

Foundations of quantum chemistry

1. The postulates of quantum mechanics

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October 2007 - Revised on June 4th, 2018



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A tiny part the theoretical frame describing our universe

We will be concerned with

Non-relativistic
quantum mech.

A tiny part the theoretical frame describing our universe

Theory of everything (String theory?, M-theory?, ...)

Grand unified theory (?)

Electroweak theory

(Standard model)

Quantum electrodynamics

Relativistic quantum mech.

Quantum theory of electrom. radiation
(Spectroscopy)

Quantum theory of weak interactions

Quantum chromodynamics

Special relativity

Non-relativistic quantum mech.

General relativity (gravity)

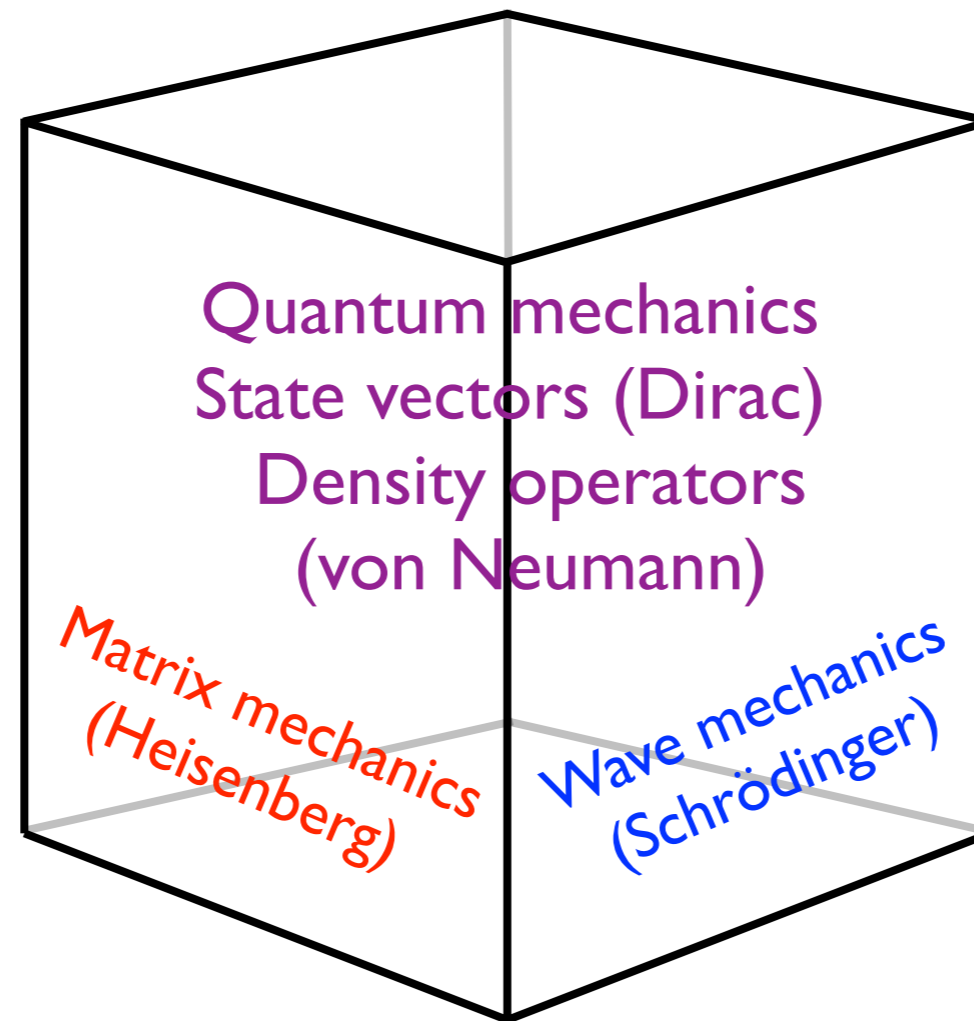
but so useful...

- The basis of the vast majority of phenomena taking place on earth
- from *physics and chemistry* to *biology, biomedicine, geology, technology...*

Some bibliography

- C. Cohen-Tannoudji, B. Diu, F. Laloë: *Mécanique quantique*, Hermann, 1977 (1973)(**pedagogical**; **french, english**).
- A. Galindo, P. Pascual: *Mecánica cuántica*, Eudema, 1989 (1978) (**mathematically rigorous**; **spanish, english**).
- L. E. Ballentine: *Quantum mechanics. A modern development*, World Scientific, 1998 (**enlightening discussion of subtle points**; **english**).
- J. J. Sakurai: *Modern quantum mechanics*, University of Bangalore Press, 1985 (**english**).
- A. Messiah, *Mécanique quantique*, 2e ed., Dunod, 1995 (1959) (**french, english, spanish**).
- R. Balian: *Du Microscopique au Macroscopique*, Ellipses, 1986 (1973) (**connection with statistical mechanics**; **french, english**).
- J. C. Paniagua: *El escenario de la química cuántica*, 2008 (1990) hdl.handle.net/2445/4961 (**spanish**).

Different views of NR-quantum mechanics



First postulate:
system \leftrightarrow *Hilbert space*
pure state \leftrightarrow *unitary ray*

*To each physical system corresponds a complex separable Hilbert space.
To each pure state of the system corresponds a unitary ray of that space.
Any element of that ray (a state vector or ket) can be used to represent
the state.*

Hilbert spaces

Quantum Hilbert spaces (\mathcal{H}) are **vector spaces** over the field \mathbb{C} .

- The **vectors** will be also referred to as **kets** and will be represented by the notations $|\Psi\rangle$, $|\Phi\rangle$, ... or simply Ψ , Φ , ...
- The **dimension** of the space can be finite or infinite, depending on the system (nothing to do with the number of coordinates).
- Hilbert spaces have a **scalar product** $(|\Psi\rangle, |\Phi\rangle) \equiv \langle\Psi|\Phi\rangle$; that is, for any vectors Ψ , Φ , ... and any complex number λ :

$$\langle\Psi|\Phi_1 + \Phi_2\rangle = \langle\Psi|\Phi_1\rangle + \langle\Psi|\Phi_2\rangle$$

$$\langle\Psi|\lambda\Phi\rangle = \lambda\langle\Psi|\Phi\rangle$$

$$\langle\Psi|\Phi\rangle = \langle\Phi|\Psi\rangle^*$$

$$\langle\Psi|\Psi\rangle \geq 0$$

$$\langle\Psi|\Psi\rangle = 0 \Leftrightarrow \Psi = 0,$$

- **Separable**: \exists a denumerable or discrete basis set: $\Psi = \sum_{r=1}^{\infty} c_r \Phi_r$
- Other requirements will not be detailed (see Galindo)

The dual space

The notation $\langle \Psi_1 | \Psi_2 \rangle$ can be interpreted in 2 ways from the mathematical point of view:

- as a *scalar product* of 2 vectors of \mathcal{H} (2 *kets* $|\Phi_1\rangle$ and $|\Phi_2\rangle$); i.e., a map

$$\mathcal{H} \times \mathcal{H} \rightarrow \mathcal{C} \quad \{ \Psi_1, \Psi_2 \} \rightarrow \langle \Psi_1 | \Psi_2 \rangle$$

- as the result of applying a *linear functional* or *linear form* (a *bra* $\langle \Psi_1 |$) to a vector of \mathcal{H} (a *ket* $|\Phi_2\rangle$): $\langle \Psi_1 | (|\Psi_2\rangle) = \langle \Psi_1 | \Psi_2 \rangle$

- A *linear form* is a linear map from a vector space \mathcal{H} to its field of scalars \mathcal{C}

$$\langle \Psi_1 | : \mathcal{H} \rightarrow \mathcal{C}$$

$$|\Psi_2\rangle \rightarrow \langle \Psi_1 | \Psi_2 \rangle$$

- The *dual space* of \mathcal{H} (\mathcal{H}^*) is the space consisting of all linear forms on \mathcal{H} .

Pure vs mixed states

- A *unitary ray*: $\{e^{i\alpha} |\Psi\rangle\}_{\alpha \in \mathbb{R}}$ with $\langle \Psi | \Psi \rangle = 1$

Complex numbers: $z = x + iy = r \cos\alpha + i r \sin\alpha = r e^{i\alpha}$

- We say that a system is in a *pure state* when we have the **maximum “degree” of information** about the properties of the system. Each *state vector* **represents** a pure state in the sense that it **“contains” all the physical information characterizing the pure state** (the third postulate deals with the way of extracting this information).
- If we have a **lower-than-maximal degree of information** about the system properties then *we cannot associate a unitary ray to the system state* and we say that this is a *statistical mixture* of pure states or, simply, a *mixed state* (later on we will introduce a mathematical tool for representing mixed states).

Pure vs mixed states

Examples:

- If we know that a **hydrogen atom** has an energy of $-1/8$ a.u. ($E_n = -1/2n^2$, $n=2$), a value of L^2 equal to 2 a.u. ($l(l+1)=2$, $l=1$), a value of L_z equal to -1 a.u. ($m_l=-1$), and a value of S_z equal to $-1/2$ a.u. ($m_s=-1/2$) then we say that it is in the **pure state** $\psi_{2p-1\beta}$.
- If we **only** know that its energy is $-1/8$ a.u. then we say that the atom is in a **mixed state**. We *cannot* associate a state vector to this state, since we would not know with to chose within the set $\{\psi_{2s\alpha}, \psi_{2s\beta}, \dots, \psi_{2p-1\beta}\}$. In fact, any linear combination of these 8 vectors would also correspond to a state with that energy, as we will see.

Basis sets

- *Denumerable* or *discrete* basis set: $\Psi = \sum_{r=1}^{\infty} c_r \Phi_r$

Examples:

- For a spin-less particle moving along the x -axis:
the eigenvectors of the hamiltonian of a uni-dimensional harmonic oscillator.
- For a spin-1/2 particle moving along the 3-D space:
the eigenvectors of the hamiltonian of a three-dimensional harmonic oscillator including the spin state (α or β).

- A *non-denumerable* "basis": $\psi = \sum_i c_i \psi_i + \int_x \psi_x c(x) dx$

Example: Eigenvectors of the hamiltonian of a hydrogen atom.

