2. Brief Review of the Basic Quantum Mechanics

Chang Woo Kim
Computational Chemistry Group
Department of Chemistry, JNU

History of Science: Classical Physics

The pre-modern physics can be roughly divided into two fields:

Newton's theory of mechanics, which describes the movement of particles and objects based on equations of motion.

Maxwell's theory of electromagnetism, which describes various phenomena involving current, magnet, and electromagnetic waves.

Development of these two fields was already finished in the 19th century, and countless number of applications have been made possible due to the predictive power of the theories.

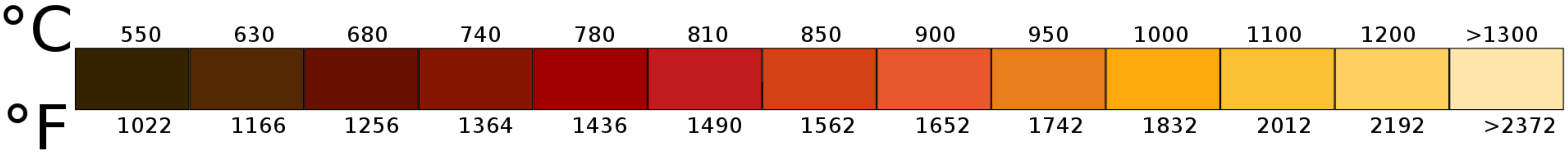
ex) mechanical and electrical engineering

Blackbody Radiation

Heated matter emits energy in the form of electromagnetic waves (light). This is modeled by blackbody radiation.

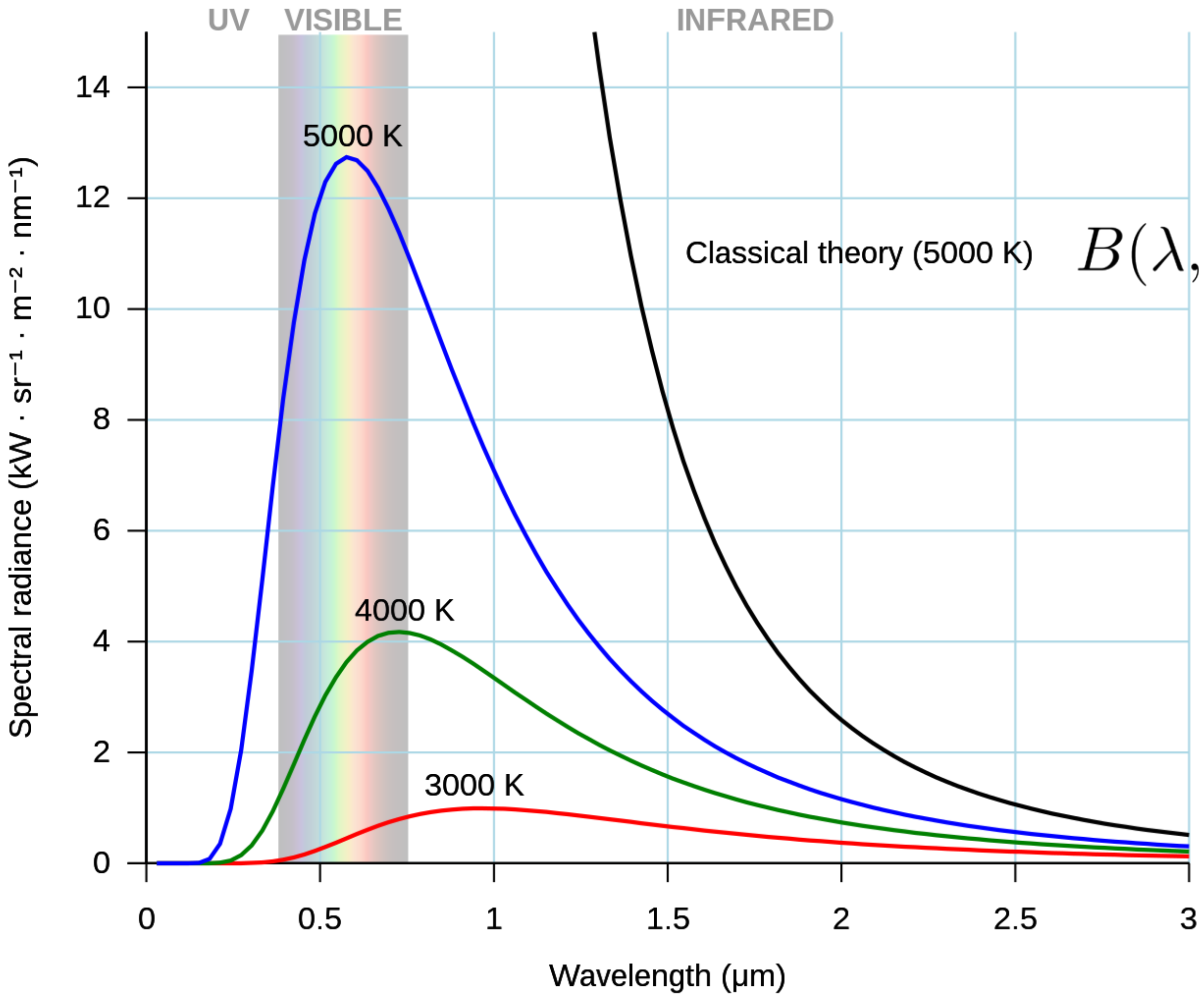
The distribution of the wavelength intensity depends on temperature, which was carefully studied for application in metallurgy.

