A ~~10-MINUTE~~ RATHER QUICK INTRODUCTION TO QUANTUM MECHANICS

1. What is quantum mechanics (as opposed to classical mechanics)?

Quantum mechanics (QM) deals with systems on atomic scale level, whose behaviours cannot be described by classical mechanics.

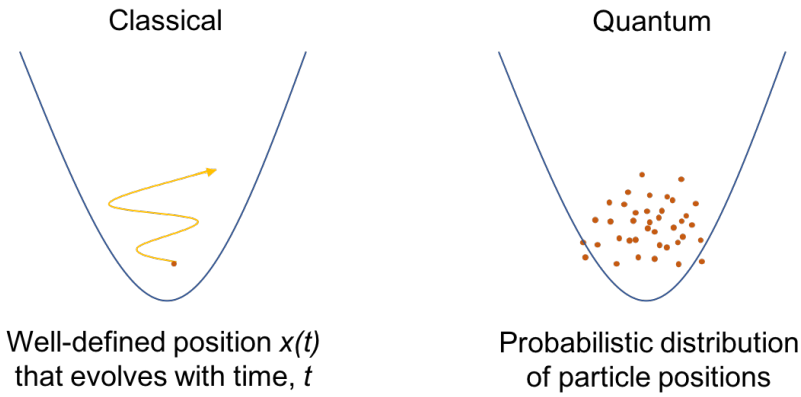

Figure 1. Left: A classical particle moves in a well-defined path, $x(t)$, governed by Newton's Laws of Motion. Right: A quantum particle has a probabilistic distribution of positions described by a wavefunction, $\Psi(x,t)$.

	Classical Mechanics	Quantum Mechanics
Size of system	Macroscopic	Atomic/sub-atomic
Nature	Deterministic	Probabilistic
Governed by	Newton's Laws of Motion	Schrödinger Equation
Energy	Continuous	Quantized

Table 1. A comparison between classical mechanics and quantum mechanics.

As we will see, many properties (e.g., energy, momentum etc) in QM are discrete; the word *quantum*[1]*/quantized/quantization* describes the fact that these properties can only have *discrete* (as opposed to continuous in classical mechanics) values.

[1]This word was first used by Planck to describe a packet of energy in his attempt to explain the blackbody catastrophe.

2. Why do we need quantum mechanics?

Classical mechanics fail when applied to systems of atomic scale:

- Emission spectra of excited atoms (Fig. 2): only certain lines are observed, implying that transitions occur between discrete energy levels.
- Blackbody radiation (Fig. 3). Classical explanation: energy radiation due to electron vibrations; expect higher radiation at higher temperature due to larger frequency of vibrations, but radiations are small at high frequency regardless of temperature *(Fig. 3 circled in red)*. Quantum: $E = hf$, so at high f, E is so large that vibrations becomes difficult.
- Photoelectric effect. Shining light on a metal induces electron emission without time delay only if the light is above certain frequency but independent of its intensity/brightness. Classically, light is a wave and it would take time for energy to build up if dim/low intensity light is used. Quantum explanation is that $E = hf$, so with high enough frequency, light (or the photon) has enough energy to induce electron emission.
- Bohr's atom confines electron motion to specific orbits. Classically, electrons are particles and moving electrons around an orbit has acceleration and thus radiates energy, this causes the electrons to continuously lose energy and spiral towards nucleus. This does *not* occur. Quantum mechanically, electrons move probabilistically.

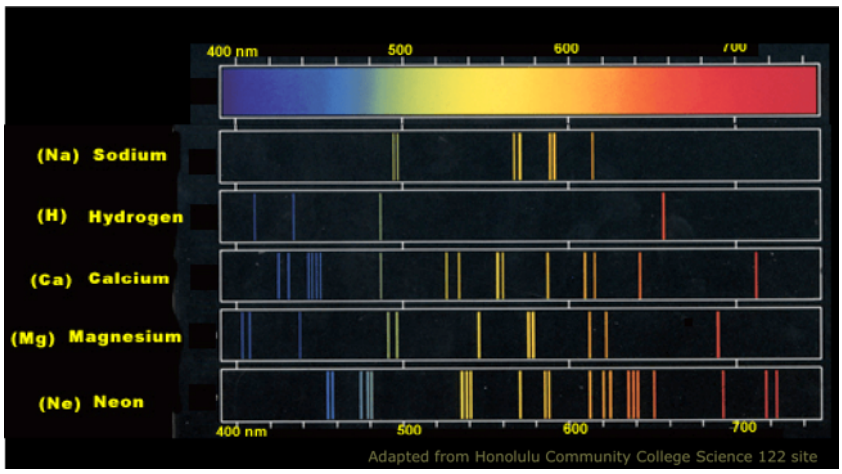

Figure 2. Emission spectra of excited atoms. Note that only specific lines, instead of a spectrum of lines, are observed.

