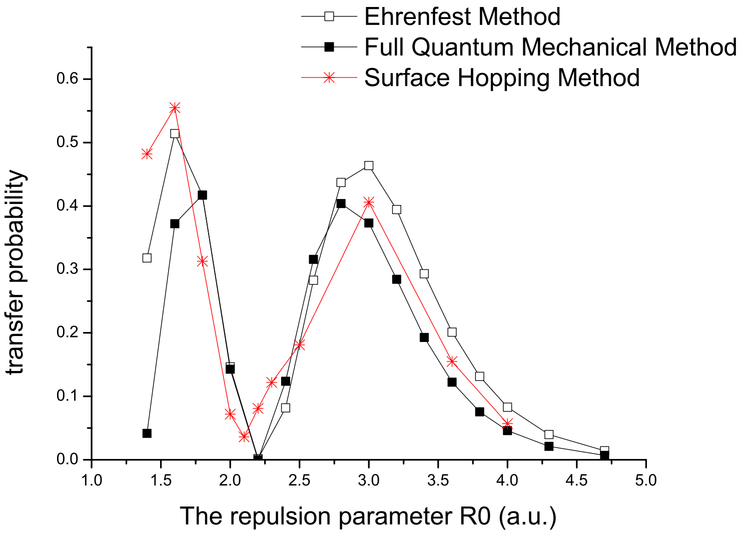

FIG. 6: The electron transfer probability as a function of repulsion parameter R_0. The total initial kinetic energy for this graph is $T_0 = 0.10a.u.$. Other parameters are the same as fig.3. For Ehrenfest and surface hopping method, tt is hard to tell which one is better than the other.

D. Surface Hopping Method

The surface hopping method is very expensive. A large number of trajectories is needed to get a statistically significant results. The convergence is very slow, as shown in fig.9. In this calculation, 10000 trajectories are calculated, giving the transfer probability to be 0.057 ± 0.003. Thus, if the number of trajectories is not large enough, the results are really not that accurate.

The consistency is also a problem for the surface hopping method. We use a swarm of trajectories to describe the nuclei, and a wave function to describe the electron. There are two ways to get the population distribution. One way

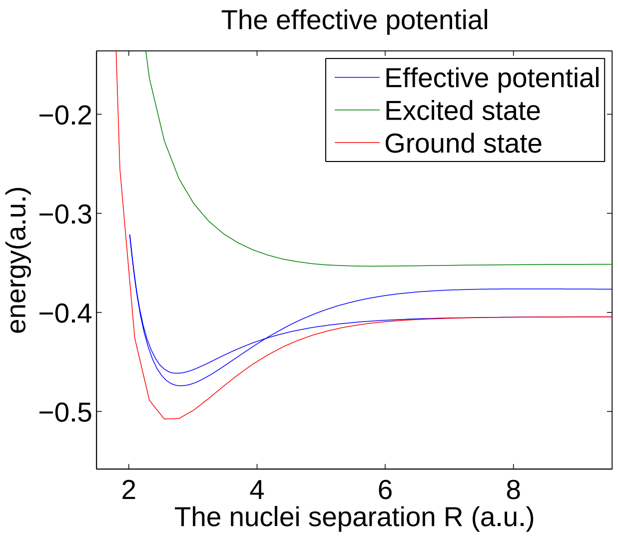

FIG. 7: The effective potential relative to the ground and effective PES. It is calculated self-consistently. The two physically distinct branches are replaced by a single trajectory.

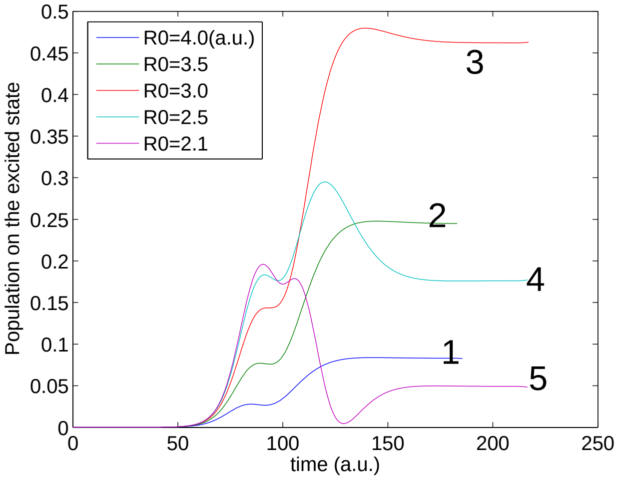

FIG. 8: The time dependence of the population on the excited state. Number 1 to 5 corresponding to decreasing R_0. The population oscillates between the ground and excited states.