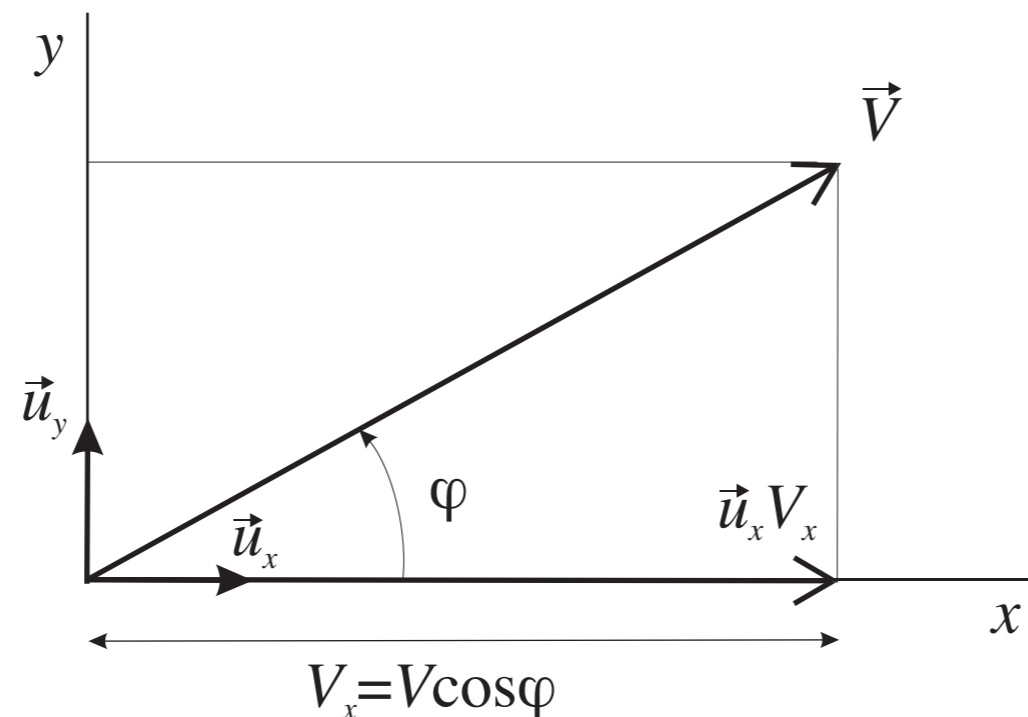
- The denumerable basis is *orthonormal* $\Leftrightarrow \langle \Phi_r | \Phi_s \rangle = \delta_{rs} \quad \forall r, s$

Vector components on an orthonormal discrete basis set

- The components of a state vector in an **orthonormal** basis can be obtained as:

$$\langle \Phi_s | \Psi \rangle = \left\langle \Phi_s \left| \sum_{r=1}^{\infty} c_r \Phi_r \right. \right\rangle = \sum_{r=1}^{\infty} c_r \langle \Phi_s | \Phi_r \rangle = \sum_{r=1}^{\infty} c_r \delta_{rs} = c_s$$

The same as for R^3 :

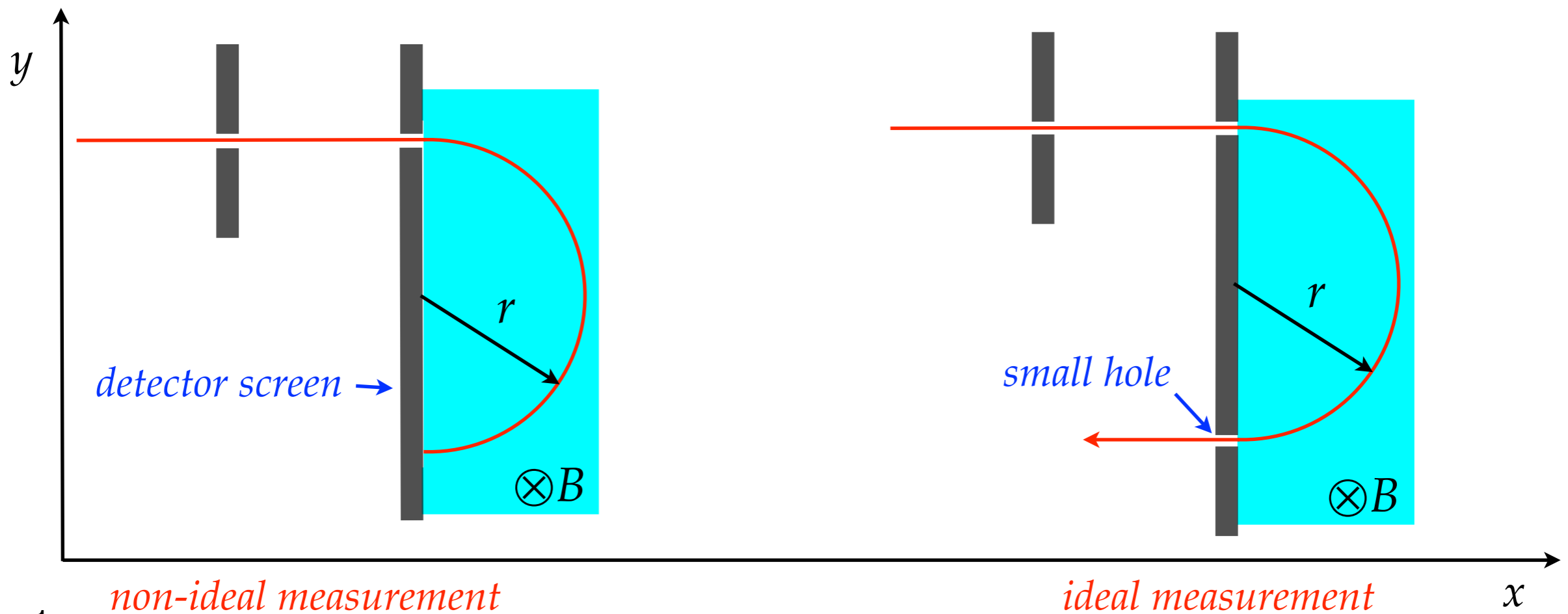


$$\vec{u}_x \cdot \vec{V} = V \cos \varphi = V_x$$

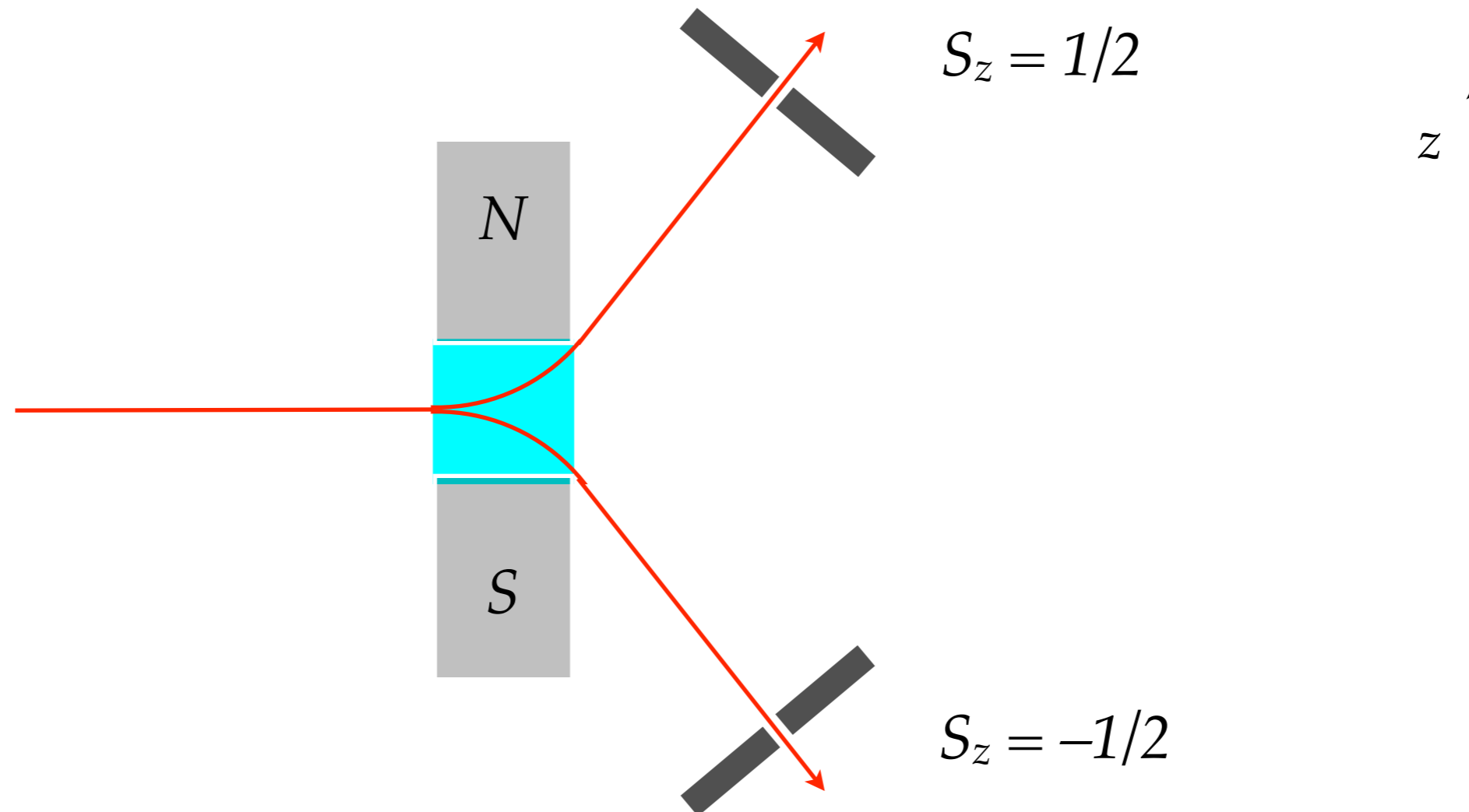
Measurements

- An *ideal* measurement of an observable is one producing a minimal disturbance on the system. A *filtering* measurement of A selects systems with a given value (or interval of values) of A .

