Time-Dependent Dynamics of a Quantum Harmonic Oscillator under an Arbitrary Temperature

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1 The Planck Atomic Units

A variable stored in the memory of a computer always has finite precision. Although the floating point system can preserve the accuracy of the calculations to some extent, it is still desirable to prevent the numbers from becoming too large or too small. Unfortunately, in the field of quantum mechanics, such situations are frequently encountered due to the key physical constants having extremely small values. Examples include the Planck's constant h $(= 6.626070\cdots\times 10^{-34}\ \mathrm{m}^2\ \mathrm{kg}\ \mathrm{s}^{-1})$ and the Boltzmann's constant k_B $(= 1.380649 \times 10^{-23}\ \mathrm{m}^2\ \mathrm{kg}\ \mathrm{s}^{-2}\ \mathrm{K}^{-1})$. One way to avoid potential problems arising from such small numbers is switching to an alternative system of units which is more suited to the problem.

Exercise 1. Consider a system of units where $\hbar = k_\mathrm{B} = 1$. Show that, if we keep the unit of temperature as the same as in the MKS system, the unit of time in this system corresponds to $7.638235\cdots$ ps.

The unit system introduced above is often referred to as *Planck atomic units*, which will be used for the rest of this exercise.

2 The Quantum Harmonic Oscillator

The Hamiltonian of a one-dimensional quantum harmonic oscillator (QHO) is written as

$$\hat{H}_\mathrm{QHO} = \frac{\hat{p}^2}{2m} + \frac{m\omega^2}{2}\hat{x}^2, \tag{1}$$

where $\hat{x}$ and $\hat{p}$ are the position and momentum operators that satisfy canonical commutation relation, $[\hat{x},\ \hat{p}] = i\hbar$. The mass of the particle m can be eliminated from the Hamiltonian by shifting to the *mass-weighted coordinate* defined by

$$\hat{X} = \sqrt{m}\hat{x}, \qquad \hat{P} = \frac{\hat{p}}{\sqrt{m}}, \tag{2}$$

which converts the original Hamiltonian [Eq. (1)] into

$$\hat{H}_\mathrm{QHO} = \frac{\hat{P}^2}{2} + \frac{\omega^2\hat{X}^2}{2}. \tag{3}$$

Exercise 2-1. Confirm that the mass-weighted operators $\hat{X}$ and $\hat{P}$ also satisfy $[\hat{X},\ \hat{P}] = i\hbar$.

At this point, we introduce the ladder operators for the QHO

$$\hat{a} = \sqrt{\frac{\omega}{2\hbar}}\left(\hat{X} + \frac{i}{\omega}\hat{P}\right), \qquad \hat{a}^\dagger = \sqrt{\frac{\omega}{2\hbar}}\left(\hat{X} - \frac{i}{\omega}\hat{P}\right), \tag{4}$$

based on which the Hamiltonian is expressed as

$$\hat{H}_{\text{QHO}} = \hbar\omega\left(\hat{a}^{\dagger}\hat{a} + \frac{1}{2}\right). \tag{5}$$

Let us adopt Dirac's braket notation and denote the nth normalized eigenstate of $\hat{H}$ as $|n\rangle$. Then, the action of the ladder operators to these eigenstates is

$$\hat{a}\,|n\rangle = \sqrt{n}\,|n-1\rangle\,, \qquad \hat{a}^{\dagger}\,|n\rangle = \sqrt{n+1}\,|n+1\rangle\,. \tag{6}$$

Exercise 2-2. Verify Eq. (6) based on the ladder operator treatment of QHO.

We now take the states $\{|n\rangle\}$ as the basis set and use it to cast the operators $\hat{X}$ and $\hat{P}$ in the matrix form. For practical purposes, it is desirable to set a certain upper bound $n_{\max}$ for the quantum number to maintain the size of the basis as finite.

Exercise 2-3. Write a code that accepts $n_{\max}$ as the input and produces the matrix representation of the operators $\hat{X}$ and $\hat{P}$.

