Basics of Quantum Theory

Quantum Chemistry

Lesson 1

Contents

1. Quantum theory, quantum mechanics, quantum field thoery
2. State, state space, wave function
3. Dynamic observables, operators
4. Hamilton operator, Schrödinger equation(s)
5. Quantum chemistry

Quantum theory, …

Quantum theory

- mathematical framework for the description of phenomena beyond the classical physics domain (microscopic, not only)

Quantum mechanics

- quantum theory applied to systems with a finite number of degrees of freedom (= finite and constant number of particles)

Quantum field theory

- quantum theory applied to systems with an infinite number of degrees of freedom (= finite to infinite number of particles, not constant)

Quantum theory, …

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State, state space, wave function

State

- a complete info about the system under study (= initial condition for equations of motion)
  - compatible / incompatible observables
  - complete set of compatible observables
  - measurement outputs $\rightarrow |a_k, a_l, \dots\rangle \subset \mathcal{H}$ (orthonormal basis set in $\mathcal{H}$)
  - in fact a linear span of $|a_k, a_l, \dots\rangle$, 1D subspace

State space

- $\mathcal{H}$, a set of all possible states
- a separable Hilbert space

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State, state space, wave function

Separable Hilbert spaces

- Hilbert space
  - linear vector space: **x**+**y**, *c***x**
  - complex valued
  - scalar (dot) product (**x**.**y** $\longrightarrow$ *c*, **x**.**x** $\longrightarrow$ Euclidean norm)
  - complete (all the Cauchy sequences do converge)
- basis
  - $\mathbf{x} = \sum_\alpha c_\alpha \mathbf{e}_\alpha$ (an infinite / or even uncountable set of $\mathbf{e}_\alpha$, but always a finite sum)
  - orthonormal basis ($\mathbf{e}_\alpha . \mathbf{e}_\beta = \delta_{\alpha\beta}$)
- separable
  - $\mathbf{x} = \sum_{k=1}^{+\infty} c_k \mathbf{e}_k$ (countable Schauder basis)
- all the separable Hilbert spaces are both algebraically and topologically equivalent
  - Dirac's *abstract Hilbert state space*
  - representations (*X*, *P*, ...)

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State, state space, wave function

Bra-ket formalism (Dirac)

- ket and bra vectors
  - $\mathbf{x} \rightarrow |x\rangle$
  - $\mathbf{x}^* \rightarrow \langle x|$
- scalar product
  - $\mathbf{x}.\mathbf{y} \rightarrow \langle x|y\rangle$

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State, state space, wave function

L_2 spaces on $\mathbb{R}^n$

- square-integrable functions
  - $\varphi: \mathbb{R}^n \to \mathbb{C}$
  - $\int_{\mathbb{R}^n} |\varphi(\mathbf{x})|^2 \mathrm{d}^n\mathbf{x} < +\infty$
- $L_2(\mathbb{R}^n)$ spaces are separable Hilbert spaces
  - $|\varphi\rangle = \varphi: \mathbb{R}^n \to \mathbb{C}$
  - $\langle\psi|\varphi\rangle = \int_{\mathbb{R}^n} \psi^*(\mathbf{x})\varphi(\mathbf{x})\mathrm{d}^n\mathbf{x}$
  - *X*-representations of the abstract Hilbert state space
- physical point of view
  - wave functions (why?)
  - $n = 3N$, where N is the number of particles ($n = 3, 6, 9, \ldots$)
  - wave function meaning: $\int_{\mathbb{R}^n} |\varphi(\mathbf{x})|^2 \mathrm{d}^n\mathbf{x} = \langle\varphi|\varphi\rangle = 1 \quad \Rightarrow \quad |\varphi(\mathbf{x})|^2$ is the *probability density* of ...
  - only the absolute value (module) of φ is measurable (physically relevant), not its argument (phase)