However, the prediction of classical electromagnetism did not match the experiment, especially towards the high frequency.



https://en.wikipedia.org/wiki/Black-body_radiation

Blackbody Radiation



$$B(\lambda, T) \propto \frac{T}{\lambda^4}$$

https://en.wikipedia.org/wiki/Black-body_radiation

Planck's Quantization

Planck proposed that, when the light is emitted, it can only carry energy which is multiple of $h\nu$ - the energy of the light is quantized.

Based on this theory, Planck could show that the blackbody radiation follows

$$B(\lambda, T) = \frac{2hc^2}{\lambda^5} \frac{1}{\exp(hc/\lambda k_{\mathrm{B}} T) - 1},$$

which perfectly described the experimental spectra.

This implied that the light can be thought as individual particles carrying the energy of $h\nu$, which was later called wave-particle duality.

de Broglie's Matter Wave

Soon after the Planck proposed his theory, Einstein arrived at the conclusion that the light energy E and its momentum p are related by

$$E = pc,$$

which can be combined with $E = hc/\lambda$ to give

$$\lambda = \frac{h}{p}.$$

Based on this result, de Broglie made a bold claim: if light can behave like particle, matter can also behave like wave whose wavelength is

$$\lambda = \frac{h}{mv},$$

as the momentum of particle of mass m and velocity v is $p = mv$.

The Schrödinger Wave Equation

Schrödinger constructed the equation of motion for the "matter waves" by combining the classical mechanics and wave equation:

$$i\hbar\frac{\partial}{\partial t}\Psi(x,t) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi(x,t) + V(x,t)\Psi(x,t).$$

This is the famous Schrödinger equation, for 1-dimensional system.

It can be compactly written as

$$i\hbar\frac{\partial}{\partial t}\Psi(x,t) = [\hat{K} + \hat{V}(x,t)]\Psi(x,t) = \hat{H}(x,t)\Psi(x,t),$$

Where $\hat{K}$ and $\hat{V}(x,t)$ are operators for kinetic and potential energy. We have also defined the Hamiltonian operator for the total energy,

$$\hat{H}(x,t) = \hat{K} + \hat{V}(x,t).$$

Solving the Schrödinger Equation

In this course, we will work with potentials that do not change with time. As a result, we have

$$i\hbar\frac{\partial}{\partial t}\Psi(x,t) = \hat{H}(x)\Psi(x,t).$$

This can be solved by separation of variables, where we assume the solution of

$$\Psi(x,t) = \psi(x)T(t).$$

Inserting this solution to the original equation and rearranging leads to

$$i\hbar\frac{1}{T(t)}\frac{dT(t)}{dt} = \frac{1}{\psi(x)}\hat{H}(x)\psi(x) = E \quad \text{(constant)}$$

This course will mostly focus on the time-independent part

$$\hat{H}(x)\psi(x) = E\psi(x).$$

Solving the Schrödinger Equation

The time-independent part of the Schrödinger equation

$$\hat{H}(x)\psi(x) = E\psi(x),$$

is in the form of eigenvalue equation. Solving this equation usually leads to infinitely many solutions $\{\psi_n(x)\}$ and energy eigenvalues $\{E_n\}$.

For each set of solution and eigenvalue, the time part can be solved as:

$$i\hbar\frac{dT_n(t)}{dt} = E_nT_n(t) \quad \rightarrow \quad T_n(t) = \exp\left(-\frac{iE_nt}{\hbar}\right).$$

The general solution can now be constructed as

$$\Psi(x,t) = \sum_j c_j\psi_j(x)T_j(t) = \sum_j c_j\psi_j(x)\exp\left(-\frac{iE_jt}{\hbar}\right),$$

where $\{c_j\}$ are complex-valued coefficients.