3 Quantum Mechanical Simulation of Molecular Vibration

The result of **Exercise 2-3** allows us to obtain the matrix representation of any time-independent Hamiltonian in one-dimension

$$\hat{H} = \frac{\hat{P}^2}{2} + V(\hat{X}), \tag{7}$$

as long as its potential energy component $\hat{V}(\hat{X})$ can be expressed as a polynomial in $\hat{X}$ to a sufficient accuracy. This machinery can be consequently utilized to study the behavior of simple systems related to chemical dynamics, when $V(\hat{X})$ is identical or close to that of QHO.

As a primitive example, we simulate the dynamics of a vibrationally excited diatomic molecule based on the displaced harmonic oscillator (DHO) model. In this model, the vibrational Hamiltonians in the ground and excited electronic states of the molecule are specified as

$$\hat{H}_g = \frac{\hat{P}^2}{2} + \frac{\omega^2\hat{X}^2}{2}, \tag{8a}$$

$$\hat{H}_e = \frac{\hat{P}^2}{2} + \frac{\omega^2(\hat{X}-d)^2}{2}, \tag{8b}$$

respectively, with d being the distance between the energy minima of the two electronic states. We assume that the state vector $|\psi(t)\rangle$ is initially in the ground eigenstate of $\hat{H}_g$, so that $|\psi(0)\rangle = |0\rangle$. The formal solution of the time-dependent Schrödinger equation (TDSE) is given by

$$|\psi(t)\rangle = \hat{U}(t)\,|\psi(0)\rangle\,, \tag{9}$$

with the propagator being

$$\hat{U}(t) = \exp(-i\hat{H}t/\hbar) \tag{10}$$

for a Hamiltonian $\hat{H}$ that is constant in time.

Exercise 3-1. Analytically solve the TDSE under $\hat{H}_g$ to obtain the expression for $|\psi(t)\rangle$ and the expectation value $\langle\hat{X}(t)\rangle$.

If we assume a sudden electronic excitation of the molecule at $t = 0$, the subsequent evolution of the state vector will be governed by $\hat{H}_e$ instead of $\hat{H}_g$. If d is nonzero, $|\psi(0)\rangle = |0\rangle$ is not an eigenstate of $\hat{H}_e$, and therefore the resulting dynamics will not be as trivial as we have seen in **Exercise 3-1**. As for the classical harmonic oscillator, the time dependence of the dynamics can be tracked by two different ways: (semi-)analytical and numerical means.

Exercise 3-2. It can be shown that the expectation value of an operator evolves under the Hamiltonian $\hat{H}$ according to the Ehrenfest's equation,

$$\frac{d}{dt}\langle\hat{A}\rangle = \frac{1}{i\hbar}\langle[\hat{A},\hat{H}]\rangle. \tag{11}$$

Construct the coupled differential equation between $\langle\hat{X}(t)\rangle$ and $\langle\hat{P}(t)\rangle$ based on the equation above, and observe their similarities to the equation of motion for the classical harmonic oscillator.

Exercise 3-3. Numerically simulate the dynamics of $|\psi(t)\rangle$ under $\hat{H}_e$ [Eq. (8b)] until $t = 10$ by both directly evaluating the propagator $\hat{U}(t)$ [Eq. (10)] by diagonalization and applying the fourth-order Runge-Kutta (RK4) method. Take the vibrational angular frequency and Huang-Rhys factor of the molecule as $\omega = 1$ and $s = \omega d^2/(2\hbar) = 0.1$, respectively, and set the maximum quantum number of the basis states as $n_{\max} = 40$. Calculate $\langle\hat{X}(t)\rangle$ and $\langle\hat{P}(t)\rangle$ at time points uniformly spaced by $\Delta t = 0.01$ (Note that Δt has nothing to do with the actual integration of the TDSE, if you use RK4 for the propagation), and confirm that the obtained result matches the analytical solution predicted by **Exercise 3-2**.

