2. Introduction to Time-Dependent Quantum Mechanics

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The Schrödinger Equation

In his 1924 thesis, de Broglie suggested that a particle can behave like a wave whose wavelength is

$$\lambda = \frac{h}{p}.$$

Based on this observation, Schrödinger constructed an equation of motion which the matter wave of a particle must satisfy.

We start from the generalized expression of a wave along the x-axis

$$\psi(x,t) = \exp\left[2\pi i\left(\frac{x}{\lambda} - \nu t\right)\right] = \exp\left(\frac{i(px - Et)}{\hbar}\right),$$

where we have used the relation $E = h\nu$ in the last step.

The Schrödinger Equation

If we calculate the derivatives with respect to x and t, we obtain

$$-i\hbar\frac{\partial\psi(x,t)}{\partial x} = p\psi(x,t), \quad i\hbar\frac{\partial\psi(x,t)}{\partial t} = E\psi(x,t).$$

From the first equation, we can deduce that the quantum operator for the momentum is

$$\hat{p} = -i\hbar\frac{\partial}{\partial x}.$$

For the second equation, we can express the total energy E as the sum of kinetic and potential energies,

$$E = \frac{p^2}{2m} + V(x,t).$$

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The Schrödinger Equation

If we substitute the classical momentum in the total energy with the momentum operator and use its definition, we get

$$i\hbar\frac{\partial\psi(x,t)}{\partial t} = \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x,t)\right)\psi(x,t) = \hat{H}(x,t)\psi(x,t)$$

which is the famous (time-dependent) Schrödinger equation.

At the last step, we have defined the Hamiltonian operator, which corresponds to the total energy of a matter wave (wavefunction).

Note: It is not possible to “derive” the TDSE, and the previous steps should be thought as just a heuristic way to validate the TDSE.

Linear Algebraic Representation

To solve the Schrödinger equation, we introduce a set of basis functions $\{\phi_j\}$ and express the wavefunction as their linear combination

$$\psi(t) = \sum_j c_j(t)\phi_j.$$

This converts the problem into finding the time-dependence of the coefficients $\{c_j(t)\}$.

We assume that the basis functions satisfy orthonormality in the whole space

$$\int \phi_k^* \phi_j \, d\tau = \delta_{jk}.$$

Linear Algebraic Representation

If we insert the basis representation of the wavefunction into the TDSE, we obtain the equation of motion for the coefficients

$$i\hbar \sum_j \phi_j \dot{c}_j(t) = \hat{H} \sum_j \phi_j c_j(t),$$

where $\dot{c}_j(t)$ is a shorthand notation for $\partial c_j(t)/\partial t$.

Multiplying by ϕ_k from the left and integrating over the entire space leads to

$$i\hbar \dot{c}_k(t) = \sum_j \left(\int \phi_k^* \hat{H} \phi_j \, d\tau \right) c_j(t).$$

which cannot be simplified any more as $\{\phi_j\}$ are not the eigenfunctions of the Hamiltonian operator.

Linear Algebraic Representation

We now represent the wavefunction as a vector $|\psi^{\phi}(t)\rangle$ whose components are the coefficients of the basis $\{c_k(t)\}$,

and consider a matrix $\hat{H}^{\phi}$ whose elements are

$$(H^{\phi})_{kj} = \int \phi_k^* \hat{H} \phi_j \, d\tau.$$

By taking this viewpoint, the TDSE is converted to an equivalent linear algebraic representation

$$i\hbar \frac{\partial}{\partial t} |\psi^{\phi}(t)\rangle = \hat{H}^{\phi} |\psi^{\phi}(t)\rangle \, .$$

The superscript $^{\phi}$ marks that the elements are evaluated by using the particular basis set $\{\phi_j\}$.

Linear Algebraic Representation

We briefly introduce some properties regarding the linear algebraic representation of quantum mechanics (matrix mechanics).

A quantum state is represented as a state vector (ket) $|\psi\rangle$.

We can also consider the conjugate-transposed vector (bra) $\langle\psi|$.

A normalized state ket $|\psi\rangle$ can be thought as a column vector of unit length in the space defined by the unit basis vectors $\{|\phi_j\rangle\}$.

The components of the generalized position vector $|\psi^{\phi}\rangle$ can be calculated as the inner product $\langle\phi_j|\psi\rangle$.

The components depend on the choice of basis (coordinate axes).