3. Is electron a particle? Is light a wave?

As we can see, although conventionally people think about electrons as being particle and light as being wave, they actually can be both. Electrons can have

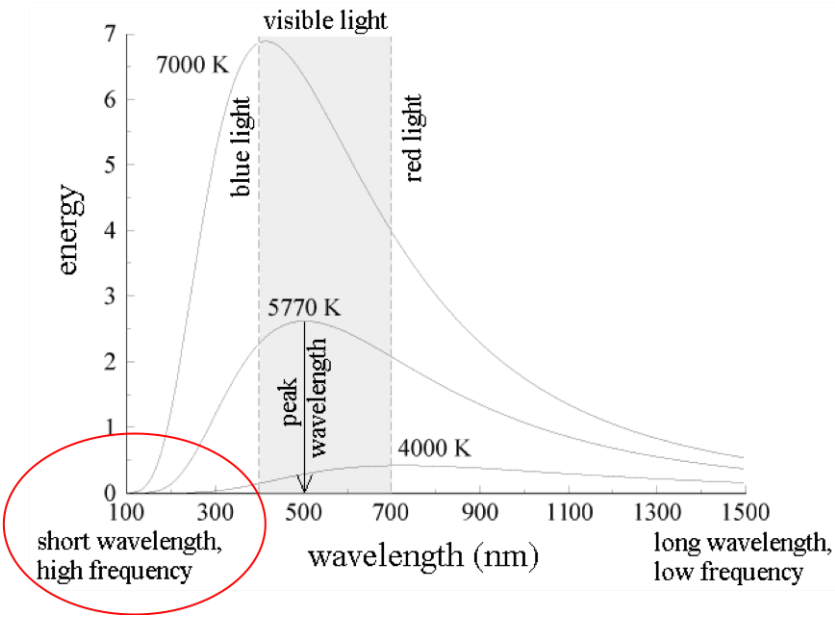

FIGURE 3. Spectra of blackbody radiation. Note that only specific lines, instead of a spectrum of lines, are observed. Adapted from *Three Failures of Classical Physics*. https://physics.weber.edu/carroll/honors/failures.htm. B. W. Carroll. Published April 08, 2014. Accessed 21 July 2018.

wave-like properties as shown by electron diffraction and interference. Light can have particle properties as seen in photoelectric effect. We really want to think of them as being both wave and particle. This is the **wave-particle duality**.

Interestingly, J. J. Thomson was awarded a Nobel prize (1906) for showing that electron is a negatively charged *particle*, while his son, George Thomson, was awarded a Nobel prize (1937) for showing that electron is a *wave* (electron diffraction experiment)!

4. So, what's a quantum system and how do we make measurements?

Richard Feynman once said "I think I can safely say that nobody understands quantum mechanics.". Fortunately, we can still *do* quantum mechanics before completely understanding it. We take postulates in quantum mechanics as given[2], and apply it to make predictions that can be tested by experiments. Indeed, QM has not failed since its formulation in agreeing with/explaining experimental observations.

[2]We will not question the validities of or going philosophical about these postulates but simply accepts them as given. This is much like accepting the axioms in mathematics before proving theorems. We simply do not question the axioms.

A quantum mechanical system is represented by its **wavefunction** – this is a mathematical function of the positions of all particles in the system and contains *all* the information about the system. In 3D, we represent this as $\Psi(x, y, z, t)$, or in 1D, we have $\Psi(x, t)$. For time-independent system we simply write $\Psi(x)$. We only consider time-independent systems here.