4 Incorporating the Effect of Temperature

Up to now, we assumed that the molecule was in its vibrational ground state prior to electronic excitation. This corresponds to the absolute zero temperature, where all molecules can be described by a single wavefunction $|\psi(t)\rangle = \exp(-i\omega t/2)\,|0\rangle$. When the temperature is raised to $T > 0$ and thermal equilibrium is established, the populations of the QHO eigenstates are dictated by Boltzmann distribution and the wavefunctions of individual molecules are not identical any more. To describe such a statistical mixture, we need to rely on the density matrix. The thermal density matrix for the QHO at $t = 0$ is expressed as

$$\hat{\rho}(0;\beta) = \sum_n R_n(\beta)\,|n\rangle\,\langle n| \tag{12}$$

where $\beta = 1/(k_\mathrm{B}T)$ is the so-called inverse temperature and $R_n(\beta)$ is the normalized thermal population for the nth eigenstate,

$$R_n(\beta) = \frac{\exp(-\beta E_n)}{\sum_k \exp(-\beta E_k)}. \tag{13}$$

Based on $\hat{\rho}$, we can express the expectation value of an operator $\hat{A}$ as

$$\langle\hat{A}\rangle = \mathrm{Tr}[\hat{A}\hat{\rho}], \tag{14}$$

where $\mathrm{Tr}[\hat{O}]$ denotes the trace of the matrix representation of the operator $\hat{O}$. Note that the trace of a matrix is independent under a unitary transformation, and therefore the value of Eq. (14) is not affected by the choice of the basis set.

Exercise 4-1. Validate Eq. (14) when $\hat{\rho}$ is given by Eq. (12).

The evolution of $\hat{\rho}(t)$ under the influence of $\hat{H}$ is governed by the Liouville-von Neumann (LvN) equation,

$$i\hbar\frac{d\hat{\rho}(t)}{dt} = [\hat{H}, \hat{\rho}(t)]. \tag{15}$$

Exercise 4-2. Validate Eq. (15) when $\hat{\rho}(0)$ is given by Eq. (12).

The evolution of $\hat{\rho}(t)$ can be simulated by direct integration of the LvN equation [Eq. (15)] by numerical algorithms, e.g. RK4 method. Alternatively, we can separately propagate the component wavefunctions $|\psi_n(t)\rangle$ by TDSE starting from $|\psi_n(0)\rangle = |n\rangle$, and construct $\hat{\rho}(t)$ according to

$$\hat{\rho}(t;\beta) = \sum_n R_n(\beta)\, |\psi_n(t)\rangle \langle\psi_n(t)|\,. \tag{16}$$

As $|\psi_n(t)\rangle = \hat{U}(t)\,|\psi_n(0)\rangle$, it follows that

$$\hat{\rho}(t) = \hat{U}(t)\hat{\rho}(0)\hat{U}^\dagger(t). \tag{17}$$

Combining this relation with Eq. (14) leads to

$$\begin{aligned}\langle\hat{A}(t)\rangle &= \mathrm{Tr}[\hat{A}\hat{U}(t)\hat{\rho}(0)\hat{U}^\dagger(t)] = \mathrm{Tr}[\hat{U}^\dagger(t)\hat{A}\hat{U}(t)\hat{\rho}(0)] \\ &= \mathrm{Tr}[\hat{A}(t)\hat{\rho}(0)],\end{aligned} \tag{18}$$

where the second inequality comes from the cyclic invariance of the trace $\mathrm{Tr}[\hat{C}\hat{D}] = \mathrm{Tr}[\hat{D}\hat{C}]$ and the third equality relies on the Heisenberg picture where $\hat{A}(t) = \hat{U}^\dagger(t)\hat{A}\hat{U}(t)$.

We are now ready to define the quantum time correlation function as

$$\langle\hat{A}(t)\hat{B}(0)\rangle = \mathrm{Tr}[\hat{A}(t)\hat{B}(0)\hat{\rho}(0)]. \tag{19}$$

Exercise 4-3. By numerical calculation, show that the quantum time correlation for the mass-weighted position operator is expressed as

$$\langle\hat{X}(t)\hat{X}(0)\rangle = \frac{\hbar}{2\omega}\left[\coth\left(\frac{\beta\hbar\omega}{2}\right)\cos(\omega t) - i\sin(\omega t)\right], \tag{20}$$

when the time evolution is dictated by $\hat{H}_g$ [Eq. (8a)]. This equation plays a crucial role in the simulation of complicated molecular quantum dynamics, such as transfer of electronic excitation in interacting chromophore molecules or solvent-induced electron transfer between redox pairs.