The Quantum Theory of Atoms and Molecules

*The postulates of quantum mechanics*

Dr Grant Ritchie

The postulates…..

1. Associated with any particle moving in a conservative field of force is a *wave function,* ψ, which determines everything that can be known about the system.

2. With every *physical observable*, *q* , there is associated an *operator*, *Q*, which, when operating upon the wavefunction associated with a definite value of that observable, will yield that value (the *eigenvalue*) times the wavefunction. The eigenvalues of a given operator are the **only** values that a measurement can take.

3. The time evolution of Ψ is given by the time dependent *Schrödinger equation*.

4. The set of *eigenfunctions* of operator *Q* will form a *complete* set of linearly independent (*orthogonal*) functions.

5. For a system described by a given wavefunction, the *expectation value* of any property *q* can be found by performing the *expectation value integral with respect to that wavefunction*.

1: The Wavefunction Postulate

✓ For a physical system consisting of a single particle there is an associated wavefunction, Ψ, which determines everything that can be known about the system.

✓ Ψ is assumed to be a single-valued function of position and time, since that is sufficient to guarantee an unambiguous value of probability of finding the particle at a particular position and time.

✓ Ψ may be complex, since it is its product with its complex conjugate which specifies the real physical probability of finding the particle in a particular state.

✓ $\Psi (x,t)$ = single-valued probability amplitude at (x,t) for finding a particle at a given point in space at a given time.

✓ $\Psi^*(x,t). \Psi(x,t) = |\Psi(x,t)|^2$ = probability of finding the particle at x at time t (*Born Interpretation*)

✓ Since the probability must be 1 for finding the particle somewhere, the wavefunction must be *normalised*. That is, the sum of the probabilities for all of space must be equal to one. This is expressed by the integral $\int \Psi^* \Psi \, dr = 1$.

Constraints on the wavefunction

- In order to represent a physically observable system, ψ must satisfy certain constraints:

  - **Must be a solution of the Schrödinger equation; This implies:**
    - Must be single-valued;
    - Must be normalisable; this implies that the $\psi \to 0$ as $x \to \infty$;
    - $\psi(x)$ must be a continuous function of x;
    - The *slope* of ψ must be continuous, specifically $d\psi(x) / dx$ must be continuous (except at points where potential is infinite).

- **These constraints are applied to the boundary conditions on the solutions, and in the process help determine the energy eigenvalues.**
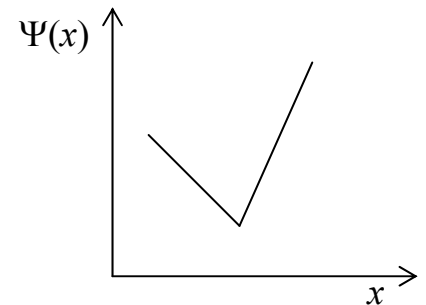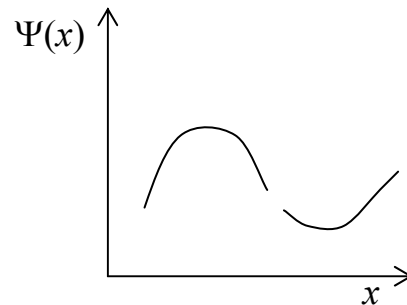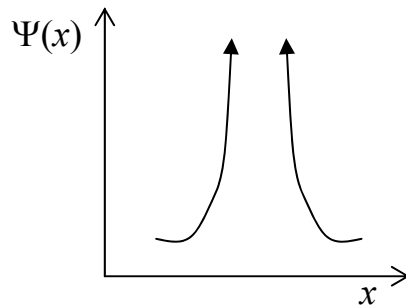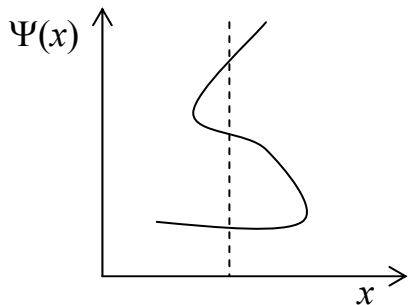
2: The Hamiltonian – the energy operator

Associated with each measurable parameter in a physical system is a quantum mechanical operator, and the operator associated with the system energy is called the Hamiltonian. The Hamiltonian contains the operations associated with the kinetic and potential energies and for a particle in one dimension can be written:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2}+V(x)\psi = E\psi$$

Operating on ψ with the Hamiltonian produces the Schrödinger equation. In the time independent Schrödinger equation, the operation may produce specific values for the energy called energy eigenvalues. This situation can be shown in the form of a eigenvalue Equation:

$$H\psi_i = E\psi_i$$

where the specific values of energy are called *energy eigenvalues* and the functions ψ_i are called *eigenfunctions*.