4.1. **Born's interpretation of wavefunction.** How is wavefunction related to the particle in the system? Max Born postulated that

$$|\Psi|^2 = \Psi^* \Psi \tag{1}$$

is the *probability density* of finding the particle. For example, for a particle confined to a one-dimensional box (imagine the particle is only allowed to move in a finite line segment), then, $|\Psi(x)|^2 dx$ gives the probability of finding the particle between the infinitesimal distances x and $x + dx$. The probability of finding the particle between two positions $x = a_0$ and $x = b_0$ is then

$$P(a_0 \leq x \leq b_0) = \int_{a_0}^{b_0} |\Psi(x)|^2 dx \tag{2}$$

Because the total probability of finding the particle is 1, the wavefunction needs to satisfy the *normalization condition*, viz.,

$$\int_{-\infty}^{\infty} |\Psi(x)|^2 dx = 1 \tag{3}$$

where the integration goes over all length of the box.

The normalized probability density of finding the particle is then given by

$$P(x) = \frac{\Psi^*(x)\Psi(x)}{\int_{-\infty}^{\infty} \Psi^*(x)\Psi(x) dx}. \tag{4}$$

4.2. **Measuring physical observables.** Any physical observable is represented by a quantum operator.[3] To obtain the information from the wavefunction, we apply the quantum operator to it. An operator is a mathematical operation that acts on a function to return another function. For example, d/dx is a differentiation operator that returns the derivative of a function when acting on it. A multiplication is another operator. All quantum operators has a caret/hat (ˆ) on top of the symbol.

[3]We will see later (in second year) that there are certain restrictions on these operators. For example, they have to be Hermitian and have associated properties.

We need the position operator and the momentum operator to construct everything else:

$$\text{Position operator: } \hat{x} \text{ (multiply by } x) \tag{5}$$

$$\text{Momentum operator: } \hat{p} = -i\hbar\frac{\partial}{\partial x} \tag{6}$$

Generally, to construct a quantum operator, write the physical quantity in terms of position and momentum variables *as in classical mechanics* and then replace them using Eq.s (5) and (6).

4.3. **A general quantum operator.** We can denote a general quantum operator as $\hat{Q}$, to measure its corresponding physical observable Q, we apply this operator to the system represented by the wavefunction Ψ. We then have

$$\hat{Q}\Psi = Q\Psi \tag{7}$$

where Q is a constant. Note that the quantum operator returns the function itself multiplied by a *constant* value, this equation is thus an eigenequation; the constant Q is the **eigenvalue** whereas the wavefunction Ψ is the **eigenfunction**.

In general, in QM, the *expectation value* (the average of a series of measurements) is given by

$$\langle Q \rangle = \frac{\int \Psi^*(x)\hat{Q}\Psi(x)dx}{\int \Psi^*(x)\Psi(x)dx} \tag{8}$$

4.4. **The total energy operator, $\hat{H}$.** The total energy of the system is an important quantity; knowing the total energy of the system allows many other properties to be calculated (Fig. 4). The total energy operator is called the **Hamiltonian** of the system and is the sum of kinetic energy operator and the potential energy operator (as per classical mechanics):

$$\hat{H} = \hat{T} + \hat{V} \tag{9}$$

where $\hat{T}$ is the kinetic energy operator and $\hat{V}$ is the potential energy operator. We need to convert this in terms of position and momentum operators using Eq.s (5) and (6). For a linear system, $\hat{T} = \hat{p}^2/2m$ where m is the mass of the particle; $\hat{V}$ is simply multiplication by the potential energy expression. Note that the potential energy expression is dictated by the system under consideration.

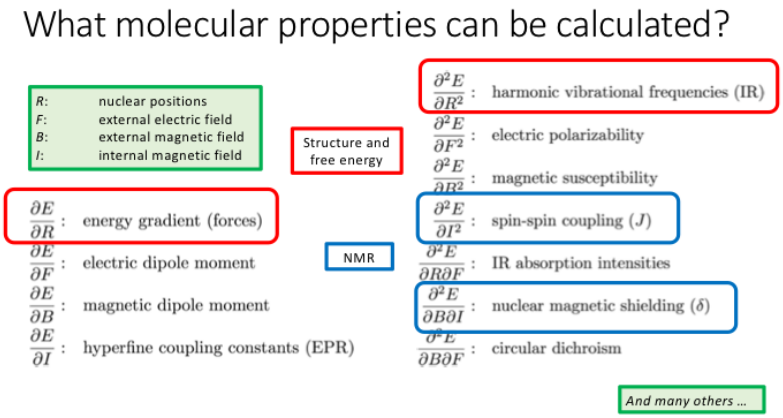

FIGURE 4. Molecular properties that can be calculated by knowing the energy of the system.

