Photo-Induced Chemistry II

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Introduction

These two lectures discuss time-dependent quantum mechanics. We aim to qualitatively describe wave packet dynamics in photochemical reactions.

Lecture 1

The basics of time-dependent quantum mechanics:

- how wave functions and expectation values vary with time

Lecture 2

The wave packet model for quantum dynamics

- the approximations involved in simple wave packet models
- how a wave packet propagates with time

1.1 Time-dependent Schrödinger equation

Quantum mechanics describes the dual wave-particle nature of matter at the molecular level.

Schrödinger's time-dependent equation for the wave function is

$$\boxed{i\hbar\frac{\partial}{\partial t}\Psi = \hat{H}\Psi}$$

- $\Psi(\mathbf{r}, \mathbf{R}, t)$ is the molecular wave function:
  - $\Psi^*(\mathbf{r}, \mathbf{R}, t)\Psi(\mathbf{r}, \mathbf{R}, t)$ is the probability of finding at time t an electron at each position $\mathbf{r} = (\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n)$ and the nuclei at positions $\mathbf{R} = (\mathbf{R}_1, \mathbf{R}_2, \ldots, \mathbf{R}_N)$
- $\hat{H}$ is the molecular Hamiltonian

$$\hat{H} = \sum_i^n \frac{-\hbar^2}{2m_e}\nabla_i^2 + \sum_I^N \frac{-\hbar^2}{2M_I}\nabla_I^2 \qquad \text{Kinetic}$$

$$+ \sum_{i<j}^n \frac{e^2}{4\pi\varepsilon_0 r_{ij}} + \sum_{I<J}^N \frac{e^2 Z_I Z_J}{4\pi\varepsilon_0 r_{IJ}} + \sum_i^n \sum_I^N \frac{-e^2 Z_I}{4\pi\varepsilon_0 r_{iI}} \qquad \text{Potential}$$

The molecular Hamiltonian is time independent.

If there is a non-zero time-dependent external potential, such as an oscillating electromagnetic field (a photon), the Hamiltonian is then time-dependent.

$$+\hat{V}(\mathbf{r}, \mathbf{R}, t)$$

- in this course we will not treat the photon explicitly

1.2 The time propagator

The time-dependent Schrödinger equation describes how a wave function propagates in time.

The formal solution is

$$\Psi(\mathbf{r},\mathbf{R},t) = e^{-\frac{i}{\hbar}\hat{H}t}\Psi(\mathbf{r},\mathbf{R},0)$$

The operator $e^{-\frac{i}{\hbar}\hat{H}t}$ evolves the wave function forwards in time from $t=0$ to time t

- $e^{-\frac{i}{\hbar}\hat{H}t}$ is called the time propagator

The simplest approximation to the time propagator is the linear approximation $e^{-\frac{i}{\hbar}\hat{H}t} \approx 1 - \frac{i}{\hbar}\hat{H}t$

- $\Psi(\mathbf{r},\mathbf{R},t+\Delta t) \approx \Psi(\mathbf{r},\mathbf{R},t) - \frac{i}{\hbar}\hat{H}\Psi(\mathbf{r},\mathbf{R},t)\Delta t$

1.3 Hamiltonian eigenstates

The eigenstates of the (time-independent) molecular Hamiltonian have a simple factorizable time dependence of the form

$$\Psi_k(\mathbf{r},\mathbf{R},t) = \psi_k(\mathbf{r},\mathbf{R})\phi_k(t)$$

- An eigenstate is an eigenfunction with eigenvalue E_k

$$\hat{H}\psi_k(\mathbf{r},\mathbf{R}) = E_k\psi_k(\mathbf{r},\mathbf{R})$$

- Therefore $i\hbar\frac{\partial}{\partial t}\Psi = \hat{H}\Psi$

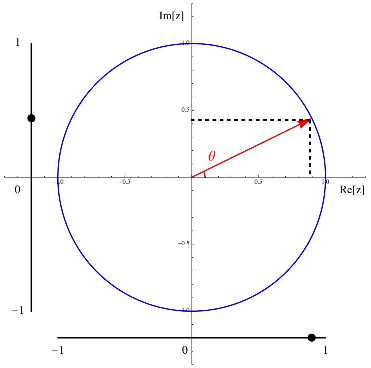
$$i\hbar\frac{\partial}{\partial t}\psi_k(\mathbf{r},\mathbf{R})\phi_k(t) = \hat{H}\psi_k(\mathbf{r},\mathbf{R})\phi_k(t)$$

