Decoherence Corrections in TSH

Elious

Lets recap the Double slit experiment

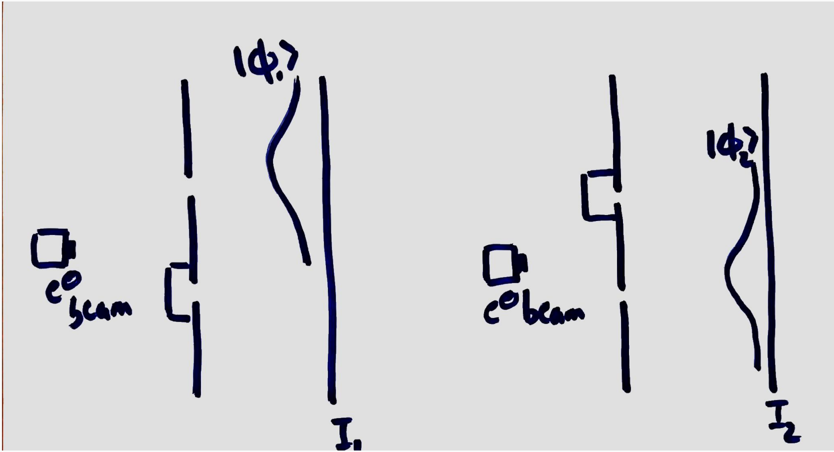

Figure 1: One of the slits is open

Double slit experiment results

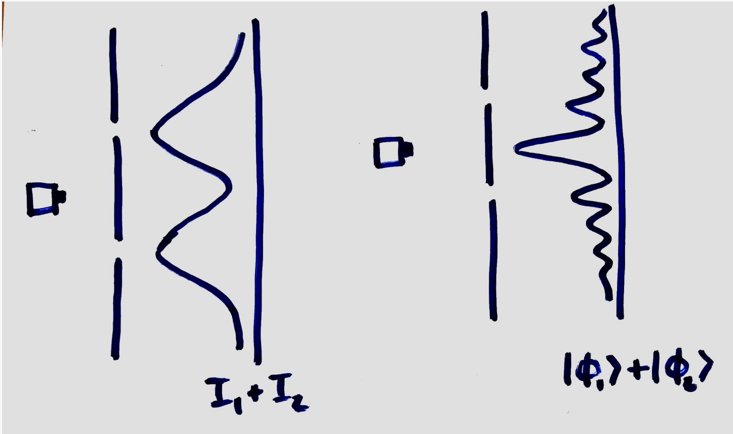

Figure 2: Both slits open: left → Classical expectation, right → Quantum reality

So what is going on?

Instead of the intensities, the quantum amplitude gets added up and we have :

$$|\Psi\rangle = c_1|\phi_1\rangle + c_2|\phi_2\rangle \tag{1}$$

and the intensity is given by:

$$\begin{aligned}\langle\Psi|\Psi\rangle = |c_1|^2\langle\Phi_1|\Phi_1\rangle + |c_2|^2\langle\Phi_2|\Phi_2\rangle + \\ c_1^* c_2\langle\Phi_1|\Phi_2\rangle + c_1 c_2^*\langle\Phi_2|\Phi_1\rangle\end{aligned} \tag{2}$$

The last two terms are what gives rise to the interference and sometimes also called **coherence**

Lets take quick look at the expansion of infinite well

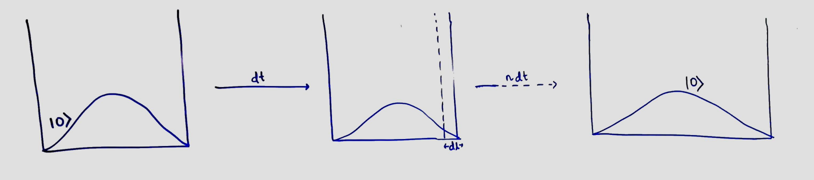

Figure 3: Slow (Adiabatic) expansion of the well

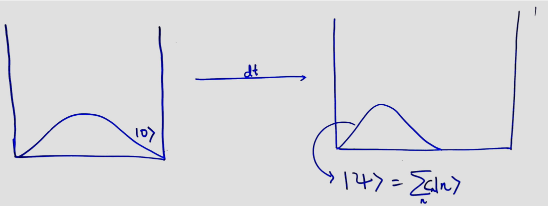

Figure 4: Sudden (Non-adiabatic) expansion of the well

Coherence

Sudden expansion $\rightarrow$ System can't adapt and the resulting wavefunction is now :