To measure the total energy of the system, we then apply the Hamiltonian operator to the wavefunction representing the system, this should return a real eigenvalue[4] that represents the physical measurement of total energy. We have the famous (time-independent) Schrödinger equation:

$$\boxed{\hat{H}\Psi = E\Psi} \tag{10}$$

5. Models in quantum mechanics

It is important at this stage to distinguish atoms from molecules. Atoms have no internal structure and have only translational and electronic degrees of freedom. This means that there are translational and electronic energy levels associated with atoms. For molecules however, on top of having translational and electronic degrees of freedom, there are also rotational and vibrational degrees of freedom, meaning that molecules have translational, rotational, vibrational and electronic energy levels associated with them (Fig. 5).

We want to be able to model each degree of freedom separately[5] in quantum mechanics. We employ simple models to treat each degree of freedom as shown in Table 2.

[4]You will see in second year that because the operators are Hermitian, their eigenvalues must be real. Physically, since they correspond to physical observables, they have to be real.

[5]We can do so due to Born-Oppenheimer approximation.

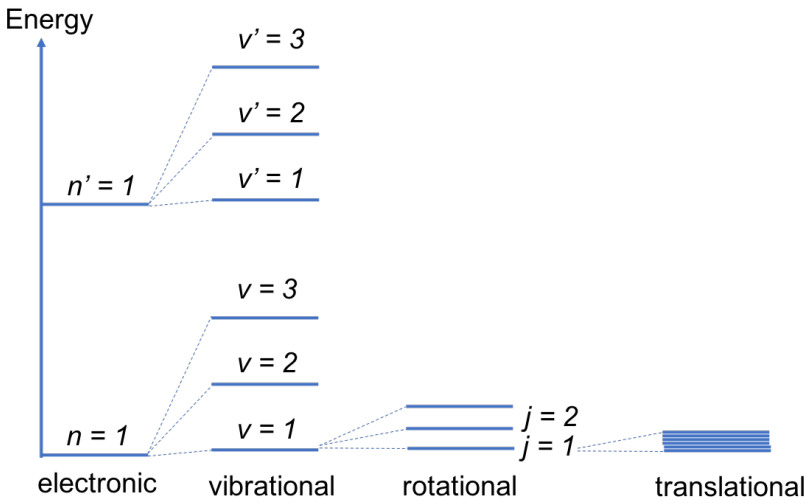

FIGURE 5. Molecular energy levels associated with each degree of freedom. The energy level spacings are not drawn to scale.

Degree of freedom	Model
Translation	Particle-in-a-box
Rotation	Rigid rotor
Vibration	Harmonic/Anharmonic oscillator
Electronic	Hydrogen Atom/Multielectronic system (very complex, no simple models)

TABLE 2. Models in quantum mechanics.

5.1. **Translation.** The quantum mechanical model for translation is the **particle-in-a-box** model. The Schrödinger equation for this system, in 1D, is

$$\hat{H}\psi = \left(\frac{\hat{p}^2}{2m} + \hat{V}\right)\psi = -\frac{\hbar^2}{2m}\frac{d}{dx}\psi + \hat{V}\psi = E\psi \tag{11}$$

where the potential V (Fig. 6) is given by

$$V = \begin{cases} 0 & \text{if } 0 < x < L \\ \infty & \text{otherwise} \end{cases}$$

where L is the box length. Within the box, we can easily solve the following second-order linear ordinary differential equation

$$-\frac{\hbar^2}{2m}\frac{d}{dx}\psi = E\psi.$$

Applying boundary conditions that the wavefunction vanishes at both ends of the box (infinite potential outside the box, so the particle cannot tunnel/move out of the box), we arrive at energy quantization with the following energy expression:

$$\boxed{E_n = \frac{n^2 h^2}{8mL^2}} \tag{12}$$

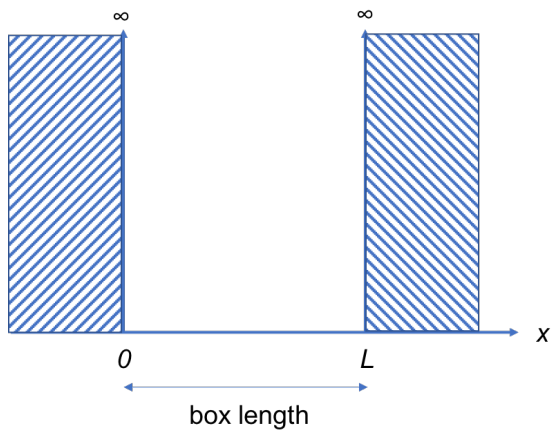

FIGURE 6. Potential energy for a particle-in-a-box.