$$i\hbar\frac{\partial}{\partial t}\psi_k(\mathbf{r},\mathbf{R})\phi_k(t) = E_k\psi_k(\mathbf{r},\mathbf{R})\phi_k(t)$$

$$i\hbar\frac{\partial}{\partial t}\phi_k(t) = E_k\phi_k(t) \quad \rightarrow \quad \boxed{\phi_k(t) = e^{-iE_kt/\hbar - i\gamma}}$$

Exercise 1

Complex numbers arise in wave mechanics since they describe rotational or oscillatory motion $e^{i\theta} = \cos\theta + i\sin\theta$



$$\phi_k(t) = e^{-iE_k t/\hbar - i\gamma}$$

$$\theta = -E_k t/\hbar - \gamma$$

The frequency of the oscillation is related to the energy

$$E_k = \hbar\omega_k = h\nu_k$$

- the time-dependence is an oscillation in the complex plane which can give rise to interference (constructive/destructive)

The nature of an eigenstate does not vary with time:

The probability of finding the electrons at positions $\mathbf{r}$ and the nuclei at positions $\mathbf{R}$ is independent of time

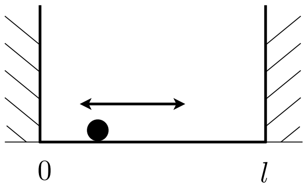
- $$\begin{aligned} |\Psi(\mathbf{r},\mathbf{R},t)|^2 &= |\psi_k(\mathbf{r},\mathbf{R})\phi_k(t)|^2 \\ &= |\psi_k(\mathbf{r},\mathbf{R})|^2 e^{\frac{i}{\hbar}E_k t + i\gamma - \frac{i}{\hbar}E_k t - i\gamma} \\ &= |\psi_k(\mathbf{r},\mathbf{R})|^2 \end{aligned}$$

All expectation values are therefore also time-independent

- $\langle\Psi(\mathbf{r},\mathbf{R},t)|\hat{A}|\Psi(\mathbf{r},\mathbf{R},t)\rangle = \langle\psi_k(\mathbf{r},\mathbf{R})|\hat{A}|\psi_k(\mathbf{r},\mathbf{R})\rangle$

Exercise 2

Example 1. A particle in a box (standing waves)



$$\hat{H} = \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \hat{V}(x)$$

$$\hat{V}(x) = \begin{cases} 0 & 0 < x < l \\ \infty & \text{otherwise} \end{cases}$$

- The spatial eigenstates for a particle in a box of length l are

$$\psi_n(x) = \sqrt{\frac{2}{l}}\sin kx \qquad E_n = \frac{\hbar^2 k^2}{2m} \qquad k = \frac{n\pi}{l}$$

$$n = 1, 2 \cdots$$

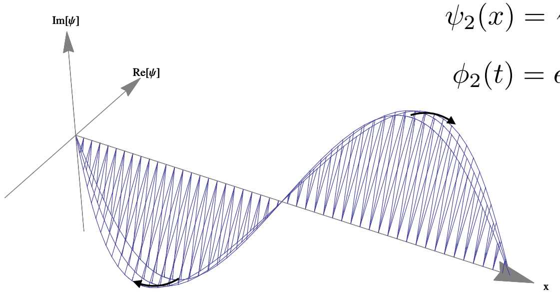
- The full time-dependent eigenstates are

$$\Psi_n(x,t) = \psi_n(x)\phi_n(t) \qquad \phi_n(t) = e^{-iE_n t/\hbar - i\gamma}$$

The time-dependence is analogous to a stationary (or standing) wave, such as the oscillations of a violin string.

