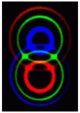

Introduction to Quantum Chemistry

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Physical Chemistry I

Index

Definintion of probability

- Discrete spectrum $\Rightarrow$ Finite number of possible measurement results
  Ex. Coin toss: Espectrum = 1,2
  Ex. Dice toss: Espectrum = 1,2,3,4,5,6

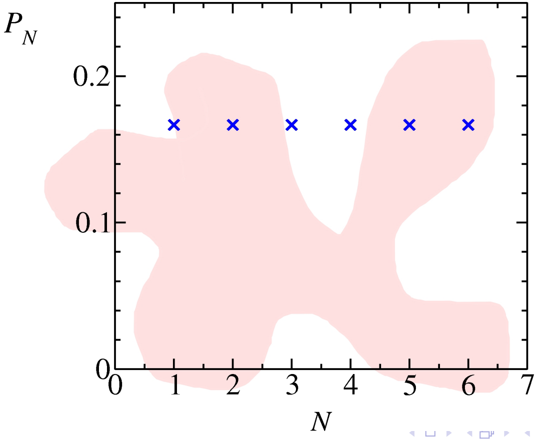
- Probability P_N $\Rightarrow$ Frequency of every result

$$P_N = \frac{\text{Number of measurements providing } N \text{ as result}}{\text{Number of possible measurements}}$$

- Normalization $\Rightarrow \sum_i P_i = 1$
  Ex. Coin toss: $P_1 = \frac{1}{2} = P_2$
  Ex. Dice toss: $P_1 = \frac{1}{6} = P_2 = P_3 = P_4 = P_5 = P_6$

Graphical representation

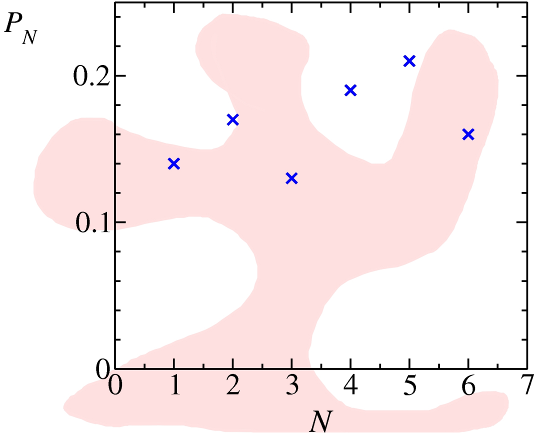
Ex. Dice toss: $P_1 = P_2 = P_3 = P_4 = P_5 = P_6 = \frac{1}{6}$



Graphical representation

Ex. Real dice toss:

$$P_1 = 0.14, P_2 = 0.17, P_3 = 0.13, P_4 = 0.19, P_5 = 0.21, P_6 = 0.16$$



Mean value of a measurement

- Mean value of a measurement $\langle f \rangle$

$$\text{N measurements} \Rightarrow \; f_5, f_3, f_1, f_1, f_3, \ldots$$

$$\begin{aligned} \text{Mean value} &= \frac{1}{N}\left(f_5 + f_3 + f_1 + f_1 + f_3 + \ldots\right) \\ &= \frac{1}{N}\left(f_1 N_1 + f_2 N_2 + \ldots\right) \\ &= f1 \frac{N_1}{N} + f_2 \frac{N_2}{N} + \ldots \end{aligned}$$

$$\langle f \rangle = \sum_i f_i \, P_i$$

Mean value of a measurement

Ex. Dice toss:

$$\langle N \rangle = 1 \cdot \frac{1}{6} + 2 \cdot \frac{1}{6} + 3 \cdot \frac{1}{6} + 4 \cdot \frac{1}{6} + 5 \cdot \frac{1}{6} + 6 \cdot \frac{1}{6} = \frac{21}{6} = 3.5$$

$$\langle \sqrt{N} \rangle = \sqrt{1} \cdot \frac{1}{6} + \sqrt{2} \cdot \frac{1}{6} + \sqrt{3} \cdot \frac{1}{6} + \sqrt{4} \cdot \frac{1}{6} + \sqrt{5} \cdot \frac{1}{6} + \sqrt{6} \cdot \frac{1}{6}$$
$$= 1.8$$

