3. Interaction Picture and Light-Matter Interaction

Chang Woo Kim
Computational Chemistry Group
Department of Chemistry, JNU

Viewpoints of Quantum Dynamics

There are three different viewpoints for quantum dynamics:

- Schrödinger picture
- Heisenberg picture
- Interaction picture

These viewpoints differ in where we put the time dependence, and each of them has unique advantage and consequence.

However, the physical behavior of the system must remain the same regardless of which picture we take.

This is equivalent to saying that the time-dependence of the expectation value $\langle A \rangle_t$ should remain constant.

Schrödinger Picture

This is what we are familiar at: the state vector evolves in time, and the operators remain constant.

$$|\psi(t)\rangle = \hat{U}(t)\,|\psi(0)\rangle\,, \quad \hat{A}(t) = \hat{A}.$$

The expectation value is expressed as

$$\langle A\rangle_t = \langle\psi(t)|\,\hat{A}\,|\psi(t)\rangle = \langle\psi(0)|\,\hat{U}^\dagger(t)\hat{A}\hat{U}(t)\,|\psi(0)\rangle\,.$$

From the TDSE, we have (note that we are allowing $\hat{H}$ to change in time)

$$\frac{d\hat{U}(t)}{dt} = -\frac{i}{\hbar}\hat{H}(t)\hat{U}(t), \quad \frac{d\hat{U}^\dagger(t)}{dt} = \frac{i}{\hbar}\hat{U}^\dagger(t)\hat{H}(t),$$

which leads to the Ehrenfest's theorem, $\dfrac{d\langle A\rangle_t}{dt} = -\dfrac{i}{\hbar}\langle[\hat{A},\hat{H}(t)]\rangle_t.$

Heisenberg Picture

We can take a different viewpoint and split the expectation value in a different way:

$$\langle A\rangle_t = \langle\psi(t)|\,\hat{U}^\dagger(t)\hat{A}\hat{U}(t)\,|\psi(0)\rangle = \langle\psi(0)|\,\hat{A}(t)\,|\psi(t_0)\rangle.$$

From this viewpoint, the state vector is fixed and the operator evolves. This is Heisenberg picture.

The equation of motion for the operator is

$$\frac{d\hat{A}(t)}{dt} = -\frac{i}{\hbar}[\hat{A}(t), \hat{H}(t)],$$

which resembles the Ehrenfest's theorem and is useful in showing quantum-classical correspondence.

Heisenberg Picture

Example: If we consider the harmonic oscillator Hamiltonian

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{m\omega^2}{2}\hat{x}^2,$$

$$\begin{aligned}\frac{d}{dt}\hat{x}(t) &= -\frac{i}{\hbar}[\hat{x}(t), \hat{H}] = -\frac{i}{\hbar}[\hat{U}^\dagger \hat{x}\hat{U}, \hat{H}] = -\frac{i}{\hbar}\hat{U}^\dagger[\hat{x}, \hat{H}]\hat{U} \\ &= -\frac{i}{\hbar}\frac{1}{2m}[\hat{x}, \hat{p}^2] = \frac{\hat{p}(t)}{m}, \\ \frac{d}{dt}\hat{p}(t) &= -\frac{i}{\hbar}[\hat{p}(t), \hat{H}] = -\frac{i}{\hbar}[\hat{U}^\dagger \hat{p}\hat{U}, \hat{H}] = -\frac{i}{\hbar}\hat{U}^\dagger[\hat{p}, \hat{H}]\hat{U} \\ &= -\frac{i}{\hbar}\frac{m\omega^2}{2}[\hat{p}, \hat{x}^2] = -m\omega^2\hat{x}(t).\end{aligned}$$

The operators evolve in a similar way to classical dynamics.

Interaction Picture

This picture is in between Schrödinger and Heisenberg pictures, and is effective in treating the dynamics under

$$\hat{H}(t) = \hat{H}_0 + \hat{V}(t)$$

where the perturbation $\hat{V}(t)$ has all the time dependence.

We start by defining

$$\hat{U}_I(t) = \hat{U}_0^\dagger(t)\hat{U}(t),$$

where $\hat{U}(t)$ exists but its form is unknown.

This splits $\hat{U}(t)$ into a product form

$$\hat{U}(t) = \hat{U}_0(t)\hat{U}_I(t).$$

Interaction Picture

If we substitute $\hat{U}(t)$, the expectation value is expressed as

$$\begin{aligned}\langle A\rangle_t &= \langle\psi(0)|\,\hat{U}_I^\dagger(t)\,\hat{U}_0^\dagger(t)\hat{A}\hat{U}_0(t)\,\hat{U}_I(t)\,|\psi(0)\rangle \\ &= \langle\psi_I(t)|\hat{A}_I(t)|\psi_I(t)\rangle.\end{aligned}$$

That is, the operator moves under the influence of $\hat{H}_0$ and the state vector is affected by the time-dependent component $\hat{V}(t)$.