Example: 2 ways of measuring p_x (and y) for a charged particle: $p_x = rqB$



An ideal measurement of a component of a magnetic moment

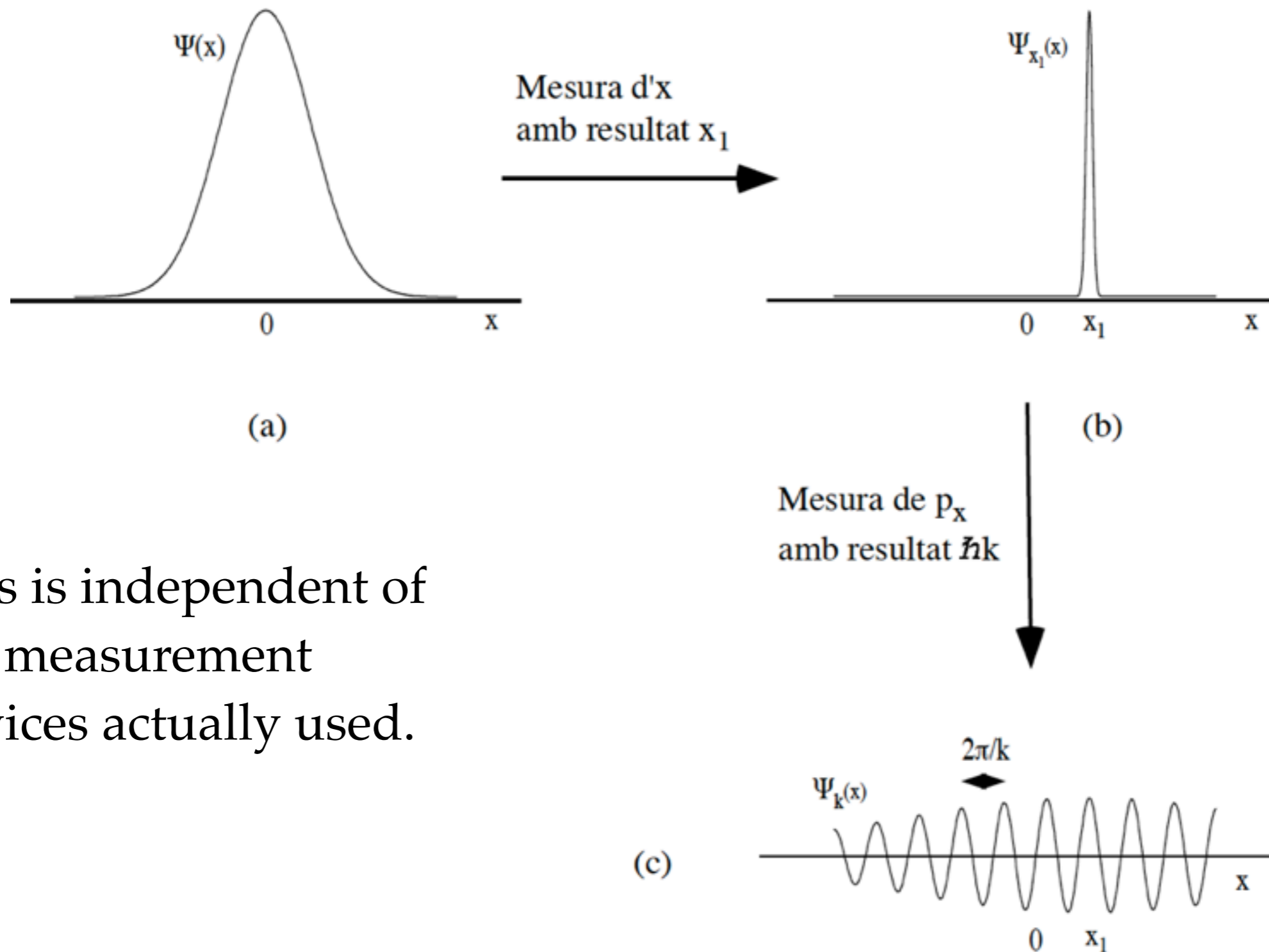


Compatible observables

- We say that an observable A of a system is *compatible* with another observable B when, for any state in which we know the value of A , an *ideal* measurement of B does not affect that value (and vice versa), so that **both observables become known**.
 - This is always assumed in classical physics, but, as we will see, it is not generally true in quantum mechanics.
- In some cases the measurements of A and B can be made **simultaneously**, in which case compatibility is evident: the values of both observables become known in the same state.

Examples: p_x and y are compatible, but p_x and x are not.

Incompatible observables



This is independent of the measurement devices actually used.

Preparation of pure states

- A way of preparing a system in certain *pure states* consists in performing ideal, *filtering* measurements of the observables of a *complete set of compatible observables* (CSCO or CCOC).
 - *Compatibility* is needed in order that the information is accumulated.
 - *Complete* means *maximal* and *non redundant*.
 - A set of compatible observables of a system is *maximal* when their values determine the values of any other observables compatible with them.
 - The set is *non redundant* if none of its observables is determined by the others for a complete set of state vectors (so it is *not* a *function* of the others).
- There are *other ways* of preparing systems in pure states: cooling, pulses of radiation, etc.

Some examples

- $T = p^2/2m$ is a function of the observables p_x , p_y and p_z , since if we know the values of these we can calculate that of $T = (p_x^2 + p_y^2 + p_z^2)/2m$.
- It can be shown that $\{x, y, z\}$ and $\{p_x, p_y, p_z\}$ are two CSCO of a spin-less particle. It is *non-redundant* because, e.g., knowledge of p_x and p_y does not fix p_z . However, $\{p_x, p_y, p_z, T\}$ is a maximal but *redundant* set.
- Different CSCO of the same system may have **different numbers of observables**. So both, $\{H\}$ and $\{x, y, z\}$, are CSCO for a spin-less, three-dimensional asymmetric harmonic oscillator.
- For the electronic state of a **hydrogen atom** $\{H, l^2, l_z\}$ is a CSCO if we are not interested in studying phenomena related to the spin. Otherwise we should add s_z to obtain a maximal set, because this is compatible with H, l^2 and l_z and cannot be obtained from them.
- **Other CSCO** for this system are $\{H, l^2, l_x\}$, $\{H, l^2, l_y\}$, etc. (same “degree” or “quantity” of information). Different states may require different CSCO to be measured in order to prepare them (ψ_{2pz} , ψ_{2px} , ψ_{2py} , etc.).

Pure-state preparation for a hydrogen atom

Exercise 1.1

Indicate what measurements should be made to obtain a hydrogen atom in the pure states corresponding to the following state vectors:

a) ψ_{2p-1}

b) ψ_{2px}

c) ψ_{2s}

It is assumed that we have devices for measuring any observable, and that spin-related observables are not relevant.

Hint: The state ψ_{2px} becomes the state $\psi_{2pz} = \psi_{2p_0}$ by a 90° rotation of the cartesian axis system.

Solution of the exercise 1.1

a) $\psi_{2p_{-1}}$ is an eigenvector of

$$\left\{ \begin{array}{ll} \hat{H} & \text{with eigenvalue } -\frac{1}{2 \times 2^2} = -\frac{1}{8} \text{ (a.u.'s)} \\ \hat{L}^2 & \text{" } l(l+1) = 1(1+1) = 2 \text{ (a.u.'s)} \\ \hat{L}_z & \text{" } m = -1 \text{ (")} \end{array} \right.$$

\Rightarrow we could heat a gas of hydrogen atoms so as to populate the $E_2 = -\frac{1}{8}$ energy level and then measure the internal energy of some of them and select those for which the result $E_2 = -\frac{1}{8}$ has been obtained. On those we should measure L^2 and select those with $L^2 = 2$, and measure L_z and select those with $L_z = -1$.

b) $\psi_{2p_z}(\vec{r}) = \psi_{2p_0}(\vec{r}) = \sqrt{\frac{1}{2^5\pi}} z e^{-r/2}$; $\psi_{2p_x}(\vec{r}) = \sqrt{\frac{1}{2^5\pi}} x e^{-r/2}$

Since $L_z = 0$ for ψ_{2p_z} , L_x should be 0 for ψ_{2p_x} (by symmetry) \Rightarrow

to prepare ψ_{2p_x} we should filter $E_2 = -\frac{1}{8}$, $L^2 = 2$ and $L_x = 0$.

c) $\psi_{2s} \left\{ \begin{array}{l} n=2 \\ l=0 \\ s=0 \end{array} \right. \Rightarrow$ to prepare it we should filter $E_2 = -\frac{1}{8}$ and $L^2 = 0$ ($L_z = 0$ is implied in this case).

(Linear) operators on \mathcal{H}

$$\hat{A} : \mathcal{H} \rightarrow \mathcal{H}$$

$$\hat{A}\Psi = \Phi \in \mathcal{H}$$

- Linearity: $\hat{A}(\lambda_1\psi_1 + \lambda_2\psi_2) = \lambda_1\hat{A}\psi_1 + \lambda_2\hat{A}\psi_2$

Dirac notation (The Principles of Quantum Mechanics, 1930)

\approx von Neumann notation (Mathematische Grundlagen der Quantenmechanik, 1932, 1949-1991 Sp, 1955 Eng., 1964 Rus.) $(A^*\Psi, \Psi')$

- Adjoint of \hat{A} : $\langle \Psi | \hat{A} \Psi' \rangle = \langle \hat{A}^\dagger \Psi | \Psi' \rangle \quad \forall \Psi, \Psi' \in \mathcal{H}$

(bra notation: $\langle \hat{A}^\dagger \Psi | \equiv \langle \Psi | \hat{A} \Rightarrow$ in $\langle \Psi | \hat{A} | \Psi' \rangle$ we

can consider that \hat{A} acts either on the ket or on the bra)

- \hat{A} self-adjoint “or” hermitian $\Leftrightarrow \langle \Psi | \hat{A} \Psi' \rangle = \langle \hat{A} \Psi | \Psi' \rangle \quad \forall \Psi, \Psi' \in \mathcal{H}$
- Commutator: $[\hat{A}, \hat{B}] \equiv \hat{A}\hat{B} - \hat{B}\hat{A}$

Second postulate: *observable* \Leftrightarrow *operator*

To each observable of a physical system corresponds a linear self-adjoint operator acting on the elements of the system Hilbert space. The operators corresponding to the cartesian position coordinates of the system particles (q_1, q_2, \dots, q_N) and to their conjugate momenta (p_1, p_2, \dots, p_N) must satisfy the following commutation relationships:

$$[\hat{q}_i, \hat{q}_j] = 0, \quad [\hat{p}_i, \hat{p}_j] = 0 \quad \text{y} \quad [\hat{q}_i, \hat{p}_j] = i\hbar \delta_{ij} \hat{1} \quad , \quad \forall i, j = 1, 2, \dots, N.$$

The operator corresponding to an observable with a classical expression $A(\dots, q_i, \dots, p_j, \dots, t)$ is obtained by substituting in this expression the coordinates and momenta by their quantum operators and symmetrizing, if needed, the resulting expression. If there are observables than cannot be expressed in that way their quantum operators are defined so as to reproduce, according to the third postulate, the experimental facts that justify their existence.