Form of the Hamiltonian

The operators representing the **position** and **momentum** of a particle are:

$$\hat{x} = x \qquad \hat{p}_x = -i\hbar \frac{\partial}{\partial x}$$

1 dimension

$$\hat{r} = r \qquad \hat{p} = -i\hbar \left(\frac{\partial}{\partial x} + \frac{\partial}{\partial y} + \frac{\partial}{\partial z} \right) = -i\hbar \nabla$$

3 dimensions

Other operators may be obtained from the corresponding classical expressions by making these replacements everywhere.

For example:

Kinetic energy:

$$T_x = \frac{p_x^2}{2m} \quad \Rightarrow \quad \hat{T}_x = \frac{1}{2m} \left(-i\hbar \frac{\partial}{\partial x} \right)^2 = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}$$

What about an angular momentum operator?

3: The Schrödinger Equation

- ✓ The SE plays the role of *Newton's laws and conservation of energy in classical mechanics* – i.e., it predicts the future behaviour of a dynamic system.

- ✓ The SE is a wave equation in terms of the wavefunction which predicts analytically and precisely the probability of events or outcome. The detailed outcome is not strictly determined, but given a large number of events, the Schrödinger equation will predict the distribution of results.

- ✓ The *kinetic and potential energies* are transformed into the *Hamiltonian* which acts upon the wavefunction to generate the *evolution* of the wavefunction in time and space.

- ✓ The SE gives the quantized energies of the system and gives the form of the wavefunction so that other properties may be calculated.

- ✓ Though the SE cannot be derived, it can be shown to be consistent with experiment.

The time dependent Schrödinger equation (TDSE)

In addition to its role in determining system energies, the Hamiltonian operator generates the time evolution of the wavefunction in the form:

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

Suppose the potential is independent of time i.e. $V(x, t) = V(x)$

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

LHS involves variation of ψ with t while RHS involves variation of ψ with x. Hence look for a separated solution:

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

Then (see earlier):

$$\Psi(x,t) = \psi(x)\,T(t) = \psi(x)e^{-iEt/\hbar}$$

The Schrödinger Equation contd.

Time Independent Schrödinger Equation:

$$\frac{d^2\psi(x)}{dx^2} + \frac{2m(E - V(x))}{\hbar^2}\psi(x) = 0$$

$$or - \frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\,\psi(x) = E\,\psi(x)$$

SE describes the motion of a particle of mass m, moving under influence of a potential field $V(x)$ (in 1-D). Solve SE for a given $V(x)$ to determine the wavefunctions ($\sim$ spatial probability distribution) and possible energies, E, of the particle.

The *Schrödinger Equation* is the form of an *Eigenvalue Equation*: $\quad \hat{H}\psi = E\psi$

where $\hat{H}$ is the Hamiltonian operator, $\qquad \hat{H} = \hat{T} + \hat{V} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)$

ψ is the wavefunction and is an *eigenfunction* of $\hat{H}$;

E is the total energy $(T + V)$ and an *eigenvalue* of $\hat{H}$.

4. "Special" properties of eigenvalues and eigenfunctions

In general the eigenvalues and eigenfunctions of a particular operator, Q, have the following important properties.

(I) The eigenvalues of a given operator are the **only** values that a measurement can take.

(II) The corresponding eigenfunctions are *orthogonal*.

(III) The eigenfunctions ϕ_i of an operator form a complete set. This means that any other function satisfying the same boundary conditions can be expanded as follows:

$$\psi(x) = \sum_i c_i \phi_i(x)$$

i.e. any ψ can be written as a *superposition* of different eigenfunctions. **(See particle in box).**

If the eigenfunctions are orthonormal then the coefficients c_i can be found as follows:

$$c_i = \int_{-\infty}^{\infty} \phi_i^*(x)\psi(x)dx$$

$NB: \int_{-\infty}^{\infty} \phi_i^*(x)\phi_j(x)dx = \delta_{ij}$ **These expansions are important for describing measurements in quantum mechanics.**

5: Expectation Values

To relate a quantum mechanical calculation to something you can observe in the laboratory, the **expectation value** of the measurable parameter is calculated. For the position x, the expectation value (for a normalised wavefunction) is defined as

$$\langle x \rangle = \int_{-\infty}^{\infty} \psi^*(x,t)\, x\, \psi(x,t)\, dx$$

Integral can be interpreted as the **average value** of x that we would expect to obtain from a large number of measurements. Alternatively, it could be viewed as the average value of position for a large number of particles which are described by the same wavefunction.