The latter becomes more apparent by observing

$$i\hbar\frac{d\hat{U}}{dt} = [\hat{H}_0 + \hat{V}(t)]\hat{U} \quad \rightarrow \quad i\hbar\frac{d\hat{U}_0}{dt}\hat{U}_I + i\hbar\hat{U}_0\frac{d\hat{U}_I}{dt} = [\hat{H}_0 + \hat{V}(t)]\hat{U}_0\hat{U}_I,$$

from which we can derive

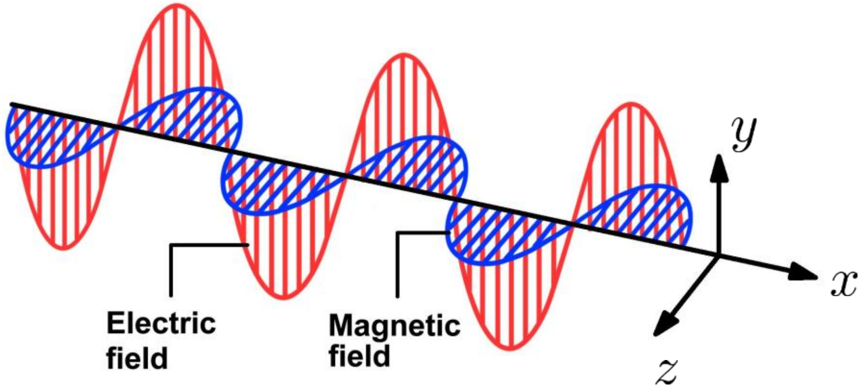
$$i\hbar\frac{d\hat{U}_I}{dt} = \hat{U}_0^\dagger\hat{V}(t)\hat{U}_0\hat{U}_I = \hat{V}_I(t)\hat{U}_I.$$

Summary of the Viewpoints

	Schrödinger	Heisenberg	Interaction
State vector $\lvert\psi(t)\rangle$	$\hat{U}(t)\lvert\psi(0)\rangle$	$\lvert\psi(0)\rangle$	$\hat{U}_I(t)\lvert\psi(0)\rangle$
Operator $\hat{A}(t)$	$\hat{A}$	$\hat{U}^\dagger(t)\hat{A}\hat{U}(t)$	$\hat{U}_0^\dagger(t)\hat{A}\hat{U}_0(t)$
Equation of motion	$i\hbar\frac{d}{dt}\hat{U}(t) = \hat{H}(t)\hat{U}(t)$	$i\hbar\frac{d}{dt}\hat{A}(t) = [\hat{A}(t), \hat{H}(t)]$	$i\hbar\frac{d}{dt}\hat{U}_I(t) = \hat{V}_I(t)\hat{U}_I(t)$ $i\hbar\frac{d}{dt}\hat{A}_I(t) = [\hat{A}_I(t), \hat{H}_0]$

Interaction of Quantum System with Light

In the classical electromagnetism, the light is represented as a combination of oscillating electric and magnetic field.



$$\vec{\mathcal{E}}(t) = \mathcal{E}_0 \cos(kx - \omega t)\hat{e}_y$$
$$\vec{\mathcal{B}}(t) = \mathcal{B}_0 \cos(kx - \omega t)\hat{e}_z$$

The ratio between the amplitudes of the electric and magnetic fields are equal to the velocity:

$$\mathcal{B}_0 = \frac{\mathcal{E}_0}{v}.$$

We can therefore neglect the effect of $\vec{\mathcal{B}}(t)$ and focus only on $\vec{\mathcal{E}}(t)$.

Interaction of Quantum System with Light

When a wavefunction of a charged particle interacts with light, the tendency of interaction can be quantified by the dipole operator

$$\hat{\mu} = q\hat{r}.$$

Its matrix elements can be calculated in terms of the wavefunctions,

$$\vec{\mu}_{ab} = \langle\psi_a|\, q\hat{r}\, |\psi_b\rangle = q\int \psi_a^*(\vec{r})\,\hat{r}\,\psi_b(\vec{r})\,d\vec{r}$$

$$= \mu_{ab}^x \mathbf{e}_x + \mu_{ab}^y \mathbf{e}_y + \mu_{ab}^z \mathbf{e}_z,$$

where q is the charge of the particle and $\hat{r}$ is the positional vector operator in three-dimensional space