Linear Algebraic Representation

The change from one basis representation to another can be easily done by using the resolution of identity

$$\hat{I} = \sum_j |\phi_j\rangle \langle\phi_j| \,.$$

The meaning of this expression becomes clear if we represent $|\phi_j\rangle$ as a unit vector $\mathbf{e}_j$ and define the outer product of the two vectors as

$$\mathbf{u} \otimes \mathbf{v}^\dagger = \begin{pmatrix} u_1 \\ u_2 \\ \vdots \\ u_N \end{pmatrix} \otimes \begin{pmatrix} v_1^* & v_2^* & \cdots & v_M^* \end{pmatrix} = \begin{pmatrix} u_1 v_1^* & u_1 v_2^* & \cdots & u_1 v_N^* \\ u_2 v_1^* & u_2 v_2^* & \cdots & u_2 v_N^* \\ \vdots & \vdots & \ddots & \vdots \\ u_M v_1^* & u_M v_2^* & \cdots & u_M v_N^* \end{pmatrix} .$$

Linear Algebraic Representation

The state vector and wavefunction are connected by

$$\psi(x) = \langle x|\psi\rangle \,,$$

where $|x\rangle$ is an eigenvector of the position operator $\hat{x}$ which satisfies the orthonormality for a continuous variable (Dirac delta function)

$$\langle x'|x\rangle = \delta(x - x').$$

For a continuous variable, the resolution of identity becomes

$$\hat{I} = \int_{-\infty}^{\infty} |x\rangle \langle x| \; dx,$$

with which we can express the inner product between two states as

$$\langle \psi_a|\psi_b\rangle = \int_{-\infty}^{\infty} \langle \psi_a|x\rangle \langle x|\psi_b\rangle \; dx = \int_{-\infty}^{\infty} \psi_a^*(x)\psi_b(x)\, dx.$$

Linear Algebraic Representation

Lastly, we consider the representation of an operator by considering the expression

$$C = \langle\psi_a|\,\hat{A}\,|\psi_b\rangle\,,$$

which can be expanded by introducing a basis set

$$C = \sum_j \sum_k \langle\psi_a|\phi_j\rangle\langle\phi_j|\,\hat{A}\,|\phi_k\rangle\langle\phi_k|\psi_b\rangle = \langle\psi_a^\phi|\hat{A}^\phi|\psi_b^\phi\rangle.$$

We notice that the operator is represented as a matrix whose elements are

$$A_{jk}^\phi = \langle\phi_j|\,\hat{A}\,|\phi_k\rangle\,.$$

The change of basis affects the representation, but does not alter the physical property (C).

Linear Algebraic Representation

In the positional basis, the expression is converted to

$$C = \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dx' \ \langle \psi_a | x \rangle \langle x | \hat{A} | x' \rangle \langle x' | \psi_b \rangle \, .$$

Almost all of the physical operators are local and satisfy the property

$$\langle x | \hat{A} | x' \rangle = \langle x | \hat{A} | x \rangle \, \delta(x - x'),$$

so that

$$C = \int_{-\infty}^{\infty} \langle \psi_a | x \rangle \langle x | \hat{A} | x \rangle \langle x | \psi_b \rangle \ dx = \int_{-\infty}^{\infty} \psi_a^*(x) \hat{A}^x \psi_b(x) \, dx,$$

where we have introduced the positional representation of an operator

$$\hat{A}^x = \langle x | \hat{A} | x \rangle \, .$$

Basis Rotation

Suppose that we have two different representations of a state vector $|\psi^{\phi}\rangle$ and $|\psi^{\phi'}\rangle$, and also an operator $\hat{A}^{\phi}$ and $\hat{A}^{\phi'}$.

How are these two representations connected?

$$|\psi\rangle = \sum_j \langle\phi_j|\psi\rangle\,|\phi_j\rangle = \sum_{j,k} \langle\phi'_k|\phi_j\rangle\,\langle\phi_j|\psi\rangle\,|\phi'_k\rangle$$

$$\hat{A} = \sum_{j,m} |\phi_j\rangle\,\langle\phi_j|\,\hat{A}\,|\phi_m\rangle\,\langle\phi_m| = \sum_{j,m}\sum_{k,n} |\phi'_k\rangle\,\langle\phi'_k|\phi_j\rangle\,\langle\phi_j|\,\hat{A}\,|\phi_m\rangle\,\langle\phi_m|\phi'_n\rangle\,\langle\phi'_n|$$