is to calculate the ratio of trajectories that are on the upper PES. The other way is to average the probabilities on the upper PES from the electronic wave function for all trajectories. The consistency requires that the population distribution of the trajectory must equal to the average state population of the electron. This is not accurately obeyed, as shown in fig.10. Surprisingly, we found that the consistancy is not related to the accuracy of the results.

Actually, because of the “frustrated” hops (hopping forbidden by the energy conservation), the consistency is not guaranteed. Also, there are issues about the decoherence effect. Thus, it is really hard to tell when surface hopping method is better than the Ehrenfest method(see fig.5 and fig.6).

V. CONCLUSION

In this project, a simple toy model is investigated. The results from various approximate methods are compared with the exact solution. Generally, the surface hopping method guarantees the energy and momentum conservation. The Ehrenfest method is easy to calculated. In our model, for small kinetic energy and weak coupling, the surface

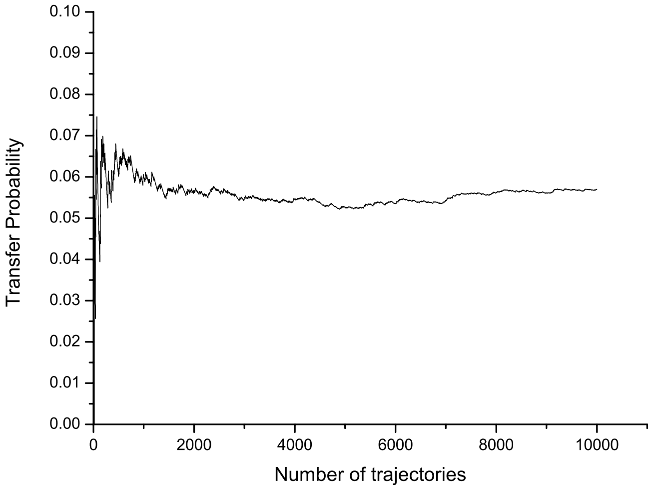

FIG. 9: The transfer probability calculated from the collection of the trajectories. KE= $0.10(a.u.)$, $R_0 = 4.0(a.u.)$. It converges slowly.

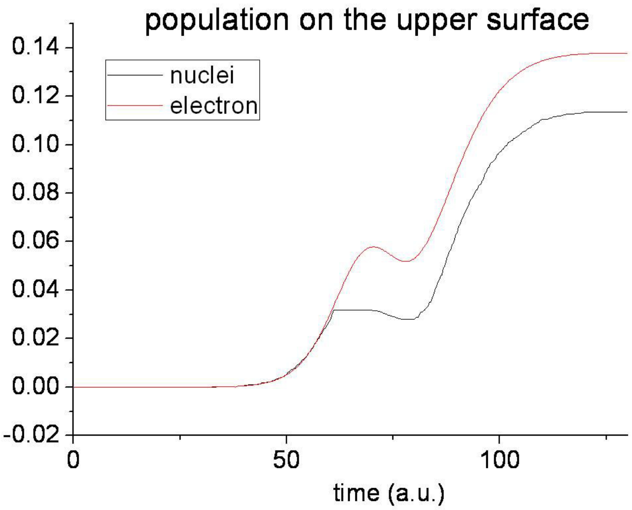

FIG. 10: The state population of the trajectories and the electrons on the excited PES. ($KE = 0.10, R_0 = 1.5(a.u.)$). They are different, which causes the consistency problem.

hopping method gives much better results. But for general cases, we don't know which one is better.

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[1] J. C. Tully, *Molecule Dynamics With Electronic Transitions*, J.Chem.Phys. **93**, 2 (1990).