$$\hat{r} = \hat{x}\mathbf{e}_x + \hat{y}\mathbf{e}_y + \hat{z}\mathbf{e}_z.$$

Interaction of Quantum System with Light

We can generalize the expression to multi-particle system,

$$\vec{\mu}_{ab} = \langle\psi_a| \left(q_1\hat{r}_1 + q_2\hat{r}_2 + \cdots q_n\hat{r}_n\right) |\psi_b\rangle$$
$$= \sum_j \left(q_j \int \psi_a^*(\vec{r}_1, \vec{r}_2 \cdots \vec{r}_n)\, \hat{r}_j\, \psi_b(\vec{r}_1, \vec{r}_2 \cdots \vec{r}_n)\, d\vec{r}_1\, d\vec{r}_2 \cdots d\vec{r}_n \right),$$

with $\hat{r}_j = \hat{x}_j\mathbf{e}_x + \hat{y}_j\mathbf{e}_y + \hat{z}_j\mathbf{e}_z$.

As a result, $\vec{\mu}$ is still a 3-dimensional vector whose components are

$$\mu_{ab}^x = \sum_j \left(q_j \int \psi_a^*(\vec{r}_1, \vec{r}_2 \cdots \vec{r}_n)\, \hat{x}_j\, \psi_b(\vec{r}_1, \vec{r}_2 \cdots \vec{r}_n)\, d\vec{r}_1\, d\vec{r}_2 \cdots d\vec{r}_n \right),$$

and so on.

Interaction of Quantum System with Light

When $a = b$, $\vec{\mu}_{aa}$ is the stationary dipole moment of the state a.

In contrast, when $a \neq b$, $\vec{\mu}_{ab}$ couples different states in the presence of electric field and is called transition dipole moment.

The time-dependent electric field $\vec{\mathcal{E}}(t)$ introduces the additional term in the Hamiltonian

$$\hat{H}(t) = \hat{H}_0 + \hat{V}(t),$$

whose matrix representation in $|\psi_a\rangle$ and $|\psi_b\rangle$ basis is

$$\hat{V}^{\psi}(t) = \begin{pmatrix} \vec{\mathcal{E}}(t) \cdot \vec{\mu}_{aa} & \vec{\mathcal{E}}(t) \cdot \vec{\mu}_{ab} \\ \vec{\mathcal{E}}(t) \cdot \vec{\mu}_{ba} & \vec{\mathcal{E}}(t) \cdot \vec{\mu}_{bb} \end{pmatrix}.$$

We can see that $\vec{\mu}_{ab}$ can indeed induce the transition.

Interaction of Quantum System with Light

However, to analyze the dynamics, we need to consider the total Hamiltonian

$$\hat{H}^{\psi}(t) = \hat{H}_0^{\psi} + \hat{V}^{\psi}(t) = \begin{pmatrix} E_a + \vec{\mathcal{E}}(t) \cdot \vec{\mu}_{aa} & \vec{\mathcal{E}}(t) \cdot \vec{\mu}_{ab} \\ \vec{\mathcal{E}}(t) \cdot \vec{\mu}_{ba} & E_b + \vec{\mathcal{E}}(t) \cdot \vec{\mu}_{bb} \end{pmatrix}.$$

where E_a and E_b are the energies of the molecular quantum states.

Usually, the energy difference $E_b - E_a$ between these states is very large compared to the dipole moment contribution, and the population transfer cannot easily take place.

However, as we will see, a resonant light wave which satisfies $\hbar\omega = E_b - E_a$ can induce a complete population transfer.

Light-Molecule Interaction in the Interaction Picture

We first neglect the diagonal contribution of the dipole, which is negligible compared to the diagonal energy difference.

$$\hat{H}^{\psi}(t) = \begin{pmatrix} E_a & \vec{\mathcal{E}}(t) \cdot \vec{\mu}_{ab} \\ \vec{\mathcal{E}}(t) \cdot \vec{\mu}_{ba} & E_b \end{pmatrix}.$$

Then we assume a resonant monochromatic light

$$\vec{\mathcal{E}}(t) = \vec{\mathcal{E}}_0 \cos(\omega t), \quad \hbar\omega = E_b - E_a,$$

and redefine the zero of energy as $E_a \to 0$. As a result, we obtain

$$\hat{H}^{\psi}(t) = \begin{pmatrix} 0 & F\cos(\omega t) \\ F\cos(\omega t) & \hbar\omega \end{pmatrix}.$$

where we have defined $F = \vec{\mathcal{E}}_0 \cdot \vec{\mu}_{ab} = \vec{\mathcal{E}}_0 \cdot \vec{\mu}_{ba}$.