This shows that the two representations are connected via

$$|\psi^{\phi'}\rangle = \hat{X}^{\dagger}\,|\psi^{\phi}\rangle\,, \quad \hat{A}^{\phi'} = \hat{X}^{\dagger}\hat{A}^{\phi}\hat{X}, \qquad \text{where} \qquad X_{jk} = \langle\phi_j|\phi'_k\rangle\,.$$

Basis Rotation

$$|\psi^{\phi'}\rangle = \hat{X}^\dagger |\psi^\phi\rangle\,, \quad \hat{A}^{\phi'} = \hat{X}^\dagger \hat{A}^\phi \hat{X}, \qquad \text{where} \qquad X_{jk} = \langle \phi_j | \phi'_k \rangle\,.$$

Note that $\hat{X}$ is unitary when the basis sets are orthonormal, as

$$\begin{aligned}(\hat{X}^\dagger \hat{X})_{jk} &= \sum_m (\hat{X}^\dagger)_{jm} \hat{X}_{mk} = \sum_m \langle \phi'_j | \phi_m \rangle \langle \phi_m | \phi'_k \rangle \\ &= \langle \phi'_j | \phi'_k \rangle = \delta_{jk},\end{aligned}$$

and similarly

$$(\hat{X}\hat{X}^\dagger)_{jk} = \delta_{jk}.$$

Combining these two results give

$$\hat{X}^\dagger \hat{X} = \hat{X}\hat{X}^\dagger = \hat{I}.$$

Two-Level System

We will now study the time-dependent behavior of a two-level quantum system, which is the most basic problem of quantum dynamics.

This model consists of two orthogonal quantum states $|\phi_1\rangle$ and $|\phi_2\rangle$ which can have different energies and properties in general.

If these two quantum states are eigenstates of the Hamiltonian, the dynamics of each quantum states will be stationary:

$$
\begin{aligned}
|\psi_1(0)\rangle = |\phi_1\rangle \quad &\rightarrow \quad |\psi_1(t)\rangle = \exp(-iE_1 t/\hbar)\,|\phi_1\rangle\,, \\
|\psi_2(0)\rangle = |\phi_2\rangle \quad &\rightarrow \quad |\psi_2(t)\rangle = \exp(-iE_2 t/\hbar)\,|\phi_2\rangle\,.
\end{aligned}
$$

However, if there are interactions (couplings) between the two states, these are not the eigenstates and there can be exchange of populations.

Two-Level System

Let us represent the quantum state at a time instance t as

$$|\psi(t)\rangle = c_1(t)\,|\phi_1\rangle + c_2(t)\,|\phi_2\rangle\,,$$

where $c_1(t)$ and $c_2(t)$ are time-dependent coefficients.

The time-dependence of the coefficients are of course governed by TDSE:

$$i\hbar\frac{\partial}{\partial t}\,|\psi(t)\rangle = \hat{H}\,|\psi(t)\rangle\,,$$

$$i\hbar[\dot{c}_1(t)\,|\phi_1\rangle + \dot{c}_2(t)\,|\phi_2\rangle] = \hat{H}[\dot{c}_1(t)\,|\phi_1\rangle + \dot{c}_2(t)\,|\phi_2\rangle].$$

Note that we are implicitly assuming that the dynamics will be confined in these two quantum states.

The TDSE

Using the matrix-vector representation, the equation of motion becomes

$$i\hbar\frac{d}{dt}\begin{pmatrix} c_1(t) \\ c_2(t) \end{pmatrix} = \begin{pmatrix} E_1 & V \\ V & E_2 \end{pmatrix}\begin{pmatrix} c_1(t) \\ c_2(t) \end{pmatrix},$$

where

$$E_1 = \langle\phi_1|\,\hat{H}\,|\phi_1\rangle\,, \quad E_2 = \langle\phi_2|\,\hat{H}\,|\phi_2\rangle\,,$$

$$V = \langle\phi_1|\,\hat{H}\,|\phi_2\rangle = \langle\phi_2|\,\hat{H}\,|\phi_1\rangle\,.$$

For convenience, we now redefine the zero of energy to be $(E_1 + E_2)/2$ and get

$$i\hbar\frac{d}{dt}\begin{pmatrix} c_1(t) \\ c_2(t) \end{pmatrix} = \begin{pmatrix} \epsilon & V \\ V & -\epsilon \end{pmatrix}\begin{pmatrix} c_1(t) \\ c_2(t) \end{pmatrix}, \quad \epsilon = \frac{E_1 - E_2}{2}.$$

We will see later that the physical behavior is not affected by this adjustment.