$$\psi_2(x) = \sqrt{\frac{2}{l}}\sin\frac{2\pi x}{l}$$

$$\phi_2(t) = e^{-iE_2 t/\hbar}$$

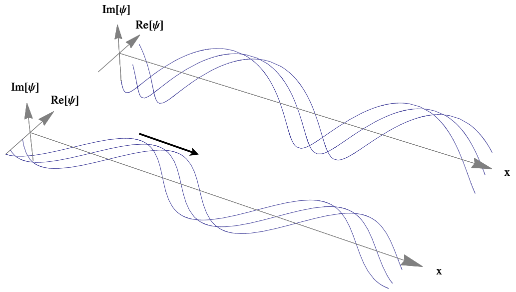


- The wavefront is stationary - it does not move with time
- Time dependence is just a rotation in the complex plane
- $|\Psi|^2$ is time-independent

Example 2. A free particle (travelling waves)

- The wave function for particle with momentum $p = \hbar k$ moving on a flat potential is a plane wave

$$\Psi_k(x,t) = e^{ikx} e^{-iE_k t/\hbar - i\gamma} \qquad E_k = \frac{\hbar^2 k^2}{2m} = \frac{p^2}{2m}$$



projection
onto real axis

motion is like
a corkscrew

The time-dependence is analogous to travelling wave, such as the waves of the ocean. The wavefront moves forward in time.

1.4 Superposition of eigenstates

Any wave function can be decomposed into a linear combination (a superposition) of the eigenstates.

$$\Psi(x,t) = \sum_k c_k \, \psi_k(x) \, e^{-iE_k t/\hbar}$$

- The amplitudes c_k take complex values (absorb the phase)

$|\Psi(x,t)|^2$ is time-dependent:

$$\begin{aligned} |\Psi(x,t)|^2 &= \sum_{kl} c_l^* c_k \; \psi_l^*(x) \psi_k(x) \; e^{-i(E_k - E_l)t/\hbar} \\ &= \sum_{kl} \Re[c_l^* c_k] \Re[\psi_l^* \psi_k](x) \cos[(E_l - E_k)t/\hbar] \end{aligned}$$

Nevertheless, physical observables with operators that commute with the Hamiltonian have time-independent expectation values

e.g. conservation of energy, conservation of momentum

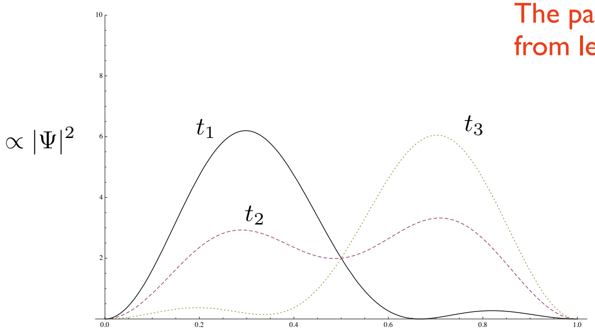
Exercises 3 and 4

Physical observables that do not commute with the Hamiltonian have time-dependent expectation values.

- e.g. superposition of two particle in a box eigenstates

$$\Psi(x,t) = \frac{1}{\sqrt{2}}\psi_1(x)e^{-iE_1t/\hbar} + \frac{1}{\sqrt{2}}\psi_2(x)e^{-iE_2t/\hbar}$$

    - position expectation value $\langle\Psi|\hat{x}|\Psi\rangle$ is time dependent



The particle moves from left to right

1 Summary

The time-dependent Schrödinger equation tells us how wave functions propagate in time.

Eigenstates of the time-independent Schrödinger equation have separable space and time dependence.

- Expectation values of pure eigenstates are time independent.

Superpositions of eigenstates have more complicated time dependence.

- Expectation values of conserved quantities, such as total energy and total momentum, are time independent.
- Expectation values for other physical observables, such as the position of a particle, vary with time.

