Advanced Quantum Mechanics & Spectroscopy (CHEM 7520)

Alexander Yu. Sokolov

Week 1: Review of foundations

I. FOUNDATIONS OF QUANTUM MECHANICS

A. Linear vector algebra

First, we briefly recap main concepts of linear algebra that will be very important later in the course.

A vector in 3 dimensions can be represented by specifying its components a_i (i = 1, 2, 3) with respect to a set of three **mutually perpendicular unit** vectors:

$$\vec{a} = a_1\vec{e}_1 + a_2\vec{e}_2 + a_3\vec{e}_3 = \sum_{i=1}^{3} a_i\vec{e}_i \tag{1}$$

The unit vectors $\vec{e}_i$ form a **basis** and are called **basis vectors**. The basis is **complete**, i.e. any three-dimensional vector can be represented as a linear combination of 3 basis vectors. Basis is not unique, we could have chosen three different mutually perpendicular vectors:

$$\vec{a} = a'_1\vec{\varepsilon}_1 + a'_2\vec{\varepsilon}_2 + a'_3\vec{\varepsilon}_3 = \sum_{i=1}^{3} a'_i\vec{\varepsilon}_i \tag{2}$$

A vector can be represented by a column matrix. For example, in the basis $\vec{e}_i$, the representation is:

$$\mathbf{a} = \begin{pmatrix} a_1 \\ a_2 \\ a_3 \end{pmatrix} \tag{3}$$

The same vector can be represented in the basis $\vec{\varepsilon}_i$ as:

$$\mathbf{a}' = \begin{pmatrix} a'_1 \\ a'_2 \\ a'_3 \end{pmatrix} \tag{4}$$

For now we assume that we always work in the same basis.

The **scalar** or **dot product** of two vectors in the same basis is defined as:

$$\vec{a}\cdot\vec{b} = a_1b_1 + a_2b_2 + a_3b_3 = \sum_{i=1}^{3} a_ib_i \tag{5}$$

The dot product of the vector on itself is just the square of the **length** of the vector ($|\vec{a}|$):

$$\vec{a}\cdot\vec{a} = a_1^2 + a_2^2 + a_3^2 \equiv |\vec{a}|^2 \tag{6}$$

We can express the product as

$$\vec{a}\cdot\vec{b} = \sum_{i=1}^{3}\sum_{j=1}^{3} a_ib_j\vec{e}_i\cdot\vec{e}_j \tag{7}$$

Thus, we require:

$$\vec{e}_i\cdot\vec{e}_j = \delta_{ij} = \begin{cases} 1 & for\ i\ =\ j \\ 0 & for\ i\ \neq\ j\ , \end{cases} \tag{8}$$

where δ_{ij} is a **Kronecker delta**. The above equation states that the basis vectors $\vec{e}_i$ are mutually perpendicular (**orthogonal**) and have unit length; in other words, **orthonormal**. Useful Properties:

$$\vec{e}_j\cdot\vec{a} = \sum_{i=1}^{3} a_i\vec{e}_j\cdot\vec{e}_i = a_j \tag{9}$$

$$\vec{a} = \sum_{i=1}^{3} \vec{e}_i\vec{e}_i\cdot\vec{a} = \sum_{i=1}^{3} \vec{e}_i a_i = \overleftrightarrow{1}\cdot\vec{a}\ , \tag{10}$$

where $\overleftrightarrow{1}$ is the **unit dyadic**:

$$\overleftrightarrow{1} = \sum_{i=1}^{3} \vec{e}_i\vec{e}_i\ . \tag{11}$$

Dyadic is a quantity, which when dotted into a vector gives another vector. The unit dyadic gives the same vector back.

All of the above equations can be generalized to more than 3 dimensions. In the general case of N dimensions, we get

$$\vec{a} = a_1\vec{e}_1 + a_2\vec{e}_2 + \ldots + a_N\vec{e}_N = \sum_{i=1}^{N} a_i\vec{e}_i \tag{12}$$

and the dot product is expressed as:

$$\vec{a}\cdot\vec{b} = a_1b_1 + a_2b_2 + \ldots + a_Nb_N = \sum_{i=1}^{N} a_ib_i \tag{13}$$

From now on, we will work with general vector spaces of N dimensions and will simplify our summation notation.