Examples

- $\vec{L} = \vec{r} \times \vec{p} = \begin{vmatrix} \vec{u}_x & \vec{u}_y & \vec{u}_z \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix} = (yp_z - zp_y)\vec{u}_x + (zp_x - xp_z)\vec{u}_y + (xp_y - yp_x)\vec{u}_z$

$$\widehat{L}_x = \widehat{y}\widehat{p}_z - \widehat{z}\widehat{p}_y \quad + \quad \text{cyclic permutations of the subscripts}$$

$$L^2 = L_x^2 + L_y^2 + L_z^2 \quad \Rightarrow \quad \widehat{L}^2 = \widehat{L}_x^2 + \widehat{L}_y^2 + \widehat{L}_z^2$$

- If $A = q_i p_i$ then $\widehat{A} = (\widehat{q}_i \widehat{p}_i + \widehat{p}_i \widehat{q}_i) / 2$

- Spin: $[\widehat{S}_x, \widehat{S}_y] = i\hbar \widehat{S}_z \quad + \quad \text{cyclic permutations}$

(arises naturally in relativistic quantum mechanics)

Exercise 1.2

Show (without using matrix representations of the operators) that

a) $(\hat{A}^\dagger)^\dagger = \hat{A}$

b) $(\hat{A}\hat{B})^\dagger = \hat{B}^\dagger\hat{A}^\dagger$

c) $(\hat{A}\hat{B})^{-1} = \hat{B}^{-1}\hat{A}^{-1}$

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

e) $[\hat{A}, \lambda_1\hat{B} + \lambda_2\hat{C}] = \lambda_1[\hat{A}, \hat{B}] + \lambda_2[\hat{A}, \hat{C}]$

f) $[\hat{A}, \hat{B}\hat{C}] = \hat{B}[\hat{A}, \hat{C}] + [\hat{A}, \hat{B}]\hat{C}$; $[\hat{A}\hat{B}, \hat{C}] = \hat{A}[\hat{B}, \hat{C}] + [\hat{A}, \hat{C}]\hat{B}$

g) $[\hat{L}_x, \hat{L}_y] = i\hbar\hat{L}_z, \dots$ (+ cyclic permutations) (don't use the specific representations of the operators; use only d) to f) and the 2nd postulate).

h) $[\hat{L}_x, \hat{L}^2] = [\hat{L}_y, \hat{L}^2] = [\hat{L}_z, \hat{L}^2] = 0$ (use only d) to g))

i) $\hat{S}_x\hat{S}_y$ is not self-adjoint, while $\frac{1}{2}(\hat{S}_x\hat{S}_y - \hat{S}_y\hat{S}_x)$ is.

Solution of the exercise 1.2

~~$(\hat{A}^\dagger)^\dagger = \hat{A}$~~

a) Adjoint operator definition: $\langle \hat{A}^\dagger \psi | \psi' \rangle = \langle \psi | \hat{A} \psi' \rangle \quad \forall \psi, \psi' \in \mathcal{H}$

$\langle (\hat{A}^\dagger)^\dagger \psi | \psi' \rangle = \langle \psi | \hat{A}^\dagger \psi' \rangle = \langle \hat{A} \psi | \psi' \rangle \quad \forall \psi, \psi' \in \mathcal{H} \Rightarrow (\hat{A}^\dagger)^\dagger = \hat{A}$

$\langle \hat{A}^\dagger \psi | \psi' \rangle^* = \langle \psi | \hat{A} \psi' \rangle^* \Rightarrow \langle \psi' | \hat{A}^\dagger \psi \rangle = \langle \hat{A} \psi' | \psi \rangle$

Note: If $\langle \psi' | \hat{A} \psi \rangle = \langle \psi' | \hat{B} \psi \rangle$ (or $\langle \hat{A} \psi | \psi \rangle = \langle \hat{B} \psi | \psi \rangle$) $\forall \psi, \psi' \in \mathcal{H}$

then, for any orthonormal basis set $\{\phi_i\}$, $\langle \phi_i | \hat{A} \psi \rangle = \langle \phi_i | \hat{B} \psi \rangle$

and, since $\hat{A} \psi = \sum_i c_i \phi_i = \sum_i \underbrace{\langle \phi_i | \hat{A} \psi \rangle}_{c_i} \phi_i$, same for $\hat{B} \psi$

$\Rightarrow \hat{A} \psi = \hat{B} \psi \quad \forall \psi \in \mathcal{H} \Rightarrow \hat{A} = \hat{B}$

Solution of the exercise 1.2 (cont.)

$$b) (\hat{A}\hat{B})^\dagger = \hat{B}^\dagger \hat{A}^\dagger$$

$$\langle (\hat{A}\hat{B})^\dagger \psi | \psi' \rangle = \langle \psi | \hat{A}\hat{B} \psi' \rangle = \langle \hat{A}^\dagger \psi | \hat{B} \psi' \rangle = \langle \hat{B}^\dagger \hat{A}^\dagger \psi | \psi' \rangle$$

$$c) (\hat{A}\hat{B})^{-1} = \hat{B}^{-1} \hat{A}^{-1} \quad (\text{Def. of } \hat{A}^{-1}: \hat{A}^{-1} \hat{A} = \hat{A} \hat{A}^{-1} = \hat{1})$$

let's see that $\hat{B}^{-1} \hat{A}^{-1}$ is the inverse of $\hat{A}\hat{B}$:

$$(\hat{B}^{-1} \hat{A}^{-1}) (\hat{A}\hat{B}) = \hat{1} \quad ; \quad \hat{A}\hat{B} (\hat{B}^{-1} \hat{A}^{-1}) = \hat{1}$$

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

$$e) [\hat{A}, \lambda_1 \hat{B} + \lambda_2 \hat{C}] = \underbrace{\hat{A} \lambda_1 \hat{B}} + \underbrace{\hat{A} \lambda_2 \hat{C}} - (\underbrace{\lambda_1 \hat{B} \hat{A}} + \underbrace{\lambda_2 \hat{C} \hat{A}}) = \lambda_1 [\hat{A}, \hat{B}] + \lambda_2 [\hat{A}, \hat{C}]$$

$$f) [\hat{A}, \hat{B}\hat{C}] = \hat{B} [\hat{A}, \hat{C}] + [\hat{A}, \hat{B}] \hat{C}$$

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

Solution of the exercise

1.2 (cont.)

g) $[\hat{L}_x, \hat{L}_y] = [\gamma p_z - z p_y, z p_x - x p_z] =$

$$= [\gamma p_z, z p_x] - [\gamma p_z, x p_z] - [z p_y, z p_x] + [z p_y, x p_z] = \oplus$$

$$\gamma [p_z, z p_x] + [\gamma, z p_x] p_z = \gamma z [\hat{p}_z, \hat{p}_x] + \gamma [p_z, z] p_x + z [\gamma, p_x] p_z +$$

$$\oplus = -i\hbar \gamma p_x + i\hbar x p_y = i\hbar L_z + [\gamma, z] p_x p_z$$

h) $[L_x, L_x^2 + L_y^2 + L_z^2] = [L_x, L_x^2] + [L_x, L_y^2] + [L_x, L_z^2] =$

~~$$= L_y [L_x, L_y] + [L_x, L_y] L_y + L_z [L_x, L_z] + [L_x, L_z] L_z = 0$$~~

i) $(S_x S_y)^\dagger = \hat{S}_y^\dagger \hat{S}_x^\dagger = \hat{S}_y \hat{S}_x \neq \hat{S}_x \hat{S}_y \quad ([\hat{S}_x, \hat{S}_y] \neq 0) \Rightarrow \hat{S}_x \hat{S}_y \text{ is not self-adjoint}$

b) S_y and S_x are observables
 $\Rightarrow \hat{S}_y$ and \hat{S}_x must be self-adjoints

$$\frac{1}{2} (\hat{S}_x \hat{S}_y + \hat{S}_y \hat{S}_x)^\dagger = \frac{1}{2} (\hat{S}_y^\dagger \hat{S}_x^\dagger + \hat{S}_x^\dagger \hat{S}_y^\dagger) = \frac{1}{2} (\hat{S}_y \hat{S}_x + \hat{S}_x \hat{S}_y) \Rightarrow \text{self-adjoint}$$

The spectrum of an operator

The *spectrum* of an operator is the set of its *eigenvalues* (in a “wide” sense)

- *Discrete* spectrum (σ_d): $\hat{A} \psi_i = a_i \psi_i$
- *Continuous* spectrum (σ_c): $\hat{A} \psi_a = a \psi_a$

- An eigenvalue a_i has a *degeneracy* d_i if there are d_i (and no more) linearly independent eigenvectors with that eigenvalue:

$$\hat{A} \Psi_{ij} = a_i \Psi_{ij} \quad \text{with} \quad j = 1, \dots, d_i$$

- **T1:** Any *linear combination* of *degenerate* eigenvectors of a linear operator is also an eigenvector with the same eigenvalue. If not all the combined eigenvectors are degenerate the linear combination is not an eigenvector.

Corollary: If $\hat{A} \Phi_{ij} = a_i \Phi_{ij}$ with $j = 1, \dots, d_i$ then $\{\Phi_{i1}, \dots, \Phi_{id_i}\}$ is the basis of a *d_i -dimensional eigenspace* of \hat{A} with eigenvalue a_i .

