Time-Dependent Dynamics of a Two-Level Quantum System

Computational Chemistry Group
Chonnam National University
Drafted on 3 Feb 2022 / Last edited on 28 May 2025

Note: either C or python language can be used for dealing with the exercises that require programming. For C language, complex numbers can be incorporated in the calculations as illustrated in `complex.c`. Alternatively, it is also possible to rely on external tools such as Intel® Math Kernel Library.

1 Time-Dependent Schrödinger Equation

Let us consider a quantum problem involving a single coordinate x. The time-dependent Schrödinger equation (TDSE) is

$$i\hbar\frac{\partial}{\partial t}\Psi(x,t) = \hat{H}(x,t)\Psi(x,t), \tag{1}$$

where $\Psi(x,t)$ is the wavefunction and $\hat{H}(x,t)$ the Hamiltonian of the system

$$\hat{H}(x,t) = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x,t). \tag{2}$$

For now, we assume that the Hamiltonian is independent on time for the sake of simplicity. Equation (1) can then be solved by separation of variables, which assumes that the wavefunction can be factorized into the spatial and temporal components,

$$\Psi(x,t) = \psi(x)T(t), \tag{3}$$

which decouples Eq. (1) into two ordinary differential equations,

$$\hat{H}(x)\psi(x) = \epsilon\psi(x), \tag{4a}$$

$$i\hbar\frac{d}{dt}T(t) = \epsilon T(t), \tag{4b}$$

where ϵ is a constant that acts as the energy.

Exercise 1-1. Derive Eq. (4).

Eq. (4a) is the time-independent Schödinger equation (TISE) which we have encountered many times in the undergraduate physical chemistry courses. If we can find its solution wavefunctions $\{\psi_n(x)\}$ and energies $\{E_n\}$, we can use them to solve Eq. (4b),

$$T(t) = e^{-i\omega_n t}, \tag{5}$$

where $\omega_n = \epsilon_n/\hbar$. We can now construct a complete set of time-dependent solutions for the TDSE,

$$\Psi_n(x,t) = \psi_n(x)e^{-i\omega_n t}. \tag{6}$$

If we specify the initial wavefunction at $t = 0$ as

$$\Psi(x,0) = \sum_n c_n\psi_n(x), \tag{7}$$

one can straightforwardly obtain the solution at arbitrary time t,

$$\Psi(x,t) = \sum_n c_n \psi_n(x) e^{-i\omega_n t}. \tag{8}$$

Exercise 1-2. Plug Eq. (8) in Eq. (1) and check the validity of the solution. How can we calculate the coefficients $\{c_n\}$?

2 Two-Level Quantum System

When the solution wavefunctions of TISE $\{\psi_n(x)\}$ are not immediately available, a general way to solve Eq. (1) is introduction of a basis set. Suppose we are trying to describe the dynamics by using two basis functions $\phi_1(x)$ and $\phi_2(x)$ which satisfy the orthonormality,

$$\int_{-\infty}^{\infty} \phi_m(x)\phi_n(x)\, dx = \delta_{mn}, \tag{9}$$

where δ_{mn} is the Kronecker delta which is unity when $m = n$ and zero when $m \neq n$. We can now represent the wavefunction at an arbitrary time t as

$$\Psi(x,t) = c_1(t)\phi_1(x) + c_2(t)\phi_2(x). \tag{10}$$

Inserting Eq. (10) in the TDSE [Eq. (1)] leads to the matrix equation for the coefficients

$$i\hbar \frac{d}{dt}\begin{pmatrix} c_1(t) \\ c_2(t) \end{pmatrix} = \begin{pmatrix} \epsilon_1 & V \\ V & \epsilon_2 \end{pmatrix}\begin{pmatrix} c_1(t) \\ c_2(t) \end{pmatrix}. \tag{11}$$

Exercise 2-1. Derive Eq. (11) and express the matrix elements ϵ_1, ϵ_2 and V in terms of $\hat{H}(x)$, $\phi_1(x)$ and $\phi_2(x)$.

Equation (11) can be re-written as

$$i\hbar \frac{d}{dt}\vec{\Psi}(t) = \hat{H}\vec{\Psi}(t), \tag{12}$$

where $\vec{\Psi}(t)$ and $\hat{H}$ are

$$\vec{\Psi}(t) = \begin{pmatrix} c_1(t) \\ c_2(t) \end{pmatrix}, \quad \hat{H} = \begin{pmatrix} \epsilon_1 & V \\ V & \epsilon_2 \end{pmatrix}. \tag{13}$$

Equations (12) and (13) are called the "linear algebraic representation" of the TDSE. Note that the wavefunction is now represented as the coefficient vector $\vec{\Psi}(t)$, and all of the information about the Hamiltonian is included in the matrix $\hat{H}$. Note that we must keep in mind that we are using $\phi_1(x)$ and $\phi_2(x)$ as the basis functions, as the elements of $\vec{\Psi}(t)$ and $\hat{H}$ become different upon the change of basis.

An exact solution of Eq. (12) can be obtained by diagonalizing the Hamiltonian matrix $\hat{H}$, which is equivalent to solving the TISE:

$$\epsilon_+ = \bar{\epsilon} + \Delta\epsilon, \quad \psi_+(x) = (\cos\theta)\phi_1(x) + (\sin\theta)\phi_2(x), \tag{14a}$$

$$\epsilon_- = \bar{\epsilon} - \Delta\epsilon, \quad \psi_-(x) = (\sin\theta)\phi_1(x) - (\cos\theta)\phi_2(x), \tag{14b}$$

where $\bar{\epsilon}$, $\Delta\epsilon$, and θ are given by

$$\bar{\epsilon} = \frac{\epsilon_1 + \epsilon_2}{2}, \quad \Delta\epsilon = \frac{\sqrt{(\epsilon_2 - \epsilon_1)^2 + 4V^2}}{2}, \quad \tan(2\theta) = \frac{2V}{\epsilon_2 - \epsilon_1}. \tag{15}$$

Exercise 2-2. Derive Eqs. (14) and (15).