$$\sqrt{\langle N \rangle} \neq \langle \sqrt{N} \rangle$$

$$\sqrt{3.5} \neq 1.8$$

Mean squared deviation

- Mean squared deviation $\Delta f \Rightarrow$ Measures the mean deviation of the values from their mean value

$$\text{Measurements: } f_1,\ f_2,\ f_3, \ldots$$

$$\text{Mean value of the deviations} = \langle f - \langle f \rangle \rangle = \langle f \rangle - \langle f \rangle = 0$$

$$(\Delta f)^2 = \langle (f - \langle f \rangle)^2 \rangle = \langle f^2 - 2f\langle f \rangle + \langle f \rangle^2 \rangle$$

$$= \langle f^2 \rangle - 2\langle f \rangle \langle f \rangle + \langle f \rangle^2$$

$$\Delta f = \sqrt{\langle f^2 \rangle - \langle f \rangle^2}$$

Probability density

- Continuous spectrum $\Rightarrow$ Infinite number of possible results of the measurements $\tau \in (a, b)$. It makes no sense to ask about the probability of a particular outcome.

- Probability density ϱ_τ $\Rightarrow$ It describes how the probability is distributed among the possible results of the measurement

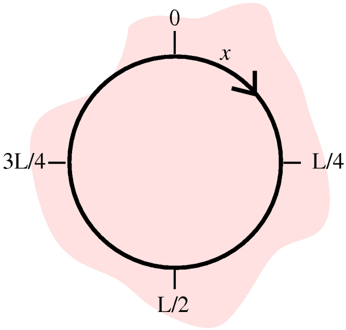
$$\varrho_\tau = \frac{dP}{d\tau}$$

$$P(\tau \in (\tau_1, \tau_2)) = \int_{\tau_1}^{\tau_2} \varrho_\tau \, d\tau$$

- Normalization $\Rightarrow \int_{\forall\tau} \varrho_\tau \, d\tau = 1$

Probability density

Ex. Ring toss $\Rightarrow \quad \rho_x = \frac{dP}{dx}$



$$P(x \in [x_1, x_2]) = \int_{x_1}^{x_2} \varrho_x \, dx$$

$$\text{Normalization} \Rightarrow \int_0^L \varrho_x \, dx = 1$$

$$\varrho_x = \text{cte.} \Rightarrow \varrho_x \int_0^L dx = 1 \Rightarrow \varrho_x = \frac{1}{L}$$

$$P(x \in [0, L/2]) = \int_0^{L/2} \varrho_x \, dx = \frac{1}{L} \int_0^{L/2} dx = \frac{1}{2}$$

Mean value of measurement

- Mean value of a measurement $\langle f \rangle$

$$\langle f \rangle = \int_{\forall \tau} f_\tau \, \varrho_\tau \, d\tau$$

Ex. Ring toss

$$\langle x \rangle = \int_0^L x \, \varrho_x \, dx = \frac{1}{L} \int_0^L x \, dx = \frac{L}{2}$$

$$\langle x^2 \rangle = \int_0^L x^2 \, \varrho_x \, dx = \frac{1}{L} \int_0^L x^2 \, dx = \frac{L^2}{3}$$

Mean squared deviation

- Mean squared deviation Δf

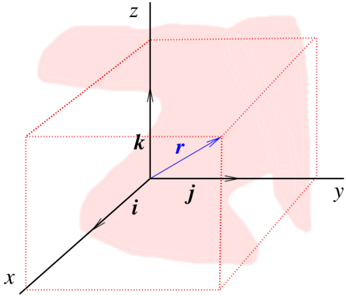
$$\Delta f = \sqrt{\langle f^2 \rangle - \langle f \rangle^2}$$

Ex. Ring toss

$$\Delta x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2} = \frac{L}{\sqrt{12}}$$