Eigenspaces in a 3D Hilbert space

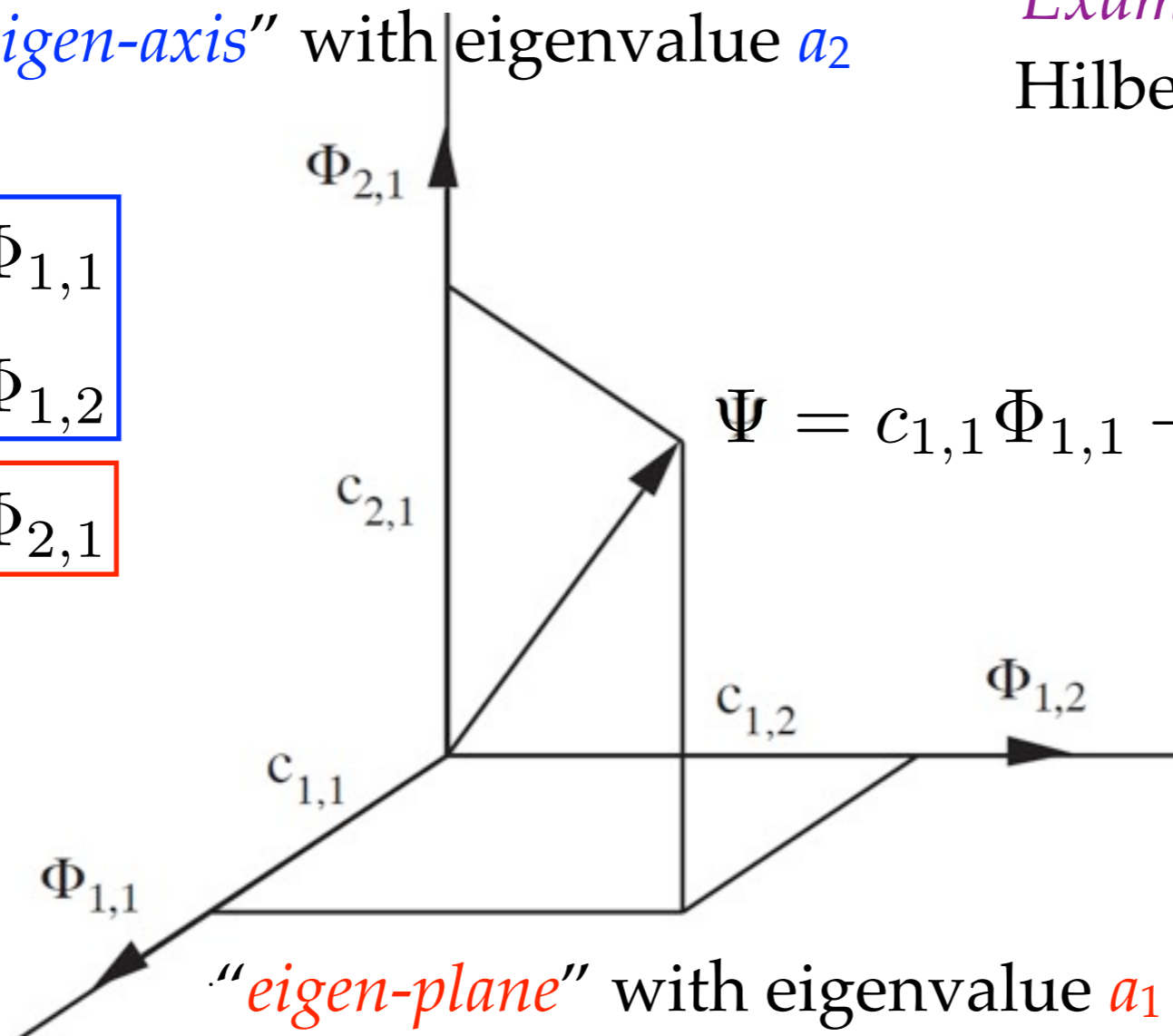
“*eigen-axis*” with eigenvalue a_2

Example: $A = I_z^2$ in the spin Hilbert space of a $I = 1$ nucleus

$$\hat{A}\Phi_{1,1} = a_1\Phi_{1,1}$$

$$\hat{A}\Phi_{1,2} = a_1\Phi_{1,2}$$

$$\hat{A}\Phi_{2,1} = a_2\Phi_{2,1}$$



$$\Psi = c_{1,1}\Phi_{1,1} + c_{1,2}\Phi_{1,2} + c_{2,1}\Phi_{2,1}$$

Example: For the hydrogen atom the hamiltonian eigenspaces corresponding to E_1, E_2, \dots have dimensions 1, 4, ... (disregarding the spin) \rightarrow complex, real, hybrid, ... AOs can be chosen in each eigenspace.

Exercise 1.3

For each of the following operators say if their spectrum is discrete, continuous, or partially discrete and partially continuous, as well as the degeneration of each value of the spectrum (do not try to solve the eigenvalue equations; use instead your previous knowledge or see the bibliography).

- a)* The linear momentum operator of a spin-less particle that moves along the x axis.
- b)* The z component of the orbital angular momentum of the electron of a hydrogen atom.
- c)* The hamiltonian of a free, spin-less, particle that moves along the x axis.
- d)* The non-relativistic hamiltonian for the internal motion of a hydrogen atom (spin excluded).

Solution of the exercise 1.3

a) $\hat{p}_x e^{ikx} = \hbar k e^{ikx}$ for any $k \in \mathbb{R} \Rightarrow$ the whole spectrum is continuous and non-degenerate

b) $\hat{L}_z e^{im\varphi} = m\hbar e^{im\varphi}$ for any $m \in \mathbb{N} \Rightarrow$ the whole spectrum is discrete and non-degenerate (if φ is the only position coordinate).

c) $\hat{H} e^{ikx} = \hat{T} e^{ikx} = \frac{\hbar^2 k^2}{2m} e^{ikx}$ for any $k \in \mathbb{R}$

The spectrum is continuous and positive. The eigenvalue 0 is non-degenerate all the others are doubly degenerate ($e^{\pm ikx}$ for $k \neq 0$ have the same eigenvalue)

d) $\hat{H} \phi(r, \theta, \varphi) = E \phi(r, \theta, \varphi)$ where E can be any real ≥ 0 number (continuous spectrum) or $E_n = -\frac{1}{2n^2}$ hartrees (negative discrete spectrum)

$\phi(r, \theta, \varphi) = R(r) Y_{lm}(\theta, \varphi)$

- for $E_n < 0$ $R_{nl}(r) Y_{lm}(\theta, \varphi)$ $\left\{ \begin{array}{l} n = 1, 2, \dots \\ l = 0, 1, \dots, n-1 \\ m = l, l-1, \dots, -l \end{array} \right\} \Rightarrow$ only E_1 is non-degen. ($n=1 \Rightarrow l=0 \Rightarrow m=0$) (if spin is not considered)

- for $E > 0$ E is, at least, independent of m (different orientations of the axes cannot affect the energy) \Rightarrow degeneration.

The spectrum of an operator

- T2: The spectrum of a self-adjoint operator is *real*.
- T3: Two eigenvectors of a self-adjoint operator with different eigenvalues are *orthogonal*.
- T4: The eigenvectors of a self-adjoint operator form a *complete set*.

Example: for an operator with discrete (σ_d) and continuous (σ_c) spectra

$$\hat{A}\Phi_{ij} = a_i\Phi_{ij} \quad j = 1 \cdots d_i \quad \text{with} \quad a_i \in \sigma_d$$

$$\hat{A}\Phi_{aj} = a\Phi_{aj} \quad j = 1 \cdots d_a \quad \text{with} \quad a \in \sigma_c$$

$$\Psi = \sum_{a_i \in \sigma_d} \sum_{j=1}^{d_i} c_{ij} \Phi_{ij} + \int_{a \in \sigma_c} \sum_{j=1}^{d_a} c_j(a) \Phi_{aj} da$$

a (wave) function of a

Commuting operators

- **T5:** Two operators commute if and only if there exists a **complete** set of eigenvectors common to both.

Corollary: Several operators have a complete set of common eigenvectors if and only if every two operators commute.

Examples:

- For a hydrogen atom the operators \widehat{H} , \widehat{L}^2 , \widehat{L}_z and \widehat{S}_z commute, and $\{\psi_{n,l,m,m_s}\}$ is a complete set of eigenvectors of all of them.

Equivalent notations: $\psi_{n,l,m,m_s} \equiv |n, l, m, m_s\rangle$

- If two observables do not commute a **complete** set of common eigenvectors cannot exist, but there might be **some** common eigenvectors.

Example: ϕ_{1s} is an eigenvector of L_x , L_y and L_z with eigenvalue 0.

General angular momentum

$$\boxed{[\widehat{J}_x, \widehat{J}_y] = i\hbar\widehat{J}_z \text{ (+ cyclic perm.)}} \quad J^2 = J_x^2 + J_y^2 + J_z^2 \Rightarrow [\widehat{J}_x, \widehat{J}^2] = [\widehat{J}_y, \widehat{J}^2] = [\widehat{J}_z, \widehat{J}^2] = 0$$

\exists a complete set of eigenvectors of $\{\widehat{J}_x, \widehat{J}^2\}$, or $\{\widehat{J}_y, \widehat{J}^2\}$, or $\{\widehat{J}_z, \widehat{J}^2\}$

$$\boxed{\begin{aligned} \widehat{J}^2\Phi_{j,m_j} &= j(j+1)\hbar^2\Phi_{j,m_j} & \text{with } j &= 0, \frac{1}{2}, 1, \frac{3}{2}, 2, \dots \\ \widehat{J}_z\Phi_{j,m_j} &= m_j\hbar\Phi_{j,m_j} & \text{with } m_j &= j, j-1, \dots, -j \end{aligned}}$$

Ladder or shift operators: $\widehat{J}_{\pm} \equiv \widehat{J}_x \pm i\widehat{J}_y$

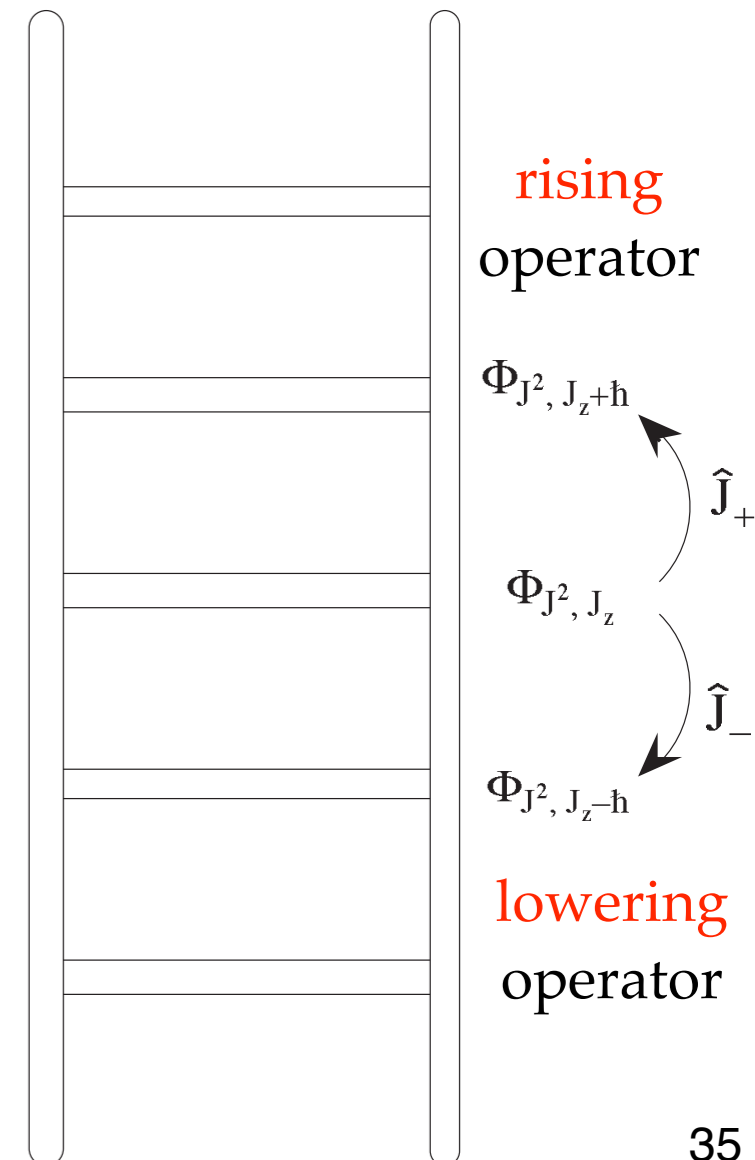
$$\widehat{J}_{\pm}\Phi_{j,m_j} = \hbar\sqrt{j(j+1) - m_j(m_j \pm 1)}\Phi_{j,m_j \pm 1}$$