An **operator** is an object that when acting on a vector converts it into another vector:

$$\hat{O}\vec{a} = \vec{c} \tag{14}$$

There are different types of operators, we will mostly encounter **linear** operators, which have the property:

$$\hat{O}(x\vec{a} + y\vec{b}) = x\hat{O}\vec{a} + y\hat{O}\vec{b} \tag{15}$$

A linear operator is completely determined in terms of its action on a basis vector $\vec{e}_i$. Since $\hat{O}\vec{e}_i$ is a vector and any vector can be represented as a linear combination of basis vectors, we get:

$$\hat{O}\vec{e}_i = \sum_j \vec{e}_j O_{ji} \tag{16}$$

The number O_{ji} is the component of the vector $\hat{O}\vec{e}_i$ along $\vec{e}_j$. These numbers can be arranged in a two-dimensional array called **matrix**:

$$\mathbf{O} = \begin{pmatrix} O_{11} & O_{12} & \ldots & O_{1N} \\ O_{21} & O_{22} & \ldots & O_{2N} \\ \ldots & \ldots & \ldots & \ldots \\ O_{N1} & O_{N2} & \ldots & O_{NN} \end{pmatrix} \tag{17}$$

This is also called as the **matrix representation** of $\hat{O}$ in the basis $\vec{e}_i$.

The matrix $\mathbf{O}$ completely specifies the action of the operator $\hat{O}$ in a given basis. For example, the action of $\hat{O}$ on a vector $\vec{a}$ can be written as:

$$\hat{O}\vec{a} = \sum_i a_i \hat{O}\vec{e}_i = \sum_{ij} a_i O_{ji} \vec{e}_j = \sum_j c_j \vec{e}_j \tag{18}$$

$$\sum_i O_{ji} a_i = c_j \tag{19}$$

$$\mathbf{Oa} = \mathbf{c} \tag{20}$$

Some important properties and definitions:

1. If $\hat{C} = \hat{A}\hat{B}$, their matrix representations are related as: $\mathbf{C} = \mathbf{AB}$.
2. In general, $\hat{A}\hat{B} \neq \hat{B}\hat{A}$ and $\mathbf{AB} \neq \mathbf{BA}$, the **commutator** is $[\mathbf{A}, \mathbf{B}] = \mathbf{AB} - \mathbf{BA}$
3. The **adjoint** operator $\hat{A}^\dagger$ of the operator $\hat{A}$ is defined such that its matrix representation $(\mathbf{A}^\dagger)_{ij} = (\mathbf{A}^*)_{ji}$, or equivalently $\mathbf{A}^\dagger = (\mathbf{A}^*)^\mathbf{T}$. If $\mathbf{A}$ is real, $\mathbf{A}^\dagger = \mathbf{A}^\mathbf{T}$.
4. If $\mathbf{a}$ is a column matrix, $\mathbf{a}^\dagger = (a_1^* a_2^* \ldots a_N^*)$ is a **row matrix**.
5. $(\mathbf{AB})^\dagger = \mathbf{B}^\dagger \mathbf{A}^\dagger$

The following properties and definitions apply only to the square matrices:

6. The matrix $\mathbf{A}$ is **diagonal** if

$$A_{ij} = A_{ii}\delta_{ij} \tag{21}$$

7. The **trace** of the matrix $\mathbf{A}$ is defined as

$$\mathrm{Tr}\,\mathbf{A} = \sum_i A_{ii} \tag{22}$$

8. The **unit** matrix $\mathbf{1}$ is defined as:

$$\mathbf{1A} = \mathbf{A1} = \mathbf{A} \tag{23}$$

   Its elements are $(\mathbf{1})_{ij} = \delta_{ij}$.

9. The **inverse** of the matrix of $\mathbf{A}$ is defined as:

$$\mathbf{A^{-1}A} = \mathbf{AA^{-1}} = \mathbf{1} \tag{24}$$

10. A **unitary** matrix is the one whose inverse is its adjoint:

$$\mathbf{A^{-1}} = \mathbf{A}^\dagger \tag{25}$$

A real unitary matrix is called **orthogonal**.