APPENDIX A: FULL QUANTUM MECHANICAL METHOD

The general process is as follows: first, by setting up a coordinate transformation, this problem can be reduced to a 2D partial differential equation. With the known asymptotic form of the solution, proper boundary conditions can be constructed. By using a standard finite element method, I can calculate the solution of this equation, then extract the coefficients $r(E)$ and $t(E)$.

1. Coordinate Transformation

A coordinate transformation will separate the center of mass coordinate of the system, reducing the problem into a 2D equation.

$$x = \sqrt{\frac{2m(M_1+M_2)}{m+M_1+M_2}}\left(r - \frac{M_1R_1+M_2R_2}{M_1+M_2}\right), \tag{A1}$$

$$y = \sqrt{\frac{2M_1M_2}{M_1+M_2}}\left(R_1 - R_2\right), \tag{A2}$$

$$z = \sqrt{2(m+M_1+M_2)}\left(\frac{mr+M_1R_1+M_2R_2}{m+M_1+M_2}\right). \tag{A3}$$

Note that the x coordinate is proportional to the distance between the electron and center of the two nuclei, the y coordinate is proportional to the distance between the two nuclei, the z coordinate is proportional to the center of mass coordinate of the whole system. The scaling factors in x, y, z make the kinetic energy operator a Laplacian operator. The unit for x, y, z is $\sqrt{mass}\cdot distance$. Under this transformation, the Hamiltonian becomes

$$\begin{aligned} H = & -\hbar^2\left(\frac{\partial^2}{\partial^2 x}+\frac{\partial^2}{\partial^2 y}+\frac{\partial^2}{\partial^2 z}\right) \\ & + V(\sqrt{\frac{m+M_1+M_2}{2m(M_1+M_2)}}\,x - \sqrt{\frac{M_2}{2M_1(M_1+M_2)}}\,y) \\ & + V(\sqrt{\frac{m+M_1+M_2}{2m(M_1+M_2)}}\,x + \sqrt{\frac{M_1}{2M_2(M_1+M_2)}}\,y) \\ & + U(\sqrt{\frac{M_1+M_2}{2M_2M_2}}\,y). \end{aligned} \tag{A4}$$

The asymptotic form of the solution becomes

$$\psi = \psi_1 + r(E)\cdot\psi_2 + t(E)\cdot\psi_3. \tag{A5}$$

Where

$$\begin{aligned} \psi_1 = & \phi_1\left(\sqrt{\frac{m+M_1+M_2}{2m(M_1+M_2)}}\,x - \sqrt{\frac{M_2}{2M_1(M_1+M_2)}}\,y\right) \\ & \times exp\left[-ik\times\sqrt{\frac{(m+M_1+M_2)m}{2(M_1+M_2)}}\frac{1}{m+M_1}\times\left(x+\sqrt{\frac{(m+M_1+M_2)M_1}{mM_2}}\,y\right)\right] \\ = & \phi_1\left(\sqrt{\frac{m+M_1+M_2}{2m(M_1+M_2)}}\,x - \sqrt{\frac{M_2}{2M_1(M_1+M_2)}}\,y\right)\times exp\left[\,-i\vec{q}\cdot\vec{r}\,\right], \end{aligned} \tag{A6}$$

$$\begin{aligned} \psi_2 = & \phi_1\left(\sqrt{\frac{m+M_1+M_2}{2m(M_1+M_2)}}\,x - \sqrt{\frac{M_2}{2M_1(M_1+M_2)}}\,y\right) \\ & \times exp\left[ik\times\sqrt{\frac{(m+M_1+M_2)m}{2(M_1+M_2)}}\frac{1}{m+M_1}\times\left(x+\sqrt{\frac{(m+M_1+M_2)M_1}{mM_2}}\,y\right)\right] \\ = & \phi_1\left(\sqrt{\frac{m+M_1+M_2}{2m(M_1+M_2)}}\,x - \sqrt{\frac{M_2}{2M_1(M_1+M_2)}}\,y\right)\times exp\left[\,i\vec{q}\cdot\vec{r}\,\right], \end{aligned} \tag{A7}$$