In terms of the eigenbasis $\psi_1(x)$ and $\psi_2(x)$ of $\hat{H}$, The TDSE becomes

$$i\hbar \frac{d}{dt} \begin{pmatrix} c_+(t) \\ c_-(t) \end{pmatrix} = \begin{pmatrix} \epsilon_+ & 0 \\ 0 & \epsilon_- \end{pmatrix} \begin{pmatrix} c_+(t) \\ c_-(t) \end{pmatrix}, \tag{16}$$

whose solution is

$$\Psi(x,t) = \psi_+(x)e^{-i\omega_+ t} + \psi_-(x)e^{-i\omega_- t}, \tag{17}$$

where $\omega_\pm = \epsilon_\pm/\hbar$. The conversion back to the original basis $\phi_1(x)$ and $\phi_2(x)$ can be accomplished by using Eq. (14).

Exercise 2-3. By setting the initial condition as $c_1(0) = 1$ and $c_2(0) = 0$, show that the time-dependent probability of the wavefunction to be $\phi_1(x)$ and $\phi_2(x)$ are expressed as

$$P_1(t) = |c_1(t)|^2 = \cos^2(\Omega t) + \cos^2(2\theta)\sin^2(\Omega t), \tag{18a}$$

$$P_2(t) = |c_2(t)|^2 = \sin^2(2\theta)\sin^2(\Omega t), \tag{18b}$$

respectively, where $\Omega = \Delta\epsilon/\hbar$.

The fact that Eq. (18) is not dependent on $\bar{\epsilon}$ shows that the zero of energy does not affect the dynamics, and only the energy difference $\epsilon_2 - \epsilon_1$ between the two quantum states matters.

Let us now numerically simulate Eq. (12). As in the classical dynamics, the most primitive method for numerical integration is the Euler's algorithm,

$$\vec{\Psi}(t + \Delta t) = \vec{\Psi}(t) + \left(\frac{d}{dt}\vec{\Psi}(t)\right)\Delta t = \vec{\Psi}(t) - \frac{i\hat{H}}{\hbar}\vec{\Psi}(t)\Delta t. \tag{19}$$

However, as you may have expected from the experience on the classical dynamics, the performance of Eq. (19) is rather poor and one needs to employ better algorithms for reliable simulation. There is no equivalent of velocity-Verlet algorithm for TDSE, and a common method of choice is the 4th-order Runge-Kutta (RK4) algorithm whose detail can be found on the wikipedia page.

Exercise 2-4. Propagate the TDSE for 2 ps by using Euler's and RK4 algorithms, with the simulation parameters of $\epsilon_2 - \epsilon_1 = 400$ cm^{-1}, $V = 200$ cm^{-1}, and $\Delta t = 0.1$ fs. The initial conditions for c_1 and c_2 are the same in **Exercise 2-3**. Plot the populations $P_1(t)$ and $P_2(t)$ and compare them to Eq. (18) to examine the accuracy. If we did not derive Eq. (18) beforehand, what is the best way to check the accuracy of the results?

3 Interaction with Monochromatic Radiation Field

An atom or molecule can absorb and emit light. A simple model for describing such processes is the time-dependent Hamiltonian matrix

$$\hat{H}(t) = \begin{pmatrix} \epsilon_1 & \boldsymbol{\vec{\mu}} \cdot \vec{\mathbf{E}}(t) \\ \boldsymbol{\vec{\mu}} \cdot \vec{\mathbf{E}}(t) & \epsilon_2 \end{pmatrix}, \tag{20}$$

where $\vec{\boldsymbol{\mu}}$ is the transition dipole moment that quantifies the tendency of a system to interact with light, and $\vec{\mathbf{E}}(t)$ is the time-dependent electric field of the light. If we assume that the incoming light is monochromatic with the angular frequency of ω, we have

$$\vec{\mathbf{E}}(t) = \vec{\mathbf{E}}_0 \cos(\omega t), \tag{21}$$

which renders Eq. (22) as

$$\hat{H}(t) = \begin{pmatrix} \epsilon_1 & F\cos(\omega t) \\ F\cos(\omega t) & \epsilon_2 \end{pmatrix}, \tag{22}$$

where we have defined $F = \vec{\boldsymbol{\mu}} \cdot \vec{\mathbf{E}}_0$.

Exercise 3-1. Simulate the TDSE [Eq. (12)] with $\hat{H}(t)$ given by Eq. (22). Set the parameters as $\epsilon_2 - \epsilon_1 = \hbar\omega = 400$ cm^{-1} and $F = 40$ cm^{-1}, while using the same simulation time and time step as in **Exercise 2-4**. Give a physical interpretation of what is happening. Confirm that the simulated dynamics approximately matches that of Eq. (13) with $\epsilon_1 = \epsilon_2$ and $V = F/2$. Finally, by gradually increasing F to 40, 100, and 200 cm^{-1}, observe that the agreement starts to break down when F becomes comparable or larger than $\hbar\omega$.

Such an interesting agreement between the time-independent and dependent Hamiltonians can be explained in terms of the interaction picture and rotating wave approximation.