11. A **Hermitian** matrix is self-adjoint:

$$\mathbf{A}^\dagger = \mathbf{A} \tag{26}$$

A real Hermitian matrix is called **symmetric**.

B. Complex vector spaces

We now generalize the concepts of linear algebra to an N-dimensional space in which vectors can be complex. In analogy to the basis $\{\vec{e}_i\}$, we consider N basis vectors denoted $|i\rangle$ called **ket vectors** or **kets**. We assume basis $|i\rangle$ is complete, so any vector can be represented as:

$$|a\rangle = \sum_{i=1}^{N} a_i |i\rangle \tag{27}$$

Similarly, $|a\rangle$ can be represented as a column matrix $\mathbf{a}$ (1D-array). We also introduce a **bra vector** $\langle a|$ whose matrix representation is $\mathbf{a}^\dagger$. The product between $\langle a|$ and $|a\rangle$ is a generalization of the dot product:

$$\langle a|\,|b\rangle \equiv \langle a|b\rangle = \mathbf{a}^\dagger\mathbf{b} = (a_1^* a_2^* \ldots a_N^*) \begin{pmatrix} b_1 \\ b_2 \\ \vdots \\ b_3 \end{pmatrix} = \sum_i a_i^* b_i \tag{28}$$

$$\langle a|a\rangle = \sum_i a_i^* a_i = \sum_i |a_i|^2 \tag{29}$$

By analogy, with real vector spaces, we obtain:

$$\langle a|b\rangle = \sum_{ij} a_i^* b_j \langle i|j\rangle \tag{30}$$

$$\langle i|j\rangle = \delta_{ij} \tag{31}$$

$$\langle j|a\rangle = \sum_i a_i \langle j|i\rangle = a_j \tag{32}$$

$$\langle a|j\rangle = \sum_i a_i^* \langle i|j\rangle = a_j^* \tag{33}$$

$$\langle a|j\rangle = (\langle j|a\rangle)^* = \langle j|a\rangle^* \tag{34}$$

$$|a\rangle = \sum_i a_i |i\rangle = \sum_i |i\rangle \langle i|a\rangle \tag{35}$$

$$\sum_i |i\rangle \langle i| = 1 \tag{36}$$

Similarly, we can introduce an operator $\hat{O}$ that converts ket $|a\rangle$ into a ket $|b\rangle$:

$$\hat{O}|a\rangle = |b\rangle \tag{37}$$

The action of the operator on the basis ket is given by:

$$\hat{O}|i\rangle = \sum_j |j\rangle O_{ji} \tag{38}$$

where O_{ji} are the elements of the matrix representation $\mathbf{O}$. The elements O_{ji} can be expressed using the braket notation either by multiplying with $\langle j|$ on the left ("**projecting**")

$$\langle j|\hat{O}|i\rangle = \sum_k \delta_{jk} O_{ki} = O_{ji} \tag{39}$$

or by introducing a **completeness relation**

$$\hat{O}|i\rangle = \sum_j |j\rangle \langle j|\hat{O}|i\rangle = \sum_j |j\rangle O_{ji} \tag{40}$$

Other useful relations:

$$C_{ij} = \langle i|\hat{C}|j\rangle = \langle i|\hat{A}\hat{B}|j\rangle = \sum_k \langle i|\hat{A}|k\rangle \langle k|\hat{B}|j\rangle = \sum_k A_{ik} B_{kj} \tag{41}$$

$$(O^\dagger)_{ij} = \langle i|\hat{O}^\dagger|j\rangle = \langle j|\hat{O}|i\rangle^* = O_{ji}^* \tag{42}$$

If $\hat{O}$ is Hermitian, the following relation is satisfied:

$$\langle a|\hat{O}^\dagger|b\rangle = \langle a|\hat{O}|b\rangle = \langle b|\hat{O}|a\rangle^* \tag{43}$$