Vectorial space

- Vector $\Rightarrow$ Member of a vectorial space



base $(\boldsymbol{i}, \boldsymbol{j}, \boldsymbol{k})$ $\left\{\begin{array}{l}\text{Normalized} \\ \quad |\boldsymbol{i}|^2 = \boldsymbol{i} \cdot \boldsymbol{i} = 1 (idem)\ \boldsymbol{j}, \boldsymbol{k}) \\ \text{Orthogonal/Perpendicular} \\ \quad \boldsymbol{i} \cdot \boldsymbol{j} = \boldsymbol{i} \cdot \boldsymbol{k} = \ldots = 0 \\ \text{Generator system} \\ \quad \boldsymbol{r} = a\boldsymbol{i} + b\boldsymbol{j} + c\boldsymbol{k}\end{array}\right.$

$$\left.\begin{array}{l} \boldsymbol{r} \cdot \boldsymbol{i} = a\, \overbrace{\boldsymbol{i} \cdot \boldsymbol{i}}^{1} + b\, \overbrace{\boldsymbol{j} \cdot \boldsymbol{i}}^{0} + c\, \overbrace{\boldsymbol{k} \cdot \boldsymbol{i}}^{0} = a \\ \boldsymbol{r} \cdot \boldsymbol{j} = a\, \overbrace{\boldsymbol{i} \cdot \boldsymbol{j}}^{0} + b\, \overbrace{\boldsymbol{j} \cdot \boldsymbol{j}}^{1} + c\, \overbrace{\boldsymbol{k} \cdot \boldsymbol{j}}^{0} = b \\ \boldsymbol{r} \cdot \boldsymbol{k} = a\, \overbrace{\boldsymbol{i} \cdot \boldsymbol{k}}^{0} + b\, \overbrace{\boldsymbol{j} \cdot \boldsymbol{k}}^{0} + c\, \overbrace{\boldsymbol{k} \cdot \boldsymbol{k}}^{1} = c \end{array}\right\} \boldsymbol{r} = (\boldsymbol{r} \cdot \boldsymbol{i})\boldsymbol{i} + (\boldsymbol{r} \cdot \boldsymbol{j})\boldsymbol{j} + (\boldsymbol{r} \cdot \boldsymbol{k})\boldsymbol{k}$$

Vectorial space

- Vector $\Rightarrow$ $f(x)$ $\Rightarrow$ Hilbert's space

David Hilbert

Dot product $\Rightarrow \langle f|g\rangle = \int_{\forall x} f^*(x)g(x)dx$

$$\text{base } (\{\phi_i(x)\}_{i=1}^N) \begin{cases} \text{Normalized} \\ \quad \langle\phi_i|\phi_i\rangle = 1, \quad i = 1,\ldots,N \\ \text{Orthogonal/Perpendicular} \\ \quad \langle\phi_i|\phi_j\rangle = 0, \quad i \neq j = 1,\ldots,N \\ \text{Generator system} \\ \quad f(x) = \sum_{i=1}^N a_i\,\phi_i(x) \end{cases}$$

$$\left.\langle\phi_j|f\rangle = \sum_{i=1}^N a_i \langle\phi_j|\phi_i\rangle \overset{\delta_{ij}}{=} a_j \right\} f(x) = \sum_{i=1}^N \langle\phi_i|f\rangle\,\phi_i(x)$$

Classic state

- Classical Mechanics ⇒ The state of the system is characterized by the positions and moments of all the particles in the system $(\vec{r}, \vec{p})$

$$\vec{p} = m \frac{d\vec{r}}{dt}$$

If these magnitudes are known at a given time $(\vec{r}(0), \vec{p}(0))$ they can be known at any later $(\vec{r}(t), \vec{p}(t))$ or earlier time $(\vec{r}(-t), \vec{p}(-t))$ using the second Newton's law

$$\overrightarrow{F} = m\frac{d^2\vec{r}}{dt^2}$$

Quantum state

- Quantum Mechanics $\Rightarrow$ Postulate 1. The state of the system is characterized by a function depending on the coordinates of the particles in the system and time $\psi(\vec{r}, t)$ referred to as state function. The squared modulus of the state function $|\psi(\vec{r}, t)|^2$ is the probability density of the system