2 Recap

The time-dependent Schrödinger equation for the wave function

$$i\hbar\frac{\partial}{\partial t}\Psi = \hat{H}\Psi$$

- $\Psi^*(\mathbf{r},\mathbf{R},t)\Psi(\mathbf{r},\mathbf{R},t)$ is the probability of finding at time t an electron at each position $\mathbf{r} = (\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n)$ and the nuclei at positions $\mathbf{R} = (\mathbf{R}_1, \mathbf{R}_2, \ldots, \mathbf{R}_N)$
- The molecular Hamiltonian $(\hat{H} = \hat{T}_e + \hat{T}_n + \hat{V}_e + \hat{V}_n + \hat{V}_{ne})$

$$\hat{H} = \sum_i^n \frac{-\hbar^2}{2m_e}\nabla_i^2 + \sum_I^N \frac{-\hbar^2}{2M_I}\nabla_I^2$$

$$+\sum_{i<j}^n \frac{e^2}{4\pi\varepsilon_0 r_{ij}} + \sum_{I<J}^N \frac{e^2 Z_I Z_J}{4\pi\varepsilon_0 r_{IJ}} + \sum_i^n\sum_I^N \frac{-e^2 Z_I}{4\pi\varepsilon_0 r_{iI}}$$

- The time propagator

$$\Psi(\mathbf{r},\mathbf{R},t) = e^{-\frac{i}{\hbar}\hat{H}t}\Psi(\mathbf{r},\mathbf{R},0)$$

2.1 Adiabatic separation of electrons and nuclei

The full molecular wave function depends on the positions of the electrons *and* the nuclei. $\Psi(\mathbf{r},\mathbf{R},t)$

- Mass of an electron: $1\ m_e = 9.11\times10^{-31}\,\mathrm{Kg}$
- Mass of a proton: $1837\ m_e = 1.67\times10^{-27}\,\mathrm{Kg}$

The forces on the electrons and nuclei are comparable.

Electrons therefore typically move $> 10^3$ times faster than nuclei.

To a good approximation the electronic wave function depends parametrically on the nuclear coordinates.

$$\Psi(\mathbf{r},\mathbf{R},t) = \Psi_e(\mathbf{r};\mathbf{R})\Psi_n(\mathbf{R},t)$$

- the nuclei are static from the perspective of the electrons
- no explicit time-dependence of the electronic wave function

Inserting into the Schrödinger equation:

$$i\hbar\frac{\partial}{\partial t}\Psi_e(\mathbf{r};\mathbf{R})\Psi_n(\mathbf{R},t) = \hat{H}\Psi_e(\mathbf{r};\mathbf{R})\Psi_n(\mathbf{R},t)$$

The right hand side is

$$\begin{aligned}
&= (\hat{T}_e + \hat{T}_n + \hat{V}_e + \hat{V}_n + \hat{V}_{ne})\Psi_e(\mathbf{r};\mathbf{R})\Psi_n(\mathbf{R},t) \\
&= \big[(\hat{T}_e + \hat{V}_e + \hat{V}_{ne})\Psi_e(\mathbf{r};\mathbf{R})\big]\Psi_n(\mathbf{R},t) \\
&\quad + \Psi_e(\mathbf{r};\mathbf{R})\big[(\hat{T}_n + \hat{V}_n)\Psi_n(\mathbf{R},t)\big] \\
&\quad + \text{ terms where } \hat{T}_n \text{ acts on } \Psi_e \qquad \longleftarrow \text{ discard}
\end{aligned}$$

- the adiabatic approximation (or Born-Oppenheimer approximation) involves discarding all effects on the electrons from the motion of the nuclei: these effects are small.

Now

$$\begin{aligned}
i\hbar\frac{\partial}{\partial t}\Psi_e(\mathbf{r};\mathbf{R})\Psi_n(\mathbf{R},t) \overset{\text{BO}}{=} &\big[(\hat{T}_e + \hat{V}_e + \hat{V}_{ne})\Psi_e(\mathbf{r};\mathbf{R})\big]\Psi_n(\mathbf{R},t) \\
&+ \Psi_e(\mathbf{r};\mathbf{R})\big[(\hat{T}_n + \hat{V}_n)\Psi_n(\mathbf{R},t)\big]
\end{aligned}$$