C. Change of basis

Consider two orthonormal bases:

$$\langle i|j\rangle = \delta_{ij} \ , \quad \sum_i |i\rangle \langle i| = 1 \tag{44}$$

$$\langle \alpha|\beta\rangle = \delta_{\alpha\beta} \ , \quad \sum_\alpha |\alpha\rangle \langle \alpha| = 1 \tag{45}$$

We can define a **transformation matrix**:

$$|\alpha\rangle = \sum_i |i\rangle \langle i|\alpha\rangle = \sum_i |i\rangle U_{i\alpha} = \sum_i |i\rangle \mathbf{U}_{i\alpha} \tag{46}$$

$$|i\rangle = \sum_\alpha |\alpha\rangle \langle \alpha|i\rangle = \sum_\alpha |\alpha\rangle U^*_{i\alpha} = \sum_\alpha |\alpha\rangle (\mathbf{U}^\dagger)_{\alpha i} \tag{47}$$

We can demonstrate that the matrix $\mathbf{U}$ is **unitary**:

$$\delta_{ij} = \langle i|j\rangle = \sum_\alpha \langle i|\alpha\rangle \langle \alpha|j\rangle = \sum_\alpha \mathbf{U}_{i\alpha}(\mathbf{U}^\dagger)_{\alpha j} = (\mathbf{U}\mathbf{U}^\dagger)_{ij} \tag{48}$$

$$\mathbf{U}\mathbf{U}^\dagger = \mathbf{U}^\dagger\mathbf{U} = \mathbf{1} \tag{49}$$

Thus, the two orthonormal bases are related by a unitary matrix. We can now consider how the matrix representations of an operator in two bases are related:

$$\hat{O}\,|i\rangle = \sum_j |j\rangle \langle j|\hat{O}|i\rangle = \sum_j |j\rangle O_{ji} \tag{50}$$

$$\hat{O}\,|\alpha\rangle = \sum_\beta |\beta\rangle \langle \beta|\hat{O}|\alpha\rangle = \sum_\beta |\beta\rangle \Omega_{\beta\alpha} \tag{51}$$

$$\Omega_{\alpha\beta} = \langle \alpha|\hat{O}|\beta\rangle = \sum_{ij} \langle \alpha|i\rangle \langle i|\hat{O}|j\rangle \langle j|\beta\rangle = \sum_{ij} (\mathbf{U}^\dagger)_{\alpha i}(\mathbf{O})_{ij}(\mathbf{U})_{j\beta} \tag{52}$$

$$\mathbf{\Omega} = \mathbf{U}^\dagger\mathbf{O}\mathbf{U} \tag{53}$$

$$\mathbf{O} = \mathbf{U}\mathbf{\Omega}\mathbf{U}^\dagger \tag{54}$$

D. Eigenvalue problem

If acting $\hat{O}$ on a vector $|\alpha\rangle$ results in the same vector multiplied by a constant we say that $|\alpha\rangle$ is an **eigenvector** of $\hat{O}$:

$$\hat{O}\,|\alpha\rangle = \omega_\alpha\,|\alpha\rangle \tag{55}$$

The constant ω_α is called **eigenvalue**.

Properties:

1. The eigenvalues of a Hermitian operator are real.

$$\langle\alpha|\hat{O}|\alpha\rangle = \langle\alpha|\hat{O}^\dagger|\alpha\rangle = \langle\alpha|\hat{O}|\alpha\rangle^* \tag{56}$$

$$\omega_\alpha = \omega_\alpha^* \tag{57}$$

2. The eigenvectors of a Hermitian operator are orthogonal.

$$\hat{O}\,|\beta\rangle = \omega_\beta\,|\beta\rangle \tag{58}$$

$$\langle\beta|\,\hat{O}^\dagger = \langle\beta|\,\omega_\beta^* \tag{59}$$

$$\langle\beta|\,\hat{O} = \langle\beta|\,\omega_\beta \tag{60}$$

$$\langle\beta|\hat{O}|\alpha\rangle = \omega_\beta\,\langle\beta|\alpha\rangle \tag{61}$$

$$\omega_\alpha\,\langle\beta|\alpha\rangle = \omega_\beta\,\langle\beta|\alpha\rangle \tag{62}$$

$$(\omega_\alpha - \omega_\beta)\,\langle\beta|\alpha\rangle = 0 \tag{63}$$

Thus, $\langle\beta|\alpha\rangle = 0$ if $\omega_\alpha \neq \omega_\beta$. Degenerate eigenvectors can always be chosen to be orthogonal.