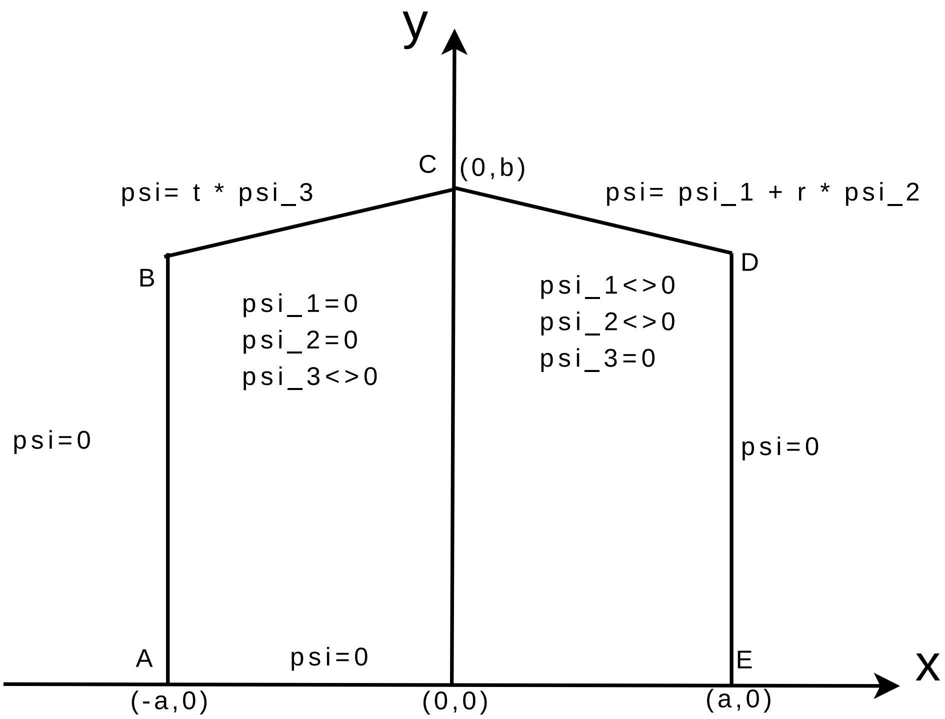

FIG. 11: the region boundary is marked as ABCDE. The parameters a and b should be large enough that the asymptotic form is accurately obtained

$$\begin{aligned}\psi_3 &= \phi_2\left(\sqrt{\frac{m+M_1+M_2}{2m(M_1+M_2)}}\,x+\sqrt{\frac{M_1}{2M_2(M_1+M_2)}}\,y\right)\\ &\times exp\left[-ik'\times\sqrt{\frac{(m+M_1+M_2)m}{2(M_1+M_2)}}\,\frac{1}{m+M_2}\times\left(x-\sqrt{\frac{(m+M_1+M_2)M_2}{mM_1}}\,y\right)\right]\\ &= \phi_2\left(\sqrt{\frac{m+M_1+M_2}{2m(M_1+M_2)}}\,x+\sqrt{\frac{M_1}{2M_2(M_1+M_2)}}\,y\right)\times exp\left[\,-i\overrightarrow{q}'\cdot\overrightarrow{r}\,\right].\end{aligned} \tag{A8}$$

The $\overrightarrow{q}$ and $\overrightarrow{q'}$ are just wave vectors in the new coordinates.

2. Construction of The Boundary Conditions

In the asymptotic form $\psi=\psi_1+r(E)\cdot\psi_2+t(E)\cdot\psi_3$, there are two unknowns. However, the boundary conditions can be constructed in a way that these two unknowns do not appear.

Considered the region shown in figure.11. On boundary AE, $y\rightarrow 0$, the two nuclei overlap with each other. If the repulsion between them is huge, then $\psi\rightarrow 0$. On boundary AB and DE, if parameter a is large enough, which means the electron is far away from the nuclei, we also get $\psi\rightarrow 0$.

