Expectation value of an operator: How to calculate from the wavefunction (General approach)

(complement to C9550, lecture 3, October 3rd, 2019)

Atkins-EN, 8th Edition (pdf in C9550/um): **Justification 8.4**

Atkins-EN, 9th Edition (hard copy in KUK Library): **Justification 7.5**

In the Czech translation (Atkins-CZ): **Odůvodnění 7.5.** In the Slovak translation: (Atkins-SK): **Zdôvodnenie 11.2**

Justification 8.4 *The expectation value of an operator*

If ψ is an eigenfunction of $\hat{\Omega}$ with eigenvalue ω, the expectation value of $\hat{\Omega}$ is

$$\langle\Omega\rangle = \int \psi^* \overbrace{\hat{\Omega}\psi}^{\omega\psi} \mathrm{d}\tau = \int \psi^* \omega\psi \mathrm{d}\tau = \omega \int \psi^* \psi \mathrm{d}\tau = \omega$$

because ω is a constant and may be taken outside the integral, and the resulting integral is equal to 1 for a normalized wavefunction. The interpretation of this expression is that, because every observation of the property Ω results in the value ω (because the wavefunction is an eigenfunction of $\hat{\Omega}$), the mean value of all the observations is also ω.

A wavefunction that is not an eigenfunction of the operator of interest can be written as a linear combination of eigenfunctions. For simplicity, suppose the wavefunction is the sum of two eigenfunctions (the general case, eqn 8.33, can easily be developed). Then

$$\begin{aligned}\langle\Omega\rangle &= \int (c_1\psi_1 + c_2\psi_2)^* \hat{\Omega}(c_1\psi_1 + c_2\psi_2)\mathrm{d}\tau \\ &= \int (c_1\psi_1 + c_2\psi_2)^* (c_1\hat{\Omega}\psi_1 + c_2\hat{\Omega}\psi_2)\mathrm{d}\tau \\ &= \int (c_1\psi_1 + c_2\psi_2)^* (c_1\omega_1\psi_1 + c_2\omega_2\psi_2)\mathrm{d}\tau \\ &= c_1^* c_1 \omega_1 \overbrace{\int \psi_1^*\psi_1 \mathrm{d}\tau}^{1} + c_2^* c_2 \omega_2 \overbrace{\int \psi_2^*\psi_2 \mathrm{d}\tau}^{1} \\ &\quad + c_2^* c_1 \omega_1 \overbrace{\int \psi_2^*\psi_1 \mathrm{d}\tau}^{0} + c_1^* c_2 \omega_2 \overbrace{\int \psi_1^*\psi_2 \mathrm{d}\tau}^{0}\end{aligned}$$

The first two integrals on the right are both equal to 1 because the wavefunctions are individually normalized. Because ψ_1 and ψ_2 correspond to different eigenvalues of an hermitian operator, they are orthogonal, so the third and fourth integrals on the right are zero. We can conclude that

$$\langle\Omega\rangle = |c_1|^2\omega_1 + |c_2|^2\omega_2$$

This expression shows that the expectation value is the sum of the two eigenvalues weighted by the probabilities that each one will be found in a series of measurements. Hence, the expectation value is the weighted mean of a series of observations.

Homework for October 17th, 2019:

Example 8.7/Atkins 8th = Example 7.7/Atkins 9th = Příklad 7.7/Atkins-CZ = Príklad 11.6/Atkins-SK