While the expectation value of a function of *position* has the appearance of an *average* of the function, the expectation value of *momentum* involves the representation of momentum as a quantum mechanical operator:

$$\langle p \rangle = \int_{-\infty}^{\infty} \psi^*(x,t)\, \frac{\hbar}{i}\frac{\partial}{\partial x}\psi(x,t)\, dx \qquad \text{where} \qquad \hat{p} = \frac{\hbar}{i}\frac{\partial}{\partial x}.$$

is the operator for the x component of momentum.

All observables *A* have associated operators *Â:*

If ψ is an eigenfunction of $\hat{A}$, then: $\hat{A}\psi = \alpha\psi$ and the observable takes on the **precise** eigenvalue α . Eigenvalues are identical with the observed values (which have been repeatedly confirmed in innumerable experiments, e.g. measurements of the energy of the electron in hydrogen have to agree with the quantum mechanically calculated eigenvalues E_n).

If ψ is **not** an eigenfunction of $\hat{A}$, then a measurement of *A* may give any of the different possible eigenvalues of the operator $\hat{A}$ with different probabilities. This 'mean value' or **expectation value** of an observable *A,* denoted $\langle A \rangle$ is defined by the integral

$$\left\langle \hat{A} \right\rangle = \int \psi * \hat{A}\, \psi\, \mathrm{d}\tau \quad \text{(only valid for normalised wavefunctions)}$$

Or more generally,

$$\left\langle \hat{A} \right\rangle = \frac{\int \psi * \hat{A}\, \psi\, \mathrm{d}\tau}{\int \psi * \psi\, \mathrm{d}\tau}$$

Uncertainty

In the special case where ψ is an eigenfunction of $\hat{A}$, of course, this integral gives the precise eigenvalue, α:

$$\left\langle \hat{A} \right\rangle = \int \psi * \hat{A} \, \psi \, \mathsf{d}\tau = \int \psi * \alpha \, \psi \, \mathsf{d}\tau = \alpha \int \psi * \psi \, \mathsf{d}\tau = \alpha$$

More generally, if the system's wavefunction is **not** an eigenfunction of the operator $\hat{A}$ then there is an *uncertainty* in the corresponding observable. The *standard deviation* of the observable is defined as follows:

$$\Delta \hat{A} = \sqrt{\left\langle \hat{A}^2 \right\rangle - \left\langle \hat{A} \right\rangle^2}$$

Example: Evaluate the product $\Delta x \Delta p_x$ for the ground state wavefunction for a particle in a box.

Simultaneous observability and commutation relations

A Ψ with a characteristic, well-defined value of some observable quantity is an eigenfunction of the corresponding operator. However, such a Ψ does not necessarily have a characteristic value of any other observable. e.g.) H and p_x for a particle in a box.

For Ψ to have characteristic values of two observables it is necessary for the corresponding operators to *commute*.

Specifically this means that the action of the two operators (say $\hat{A}$ and $\hat{C}$) taken in succession on any Ψ is identical to the action of the two operators taken in the reverse order, $\hat{A}\,\hat{C} = \hat{C}\,\hat{A}$, or equivalently the *commutator* of the two operators is zero:

$$\left[\hat{A}, \hat{C}\right] = \hat{A}\hat{C} - \hat{C}\hat{A} = 0.$$

If two operators commute it is possible to find a Ψ which has characteristic values of both observables, i.e. Ψ which is simultaneously an eigenfunction of both operators.

Example

Consider the position and momentum operators:

$$[\hat{x},\hat{p}_x]\psi = \hat{x}(\hat{p}_x\psi) - (\hat{p}_x\psi)\hat{x} = \frac{\hbar}{i}\left\{x\left(\frac{d\psi}{dx}\right) - \left(\frac{d(x\psi)}{dx}\right)\right\} = \frac{\hbar}{i}\left\{x\left(\frac{d\psi}{dx}\right) - x\left(\frac{d\psi}{dx}\right) - \psi\right\} = i\hbar\psi.$$

These two operators **do not** commute (the value of the expression is $i\hbar \neq 0$), and therefore their observables (position and linear momentum) are **complementary**: it is **not** possible to specify the values of the two corresponding observables simultaneously. This is the origin of the **Uncertainty Principle**.