5.2. **Rotation.** The quantum mechanical model for rotation is the **rigid rotor** model. In 3D, the full Schrödinger equation for this system is

$$\hat{H}\psi = \left(\frac{\hat{J}^2}{2I} + \hat{V}\right)\psi = \frac{\hat{J}^2}{2I}\psi = E\psi \tag{13}$$

where the potential V is zero, I is the moment of inertia and $I = \mu r^2$ for a diatomic and $I = \sum_i m_i r_i^2$ for a polyatomic. We consider only diatomic and linear polyatomics here. $\hat{J}^2$ is angular momentum operator and is given, in spherical polar coordinates, by

$$\hat{J}^2 = -\hbar^2 \left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)$$

Note that the eigenfunctions of the rigid rotor are also the *spherical harmonics*, Y_{JM_J}.

We can solve this differential equation (see here for the maths if interested) to get the energy for the rigid rotor, but it is enough to know that

$$\hat{J}^2 Y_{JM_J} = \hbar^2 J(J+1) Y_{JM_J} \tag{14}$$

so that the energy E in the Schrödinger equation Eq. (13) is given by

$$\boxed{E_J = \frac{\hbar^2}{2I} J(J+1) = BJ(J+1)} \tag{15}$$

where $B = \hbar^2/(2I)$ is the **rotational constant**. The *degeneracy* of each rotational energy level J is given by $g_J = 2J + 1$ due to the number of possible M_J values.

5.3. **Vibration.** The quantum mechanical model for a vibrating bond is the **simple harmonic oscillator** (SHO). The kinetic energy operator is the same as in the particle-in-a-box, $\hat{T} = \hat{p}^2/2m = -\hbar^2/2m$ whereas the potential energy operator is now $\hat{V} = (1/2)kx^2$, this is simply the potential energy for a SHO. The Schrödinger equation for the simple harmonic oscillator then becomes

$$\hat{H}\psi = \left(\frac{\hat{p}^2}{2m} + \hat{V}\right)\psi = \left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}kx^2\right)\psi = E\psi \tag{16}$$

This is a complicated second order differential equation. Solving this yields the energy expression for the SHO:

$$\boxed{E_v = \left(v + \frac{1}{2}\right)\hbar\omega = \left(v + \frac{1}{2}\right)h\nu} \tag{17}$$

where v is the vibrational quantum number and ν is the vibrational frequency, ω is the angular frequency.

5.4. **Electronic.** Except for the simple case of hydrogen atom, there is no quantum mechanical model for the energies of electronic levels; these have to be determined experimentally, usually by spectroscopy, or more recently, from computation (solving the Schrödinger equation numerically).

6. How do we obtain thermodynamic properties from quantum mechanics and statistical mechanics?

Consider a molecule. It has associated translational, rotational, vibrational energy and electronic energy levels. Now, we can apply quantum mechanics to solve for the translational, rotational and vibrational energy levels using simple models as outlined before. The electronic energy can be obtained from spectroscopy (via experiments) or theoretical calculations (via computation). With these energies,

we can form the *canonical partition function* of the system

$$\boxed{Q = \sum_i e^{-E_i/kT} = \sum_j g_j e^{-E_j/kT}} \tag{18}$$

where E_i is the energy of the ith quantum state and the summation index i goes over all states; alternatively, we can sum over all levels j, each having energy E_j and degeneracy g_j.

We can then use the "bridge equation" for the canonical ensemble

$$\boxed{A = -kT \ln Q} \tag{19}$$

to link the macroscopic thermodynamic quantity A to the partition function, Q, arising from the microscopic microstates. We will therefore be able to find all thermodynamic properties by simply knowing the energy levels of the molecule (see Statistical Mechanics in year 2).