$$|\Psi\rangle = \sum_n c_n |\phi_n\rangle \tag{3}$$

If we construct the density matrix:

$$|\Psi\rangle\langle\Psi| = \begin{pmatrix} c_1 c_1^* & c_1 c_2^* & \dots & c_1 c_n^* \\ c_2 c_1^* & c_2 c_2^* & \dots & c_2 c_n^* \\ \vdots & \vdots & \ddots & \vdots \\ c_n c_1^* & c_n c_2^* & \dots & c_n c_n^* \end{pmatrix} \tag{4}$$

Diagonal terms $\rightarrow$ **Populations**

Off-diagonal terms $\rightarrow$ **Coherence** $\rightarrow$ reason for interference patterns and a measure of how much one state interferes with the other states.

Just a recap of TSH

The basic priciple is that the nuclear coordinates and traverse classically along an adiabatic surface by:

$$M_I \ddot{\mathbf{R}} = -\nabla E_k^{el}(\mathbf{R}) \tag{5}$$

and the electronic coefficients are propagated according to

$$i\hbar \dot{c}_k^{\alpha}(t) = c_k^{\alpha}(t) E_k^{\alpha}(\mathbf{R}^{\alpha}) - i\hbar \sum_j c_j^{\alpha} \mathbf{d}_{kj}^{\alpha} . \dot{\mathbf{R}}^{\alpha} \tag{6}$$

The hops are allowed between different PES only when:

$$\sum_{m=1}^{k-1} P_{j \to m} < \zeta < \sum_{m=1}^{k} P_{j \to m} \tag{7}$$

where $P_{j \to m}$ just depends on the Non-adiabatic coupling in eqn(6) and ζ is a random number within $(0, 1)$.

Over-coherence in TSH

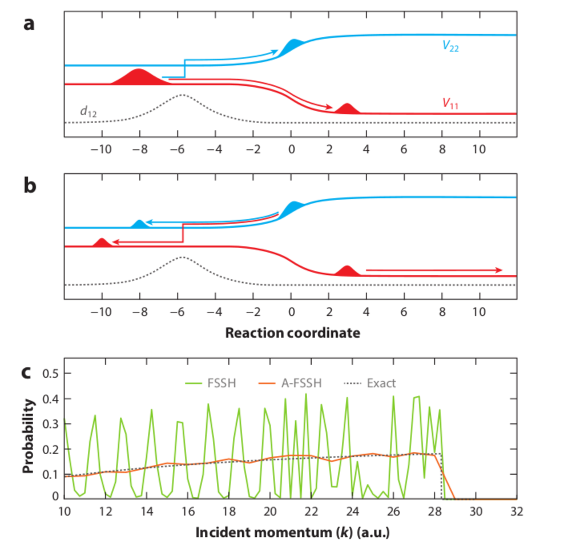

Figure 5: (c) Probability of reflection to lower surfaces

Why overcoherence happens???

Consider the Born-Huang ansatz for total wavefunction of the combined nuclei-electron system:

$$|\Psi\rangle = \sum_i |\chi_i\rangle|\phi_i\rangle \tag{8}$$

The density matrix will be;

$$|\Psi\rangle\langle\Psi| = \sum_{i,j} |\chi_i\rangle|\phi_i\rangle\langle\phi_j|\langle\chi_j| \tag{9}$$

Now to bring out the electronic density matrix from this;

$$\sigma_{el} = \sum_{i,j} \int |\mathbf{R}\rangle\langle\mathbf{R}||\Psi\rangle\langle\Psi| d\mathbf{R} \tag{10}$$

Overcoherence...