In anticipation of the 2nd year QM course……In general, if the commutation relation $[\hat{A},\hat{C}] = i\,\hat{E}$, then $\hat{E}$ is called the *commutator* of $\hat{A}$ and $\hat{C}$. The uncertainty in the simultaneous measurement of $\hat{A}$ and $\hat{C}$ is determined by the value of their commutator $\hat{E}$: $\langle[\hat{A},\hat{C}]\rangle = i\langle\hat{E}\rangle$, and a mathematical proof can be given that $\Delta\hat{A}\,\Delta\hat{C} \geq \frac{1}{2}|\langle\hat{E}\rangle|$.

For the above example we get: $\hat{E} = \hbar\,\hat{I}$, so: $\Delta\boldsymbol{x}\,\Delta\boldsymbol{p}_x \geq \frac{1}{2}\hbar$.

(N.B.: $\hat{I}$ is the unity operator, 'multiply by one')

Summary of the Uncertainty Principle

3 ways to think of the Uncertainty Principle:

1. As the inherent disturbance of the system by a measurement (e.g. electron diffraction).

2. As a consequence of Fourier transforms – a highly localised wavepacket in space is constructed from individual waves having a wide range of wavevectors *i.e.* momentum states.

3. As a consequence of the fact that the operators x and p_x do not commute and therefore cannot share eigenfunctions. Hence the corresponding observables, position and momentum, cannot have precisely defined values simultaneously.

Do you get it?

1. What is the eigenvalue of $\psi = (2\pi)^{-1/2}e^{-i4\phi}$, with respect to the operator $\hat{A} = (\hbar/i)d/d\phi$?

2. The Hamiltonian for the system above is $\hat{H} = -(\hbar^2/2I)(d^2/d\phi^2)$ where I is a constant. What is the energy of the state with the wavefunction given above?

3. Another wavefunction for the system above is $\psi = (2\pi)^{-1/2} e^{-i3\phi}$. Is this wavefunction orthogonal to $\psi = (2\pi)^{-1/2} e^{-i4\phi}$?

4. If the system is found in the state $\psi = (2\pi)^{-1/2} [(3)^{-1/2} e^{-i3\phi} + c\, e^{-i4\phi}]$, what value(s) for the constant c normalises ψ?

5. What is $< \hat{A} >$ for the operator $\hat{A}$ with $\psi = (2\pi)^{-1/2} [(3)^{-1/2} e^{-i3\phi} + c\, e^{-i4\phi}]$?

6. What is ΔA for the system in question 5 above?

7. If $\mathbf{B} = \phi$ and $\mathbf{A} = (\hbar/i)d/d\phi$, then $[\mathbf{A}, \mathbf{B}] = (\hbar/i)$. What is the smallest allowed ΔB for the ΔA above?

Answers

(1) $\hat{A}\psi = \dfrac{\hbar}{i}\dfrac{d}{d\phi}\left(\dfrac{1}{\sqrt{2\pi}}\exp{-i4\phi}\right) = \dfrac{\hbar}{i}-i4\left(\dfrac{1}{\sqrt{2\pi}}\exp{-i4\phi}\right) = -4\hbar\left(\dfrac{1}{\sqrt{2\pi}}\exp{-i4\phi}\right) = -4\hbar\psi$

(2) $\hat{H}\psi = -\dfrac{\hbar^2}{2I}\dfrac{d^2}{d\phi^2}\left(\dfrac{1}{\sqrt{2\pi}}\exp{-i4\phi}\right) = -\dfrac{\hbar^2}{2I}(-i4)^2\left(\dfrac{1}{\sqrt{2\pi}}\exp{-i4\phi}\right) = \dfrac{8\hbar^2}{I}\psi = E\psi$

(3) $\displaystyle\int_0^{2\pi}\psi_1^*\psi_2\,d\phi = \dfrac{1}{2\pi}\int_0^{2\pi}e^{4i\phi}e^{-3i\phi}\,d\phi = \dfrac{1}{2\pi}\int_0^{2\pi}e^{i\phi}\,d\phi = \dfrac{1}{2\pi}\left[\dfrac{1}{i}e^{i\phi}\right]_0^{2\pi} = 0$