On boundary CD, as shown on figure2(a).2(b), the electron is far away from the left nucleus, $r-R_2$ is large, so $\phi_3(r-R_2)\rightarrow 0$, which means $\psi_3\rightarrow 0$, if we choose CD as $y=-\sqrt{\frac{mM_2}{(m+M_1+M_2)M_1}}\,x+b$, then, on CD, ψ becomes

$$\psi|_{CD}\rightarrow\psi_1+r(E)\psi_2 \tag{A9}$$

$$=\phi_1(\sqrt{\frac{m+M_1+M_2}{2m(M_1+M_2)}}\,x-\sqrt{\frac{M_2}{2M_1(M_1+M_2)}}\,y)\times\left(e^{-iq_yb}+r(E)e^{iq_yb}\right) \tag{A10}$$

$$=\phi_1(...x-...y)\times C(b,E). \tag{A11}$$

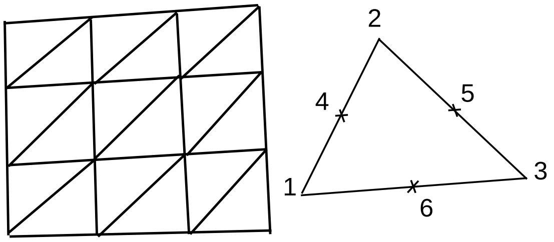

FIG. 12: An example of decomposition of the domain. In our case the domain shown in fig11 is a little more irregular, but it can be decomposed into triangles in a similar way. Each triangle is a 6-nodes quadratic element, with half of its nodes located at the center of the edges.

The coefficient $C(b, E)$ is a constant depending on b and E, it can be assigned as 1, because the wave function can be scaled by an arbitrary constant. Thus, on CD, the boundary values are known.

On boundary BC, similar to CD, the electron is far away from the right nucleus, $\phi_1(r - R_1) \rightarrow 0$. This leads to $\psi_1 \rightarrow 0, \psi_2 \rightarrow 0$, and ψ becomes

$$\psi|_{BC} \rightarrow t(E) \cdot \psi_3. \tag{A12}$$

Choose BC as $y = \sqrt{\frac{mM_1}{(m+M_1+M_2)M_2}}\ x + b$, then, on BC

$$\begin{aligned} \frac{\partial \psi}{\partial \overrightarrow{n}} &\rightarrow t(E) \frac{\partial \psi_3}{\partial \overrightarrow{n}} && \text{(A13)} \\ &= t(E)\psi_3 \times (ik') \left(\frac{m + M_1 + M_2}{m + M_2} \sqrt{\frac{M_2}{2(M_1 + M_2)M_1}} \right) && \text{(A14)} \\ &= \psi \times (ik') \left(\frac{m + M_1 + M_2}{m + M_2} \sqrt{\frac{M_2}{2(M_1 + M_2)M_1}} \right) && \text{(A15)} \\ &= D(E) \times \psi. && \text{(A16)} \end{aligned}$$

So, on BC, the value of the normal logarithmic derivitive $(\partial\psi/\partial\overrightarrow{n})/\psi$ is known.

In conclusion, on $AB, DE, AE,\ \psi \rightarrow 0$, on BC, $\frac{\partial \psi}{\partial \overrightarrow{n}} \rightarrow D(E) \times \psi$, on CD, $\psi = \phi_1(...x - ...y) \times C(b, E)$. For a definite energy E, $D(E)$ is fixed, only $C(b, E)$ is unknown, but it can be set to any constant like 1.

3. Discretization of The Differential Equation

The partial differential equation is discretized by a standard finite element method. Here are some details in the discretization process. First, the domain is decomposed into triangles shown in fig12. Each triangle have six nodes. The nodes are shared by the adjacent triangles. (Normally, 3-nodes triangle is used. But in this calculation, 6-nodes triangle is much better.) The values of $\psi(r)$ on each nodes form an unknown vector ψ_i, i is used to label each nodes on the entire domain. By choosing a proper set of basis $\{v_i(r)\}$, $\psi(r)$ can be written as

$$\psi(r) \approx \sum_i \psi_i \cdot v_i(r) \tag{A17}$$

$$\text{apparently, } v_i(r) \text{ satisfy : } v_i(r_j) = \delta_{ij}. \tag{A18}$$

In our calculation, the basis function $v_i(r)$ is quadratic on each triangles. By Eq(A18), they can be uniquely decided. Thus, $\sum_i \psi_i \cdot v_i(r)$ is unique, continuous and piecewise-quadratic throughout the domain.