Solving the Schrödinger Equation

ex) Show that the solution

$$\Psi(x,t) = \sum_j c_j \psi_j(x) \exp\left(-\frac{iE_j t}{\hbar} \right)$$

satisfies the Schrödinger equation

$$i\hbar \frac{\partial}{\partial t}\Psi(x,t) = \hat{H}(x)\Psi(x,t).$$

Postulates of Quantum Mechanics

There are different interpretations of quantum mechanics, but the most commonly accepted sets of basic rules (postulates) are as follows.

- The state of a quantum system is completely specified by its wavefunction $\Psi(x,t)$.
- The wavefunction evolves by following the Schrödinger equation.
- To every physical observable, there is a corresponding Hermitian operator. ex) $\hat{x}$ (position), $-i\hbar\frac{d}{dx}$ (momentum), $\hat{H}$ (energy) $\cdots$
- When a physical observable $\hat{A}$ is measured, the outcome is always an eigenvalue of the equation

$$\hat{A}\psi_k(x) = A_k\psi_k(x).$$

Postulates of Quantum Mechanics

- If the wavefunction was in a superposition state

$$\psi(x) = \sum_k c_k \psi_k(x)$$

before the measurement, and an eigenvalue A_n is measured as an outcome, it means that the wavefunction has been immediately collapsed into $\psi_n(x)$ after the measurement. The probability of measuring A_n is proportional to $|c_n|^2$.

- For a general wavefunction, the average (expectation value) of the measurement can be calculated as

$$\langle A \rangle = \frac{\int \psi^*(x) \hat{A} \psi(x)\, dx}{\int \psi^*(x) \psi(x)\, dx}.$$

Postulates of Quantum Mechanics

ex) Show that eigenvalues of a Hermitian operator are always real.
Recall that a Hermitian operator $\hat{A}$ satisfies

$$\int f^* \hat{A} g \, d\tau = \left(\int g^* \hat{A} f \, d\tau \right)^* .$$

Normalization

To make the calculations more compact, we will always assume that the wavefunction is normalized, which means it satisfies

$$\int_{-\infty}^{\infty} |\psi(x)|^2 \, dx = 1.$$

Even when this condition is not met, we can always multiply a normalization factor N to get a new scaled wavefunction

$$\tilde{\psi}(x) = N\psi(x).$$

It will not be difficult to prove that $\tilde{\psi}(x)$ satisfies the normalization condition if

$$N = \left(\int_{-\infty}^{\infty} |\psi(x)|^2 \, dx \right)^{-1/2}.$$

Orthonormality of the Eigenfunctions

For a Hermitian operator $\hat{A}$, the normalized solution of the eigenvalue equation

$$\hat{A}\psi_k(x) = A_k\psi_k(x)$$

satisfies the orthonormality

$$\int_{-\infty}^{\infty} \psi_j^*(x)\psi_k(x)\,dx = \delta_{jk}.$$

Then, for a normalized superposition state $\psi(x) = \sum_k c_k\psi_k(x)$, the coefficients $\{c_k\}$ can be found by

$$c_k = \int_{-\infty}^{\infty} \psi_k^*(x)\psi(x)\,dx,$$

and satisfies $\sum_k |c_k|^2 = 1.$

Orthonormality of the Eigenfunctions

ex) Show that the following two functions are orthonormal:

$$\psi_0(x) = \left(\frac{1}{\pi}\right)^{1/4} e^{-x^2/2}, \quad \psi_1(x) = \left(\frac{4}{\pi}\right)^{1/4} x e^{-x^2/2}.$$

You can use the following integration formulae:

$$\int_{-\infty}^{\infty} e^{-\alpha x^2}\, dx = \sqrt{\frac{\pi}{\alpha}}, \quad \int_{-\infty}^{\infty} x^2 e^{-\alpha x^2}\, dx = \frac{1}{2\alpha}\sqrt{\frac{\pi}{\alpha}}.$$

Probabilistic Interpretation of the Wavefunction

The probabilities for all instances must be real and add up to unity.

For a normalized superposition state, $|c_k|^2$ can be directly interpreted as the probability to measure the k-th eigenvalue as we now have

$$\sum_k |c_k|^2 = 1,$$

and the meaning of the expectation value formula should now become clear:

$$\langle A \rangle = \int_{-\infty}^{\infty} \psi^*(x) \hat{A} \psi(x)\, dx = \sum_k |c_k|^2 A_k.$$

The absolute square of the wavefunction $|\psi(x)|^2$ can be also interpreted as the probability for a particle to exist at x, as

$$\int_{-\infty}^{\infty} |\psi(x)|^2\, dx = 1.$$