

Appendix 4: the Ehrenfest Theorem

Here is a modern version of the Ehrenfest theorem. The rate of change of the expected value of the observable O is

$$\frac{\partial}{\partial t} \langle O \rangle = \frac{\partial}{\partial t} \langle \Psi | \hat{O} \Psi \rangle = \frac{\partial}{\partial t} \left(\langle \Psi^* | \hat{O} | \Psi \rangle \right). \quad (\text{A4.1})$$

By applying the product rule to the time derivative, one gets

$$\frac{\partial}{\partial t} \langle O \rangle = \frac{\partial \langle \Psi^* |}{\partial t} \hat{O} | \Psi \rangle + \langle \Psi^* | \frac{\partial \hat{O}}{\partial t} | \Psi \rangle + \Psi^* \hat{O} \frac{\partial | \Psi \rangle}{\partial t}. \quad (\text{A4.2})$$

However, from TDSE and its conjugate, one gets

$$\frac{\partial \Psi}{\partial t} = -\frac{i}{\hbar} \hat{H} \Psi \quad (\text{A4.3})$$

and

$$\frac{\partial \Psi^*}{\partial t} = \frac{i}{\hbar} \hat{H}^* \Psi^*. \quad (\text{A4.4})$$

Plugging these into (A4.2), we get

$$\begin{aligned} \frac{\partial}{\partial t} \langle O \rangle &= \frac{i}{\hbar} H^* | \Psi \rangle^* \hat{O} | \Psi \rangle + | \Psi \rangle^* \frac{\partial \hat{O}}{\partial t} | \Psi \rangle - \frac{i}{\hbar} \Psi^* \hat{O} H | \Psi \rangle = \\ &= \frac{i}{\hbar} \left\{ H^* | \Psi \rangle^* \hat{O} | \Psi \rangle - \Psi^* \hat{O} H | \Psi \rangle \right\} + \left\langle \frac{\partial \hat{O}}{\partial t} \right\rangle, \end{aligned} \quad (\text{A4.5})$$

or

$$\frac{\partial}{\partial t} \langle O \rangle = \frac{i}{\hbar} \left\{ \langle H \Psi | \hat{O} \Psi \rangle - \langle \Psi | \hat{O} | H \Psi \rangle \right\} + \left\langle \frac{\partial \hat{O}}{\partial t} \right\rangle, \quad (\text{A4.6})$$

where the last term is the expectation value of $\partial \hat{O} / \partial t$.

But \hat{H} is Hermitian, and therefore

¹ Remember that TDSE is $i\hbar \frac{\partial \Psi}{\partial t} = \hat{H} \Psi$.

$$\langle \hat{H}\Psi | \hat{O}\Psi \rangle = \langle \Psi | \hat{H}\hat{O}\Psi \rangle. \quad (\text{A4.6})$$

Plugging this back into (A4.6), we obtain

$$\frac{\partial}{\partial t} \langle O \rangle = \frac{i}{\hbar} \left\{ \langle \Psi | H\hat{O}\Psi \rangle - \langle \Psi | \hat{O}H\Psi \rangle \right\} + \left\langle \frac{\partial \hat{O}}{\partial t} \right\rangle. \quad (\text{A4.7})$$

But

$$\langle \Psi | H\hat{O}\Psi \rangle = \langle H\hat{O} \rangle \quad (\text{A4.8})$$

and

$$\langle \Psi | \hat{O}H\Psi \rangle = \langle \hat{O}H \rangle. \quad (\text{A4.9})$$

Hence,

$$\frac{\partial}{\partial t} \langle O \rangle = \frac{i}{\hbar} \left\{ \langle \hat{H}\hat{O} \rangle - \langle \hat{O}\hat{H} \rangle \right\} + \left\langle \frac{\partial \hat{O}}{\partial t} \right\rangle. \quad (\text{A4.10})$$

Given that the difference of the averages is equal to the average of the differences,

$$\frac{\partial}{\partial t} \langle O \rangle = \frac{i}{\hbar} \langle \hat{H}\hat{O} - \hat{O}\hat{H} \rangle + \left\langle \frac{\partial \hat{O}}{\partial t} \right\rangle, \quad (\text{A4.11})$$

or

$$\frac{\partial}{\partial t} \langle O \rangle = \frac{i}{\hbar} \langle [\hat{H}, \hat{O}] \rangle + \left\langle \frac{\partial \hat{O}}{\partial t} \right\rangle, \quad (\text{A4.12})$$

which is the Ehrenfest theorem.