The differential equation is discretized by projecting on to each basis function, starting from

$$\nabla^2\ \psi(r) + u(r)\ \psi(r) = 0, \tag{A19}$$

project on to $v_i(r)$

$$\iint v_i\ \nabla^2\ \psi + \iint v_i\ u\ \psi = 0, \tag{A20}$$

apply the Gauss divergence theorem

$$\oint v_i \, \frac{\partial \psi}{\partial \overrightarrow{n}} - \iint \nabla v_i \cdot \nabla \psi + \iint v_i \; u \; \psi = 0, \tag{A21}$$

put in the discretization form of $\psi(r) = \sum_j \psi_j \cdot v_j(r)$,

$$\oint v_i \, \frac{\partial \psi}{\partial \overrightarrow{n}} - \left(\iint \nabla v_i \cdot \nabla v_j \right) \cdot \psi_j + \left(\iint v_i \; u \; v_j \right) \cdot \psi_j = 0 \;\; \text{(sum over j)}. \tag{A22}$$

The exact form of all $v_i(r)$ are known. By put in the boundary conditions, finally we get

$$\sum_j A_{ij} \cdot \psi_j = b_i. \tag{A23}$$

This is the discretizaton process.

4. Numerical Solution and Calculation of $R(E)$ and $T(E)$

In our calculation, typically, the linear equation eq(A23) contains half million unknowns, the sparse matrix A_{ij} contains ten million non-zeros. This equation is solved by direct LU decomposition method using PETSC and SuperLU on Seawulf Cluster.

Fig13 is a typical solution of this equation, with the potenital between the nuclus and the electron as $-e^{-|x|}$. and the potential between the nuclei as $\frac{1}{(r/R_0)^6}$. Both nuclei have the same mass, 30 atomic unit. The total kinetic energy is 0.1 Hartree, which is much lower than the gap between the ground state and excited state.

When the solution is ready, coefficients $r(E)$ and $t(E)$ can be calculated by fitting the solution to the asymtotic form as shown in fig13. Because of the scaling factor when we deal with the boundary condition on CD in fig11, the actual solution we get is

$$\psi = \frac{\psi_1 + r(E) \cdot \psi_2 + t(E) \cdot \psi_3}{e^{-iq_y b} + r(E) e^{iq_y b}}. \tag{A24}$$

In the top right area in fig11, the solution is

$$\begin{aligned} \psi_{\text{asymptotic}} &= \frac{\psi_1 + r(E) \cdot \psi_2}{e^{-iq_y b} + r(E) e^{iq_y b}} \\ &= \phi_1(...x - ...y) \times \frac{exp\left[-i\overrightarrow{q} \cdot \overrightarrow{r}\right] + r(E) exp\left[i\overrightarrow{q} \cdot \overrightarrow{r}\right]}{exp\left[-iq_y b\right] + r(E) exp\left[iq_y b\right]}. \end{aligned} \tag{A25}$$

The only parameter that needs to be fitted is r(E). (I also fit/relax the $\overrightarrow{q}$. It is proportional to the momentum, because $\overrightarrow{q}$ is related to the phase in eq(A25). A very small difference will result in huge error. It turns out that if I relax $\overrightarrow{q}$ a little, usually less than 1% , the results can be improved a lot). The fitting is done by minimizing the sum $\sum_i |\psi_{\text{asymptotic}} - \psi_{\text{calculated}}|^2$ in the top right area in fig11. The minimization is done by using the multidimensional minimization function in the GSL library. The transfer amplitude $t(E)$ can be calculated in a similar way.

Typically, the differences between the calculated solution and the asymptotic form can be kept under 1%, namely $max(|\psi_{\text{calculated}}(r) - \psi_{\text{asymptotic}}(r)|) \;/\; max(|\psi_{\text{calculated}}(r)|) < 1\%$. Both the magnitude and phase of $r(E)$ and $t(E)$ can be calculated, however, the magnitude is more stable, while the phase is less stable.

When $r(E)$ and $t(E)$ are known, the calculation of reflection and transmission probability $R(E)$ and $T(E)$ is straightforwad using eq(11)(12). And the conservation law $R + T = 1$ can be tested.