The equation factorizes into a time-independent Schrödinger equation for the electrons (at every $\mathbf{R}$)

$$(\hat{T}_e + \hat{V}_e + \hat{V}_{ne})\Psi_e(\mathbf{r};\mathbf{R}) = W_e(\mathbf{R})\Psi_e(\mathbf{r};\mathbf{R})$$

and a time-dependent Schrödinger equation for the nuclei in the presence of the electronic potential $W_e(\mathbf{R})$

$$i\hbar\frac{\partial}{\partial t}\Psi_n(\mathbf{R},t) = (\hat{T}_n + \hat{V}_n + \hat{W}_e)\Psi_n(\mathbf{R},t)$$

- $\hat{V}_n(\mathbf{R}) + \hat{W}_e(\mathbf{R})$ is the potential energy surface
  - electrons affect the nuclei through this effective potential

Summary of the Born-Oppenheimer approximation:

The electrons follow the nuclei adiabatically (fully relaxed).

- The wave function for the electrons is time-independent, but it depends on the positions of the nuclei.

The nuclei respond to the effective interaction with the fully relaxed electron cloud (the electronic potential energy surface).

- The nuclear wave function is time-dependent.

Within the BO picture, any change in the electronic wave function (e.g. photo excitation) is instantaneous from the point of view of the nuclei (sudden approximation).

2.2 Gaussian wave packets

Plane waves $\Psi_k(x,t) = e^{ikx}e^{-iE_k t/\hbar - i\gamma}$ describe a particle with a precise (certain) momentum: $p = \hbar k, \qquad \Delta p = 0$

As required by the uncertainty principle, $\Delta p \Delta x \geq \frac{\hbar}{2}$ they are therefore completely delocalised in space $\Delta x = \infty$

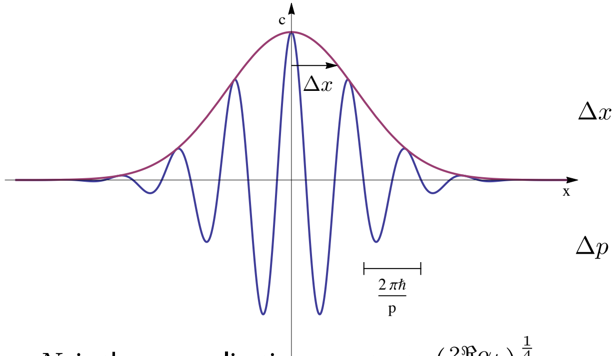
Wave packets describe a particle that is localised in space, but that has uncertain position and uncertain momentum.

$$\Psi(x,t) = \left(\frac{2\Re\alpha_t}{\pi}\right)^{\frac{1}{4}} e^{-\alpha_t(x-c_t)^2 + \frac{i}{\hbar}p_t(x-c_t) + \frac{i}{\hbar}\gamma_t}$$

- A Gaussian distribution of positions
- A Gaussian distribution of momenta

$$\Psi(k,t) = \left(\frac{1}{4\pi\alpha_t}\right)^{\frac{1}{2}} \left(\frac{2\Re\alpha_t}{\pi}\right)^{\frac{1}{4}} e^{-\frac{1}{4\alpha_t}(k-\frac{p_t}{\hbar})^2 - ikc_t + \frac{i}{\hbar}\gamma_t}$$

$$\Psi(x,t) = N e^{-\alpha_t (x-c_t)^2 + \frac{i}{\hbar} p_t (x-c_t) + \frac{i}{\hbar}\gamma_t}$$



$$\Delta x = \sqrt{\frac{1}{4\Re\alpha_t}}$$

$$\Delta p = \sqrt{\frac{\hbar^2 \alpha_t^* \alpha_t}{\Re\alpha_t}}$$

- N is the normalisation constant $\left(\frac{2\Re\alpha_t}{\pi}\right)^{\frac{1}{4}}$
- α_t is the width parameter that determines Δx and Δp
- c_t is the centre of the Gaussian in position space
- p_t is the centre of the Gaussian in momentum space
- γ_t is the phase factor