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Observables, operators

classical point of view

- measurable quantities (**r**, **p**, E_k, E_p,$\vec{L}$, ...)
- importantly (!), $A = A(\mathbf{r}, \mathbf{p})$

quantum point of view

- self-adjoint operators ($\hat{A}$): $\hat{A} = \hat{A}^{+}$, specifically $\langle\psi|\hat{A}\varphi\rangle = \langle\hat{A}\psi|\varphi\rangle$
- measurable / allowed values of A = spectrum (eigenvalues) of $\hat{A}$: $\hat{A}|a\rangle = a|a\rangle$
  - $a \in \mathbb{R}$ (always!)
  - the discrete part and continuous part of a spectrum
  - the mean value of A in state $|\varphi\rangle$: if $\langle\varphi|\varphi\rangle = 1$ then $\bar{a} = \langle\varphi|\hat{A}|\varphi\rangle$
- correspondence principle (Dirac)
  - $A = f(B, C) \Rightarrow \hat{A} = f(\hat{B}, \hat{C})$
  - $\widehat{\mathbf{X}} = \mathbf{r} \wedge \widehat{\mathbf{P}} = -i\hbar\nabla \wedge A = A(\mathbf{r}, \mathbf{p}) \Rightarrow \hat{A} = A(\mathbf{r}, -i\hbar\nabla)$

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Observables, operators

Compatible / incompatible observables

- commutator: $[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$
- uncertainty relations: $\Delta a \Delta b \geq 1/2 |\langle \varphi | [\hat{A}, \hat{B}] | \varphi \rangle|$ $(\langle \varphi | \varphi \rangle = 1)$
  - specifically, the Heisenberg uncertainty relations for $\hat{X}$ and $\hat{P}$
  - see also Annex 1
- compatibility of observables
  - commuting operators → compatible observables
  - non-commuting operators → incompatible observables

Hamilton operator

Classical Hamilton function (a single particle)

- $H(\vec{p},\vec{r}) = \frac{\vec{p}^2}{2m} + V(\vec{r})$
- the overall / total energy of the system
- a sum of the (classical) kinetic energy and potential energy

Quantum Hamilton operator (a single particle, *X*-representation)

- $\hat{H} = \frac{(-i\hbar\nabla)^2}{2m} + V(\vec{r}) = -\frac{\hbar^2}{2m}\Delta + V(\vec{r})$
- the operator of the total energy of the system under study
- a sum of the kinetic energy operator and the potential energy operator

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Schrödinger equations

Stationary (time-independent) Schrödinger equation

- in general: $\hat{H}|\psi\rangle = E|\psi\rangle$
  - stationary states (time-independent)
  - measurable / allowed values of the system total energy
  - pivotal equation of quantum chemistry
- *X*-representation (a single particle): $-\frac{\hbar^2}{2m}\Delta\psi(\vec{r}) + V(\vec{r})\psi(\vec{r}) = E\psi(\vec{r})$
  - partial differential equation
  - boundary conditions – square-integrability of ψ: $\psi \to 0$ for $r \to +\infty$, ...
  - ... lead to measurable values of the total energy (energy quantization, energetic spectrum)
  - discrete and continuous part of the energetic spectrum (in quantum chemistry, we are interested in the discrete part only, why?)
  - ground state, excited states

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Schrödinger equations

Non-stationary (time-dependent) Schrödinger equation

- in general: $\hat{H}(t)|\psi(t)\rangle = i\hbar\frac{\mathrm{d}}{\mathrm{d}t}|\psi(t)\rangle$
  - equation of motion → time evolution
  - in quantum chemistry: time-dependent Hamiltonians (interaction with light→photochemistry, collisions →reaction dynamics)
- *X*-representation (a single particle): $-\frac{\hbar^2}{2m}\Delta\psi(\vec{r},t) + V(\vec{r})\psi(\vec{r},t) = i\hbar\frac{\partial}{\partial t}\psi(\vec{r},t)$
  - partial differential equation
  - boundary conditions – square-integrability of ψ: $\psi \to 0$ for $r \to +\infty$
  - initial condition: $\psi(\vec{r},t=0) = \psi_0(\vec{r})$
  - solution is unique → quantum determinism

Quantum chemistry

Main subject(s)

- finding solutions to stationary SE for atoms and molecules
  - only electrons participate, atomic nuclei play a role of spectators (*Born-Oppenheimer separation*)
  - the total energy of the system is parametrically dependent on the positions of nuclei, *potential energy surface* (PES)
  - mainly, the ground state is needed only (thermal conditions), but for some specific problems, also excited states get into play (photoexcitation)
- PES exploration
  - molecular equilibrium geometries (molecular rotations)
  - (harmonic) molecular vibrations
  - gas-phase thermodynamic properties
- other calculations
  - other molecular properties (electric and/or magnetic dipole etc. moments, polarizability, ...)