3. Matrix representation of an operator in its eigenvector basis is diagonal. The problem of diagonalizing a matrix $\mathbf{O}$ is equivalent to finding the unitary matrix that converts $\mathbf{O}$ into a diagonal matrix

$$\mathbf{U}^\dagger\mathbf{O}\mathbf{U} = \boldsymbol{\omega} = \begin{pmatrix} \omega_1 & 0 & \dots & 0 \\ 0 & \omega_2 & \dots & 0 \\ \dots & \dots & \dots & 0 \\ 0 & 0 & 0 & \omega_N \end{pmatrix} \tag{64}$$

E. Orthogonal functions, eigenfunctions, and operators

We discussed how a vector can be represented using a complete set of orthonormal basis vector. Similarly, we can represent a sufficiently well-behaved function on some interval as an infinite linear combination of orthogonal functions.

We consider an infinite set of functions $\{\psi_i(x), i = 1, 2, \dots\}$ that satisfy orthonor-

mality condition

$$\int_{x_1}^{x_2} \mathrm{d}x\, \psi_i^*(x)\psi_j(x) = \delta_{ij} \tag{65}$$

We will drop the integration limits. We assume that any function can be expressed as a linear combination of $\{\psi_i(x)\}$:

$$a(x) = \sum_i a_i \psi_i(x) \tag{66}$$

This means that the basis $\psi_i(x)$ is complete. We can determine the coefficients of the linear combination as follows:

$$\int \mathrm{d}x\, \psi_j^*(x)a(x) = \sum_i \int \mathrm{d}x\, \psi_j^*(x)\psi_i(x)a_i = \sum_i \delta_{ji}a_i = a_j \tag{67}$$

We now insert the expression for the coefficients into the original expression:

$$a(x) = \int \mathrm{d}x' \left[\sum_i \psi_i(x)\psi_i^*(x')\right] a(x') \tag{68}$$

The function in square brackets is called **Dirac delta function**:

$$\sum_i \psi_i(x)\psi_i^*(x') = \delta(x-x') \tag{69}$$

The function $\delta(x-x')$ is a continuous generalization of the Kronecker delta. The delta function has the following properties:

$$\delta(x-x') = \delta(x'-x) \tag{70}$$

$$\int \mathrm{d}x'\, \delta(x') = 1 \tag{71}$$

We can consider the theory of complete orthonormal functions as a generalization of ordinary linear algebra. To see the analogy, we introduce the following defintions:

$$\psi_i(x) \equiv |i\rangle \qquad \psi_i^*(x) \equiv \langle i| \tag{72}$$

$$a(x) \equiv |a\rangle \qquad a^*(x) \equiv \langle a| \tag{73}$$

$$\int \mathrm{d}x a^*(x)b(x) = \langle a|b\rangle \tag{74}$$

$$\langle i|j\rangle = \delta_{ij} \tag{75}$$

$$\langle j|a\rangle = a_j \tag{76}$$
$$|a\rangle = \sum_i |i\rangle \langle i|a\rangle \tag{77}$$

Similarly, we can define an operator that converts a function into another function

$$\hat{O}a(x) = b(x) \tag{78}$$
$$\hat{O}|a\rangle = |b\rangle \tag{79}$$

Nonlocal operator:

$$b(x) = \hat{O}a(x) = \int \mathrm{d}x' O(x,x')a(x') \tag{80}$$
$$b_i = \sum_j O_{ij}a_j \tag{81}$$

Eigenfunctions:

$$\hat{O}\phi_\alpha(x) = \omega_\alpha \phi_\alpha(x) \tag{82}$$
$$\hat{O}|\alpha\rangle = \omega_\alpha |\alpha\rangle \tag{83}$$

The beauty of the Dirac notation is that it allows to manipulate vectors and functions, as well as operators acting on them, in a formally identical way. Thus, many results obtain in linear algebra of vector spaces can be directly applied to orthonormal functions.