The Propagator

The TDSE is then expressed as

$$i\hbar \frac{d}{dt} \begin{pmatrix} c_1(t) \\ c_2(t) \end{pmatrix} = \hat{H}^\phi \begin{pmatrix} c_1(t) \\ c_2(t) \end{pmatrix}, \quad \hat{H}^\phi = \begin{pmatrix} \epsilon & V \\ V & -\epsilon \end{pmatrix}.$$

To find the solution, we define the propagator $\hat{U}^\phi(t)$ which satisfies

$$\begin{pmatrix} c_1(t) \\ c_2(t) \end{pmatrix} = \hat{U}^\phi(t) \begin{pmatrix} c_1(0) \\ c_2(0) \end{pmatrix}$$

and find the expression for $\hat{U}^\phi(t)$.

The formal solution is

$$\hat{U}^\phi(t) = \exp\left(-\frac{i\hat{H}^\phi t}{\hbar} \right).$$

Note that this is only valid when $\hat{H}^\phi$ does not depend on time.

Eigenbasis of the Two-Level System

In short, solving the TDSE is equivalent to calculating the propagator

$$\hat{U}^{\phi}(t) = \exp\left(- \frac{i\hat{H}^{\phi}t}{\hbar} \right).$$

To evaluate the exponential, we first need to calculate the eigenvalues and eigenvectors of the Hamiltonian $\hat{H}^{\phi}$.

The eigenvalues are calculated by solving

$$\det \begin{pmatrix} \epsilon - \lambda & V \\ V & -\epsilon - \lambda \end{pmatrix} = -(\epsilon^2 - \lambda^2) - V^2 = 0,$$

which yields

$$\lambda_1 = \sqrt{\epsilon^2 + V^2} = \tilde{\epsilon},$$

$$\lambda_2 = -\sqrt{\epsilon^2 + V^2} = -\tilde{\epsilon}.$$

Eigenbasis of the Two-Level System

We denote the corresponding normalized eigenvectors as

$$|\phi_1'\rangle = d_{11}\,|\phi_1\rangle + d_{12}\,|\phi_2\rangle\,, \qquad |\phi_2'\rangle = d_{21}\,|\phi_1\rangle + d_{22}\,|\phi_2\rangle\,.$$

By defining

$$\frac{\epsilon}{\sqrt{\epsilon^2+V^2}} = \cos\alpha, \quad \frac{V}{\sqrt{\epsilon^2+V^2}} = \sin\alpha,$$

the two sets of simultaneous equations become

$$(\cos\alpha)d_{11} + (\sin\alpha)d_{12} = d_{11}, \qquad (\cos\alpha)d_{21} + (\sin\alpha)d_{22} = -d_{21},$$

$$d_{11}^2 + d_{12}^2 = 1, \qquad d_{21}^2 + d_{22}^2 = 1.$$

If we assume $\epsilon > 0$ without the loss of generality, the solutions are

$$|\phi_1'\rangle = \cos\left(\frac{\alpha}{2}\right)|\phi_1\rangle + \sin\left(\frac{\alpha}{2}\right)|\phi_2\rangle\,, \quad |\phi_2'\rangle = -\sin\left(\frac{\alpha}{2}\right)|\phi_1\rangle + \cos\left(\frac{\alpha}{2}\right)|\phi_2\rangle\,.$$

Mixing Angle and Basis Transformation

It is convenient to define the "mixing angle"

$$\theta = \frac{\alpha}{2} = \frac{1}{2}\tan^{-1}\left(\frac{V}{\epsilon}\right),$$

which leads to a convenient expression

$$|\phi_1'\rangle = \cos\theta\,|\phi_1\rangle + \sin\theta\,|\phi_2\rangle\,, \quad |\phi_2'\rangle = -\sin\theta\,|\phi_1\rangle + \cos\theta\,|\phi_2\rangle\,.$$

The state vector and Hamiltonian in the original and eigenvector basis sets are connected by

$$|\psi^{\phi'}(t)\rangle = \hat{X}^\dagger\,|\psi^{\phi}(t)\rangle\,, \quad \hat{H}^{\phi'} = \hat{X}^\dagger \hat{H}^{\phi}\hat{X},$$

where $\hat{X}$ is the rotational transformation matrix

$$\hat{X} = \begin{pmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{pmatrix}.$$