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Quantum chemistry

Main issues

- many-particle systems of a specific (complex) behavior (electrons = fermions)

- numerical methods are needed (analytic solutions are available for textbook problems only)
- approximations are to be made should the numerical calculations be practicable

- powerful computers are needed for realistic calculations
- involved software implementations are required which are far beyond the capability of a common user

- fortunately, such numerical methods, approximations, implementations, and computers exist
- but, the use of software packages (usually as black- or grey-boxes) requires a solid background

The end of lesson 1.

Annex 1: Proof of the uncertainty relations

Theorem

$$\Delta a \Delta b \geq \frac{1}{2}\left|\langle\varphi\left|[\hat{A},\hat{B}]\right|\varphi\rangle\right| \quad \text{with } \langle\varphi|\varphi\rangle = 1$$

Proof

- $\Delta\hat{A} \stackrel{\text{def}}{=} \hat{A} - a\hat{I}$, $\Delta\hat{B} \stackrel{\text{def}}{=} \hat{B} - b\hat{I}$, where $a = \langle\varphi|\hat{A}|\varphi\rangle$, $b = \langle\varphi|\hat{B}|\varphi\rangle$, and $\hat{I}$ is a unity (identity) operator
- $|\varphi_A\rangle \stackrel{\text{def}}{=} \Delta\hat{A}|\varphi\rangle$, $|\varphi_B\rangle \stackrel{\text{def}}{=} \Delta\hat{B}|\varphi\rangle$
- $(\Delta a)^2 \stackrel{\text{def}}{=} \langle\varphi\left|(\Delta\hat{A})^2\right|\varphi\rangle = \langle\varphi_A|\varphi_A\rangle = \|\varphi_A\|^2$, $\quad (\Delta b)^2 \stackrel{\text{def}}{=} \langle\varphi\left|(\Delta\hat{B})^2\right|\varphi\rangle = \langle\varphi_B|\varphi_B\rangle = \|\varphi_B\|^2$
- $(\Delta a)^2(\Delta b)^2 = \|\varphi_A\|^2\|\varphi_B\|^2 \geq |\langle\varphi_A|\varphi_B\rangle|^2$ (Cauchy- Schwartz-Bunyakovsky inequality)
- $\langle\varphi_A|\varphi_B\rangle = \langle\varphi|\Delta\hat{A}\Delta\hat{B}|\varphi\rangle = \frac{1}{2}\underbrace{\langle\varphi|\{\Delta\hat{A},\Delta\hat{B}\}|\varphi\rangle}_{\substack{\text{anticommutator }*,\\ \text{self-adjoint},\\ \text{real-valued diagonal}}} + \frac{1}{2}\underbrace{\langle\varphi|[\Delta\hat{A},\Delta\hat{B}]|\varphi\rangle}_{\substack{\text{commutator},\\ \text{anti-self-adjoint }**,\\ \text{imaginary-valued diagonal }***}}$
- $|\langle\varphi_A|\varphi_B\rangle|^2 = \frac{1}{4}\left|\langle\varphi|\{\Delta\hat{A},\Delta\hat{B}\}|\varphi\rangle\right|^2 + \frac{1}{4}\left|\langle\varphi|[\Delta\hat{A},\Delta\hat{B}]|\varphi\rangle\right|^2 \geq \frac{1}{4}\left|\langle\varphi|[\Delta\hat{A},\Delta\hat{B}]|\varphi\rangle\right|^2$
- $\Delta a\Delta b = \|\varphi_A\|\|\varphi_B\| \geq |\langle\varphi_A|\varphi_B\rangle| \geq \frac{1}{2}\left|\langle\varphi\left|[\Delta\hat{A},\Delta\hat{B}]\right|\varphi\rangle\right| = \cdots = \frac{1}{2}\left|\langle\varphi\left|[\hat{A},\hat{B}]\right|\varphi\rangle\right|$

* $\{\hat{P},\hat{Q}\} \stackrel{\text{def}}{=} \hat{P}\hat{Q} + \hat{Q}\hat{P}$ $\qquad$ ** $\hat{P}^+ = -\hat{P}$ $\qquad$ *** $\langle\varphi|\hat{P}\varphi\rangle = \langle\hat{P}^+\varphi|\varphi\rangle = -\langle\hat{P}\varphi|\varphi\rangle = -\overline{\langle\varphi|\hat{P}\varphi\rangle}$