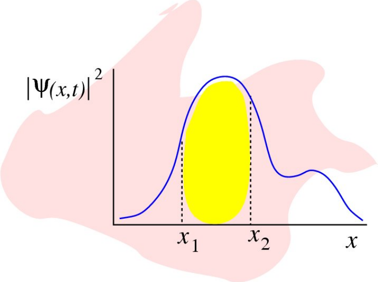
$$dP(\vec{r} \in [\vec{r}, \vec{r} + d\vec{r}]) = |\psi(\vec{r}, t)|^2 \, d\vec{r}$$

Modulus of a complex number

$$a = a_r + ia_i \Rightarrow |a|^2 = a \cdot a^* = (a_r + ia_i)(a_r - ia_i) = a_r^2 + a_i^2$$

State function

- Probabilistic interpretation



$$P(x \in [x_1, x_2]) = \int_{x_1}^{x_2} |\psi(x,t)|^2 \, dx$$

- State function must be *well behaved*:

  a) Normalizable $\Rightarrow$ $\int_{\forall \vec{r}} |\psi(\vec{r},t)|^2 \, d\vec{r} = 1$

  b) Single valued $\Rightarrow$ Probability density has only one value in any space point

  c) Continuous $\Rightarrow$ No jumps

Operators

- Postulate 2. Every measurable physical quantity is described by a lineal and hermitian operator obtained from the clasic expression of the magnitude using the correspondence principle
  - $x \rightarrow \hat{x}$
  - $p_x \rightarrow \hat{p}_x = \frac{\hbar}{i}\frac{d}{dx}$

Operators

- Operator

$$\hat{A} = \frac{d}{dx} \qquad f(x) = e^{-2x} \qquad \hat{B} = x^2$$

$$\hat{A}f = \frac{d}{dx}e^{-2x} = -2e^{-2x} \qquad \hat{B}f = x^2 e^{-2x}$$

- Lineal $\begin{cases} \hat{A}(f(x) + g(x)) = \hat{A}f(x) + \hat{A}g(x) \\ \hat{A}(c\, f(x)) = c\, \hat{A}f(x) \end{cases}$

- Hermitian $\Rightarrow \langle f|\hat{A}g\rangle = \langle \hat{A}f|g\rangle$

$$\langle f|\hat{A}g\rangle = \int_{\forall x} f^* \hat{A}g dx$$

$$\langle \hat{A}f|g\rangle = \int_{\forall x} (\hat{A}f)^* g dx = \left[\int_{\forall x} (\hat{A}f) g^* dx\right]^* = \left[\int_{\forall x} g^* (\hat{A}f) dx\right]^* = \langle g|\hat{A}f\rangle^*$$

Operators

Ex. Kinetic energy operator

$$T = \frac{p^2}{2m} \rightarrow \hat{T} = \frac{\hat{p}^2}{2m} = \frac{1}{2m}\left(\frac{\hbar}{i}\frac{d}{dx}\right)^2 = \frac{-\hbar^2}{2m}\frac{d^2}{dx^2}$$

Ex. Potential energy operator

$$V(x) \rightarrow \hat{V} = V(x)$$

Ex. Hamiltonian operator

$$E = \frac{p^2}{2m} + V(x) \rightarrow \hat{H} = \hat{T} + \hat{V}(x) = \frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + \hat{V}(x)$$

Operators: Result of a measurement

- Postulate 3. The only possible result of the measurement of a physical quantity A is one of the eigenvalues of the corresponding eigenvalue equation

$$\hat{A}\,\varphi_i = a_i\,\varphi_i \qquad\qquad i = 1, 2, \ldots$$

The numbers $a_1, a_2, \ldots$ are known as eigenvalues of the $\hat{A}$ operator and the functions φ_i are their corresponding eigenfunctions. The eigenfunctions define a basis set in the Hilbert's space.

$$\psi = \sum_i \langle \varphi_i | \psi \rangle \, \varphi_i$$

Result of a measurement

- When the system is described by the state function ψ, the measurement of the A magnitude will provide the result a_i with a probability equal to $P_{a_i} = |\langle\varphi_i|\psi\rangle|^2$.