Evaluating the Propagator

We can now calculate the propagator matrix by using

$$\hat{H}^{\phi'} = \begin{pmatrix} \tilde{\epsilon} & 0 \\ 0 & -\tilde{\epsilon} \end{pmatrix}, \quad \hat{U}^{\phi'}(t) = \exp\left(- \frac{i\hat{H}^{\phi'} t}{\hbar} \right) = \begin{pmatrix} e^{-i\tilde{\omega}t} & 0 \\ 0 & e^{i\tilde{\omega}t} \end{pmatrix},$$

where we have defined $\tilde{\omega} = \tilde{\epsilon}/\hbar$.

The next step is transforming back to the original basis

$$\begin{aligned} \hat{U}^{\phi}(t) &= \hat{X}\hat{U}^{\phi'}(t)\hat{X}^{\dagger} \\ &= \begin{pmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{pmatrix} \begin{pmatrix} e^{-i\tilde{\omega}t} & 0 \\ 0 & e^{i\tilde{\omega}t} \end{pmatrix} \begin{pmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{pmatrix} \\ &= \begin{pmatrix} \cos(\tilde{\omega}t) - i\cos(2\theta)\sin(\tilde{\omega}t) & -i\sin(2\theta)\sin(\tilde{\omega}t) \\ -i\sin(2\theta)\sin(\tilde{\omega}t) & \cos(\tilde{\omega}t) + i\cos(2\theta)\sin(\tilde{\omega}t) \end{pmatrix}, \end{aligned}$$

which can be multiplied to an arbitrary initial condition $|\psi(0)\rangle$.

Characteristics of the Dynamics

If we assume a localized initial state $|\psi(0)\rangle = |\phi_1\rangle$,

$$\begin{aligned}|\psi(t)\rangle &= \hat{U}(t)\,|\psi(0)\rangle \\ &= [\cos(\tilde{\omega}t) - i\cos(2\theta)\sin(\tilde{\omega}t)]\,|\phi_1\rangle - i\sin(2\theta)\sin(\tilde{\omega}t)\,|\phi_2\rangle\,,\end{aligned}$$

so the populations of the states are

$$\begin{aligned}p_1(t) &= |\,\langle\phi_1|\psi(t)\rangle\,|^2 = \cos^2(\tilde{\omega}t) + \cos^2(2\theta)\sin^2(\tilde{\omega}t), \\ p_2(t) &= |\,\langle\phi_2|\psi(t)\rangle\,|^2 = \sin^2(2\theta)\sin^2(\tilde{\omega}t).\end{aligned}$$

It is not difficult to see that the sum of the populations is conserved,

$$p_1(t) + p_2(t) = 1,$$

and the dynamics is periodic with the period of $\dfrac{2\pi}{\tilde{\omega}} = \dfrac{h}{\tilde{\epsilon}}$.

Characteristics of the Dynamics

It is better to analyze the behavior of the population by expressing

$$p_2(t) = \sin^2(2\theta)\sin^2(\tilde{\omega}t) = \frac{\sin^2(2\theta)}{2}[1-\cos(2\tilde{\omega}t)],$$
$$p_1(t) = 1 - p_2(t).$$

This shows that $p_2(t)$ oscillates between 0 and $\sin^2(2\theta)$.