Exercises 5 and 6

2.3 Gaussian wave packet propagation

Gaussian wave packets remain Gaussian when propagated on a potential of the form $V(x) = \frac{1}{2}Ax^2 + Bx + C$

- This can be seen by inserting the general form for the Gaussian wave packet into Schrödinger's equation

$$i\hbar\frac{\partial\Psi}{\partial t} = \Big[-i\hbar\dot{\alpha}_t (x-c_t)^2 - \dot{p}_t (x-c_t) - \dot{\gamma}_t \\ + \tfrac{i\hbar\dot{\alpha}_t}{4\alpha_t} + i\dot{c}_t 2\hbar\alpha_t (x-c_t) - \dot{c}_t p_t \Big]\Psi$$

$$\hat{H}\Psi = \Big[\tfrac{\hbar^2}{m}\alpha_t - \tfrac{2\hbar^2}{m}\alpha_t^2 (x-c_t)^2 + i\tfrac{2\hbar}{m}\alpha_t p_t (x-c_t) \\ + \tfrac{1}{2m}p_t^2 + V(x) \Big]\Psi$$

- Can equate powers of $(x-c_t)$ so that $i\hbar\frac{\partial\Psi}{\partial t} = \hat{H}\Psi$

Free particles: Gaussian wave packets on a flat potential

For a flat potential $V(x) = 0$

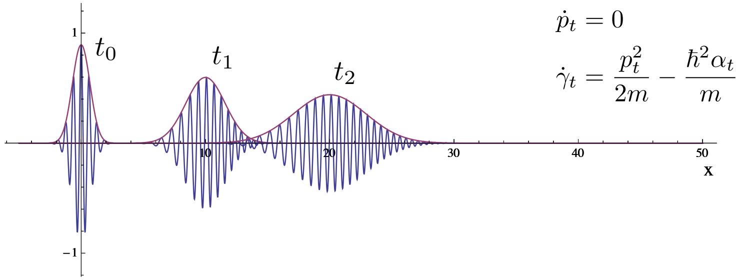
- working up the equations we obtain

$$\dot{\alpha}_t = -i\frac{2\hbar\alpha_t^2}{m}$$

$$\dot{c}_t = \frac{p_t}{m}$$

$$\dot{p}_t = 0$$

$$\dot{\gamma}_t = \frac{p_t^2}{2m} - \frac{\hbar^2\alpha_t}{m}$$



- The wave packet spreads (disperses) $\Re\alpha_t = \dfrac{\alpha_0}{1 + \frac{4\hbar^2\alpha_0^2}{m^2}t^2}$
- c_t and p_t obey classical equations of motion

$$F = \dot{p} \qquad p = m\dot{c}$$

Exercise 7

The harmonic oscillator: Coherent states

For a harmonic potential we have

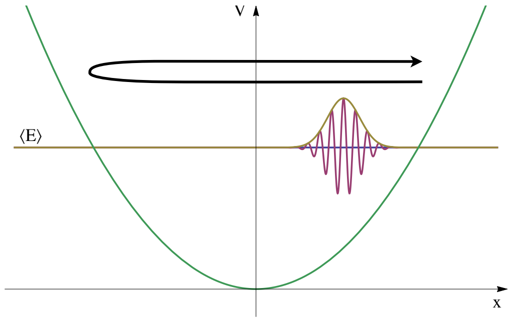
$$V(x) = \tfrac{1}{2}m\omega^2x^2$$

$$\dot{\alpha}_t = -i\frac{2\hbar\alpha_t^2}{m} + i\frac{m\omega^2}{2\hbar}$$

$$\dot{c}_t = \frac{p_t}{m}$$

$$\dot{p}_t = -m\omega c_t$$

$$\dot{\gamma}_t = \frac{p_t^2}{2m} - \frac{\hbar^2\alpha_t}{m} - \frac{m\omega^2}{2\hbar}c_t^2$$