This would give;

$$\begin{aligned}\sigma_{el} &= \sum_{i,j} \int \langle \chi_j | \mathbf{R} \rangle \langle \mathbf{R} | \chi_i \rangle | \phi_i \rangle \langle \phi_j | d\mathbf{R} \\ &= \sum_{i,j} \langle \chi_j | \chi_i \rangle | \phi_i \rangle \langle \phi_j |\end{aligned} \tag{11}$$

The electronic wavefunction in TSH is;

$$|\Psi_{el}\rangle = \sum_i c_i |\phi_i\rangle \tag{12}$$

From this we have the electronic density matrix as;

$$\sigma_{el} = \sum_{i,j} c_i c_j^* |\phi_i\rangle\langle\phi_j| \tag{13}$$

Overcoherence continued...

Comparing equations (11) and (13) we can see that the coherence terms in TSH wave-function represents the nuclear overlap of the total-wavefunction, i.e.,

$$\langle \chi_j | \chi_i \rangle = c_i c_j^* \tag{14}$$

1. After branching off of the nuclear wavepackets from strong coupling regions, when these wavepackets are far enough in phase space, then the effective overlap should go to 0 i.e., $\langle \chi_j | \chi_i \rangle \to 0$.
2. BUT, there is no term in equation(6) which will make the coherence terms $\to 0$ after the hops.
3. This leads to overcoherence.

What should be happening ideally...

1. In strong coupling regions, the nuclear wavepackets can branch into multiple wavepackets
2. Following a hop, the wavepackets remain in region of nonadiabatic coupling and continue exchanging populations.
3. After enough seperation of the wavepackets in phase-space, these should evolve independent of each other.
4. At ant time we should have:

$$\frac{N^{\alpha}}{N^{T}} = \frac{1}{N^{T}} \sum_{j=1}^{N^{T}} \rho^{j}_{\alpha\alpha} \tag{15}$$

This is called internal consistency of FSSH.

Instantaneous Decoherence Correction (IDC)

1. **ID-S:** After each successful hop, the electronic wavefunction is reinitialised as a pure state in the current state
2. **ID-A:** If a hop is accepted, the wavefunction is made to collapse at the current state and if a hop is forbidden, the wavefunction is collapsed back to the current running state.

If a hop $S_2 \rightarrow S_1$ is predicted:

if successful hop:

set $c_1 = 1$ and $c_2 = 0$

else:

set $c_2 = 1$ and $c_1 = 0$

Energy Based Decoherence Correction (EDC)

Instead of instantaneous collapse, here we allow for decay of the electronic wavefunction to a particular state.

$$c'_\beta(t) = c_\beta(t) e^{\frac{-\Delta t}{\tau_{\beta\alpha}(t)}} \tag{16}$$

and the loss gets accumulated in the current state as:

$$c'_\alpha(t) = c_\alpha(t) \left[\frac{1 - \sum_{\beta \neq \alpha} |c'_\beta(t)|^2}{|c'_\alpha(t)|^2} \right]^{\frac{1}{2}} \tag{17}$$

$\tau_{\beta\alpha}$ is known as the decoherence time and Truhlar *et al.* suggested it to be:

$$\tau_{\beta\alpha}(t) = \frac{\hbar}{|E_\beta(t) - E_\alpha(t)|} \left(C + \frac{E_0}{(\mathbf{P.d}_{\alpha\beta})^2/2\mu} \right) \tag{18}$$

Later on Granucci *et al.* found, this can be approximated as:

$$\tau_{\beta\alpha}(t) = \frac{\hbar}{|E_\beta(t) - E_\alpha(t)|} \left(C + \frac{E_0}{E_{kin}} \right) \tag{19}$$

Visualisation of the Decoherence corrections

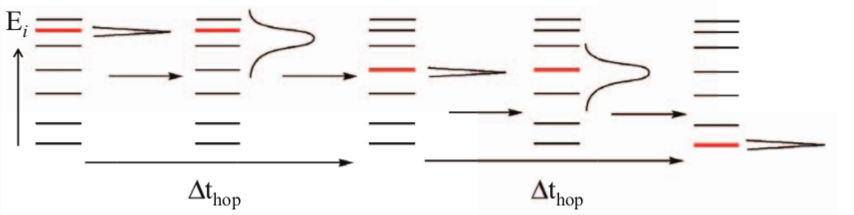

Figure 6: Instantaneous Decoherence Correction