Particular cases:

- *orbital* angular momentum L : $j = l = 0, 1, 2, \dots$
- *spin* angular momentum S (electrons) or I (nuclei):
 j (s or I) takes a single value for each particle

among: $0, 1/2, 1, 3/2, \dots$ For electrons $s = 1/2$ and

$$\widehat{S}_+\beta = \hbar\alpha \quad \widehat{S}_+\alpha = 0 \quad \widehat{S}_-\alpha = \hbar\beta \quad \widehat{S}_-\beta = 0$$



Projectors

- Let \mathcal{H}_1 and \mathcal{H}_2 be subspaces of a vector space \mathcal{H} . We say that \mathcal{H} is the *direct sum* of \mathcal{H}_1 and \mathcal{H}_2 ($\mathcal{H} = \mathcal{H}_1 \oplus \mathcal{H}_2$) if every vector ψ of \mathcal{H} admits a *unique decomposition* of the form $\psi = \psi_1 + \psi_2$ with $\psi_1 \in \mathcal{H}_1$ and $\psi_2 \in \mathcal{H}_2$
- **T6:** $\mathcal{H} = \mathcal{H}_1 \oplus \mathcal{H}_2 \iff \mathcal{H}_1 \cap \mathcal{H}_2 = \{0\}$ and $\dim(\mathcal{H}) = \dim(\mathcal{H}_1) + \dim(\mathcal{H}_2)$
- The *projector* onto \mathcal{H}_1 associated to the decomposition $\mathcal{H} = \mathcal{H}_1 \oplus \mathcal{H}_2$ is an operator that assigns to each vector of \mathcal{H} its component in \mathcal{H}_1 : $\hat{P}\Psi = \Psi_1$
- The *orthogonal complement* (\mathcal{H}_1^\perp) of \mathcal{H}_1 is the set of the vectors of \mathcal{H} orthogonal to every vector of \mathcal{H}_1 . It is easily verified that $\mathcal{H} = \mathcal{H}_1 \oplus \mathcal{H}_1^\perp$.
- The *orthogonal projector* onto \mathcal{H}_1 is the *projector* onto \mathcal{H}_1 associated to the decomposition $\mathcal{H} = \mathcal{H}_1 \oplus \mathcal{H}_1^\perp$ (the qualifier “orthogonal” is often implicit).

Basis-set expansions of projectors

- Let $\{\Phi_1, \dots, \Phi_m\}$ and $\{\Phi_{m+1}, \dots, \Phi_n\}$ be **discrete orthonormal** basis sets of \mathcal{H}_1 and \mathcal{H}_1^\perp (m and/or n could be ∞). Then

$$\hat{1}\Psi = \sum_{r=1}^n c_r \Phi_r = \sum_{r=1}^m c_r \Phi_r + \sum_{r=m+1}^n c_r \Phi_r = \hat{P}\Psi + (\hat{1} - \hat{P})\Psi$$

Using $c_r = \langle \Phi_r | \Psi \rangle$ (see [this slide](#)):

$$\hat{P}\Psi = \sum_{r=1}^m \Phi_r \langle \Phi_r | \Psi \rangle = \left(\sum_{r=1}^m |\Phi_r\rangle \langle \Phi_r| \right) \Psi \quad \Rightarrow \quad \hat{P} = \sum_{r=1}^m |\Phi_r\rangle \langle \Phi_r|$$

- Likewise (*resolution of the identity* or *closure relation*):

$$\hat{1}\Psi = \sum_{r=1}^n \Phi_r \langle \Phi_r | \Psi \rangle = \left(\sum_{r=1}^n |\Phi_r\rangle \langle \Phi_r| \right) \Psi \quad \Rightarrow \quad \hat{1} = \sum_{r=1}^n |\Phi_r\rangle \langle \Phi_r|$$

(in \mathbb{R}^3 : $\hat{1} = \hat{P}_x + \hat{P}_y + \hat{P}_z$)

- For **non-orthonormal** discrete basis sets: $\hat{1} = \sum_{r,s=1}^n |\Phi_r\rangle (\mathbf{S}_{rs}^{-1}) \langle \Phi_s|$; $S_{rs} = \langle \Phi_r | \Phi_s \rangle$

Projectors

- **T7:** A **linear combination** of projectors onto orthogonal subspaces is a projector \Leftrightarrow **all the coefficients are 1.**

- *Example:*

$\hat{A}\Phi_{ij} = a_i\Phi_{ij}$ with $\{\Phi_{i1} \cdots \Phi_{id_i}\}$ orthonormal \Rightarrow $\hat{P}_{a_i} = \sum_{j=1}^{d_i} |\Phi_{ij}\rangle \langle \Phi_{ij}|$
 projector onto the eigenspace of \hat{A} with eigenvalue a_i

- **T8:** Projectors are **self-adjoint, idempotent**, linear, bounded operators, and *vice versa*: $\hat{P}^\dagger = \hat{P} = \hat{P}^2$; $\|\hat{P}\Psi\| \leq c\|\Psi\| \forall \Psi$

- Hence
$$\begin{aligned} \langle \Psi | \hat{P}\Psi \rangle &= \langle \Psi | \hat{P}^2\Psi \rangle = \langle \hat{P}\Psi | \hat{P}\Psi \rangle = \|\hat{P}\Psi\|^2 \\ &= \left\langle \sum_{r=1}^m c_r \Phi_r \left| \sum_{s=1}^m c_s \Phi_s \right. \right\rangle = \sum_{r=1}^m c_r^* \sum_{s=1}^m c_s \langle \Phi_r | \Phi_s \rangle = \sum_{r=1}^m |c_r|^2 \end{aligned}$$

\uparrow
 $\{\Phi_1, \dots, \Phi_m\}$ orthonormal

Third postulate: *results of measurements*

If we measure at a time t an observable A of a system in the pure state described by the vector state Ψ_t

i) the probability of obtaining the value a_i of the discrete spectrum of \hat{A} is

$$P_t(A=a_i) = \langle \Psi_t | \hat{P}_{a_i} \Psi_t \rangle$$

ii) the probability density of obtaining the value a of the continuous spectrum of \hat{A} is

$$\frac{d P_t(A=a)}{d a} = \langle \Psi_t | \hat{P}_a \Psi_t \rangle$$

iii) the probability density of obtaining a value not belonging to the spectrum of A is zero.

Continuous spectrum: $\hat{A}\Phi_{aj} = a\Phi_{aj}$ with $\{\Phi_{a1} \cdots \Phi_{ad_a}\}$ orthonormal $\Rightarrow \hat{P}_a = \sum_{j=1}^{d_a} |\Phi_{aj}\rangle \langle \Phi_{aj}|$

Probabilities in terms of coefficients

Any Ψ can be expanded in terms of an orthonormal basis set made of eigenvectors of \hat{A} (see T4):

$$\Psi = \sum_{a_i \in \sigma_d} \sum_{j=1}^{d_i} c_{ij} \Phi_{ij} + \int_{a \in \sigma_c} \sum_{j=1}^{d_a} c_j(a) \Phi_{aj} da$$

then (see T8):

$$P_{\Psi}(A = a_i) = \sum_{j=1}^{d_i} |c_{ij}|^2 \quad \frac{dP_{\Psi}(A = a)}{da} = \sum_{j=1}^{d_a} |c_j(a)|^2$$

Exercise 1.4

Indicate which values can be obtained and with what probabilities when measuring the total energy, L^2 , L_z and S_z of the electron of a

hydrogen atom in the state $\Psi_{t=0} = \frac{\sqrt{3}}{2} \phi_{1s} \alpha + \frac{1}{2} e^{i\pi/4} \phi_{2p_0} \beta$

Solution of the exercise 1.4

$$\Psi_{t=0} = \frac{\sqrt{3}}{2} \phi_{1s} \alpha + \frac{1}{2} e^{i\pi/4} \phi_{2p_0} \beta$$

Since $\phi_{1s} \alpha$ and $\phi_{2p_0} \beta$ are eigenvectors of \hat{H} with eigenvalues $-\frac{1}{2}$ and $-\frac{1}{8}$ (in a.u.) $P_{\pm}(E = -\frac{1}{2}) = \left| \frac{\sqrt{3}}{2} \right|^2 = \frac{3}{4}$; $P_{\pm}(E = -\frac{1}{8}) = \left| \frac{1}{2} e^{i\pi/4} \right|^2 = \left(\frac{1}{2} e^{i\pi/4} \right) \left(\frac{1}{2} e^{i\pi/4} \right)^* = \frac{1}{4}$ and $P_{\pm}(E = E_{n>2}) = |0|^2 = 0$

Since $\phi_{1s} \alpha$ and $\phi_{2p_0} \beta$ are eigenvectors of \hat{L}^2 with eigenvalues $0(0+1) = 0$ and $1(1+1) = 2$ (in a.u.):

$$P_{\pm}(L^2 = 0) = \left| \frac{\sqrt{3}}{2} \right|^2 = \frac{3}{4}; \quad P_{\pm}(L^2 = 2) = \left| \frac{1}{2} e^{i\pi/4} \right|^2 = \frac{1}{4}; \quad P_{\pm}(L^2 > 2) = |0|^2 = 0$$