(4) $\displaystyle\int_0^{2\pi}\psi^*\psi\,d\phi = \dfrac{1}{2\pi}\int_0^{2\pi}\left(\dfrac{1}{\sqrt{3}}e^{3i\phi}+c^*e^{4i\phi}\right)\left(\dfrac{1}{\sqrt{3}}e^{-3i\phi}+ce^{-4i\phi}\right)d\phi$

$= \dfrac{1}{2\pi}\displaystyle\int_0^{2\pi}\left(\tfrac{1}{3}+c^*c+\tfrac{1}{\sqrt{3}}c^*e^{i\phi}+\tfrac{1}{\sqrt{3}}ce^{4i\phi}\right)d\phi = \dfrac{1}{2\pi}\int_0^{2\pi}\left(\tfrac{1}{3}+c^*c\right)d\phi = \left(\tfrac{1}{3}+c^*c\right)$

$\left(\tfrac{1}{3}+c^*c\right)=1 \qquad \Rightarrow \qquad c=\pm\sqrt{\dfrac{2}{3}}$

Answers contd.

(5) $\langle A \rangle = \int_0^{2\pi} \psi^* \left(\frac{\hbar}{i} \frac{d}{d\phi} \right) \psi \ d\phi = \frac{1}{2\pi} \frac{\hbar}{i} \int_0^{2\pi} \left(\frac{1}{\sqrt{3}} e^{3i\phi} + \sqrt{\frac{2}{3}} e^{4i\phi} \right) \left(\frac{d}{d\phi} \right) \left(\frac{1}{\sqrt{3}} e^{-3i\phi} + \sqrt{\frac{2}{3}} e^{-4i\phi} \right) d\phi$

$= \frac{1}{2\pi} \frac{\hbar}{i} \int_0^{2\pi} \left(\frac{1}{\sqrt{3}} e^{3i\phi} + \sqrt{\frac{2}{3}} e^{4i\phi} \right) \left(\frac{-3i}{\sqrt{3}} e^{-3i\phi} + (-4i) \sqrt{\frac{2}{3}} e^{-4i\phi} \right) d\phi$

$= \frac{1}{2\pi} \int_0^{2\pi} \left(-1 - \frac{8}{3} - \sqrt{2} e^{i\phi} - \frac{4\sqrt{2}}{3} e^{4i\phi} \right) d\phi = \frac{1}{2\pi} \hbar \int_0^{2\pi} \left(-\frac{11}{3} \right) d\phi = -\frac{11}{3} \hbar.$

(6) $\langle A^2 \rangle = \int_0^{2\pi} \psi^* \left(\frac{\hbar}{i} \frac{d}{d\phi} \right)^2 \psi \ d\phi = -\frac{1}{2\pi} \hbar^2 \int_0^{2\pi} \left(\frac{1}{\sqrt{3}} e^{3i\phi} + \sqrt{\frac{2}{3}} e^{4i\phi} \right) \left(\frac{d^2}{d\phi^2} \right) \left(\frac{1}{\sqrt{3}} e^{-3i\phi} + \sqrt{\frac{2}{3}} e^{-4i\phi} \right) d\phi$

$= \frac{1}{2\pi} \hbar^2 \int_0^{2\pi} \left(\frac{1}{\sqrt{3}} e^{3i\phi} + \sqrt{\frac{2}{3}} e^{4i\phi} \right) \left(\frac{-9}{\sqrt{3}} e^{-3i\phi} + (-16) \sqrt{\frac{2}{3}} e^{-4i\phi} \right) d\phi$

$= -\frac{1}{2\pi} \hbar^2 \int_0^{2\pi} \left(-3 - \frac{32}{3} \right) d\phi = -\frac{1}{2\pi} \hbar^2 \int_0^{2\pi} \left(-\frac{41}{3} \right) d\phi = \frac{41}{3} \hbar^2. \quad \Rightarrow \quad \Delta A = \sqrt{\langle A^2 \rangle - \langle A \rangle^2} = \sqrt{\frac{41}{3} \hbar^2 - \left(\frac{11}{3} \hbar \right)^2} = \sqrt{\frac{2}{9}} \hbar$

(7) $\left(\Delta A \Delta B \right)_{\min} = \frac{\hbar}{2} \qquad \Rightarrow \qquad \left(\Delta B \right)_{\min} = \frac{\hbar}{2} \frac{1}{\Delta A} = \frac{9}{2\sqrt{2}}.$