If we recall that

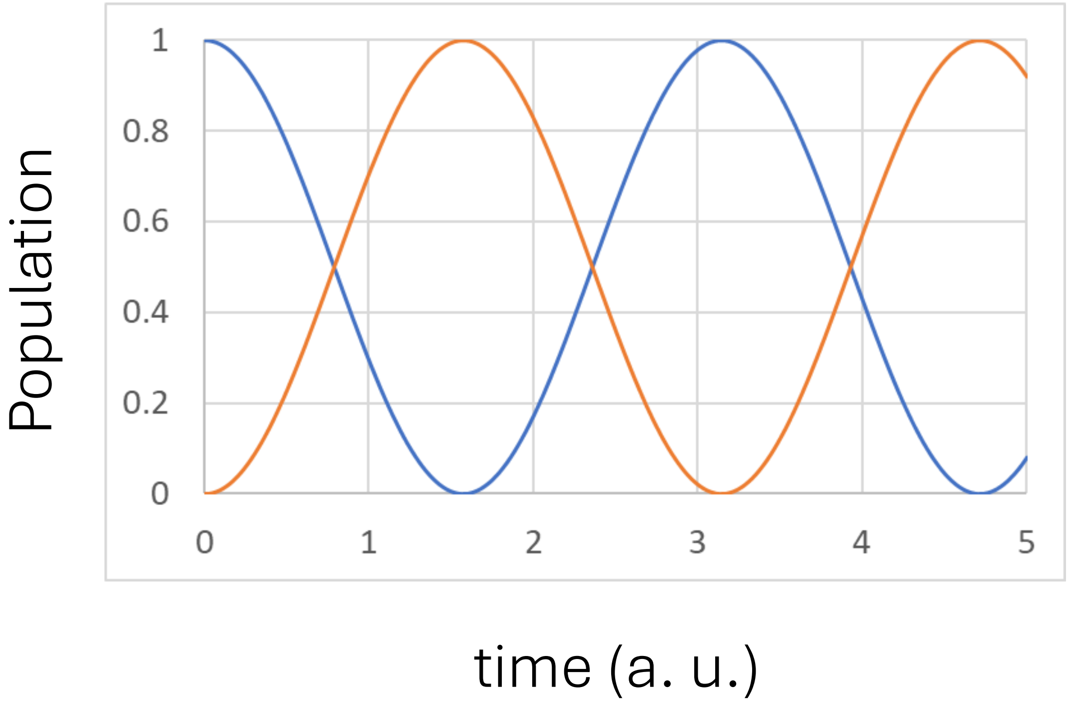
$$2\theta = \tan^{-1}\left(\frac{V}{\epsilon}\right),$$

we can observe that the population exchange becomes maximized when $\epsilon = 0$ or $V \to \infty$, and minimized when $\epsilon \to \infty$ or $V = 0$.

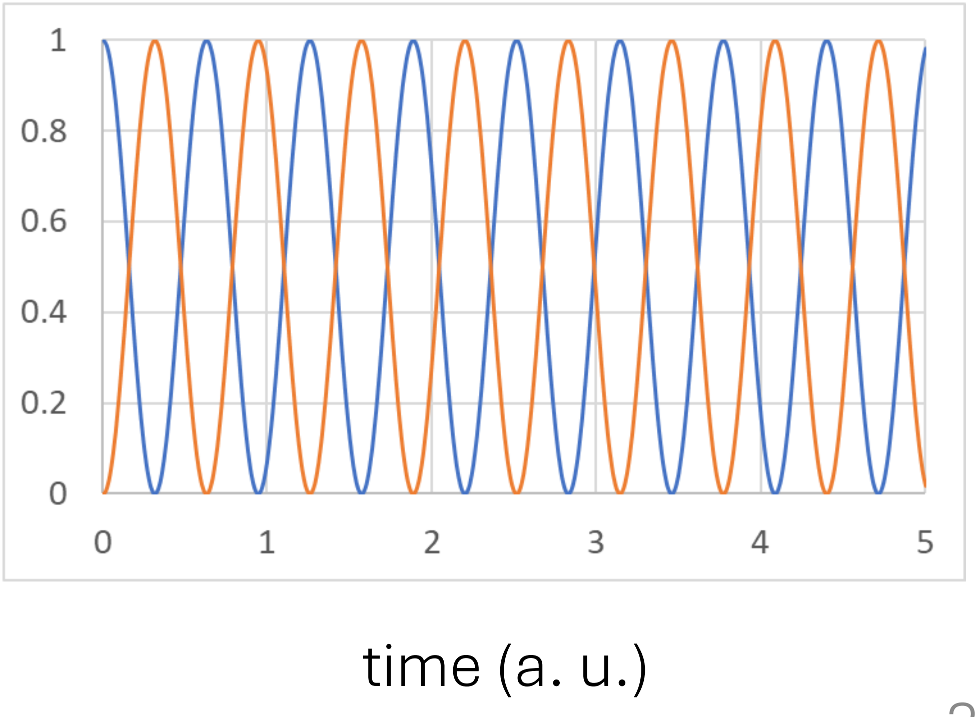
Simulation Results

The quantum dynamics simulations are usually performed by using Planck atomic units which sets $h = k_{\mathrm{B}} = 1.$

$\epsilon = 0, \quad V = 1$



$\epsilon = 0, \quad V = 5$



Simulation Results