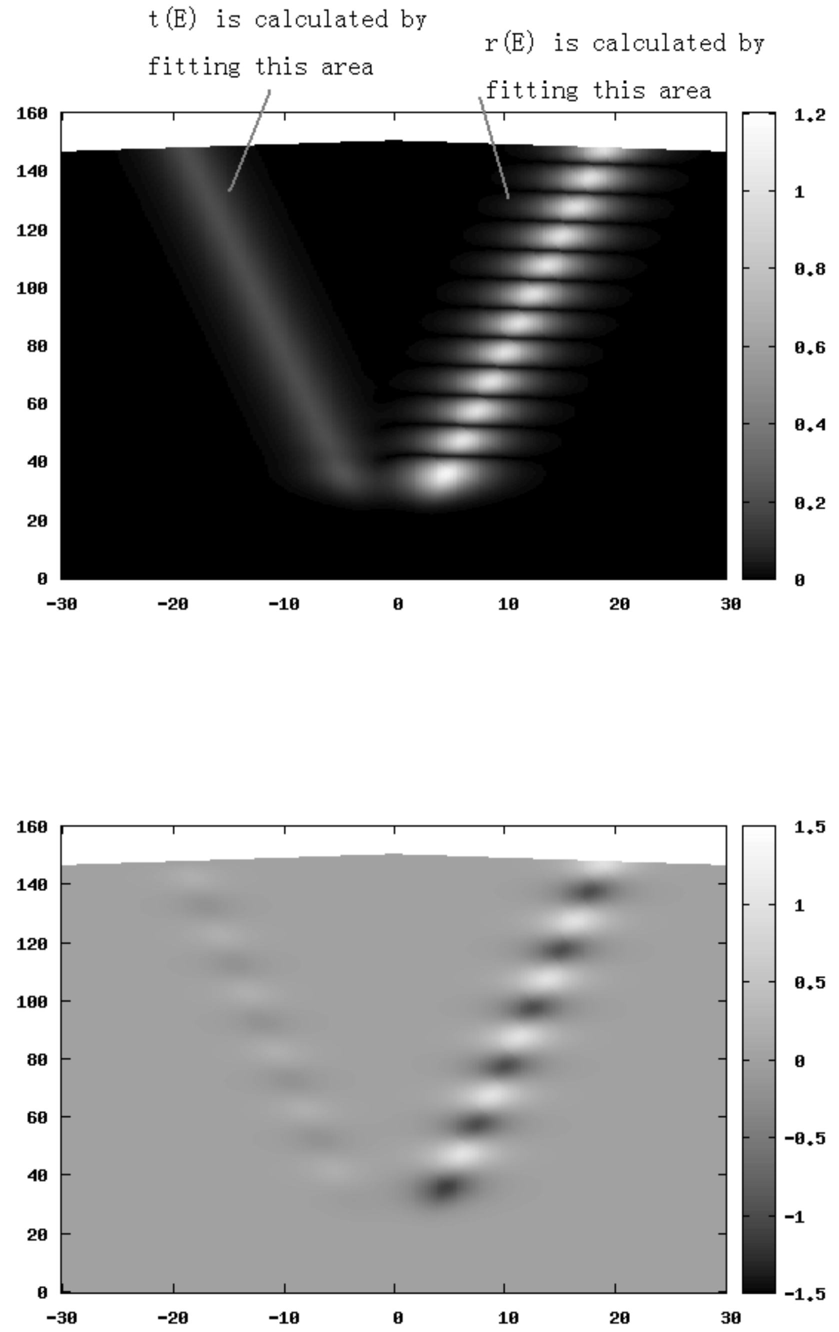

FIG. 13: A typical solution, shown as $abs(\psi)$ and $real(\psi)$, respectively. Note that the coordinates are the transformed ones(eq(A3)). The potenital between the nuclus and the electron is $-e^{-|x|}$. The potential between the nuclei is $\frac{1}{(r/R_0)^6}$. Both nuclei have the same mass, 30 electron masses. The total kinetic energy is 0.1 Hartree, which is a little higher than the gap between the ground state and excited state(0.5 Hatree).