Annex 1: Proof of the uncertainty relations

Theorem

$\Delta a \Delta b \geq \frac{1}{2}\left|\left\langle\varphi\middle|[\hat{A},\hat{B}]\middle|\varphi\right\rangle\right|$ with $\langle\varphi|\varphi$

<u>*Proof*</u>

- $\Delta\hat{A} \stackrel{\text{def}}{=} \hat{A} - a\hat{I}$, $\Delta\hat{B} \stackrel{\text{def}}{=} \hat{B} - b\hat{I}$, where $a = \langle\varphi|\hat{A}|\varphi$
- $|\varphi_A\rangle \stackrel{\text{def}}{=} \Delta\hat{A}|\varphi\rangle$, $|\varphi_B\rangle \stackrel{\text{def}}{=} \Delta\hat{B}|\varphi\rangle$
- $(\Delta a)^2 \stackrel{\text{def}}{=} \left\langle\varphi\middle|(\Delta\hat{A})^2\middle|\varphi\right\rangle = \langle\varphi_A|\varphi_A\rangle = \|\varphi_A\|^2$, $\quad (\Delta b)^2 \stackrel{\text{def}}{=} \langle\varphi|(\Delta \ldots \varphi_B|\varphi_B\rangle = \|\varphi_B\|^2$
- $(\Delta a)^2(\Delta b)^2 = \|\varphi_A\|^2\|\varphi_B\|^2 \geq |\langle\varphi_A|\varphi_B\rangle|^2$ (Cauchy- Schwartz-Bunyakovsky inequality)

> - $0 \leq \langle\varphi_A - \alpha\varphi_B|\varphi_A - \alpha\varphi_B\rangle = \cdots =$
> $= \|\varphi_A\|^2 + |\alpha|^2\|\varphi_B\|^2 - \alpha\langle\varphi_A|\varphi_B\rangle - \bar{\alpha}\langle\varphi_B|\varphi_A\rangle$
> - $\alpha \stackrel{\text{def}}{=} \frac{\langle\varphi_B|\varphi_A\rangle}{\|\varphi_B\|^2} = \frac{\overline{\langle\varphi_A|\varphi_B\rangle}}{\|\varphi_B\|^2}$
> - $\langle\varphi_A - \alpha\varphi_B|\varphi_A - \alpha\varphi_B\rangle = \cdots = \|\varphi_A\|^2 - \frac{|\langle\varphi_A|\varphi_B\rangle|^2}{\|\varphi_B\|^2} \geq 0$

- $\langle\varphi_A|\varphi_B\rangle = \left\langle\varphi\middle|\Delta\hat{A}\Delta\hat{B}\middle|\varphi\right\rangle = \underbrace{\frac{1}{2}\left\langle\varphi\middle|\{\Delta\hat{A},\Delta\hat{B}\}\middle|\varphi\right\rangle}_{\substack{\text{anticommutator }*,\\ \text{self-adjoint},\\ \text{real-valued diagonal}}} + \underbrace{\frac{1}{2}\left\langle\varphi\middle|[\Delta\hat{A},\Delta\hat{B}]\middle|\varphi\right\rangle}_{\substack{\text{commutator},\\ \text{anti-self-adjoint }**,\\ \text{imaginary-valued diagonal }***}}$
- $|\langle\varphi_A|\varphi_B\rangle|^2 = \frac{1}{4}\left|\left\langle\varphi\middle|\{\Delta\hat{A},\Delta\hat{B}\}\middle|\varphi\right\rangle\right|^2 + \frac{1}{4}\left|\left\langle\varphi\middle|[\Delta\hat{A},\Delta\hat{B}]\middle|\varphi\right\rangle\right|^2 \geq \frac{1}{4}\left|\left\langle\varphi\middle|[\Delta\hat{A},\Delta\hat{B}]\middle|\varphi\right\rangle\right|^2$
- $\Delta a\Delta b = \|\varphi_A\|\|\varphi_B\| \geq |\langle\varphi_A|\varphi_B\rangle| \geq \frac{1}{2}\left|\left\langle\varphi\middle|[\Delta\hat{A},\Delta\hat{B}]\middle|\varphi\right\rangle\right| = \cdots = \frac{1}{2}\left|\left\langle\varphi\middle|[\hat{A},\hat{B}]\middle|\varphi\right\rangle\right|$

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