Since $\phi_{1s} \alpha$ and $\phi_{2p_0} \beta$ are eigenvectors of \hat{L}_z with eigenvalue 0 Ψ is also an eigenvector of \hat{L}_z with eigenvalue 0 $\Rightarrow P_{\pm}(L_z = 0) = 1$

(Theorem T1) \nearrow

Since $\phi_{1s} \alpha$ and $\phi_{2p_0} \beta$ are eigenvectors of \hat{S}_z with eigenvalues $\frac{1}{2}$ and $-\frac{1}{2}$

$$P_{\pm}(S_z = \frac{1}{2}) = \frac{3}{4}; \quad P_{\pm}(S_z = -\frac{1}{2}) = \frac{1}{4}$$

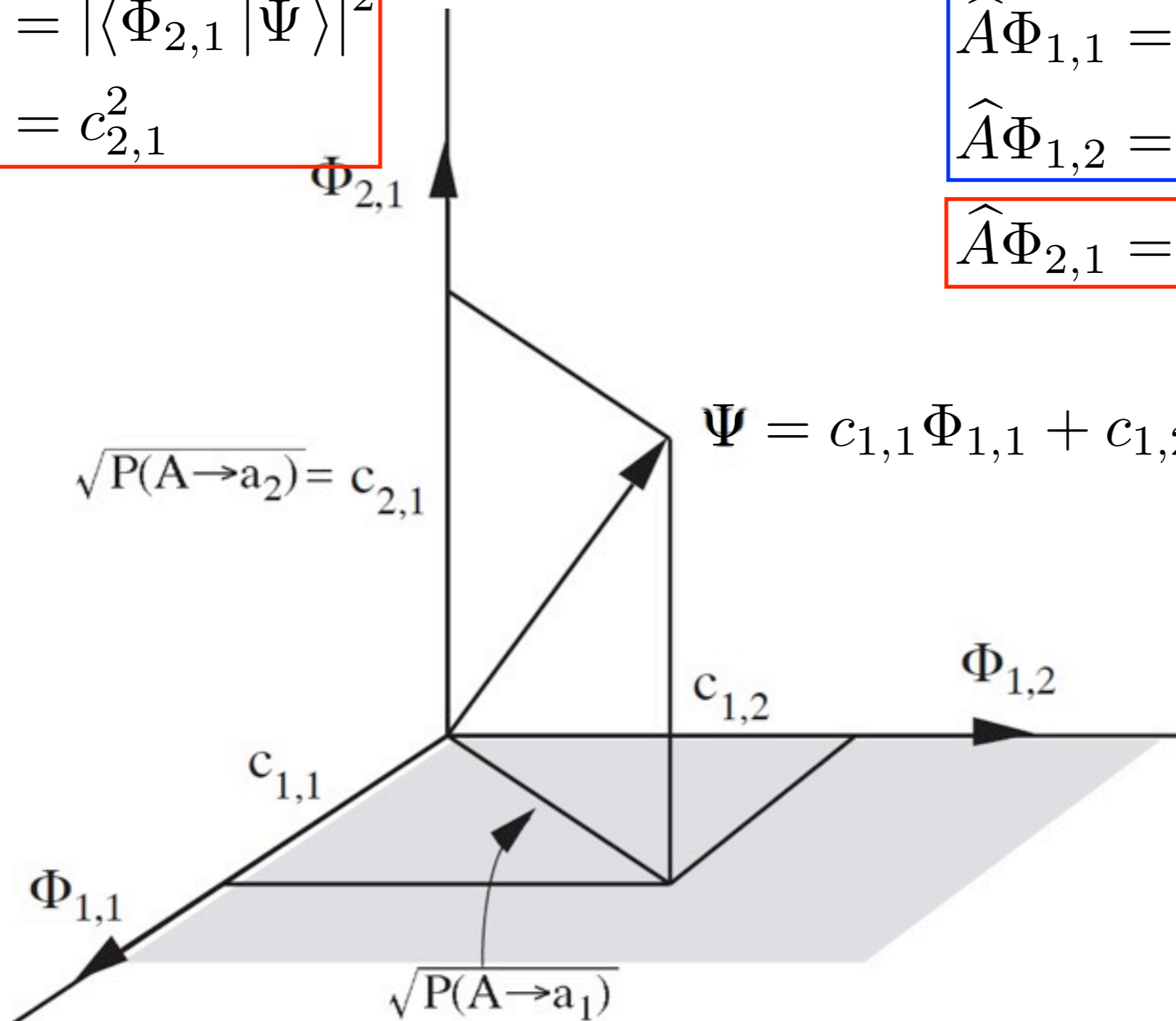
Probabilities in a 3D Hilbert space

$$P(A \rightarrow a_2) = |\langle \Phi_{2,1} | \Psi \rangle|^2 = c_{2,1}^2$$

$$\hat{A}\Phi_{1,1} = a_1\Phi_{1,1}$$

$$\hat{A}\Phi_{1,2} = a_1\Phi_{1,2}$$

$$\hat{A}\Phi_{2,1} = a_2\Phi_{2,1}$$



$$\Psi = c_{1,1}\Phi_{1,1} + c_{1,2}\Phi_{1,2} + c_{2,1}\Phi_{2,1}$$

$$\mathcal{H} = \mathcal{H}_1 \oplus \mathcal{H}_2$$

$$P(A \rightarrow a_1) = |\langle \Phi_{1,1} | \Psi \rangle|^2 + |\langle \Phi_{1,2} | \Psi \rangle|^2 = c_{1,1}^2 + c_{1,2}^2$$

Spectral decomposition

- *Spectral decomposition* of an operator:

$$\hat{A} = \sum_{a_i \in \sigma_d} a_i \hat{P}_{a_i} + \int_{a \in \sigma_c} a \hat{P}_a da$$

Demonstration for an operator with discrete spectrum:

$$\hat{A}\Psi = \sum_{a_i \in \sigma_d} \sum_{j=1}^{d_i} c_{ij} \hat{A}\Phi_{ij} = \sum_{a_i \in \sigma_d} \sum_{j=1}^{d_i} c_{ij} a_i \Phi_{ij} = \sum_{a_i \in \sigma_d} a_i \left(\sum_{j=1}^{d_i} c_{ij} \Phi_{ij} \right) = \sum_{a_i \in \sigma_d} a_i \hat{P}_{a_i} \Psi$$

see [this slide](#)

- *Resolutions of the identity*:

$$\hat{1} = \sum_{a_i \in \sigma_d} \hat{P}_{a_i} + \int_{a \in \sigma_c} \hat{P}_a da$$

- Given a function $f(x)$ of a real variable x we define the **function $f(\hat{A})$ of an operator \hat{A}** as:

$$f(\hat{A}) = \sum_{a_i \in \sigma_d} f(a_i) \hat{P}_{a_i} + \int_{a \in \sigma_c} f(a) \hat{P}_a da \quad \Rightarrow [\hat{A}, f(\hat{A})] = 0 \quad (\mathbf{T5})$$

If $f(x)$ is *analytical*: $f(\hat{A}) = f(0) + f'(0) \hat{A} + f''(0) \hat{A}^2 / 2! + f'''(0) \hat{A}^3 / 3! + \dots$

$f(x)$ may **not** have an **analytical** expression:

Exercise 1.5

When no relativistic effects are included in the hamiltonian of a poly-electronic atom (*i.e.*, only the kinetic energy and the Coulomb potential energy are considered) the corresponding energy levels are known as *spectral terms*. A usual notation for these includes the electron configuration and the eigenvalues of L^2 and S^2 for the states of the term; e. g.: the ground spectral term of a carbon atom is named $(1s^2 2s^2 2p^2) ^3P$.

a) It can be shown that that hamiltonian, L^2 , L_z , S^2 and S_z are mutually compatible observables. Which of the operators \widehat{L}^2 , \widehat{L}_z , \widehat{S}^2 and \widehat{S}_z are functions of that hamiltonian? *Hint*: there are no states with the same energy and different values for L^2 or S^2 .

b) Specify three different CSCO for the system.

Solution of the exercise 1.5a

a) $\{H, L^2, L_z, S^2, S_z\}$ are compatible $\Rightarrow \exists$ a common set of eigenvectors
 Since there are not states with the same E and $\neq L^2$ or S^2 , E determines L^2 γ S^2 ; that is, if $\Psi_{E, L, S}$ is an eigenvector of \hat{H}, \hat{L}^2 and \hat{S}^2 , once E is specified L and S could be obtained by applying \hat{L}^2 and \hat{S}^2 to $\Psi_{E, L, S} \Rightarrow L$ and S are functions of E : $L(E)$ and $S(E)$.

According to the definition of $f(\hat{A})$ (slide 1.45) \hat{L}^2 and \hat{S}^2 are functions of \hat{H} : $L^2(\hat{H})$ and $S^2(\hat{H})$.

However, since the eigenvalues E are degenerate with respect to L_z and S_z , E does NOT determine M_L nor M_S and L_z, S_z are NOT functions of $E \Rightarrow \hat{L}_z$ and \hat{S}_z are not functions of \hat{H} .

$\Rightarrow L_z$ and S_z are necessary for - together with E - determine a single state: Ψ_{E, M_L, M_S} (L and S are not strictly needed).

Solution of the exercise 1.5b

b) CSOC: $\{H, L_z, S_z\}$, $\{H, L_x, S_x\}$, $\{H, L_y, S_y\}$ } the 3 directions x, y, z are equivalent due to space isotropy.

other CSOC (n is the number of electrons):

$\{x_1, \gamma_1, z_1, w_1, \dots, x_n, \gamma_n, z_n, w_n\}$, $\{P_{x_1}, P_{y_1}, P_{z_1}, w_1, \dots, P_{x_n}, P_{y_n}, P_{z_n}, w_n\}$,
 \uparrow
 spin coordinate = m_{S_1}

and many others.

Addition of angular momenta

- Let \vec{L} and \vec{S} be 2 angular momenta of any type such that the components of one of them are compatible with those of the other. Then
 - $\vec{J} = \vec{L} + \vec{S}$ is **also an angular momentum** (in the generalized sense),
 - for any given values of the quantum numbers l and s associated to S^2 and L^2 the quantum number j associated with J^2 can take the values **$j = l+s, l+s-1, \dots, |l-s|$** (non-rigorous statement).