F. Schrödinger equation, measurements, observables

Let us briefly review the main concepts of quantum mechanics. We will be studying molecules - quantum mechanical systems with N number of particles. A system with N particles is described using a wavefunction $|\Psi(\tau,t)\rangle$, where τ symbolizes the $3N$ spatial and N spin coordinates, t is time. Properties of $|\Psi(\tau,t)\rangle$:

- Single-valued and continuous
- Quadratically-integrable ($\int \Psi^*\Psi \mathrm{d}\tau$ is finite)

This means that $|\Psi(\tau,t)\rangle$ must be well-behaved (remember requirements for expanding a function in a basis).

Each physical property corresponds to a quantum-mechanical operator. Let's assume that $|\Psi(\tau,t)\rangle$ describes a quantum-mechanical system. Measurement of an

operator $\hat{O}$ gives result that is one of the eigenvalues of this operator.

$$\hat{O}\,|\Phi_i\rangle = O_i\,|\Phi_i\rangle \tag{84}$$

In this case, we say that the measurement **collapses** the wavefunction of the system ($|\Psi(\tau,t)\rangle$) onto one of the eigenvectors of $\hat{O}$. Taking a large number of measurements will result in different outcomes (i.e., different eigenvalues), the average measurement is given by:

$$\langle O\rangle = \langle\Psi|\hat{O}|\Psi\rangle = \sum_{ij}\langle\Psi\,|\Phi_i\rangle\,\langle\Phi_i|\,\hat{O}\,|\Phi_j\rangle\,\langle\Phi_j|\,\Psi\rangle \tag{85}$$

$$= \sum_{ij}\delta_{ij}O_i|\,\langle\Phi_j|\Psi\rangle\,|^2 = \sum_i O_i|\,\langle\Phi_i|\Psi\rangle\,|^2 = \sum_i O_i P(O_i) \tag{86}$$

All operators that describe a physical system must be linear and Hermitian (recall the definitions that we discussed). Their eigenfunctions form a complete set. Thus, any wavefunction can be expanded in terms of these eigenfunctions.

$$|\Psi\rangle = \sum_i |\Phi_i\rangle\,\langle\Phi_i|\Psi\rangle = \sum_i |\Phi_i\rangle\,C_i \tag{87}$$

The time dependence of $|\Psi(\tau,t)\rangle$ is given by the **time-dependent Schrödinger equation**:

$$-\frac{\hbar}{i}\frac{\partial\,|\Psi\rangle}{\partial t} = \hat{H}\,|\Psi\rangle \tag{88}$$

where $\hat{H}$ is the **Hamiltonian** (or energy) operator. For the N-particle system, the Hamiltonian operator is given by:

$$\hat{H} = -\sum_{i=1}^{N}\frac{\hbar}{2m_i}\nabla_i^2 + \hat{V}(x_1,y_1,z_1,\ldots,x_N,y_N,z_N,t) \tag{89}$$

$$\nabla_i^2 = \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2} \tag{90}$$

The operator ∇_i is called **nabla**, while ∇_i^2 is called **Laplacian**. Note that in this (non-relativistic) formulation of quantum mechanics the Hamiltonian written above does not depend on spin, while the wavefunction $|\Psi(\tau,t)\rangle$ does. If the potential energy $\hat{V}$ does not depend on time, then the solution of the Schrödinger

equation will have the form:

$$|\Psi(\tau,t)\rangle = f(t)\,|\Psi(\tau)\rangle \tag{91}$$

where $f(t)$ is a function of only time. Inserting this form into the Schrödinger equation, we get:

$$-\frac{\hbar}{i}\frac{f'(t)}{f(t)} = \frac{\hat{H}\,|\Psi(\tau)\rangle}{|\Psi(\tau)\rangle} = E \tag{92}$$

where we set the right-hand side to a constant E by the usual separation-of-variables argument. We obtain:

$$-\frac{\hbar}{i}f'(t) = Ef(t) \tag{93}$$

$$f(t) = Ae^{\frac{-iEt}{\hbar}} \tag{94}$$

We also get:

$$\hat{H}\,|\Psi(\tau)\rangle = E\,|\Psi(\tau)\rangle \tag{95}$$

which is the **time-independent Schrödinger equation**. We see that it has the form of the eigenvalue equation where E is the eigenvalue of the Hamiltonian $\hat{H}$. Thus, E are the possible energies of the system. States of the form $|\Psi(\tau,t)\rangle = f(t)\,|\Psi(\tau)\rangle$ are called **stationary states**. For a stationary state,

$$|\Psi(\tau,t)\rangle = e^{\frac{-iEt}{\hbar}}\,|\Psi(\tau)\rangle \tag{96}$$

where E is the energy of the state and $|\Psi(\tau)\rangle$ is the wavefunction of the stationary state.

When discussing operators in linear algebra, we have defined a commutator of two operators $[\hat{A},\hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$. If $[\hat{A},\hat{B}] = 0$ we say that the two operators commute. If two Hermitian operators $\hat{A}$ and $\hat{B}$ commute, then it can be proven that there exists a common complete set of eigenfunctions for them. We say that the operators describe **compatible observables**. Let's assume that $[\hat{A},\hat{B}] = 0$ and that the operator $\hat{B}$ is nondegenerate in the basis of its eigenfunctions:

$$\hat{B}\,|\Phi_i\rangle = B_i\,|\Phi_i\rangle \tag{97}$$

$$\hat{A}\hat{B}\,|\Phi_i\rangle - \hat{B}\hat{A}\,|\Phi_i\rangle = 0 \tag{98}$$

$$\langle\Phi_j|\,\hat{A}\hat{B}\,|\Phi_i\rangle - \langle\Phi_j|\,\hat{B}\hat{A}\,|\Phi_i\rangle = 0 \tag{99}$$

$$(B_i - B_j)\langle\Phi_j|\hat{A}|\Phi_i\rangle = 0 \tag{100}$$

Since the eigenvalues of $\hat{B}$ are nondegenerate, $(B_i - B_j) \neq 0$ if $i \neq j$. Thus, the off-diagonal matrix elements $\langle\Phi_j|\hat{A}|\Phi_i\rangle = 0$, which means that the operator $\hat{A}$ is diagonal in the basis of $|\Phi_i\rangle$:

$$\langle\Phi_i|\hat{A}|\Phi_j\rangle = \delta_{ij}A_j = A_j\langle\Phi_i|\Phi_j\rangle \tag{101}$$

$$\hat{A}|\Phi_j\rangle = A_j|\Phi_j\rangle \tag{102}$$

In our course, we will pay particular attention to the observables that commute with the Hamiltonian. These observables will allow us to obtain important information about solutions of the Schrödinger equation.

G. Atomic units

To see how atomic units naturally arise, consider the Schrödinger equation for the H atom in SI units:

$$\left[-\frac{\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r}\right]|\phi\rangle = \mathscr{E}|\phi\rangle \tag{103}$$

To cast this equation into dimensionless form, we let $x, y, z \to \lambda x', \lambda y', \lambda z'$ and obtain:

$$\left[-\frac{\hbar^2}{2m_e\lambda^2}\nabla'^2 - \frac{e^2}{4\pi\varepsilon_0\lambda r'}\right]|\phi'\rangle = \mathscr{E}|\phi'\rangle \tag{104}$$

We can factor out the constant in front of the kinetic and potential energy, provided we choose λ such that

$$\frac{\hbar^2}{m_e\lambda^2} = \frac{e^2}{4\pi\varepsilon_0\lambda} = \mathscr{E}_a \tag{105}$$

where $\mathscr{E}_a$ is the unit of energy called **Hartree**. Solving for λ, we obtain:

$$\lambda = \frac{4\pi\varepsilon_0\hbar^2}{m_e e^2} = a_0 \tag{106}$$

Thus, λ is just the Bohr radius a_0 which is the atomic unit of length called **Bohr**. For the Schrödinger equation, we obtain:

$$\left(-\frac{1}{2}\nabla'^2 - \frac{1}{r'}\right)|\phi'\rangle = \frac{\mathscr{E}}{\mathscr{E}_a}|\phi'\rangle = \mathscr{E}'|\phi'\rangle \tag{107}$$