Light-Molecule Interaction in the Interaction Picture

We now switch to the interaction picture by splitting the time-independent and dependent parts

$$\hat{H}^{\psi}(t) = \hat{H}_0^{\psi} + \hat{V}^{\psi}(t) = \begin{pmatrix} 0 & 0 \\ 0 & \hbar\omega \end{pmatrix} + \begin{pmatrix} 0 & F\cos(\omega t) \\ F\cos(\omega t) & 0 \end{pmatrix}.$$

Our goal is to obtain the propagator in the interaction picture $\hat{U}_I^{\psi}(t)$.

We start by transforming the Hamiltonian according to

$$\hat{V}_I(t) = \hat{U}_0^{\dagger}\hat{V}(t)\hat{U}_0,$$

with the matrix representations of the operators

$$\hat{U}_0^{\psi}(t) = \begin{pmatrix} 1 & 0 \\ 0 & e^{-i\omega t} \end{pmatrix}, \quad \hat{V}^{\psi}(t) = \frac{F}{2}\begin{pmatrix} 0 & e^{i\omega t} + e^{-i\omega t} \\ e^{i\omega t} + e^{-i\omega t} & 0 \end{pmatrix}.$$

Light-Molecule Interaction in the Interaction Picture

Therefore, we have

$$\begin{aligned}\hat{V}_I(t) &= \hat{U}_0^\dagger \hat{V}(t)\hat{U}_0 \\ &= \frac{F}{2}\begin{pmatrix}1 & 0 \\ 0 & e^{i\omega t}\end{pmatrix}\begin{pmatrix}0 & e^{i\omega t}+e^{-i\omega t} \\ e^{i\omega t}+e^{-i\omega t} & 0\end{pmatrix}\begin{pmatrix}1 & 0 \\ 0 & e^{-i\omega t}\end{pmatrix} \\ &= \frac{F}{2}\begin{pmatrix}0 & 1+e^{-2i\omega t} \\ 1+e^{2i\omega t} & 0\end{pmatrix} \sim \begin{pmatrix}0 & F/2 \\ F/2 & 0\end{pmatrix},\end{aligned}$$

The last step is called rotating wave approximation (RWA), which is satisfied when $F/2 \ll \hbar\omega$ (weak light).

We notice that the interaction Hamiltonian now allows a complete population exchange in the evolution of $|\psi_I(t)\rangle$.

Light-Molecule Interaction in the Interaction Picture

By using the expression

$$i\hbar \frac{d}{dt}\hat{U}_I(t) = \hat{V}_I(t)\hat{U}_I(t),$$

and that the mixing angle is $\theta = \pi/4$, we can derive the propagator (chapter 2, slide 23)

$$\hat{U}_I^{\psi}(t) = \begin{pmatrix} \cos(\Omega t) & -i\sin(\Omega t) \\ -i\sin(\Omega t) & \cos(\Omega t) \end{pmatrix}, \quad \Omega = \frac{F}{2\hbar}.$$

If we assume that the molecular state is $|\psi_a\rangle$ at $t = 0$, the evolution of the state follows

$$|\psi(0)\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad |\psi_I(t)\rangle = \hat{U}_I^{\psi}|\psi(0)\rangle = \begin{pmatrix} \cos(\Omega t) \\ -i\sin(\Omega t) \end{pmatrix}.$$

Light-Molecule Interaction in the Interaction Picture

We finally go back to the Schrödinger picture by using

$$\hat{U}(t) = \hat{U}_0(t)\hat{U}_I(t),$$

which indicates that

$$\begin{aligned}|\psi(t)\rangle &= \hat{U}^{\psi}(t)\,|\psi(0)\rangle = \hat{U}_0^{\psi}(t)\hat{U}_I^{\psi}(t)\,|\psi(0)\rangle \\ &= \begin{pmatrix}1 & 0 \\ 0 & e^{-i\omega t}\end{pmatrix}\begin{pmatrix}\cos(\Omega t) \\ -i\sin(\Omega t)\end{pmatrix} = \begin{pmatrix}\cos(\Omega t) \\ -ie^{-i\omega t}\sin(\Omega t)\end{pmatrix}.\end{aligned}$$

Therefore the time-dependent populations of individual states are

$$P_a(t) = \cos^2(\Omega t), \quad P_b(t) = \sin^2(\Omega t),$$

which oscillates with the period $T = \dfrac{h}{F}$.

Summary

By using the interaction picture, we could see how an oscillating electric field can induce transition between different quantum states.

The derivation utilized rotating wave approximation, which requires the light-molecule interaction strength F to be much smaller than $\hbar\omega$.

If this condition is satisfied, the dynamics is slow enough so that the effect of the rotating term $e^{2i\omega t}$ averages out to zero during the dynamics.

The light can induce both absorption and stimulated emission.

Question: how about spontaneous emission?