- A coherent state has $\dot{\alpha}_t = 0$ so $\alpha = \dfrac{m\omega}{2\hbar}$ is constant
- c_t and p_t obey classical equations of motion $c_t = c\cos(\omega t + \theta)$

$$p_t = -m\omega c\sin(\omega t + \theta)$$

Exercise 8

Coherent states

Coherent states are convenient approximate wave functions

- They are maximally compact $\Delta x \Delta p = \frac{\hbar}{2}$
- They are exact for harmonic potentials and are therefore accurate for short time propagations on non-harmonic potentials.
- A wave packet in all nuclear coordinates $\mathbf{R}$ is a product of wave packets in each degree of freedom

$$\Psi(\mathbf{R}, t) = \prod_q^M \Psi_q(q, t)$$

- This can more generally be written as a multidimensional Gaussian wave packet

$$\Psi(\mathbf{R}, t) = N e^{-(\mathbf{R}-\mathbf{c}_t)\boldsymbol{\alpha}(\mathbf{R}-\mathbf{c}_t)^2 + \frac{i}{\hbar}\mathbf{p}_t(\mathbf{R}-\mathbf{c}_t) + \frac{i}{\hbar}\gamma_t}$$

2.4 The Ehrenfest theorem

The Ehrenfest theorem is the basis for the correspondence between classical and quantum dynamics.

- The time evolution of the position expectation value is determined by the momentum expectation value

$$\frac{d\langle x\rangle}{dt} = \frac{\langle p\rangle}{m}$$

- The time evolution of the momentum expectation value is determined by the expected force

$$\frac{d\langle p\rangle}{dt} = -\left\langle \frac{\partial V}{\partial x} \right\rangle$$

- Gaussian wave packets on a harmonic V is a special case where $\langle x\rangle = c_t$ $\quad \langle p\rangle = p_t$ $\quad \left\langle \frac{\partial V}{\partial x} \right\rangle = \frac{\partial V}{\partial x}\Big|_{x=c_t}$

Proof of Ehrenfest's theorem

Consider the time evolution of an observable A

$$\frac{d}{dt}\langle A\rangle = \langle \tfrac{\partial\Psi}{\partial t}|\hat{A}|\Psi\rangle + \langle\Psi|\hat{A}|\tfrac{\partial\Psi}{\partial t}\rangle + \langle\Psi|\tfrac{\partial\hat{A}}{\partial t}|\Psi\rangle$$

Inserting $i\hbar\frac{\partial\Psi}{\partial t} = \hat{H}\Psi$ gives (for time independent $\hat{A}$)

$$\begin{aligned}\frac{d}{dt}\langle A\rangle &= \tfrac{i}{\hbar}\langle\Psi|\hat{H}\hat{A}|\Psi\rangle - \tfrac{i}{\hbar}\langle\Psi|\hat{A}\hat{H}|\Psi\rangle \\ &= \tfrac{i}{\hbar}\langle\Psi|[\hat{H},\hat{A}]|\Psi\rangle\end{aligned}$$

- Evaluating the commutators for position and momentum, we find

$$[\hat{H},\hat{x}] = \frac{\hat{p}}{m}$$

$$[\hat{H},\hat{p}] = i\hbar\frac{\partial V}{\partial x}$$

So finally, $\quad \frac{d\langle x\rangle}{dt} = \frac{\langle p\rangle}{m} \qquad \frac{d\langle p\rangle}{dt} = -\left\langle\frac{\partial V}{\partial x}\right\rangle$

A simple model for wave packet propagation

Putting it all together, we have

- BO approximation: time-dependent nuclear wave function on an adiabatic potential energy surface

$$\hat{H}_e\Psi_e = W_e\Psi_e \qquad i\hbar\frac{\partial\Psi_n}{\partial t} = \hat{H}_n\Psi_n$$

- A time-dependent nuclear wave function can be modelled as a coherent state Gaussian wave packet

$$\Psi_n(x,t) = Ne^{-\alpha(x-c_t)^2 + \frac{i}{\hbar}p_t(x-c_t) + \frac{i}{\hbar}\gamma_t}$$

- Photo-excitations are assumed to change the electronic state Ψ_e but leave the nuclear wave packet unchanged.
- The wave packet propagates on the excited state potential according to classical equations of motion of c_t and p_t