$$\psi = \sum_i \langle\varphi_i|\psi\rangle\,\varphi_i \Rightarrow P_{a_i} = |\langle\varphi_i|\psi\rangle|^2$$

Consequences

- Consequence 1 $\Rightarrow \hat{A}\varphi_i = a_i\,\varphi_i$ y $\psi = \varphi_i$

$$P_{a_i} = |\,\langle\varphi_i|\psi\rangle\,|^2 = 1$$

- Consecuence 2 $\Rightarrow$ the mean value of a measurement of the A magnitude is

$$\langle\hat{A}\rangle = \sum_i P_{a_i}\,a_i = \sum_i |\,\langle\varphi_i|\psi\rangle\,|^2\,a_i = \langle\psi|\hat{A}|\psi\rangle$$

$\Rightarrow$ Mean squared deviation $\Delta A = \sqrt{\langle\hat{A}^2\rangle - \langle\hat{A}\rangle^2}$

Consequences

- Consequence 3 $\Rightarrow f \equiv g,\ \hat{A}f = a\,f$

$$\langle f|\hat{A}f\rangle = \left[\langle f|\hat{A}f\rangle\right]^*$$
$$\langle f|a\,f\rangle = [\langle f|a\,f\rangle]^*$$
$$a\,\langle f|f\rangle = a^*\,[\langle f|f\rangle]^* \Rightarrow a = a^* \Rightarrow a \text{ real}$$

- Consequence 4 $\Rightarrow \hat{A}f = a\,f,\ \hat{A}g = b\,g,\ a \neq b$

$$\langle f|\hat{A}g\rangle = \left[\langle g|\hat{A}f\rangle\right]^*$$
$$b\,\langle f|g\rangle = a\,\langle g|f\rangle^*$$
$$\downarrow \qquad \langle g|f\rangle^* = \left[\int_{\forall x} g^* f dx\right]^* = \int_{\forall x} f^* g dx = \langle f|g\rangle$$
$$(b-a)\,\langle f|g\rangle = 0 \Rightarrow f, g \text{ orthogonals}$$

Commutators

- The commutator between two operators is defined by

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$$

Ex. $\hat{A} = \frac{d}{dx}$ y $\hat{B} = x^2$

$$[\hat{A}, \hat{B}]f = \hat{A}\hat{B}f - \hat{B}\hat{A}f = \frac{d}{dx}\left(x^2 f\right) - x^2\frac{df}{dx}$$

$$= 2xf + \cancel{x^2\frac{df}{dx} - -x^2\frac{df}{dx}} = 2xf$$

$$[\hat{A}, \hat{B}] = 2x$$

Simultaneous measurement

- Consequence. If the hermitian operators $\hat{A}$ and $\hat{B}$ commute, then there is a common set of eigenfunctions.

$$[\hat{A}, \hat{B}] = 0 \;\Rightarrow\; \hat{A}\hat{B}f = \hat{B}\hat{A}f$$

$$\hat{A}f_i = a_i f_i$$

$$\downarrow$$

$$\hat{B}\hat{A}f_i = \hat{B}(a_i f_i)$$

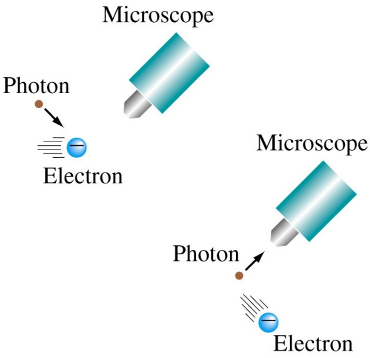
$$\hat{A}(\hat{B}f_i) = a_i(\hat{B}f_i)$$

$$\downarrow \quad \hat{B}f_i \text{ is eigenfunction of } \hat{A} \text{ with eigenvalue } a_i$$

$$\hat{B}f_i = kf_i$$

Uncertainty principle

- Heisenberg's uncertainty principle



$$\Delta A \Delta B \geq \frac{1}{2} \langle [\hat{A}, \hat{B}] \rangle$$

$$[\hat{x}, \hat{p}] = i\hbar$$

$$\Delta x \, \Delta p \geqslant \frac{\hbar}{2}$$