Spectral term degeneracy breaking

Exercise 1.6

a) Specify a CSCO for a poly-electronic atom including the spin-orbit interaction in the hamiltonian (E , J^2 , and J_z are then compatible, but E is incompatible with L^2 , S^2 , L_z and S_z). *Hint:* there are no states with the same energy and different values for J^2 .

b) Specify a CSCO for a poly-electronic atom subjected to a uniform magnetic field, which breaks completely the energy degeneracy.

Solution of the exercise 1.6

a) A reasoning like that made in the previous exercise can be applied to the energy levels (including spin-orbit interaction) to conclude that J^2 is now a function of E but J_z is not \Rightarrow a CSCO could now be $\{E, J_z\}$.

b) The magnetic field adds to the hamiltonian the term

$$\hat{H}_B = B \frac{e}{2m_e} (\hat{J}_z + \hat{S}_z) \quad (\text{Zeeman effect})$$

The corresponding first order correction to the energy levels is (eqn. 6.393)

of my book):
$$E_B = B \frac{e\hbar}{2m_e} g M_J \quad \text{with } g = 1 + \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)}$$

\Rightarrow different values of M_J now correspond to different energies \Rightarrow

\Rightarrow the energy now completely determines a single state-vector \Rightarrow

$\Rightarrow \{E\}$ is now a CSCO.

Expected values

- From probability theory:

$$\langle A \rangle_{\Psi_t} = \sum_{a_i \in \sigma_d} a_i \langle \Psi_t | \hat{P}_{a_i} \Psi_t \rangle + \int_{a \in \sigma_c} a \langle \Psi_t | \hat{P}_a \Psi_t \rangle da$$

$$\langle A \rangle_{\Psi_t} = \langle \Psi_t | \hat{A} \Psi_t \rangle \equiv \langle \Psi_t | \hat{A} | \Psi_t \rangle$$

- If $\hat{A}\Psi_i = a_i \Psi_i$ then $\langle A \rangle_{\Psi_i} = \langle \Psi_i | \hat{A} \Psi_i \rangle = \langle \Psi_i | a_i \Psi_i \rangle = a_i \langle \Psi_i | \Psi_i \rangle = a_i$
- The **probability** of obtaining a_i when measuring A in a pure state Ψ is the expected value of the **dichotomous observable** P_{a_i} that takes the value 1 for the states of the eigenspace of \hat{A} with eigenvalue a_i and 0 for those of its orthogonal complement: $P(A = a_i) = \langle \Psi | \hat{P}_{a_i} \Psi \rangle = \langle P_{a_i} \rangle_{\Psi}$
- **Any testable** physical information about a quantum system is an expected value.

Uncertainty, indetermination, dispersion or standard deviation

$$\Delta_{\Psi} A = \sqrt{\langle \Psi | (\hat{A} - \langle A \rangle_{\Psi})^2 | \Psi \rangle} = \sqrt{\langle A^2 \rangle_{\Psi} - (\langle A \rangle_{\Psi})^2}$$

- If Ψ is an eigenstate of \hat{A} with eigenvalue a then any measurement of A must give a , so that $\Delta_{\Psi} A = 0$.
- If $\Delta_{\Psi} A = 0$ then any measurement of A in the state Ψ gives the result $\langle A \rangle_{\Psi}$ which, according to the 3rd postulate, must be an eigenvalue of \hat{A} . This can only happen if Ψ is an eigenvector of \hat{A} with eigenvalue $\langle A \rangle_{\Psi}$ since the projection of Ψ into the eigenspace of \hat{A} with eigenvalue $\langle A \rangle_{\Psi}$ must have length 1.
- Therefore $\Delta_{\Psi} A = 0 \iff \hat{A}\Psi = a\Psi$

- Quantum indetermination is **not a problem of imperfection of measurement devices** or **lack of knowledge**: indeterminate observables are *undefined* until they are measured (*Schrödinger cat!*)

Examples: cartesian components of particles with spin 1/2 and 3/2.

Uncertainty relationships

- T9:

$$\Delta_{\Psi} A \Delta_{\Psi} B \geq \frac{1}{2} \left| \langle \Psi | [\hat{A}, \hat{B}] | \Psi \rangle \right|$$

Exercise 1.7

a) $\Delta x \Delta p \geq ?$ Can there be (realizable) states with Δx or $\Delta p = 0$?

b) $\Delta L_x \Delta L_y \geq ?$ Apply this relation to the states $2p_1$, $2s$ and $2p_0$ of a hydrogen atom. Can there be states with ΔL_x and / or $\Delta L_y = 0$?

Solution of the exercise 1.7

$$a) \Delta x \Delta p \geq \frac{1}{2} \left| \langle \Psi | \overbrace{[\hat{x}, \hat{p}]}^{i\hbar} \Psi \rangle \right| = \frac{1}{2} \left| \underset{\substack{\uparrow \\ |i|=1}}{i\hbar} \langle \overbrace{\Psi | \Psi}^1 \rangle \right| = \frac{1}{2}$$

\Rightarrow neither Δx nor Δp can be $= 0$.

$$b) \Delta L_x \Delta L_y \geq \frac{1}{2} \left| \langle \Psi | \overbrace{[\hat{L}_x, \hat{L}_y]}^{i\hbar \hat{L}_z} \Psi \rangle \right| = \frac{\hbar}{2} \left| \langle \Psi | \hat{L}_z \Psi \rangle \right|$$

$$\text{Für } 2p_1 \quad \hat{L}_z \phi_{2p_1} = 1\hbar \Rightarrow \Delta L_x \Delta L_y \geq \frac{\hbar}{2}$$

$$\text{Für } 2s \quad \hat{L}_z \phi_{2s} = 0 \Rightarrow \Delta L_x \Delta L_y \geq 0$$

$$\text{Für } 2p_0 \quad \hat{L}_z \phi_{2p_0} = 0 \Rightarrow \Delta L_x \Delta L_y \geq 0$$

} no information about ΔL_x nor ΔL_y

Solution of the exercise 1.7 (cont.)

- ϕ_{2s} is an eigenstate of \hat{L}^2 , \hat{L}_z , \hat{L}_x and \hat{L}_y with all the eigenvalues = 0 $\textcircled{*}$
 \Rightarrow the 4 observables are completely determined.
- ϕ_{2p} is an eigenvector of \hat{L}^2 with eigenvalue $1(1+1)\hbar^2 = 2\hbar^2$ and of \hat{L}_z with eigenvalue $0 (=m\hbar)$, but it is not an eigenvector of \hat{L}_x nor \hat{L}_y $\textcircled{*}$

$\textcircled{*}$ The effect of \hat{L}_x and \hat{L}_y on an orbital ϕ_{nlm} can be readily obtained by expressing \hat{L}_x and \hat{L}_y in terms of the ladder operators \hat{L}_+ and \hat{L}_-

Density operator

If we know that a system has probabilities p_1, p_2, \dots, p_n of being in the pure states $\psi_1, \psi_2, \dots, \psi_n$ then

$$\begin{aligned}
 \langle A \rangle_{\rho_t} &= \sum_i p_i \langle \psi_i | \hat{A} \psi_i \rangle \\
 &= \sum_i \sum_j p_i \langle \psi_i | \underbrace{|\phi_j\rangle \langle \phi_j|}_{\text{Resolution of the identity in any denumerable orthonormal basis set } \{\phi_j\}} \hat{A} \psi_i \rangle \\
 &= \sum_i \sum_j p_i \langle \phi_j | \hat{A} \underbrace{|\psi_i\rangle \langle \psi_i|}_{\text{Resolution of the identity in any denumerable orthonormal basis set } \{\psi_i\}} \phi_j \rangle \\
 &= \sum_j \langle \phi_j | \hat{A} \hat{\rho}_t \phi_j \rangle,
 \end{aligned}$$

where the *statistical operator* or *density operator* or *density matrix*:

$$\hat{\rho}_t = \sum_i p_i |\psi_i\rangle \langle \psi_i|$$

describes or represents the *statistical mixture of pure states* (mixed state).

Trace of an operator

The *trace of an operator* \hat{B} is defined as $\text{Tr } \hat{B} \equiv \sum_j \langle \phi_j | \hat{B} | \phi_j \rangle$

$$\langle A \rangle_{\rho_t} = \text{Tr} (\hat{A} \hat{\rho}_t)$$

where $\{\phi_j\}$ is any denumerable orthonormal basis set.

- The trace is independent of the chosen denumerable orthonormal basis set (exercise 2.3).
- The trace of an self-adjoint operator is the sum of its eigenvalues.
- $\text{Tr}(\hat{A}_1 \dots \hat{A}_n) = \text{Tr}(\hat{A}_{i_1} \dots \hat{A}_{i_n})$ (cyclic permutations).
- $\text{Tr} \hat{\rho} = 1$ (normalization)
- $\text{Tr} (\hat{A} |\Psi\rangle \langle \Psi|) = \langle \Psi | \hat{A} | \Psi \rangle$ (**pure** states)

Density operator

Example:

A beam of hydrogen atoms emerges from an isotropic chamber (we neglect gravitational effects) at a temperature low enough that we can assume that **all of them are in the ground level: $E_1 = -1/2$ a.u.** If the electronic **spin is a relevant** observable, the state is not pure, because we have no information about S_z , which is compatible with E , L^2 and L_z if relativistic effects are neglected, and is not a function of them. Since there are no preferred directions, the density operator describing the state of the atoms is

$$\hat{\rho} = \frac{1}{2} |\psi_{1s\alpha}\rangle \langle\psi_{1s\alpha}| + \frac{1}{2} |\psi_{1s\beta}\rangle \langle\psi_{1s\beta}|$$

- A state is **pure** \Leftrightarrow its density operator is **a projector** on a unidimensional space: $\{e^{i\alpha} \Psi\} \Leftrightarrow$ pure state $\Leftrightarrow |\Psi\rangle\langle\Psi|$

Different statistical mixtures may be indistinguishable

Exercise 1.8

a) Show that the state vectors $\psi_{1s\pm} = (\psi_{1s\alpha} \pm \psi_{1s\beta}) / \sqrt{2}$ of a hydrogen atom are eigenvectors of \widehat{S}_x with eigenvalues $\pm 1/2$ a.u. respectively.

Hint: put \widehat{S}_x in terms of ladder operators.

b) Write the density operator describing the atoms emerging from an isotropic chamber in terms of $\psi_{1s\pm}$ and show that it is equal to

$$\widehat{\rho} = 0.5 |\psi_{1s\alpha}\rangle \langle\psi_{1s\alpha}| + 0.5 |\psi_{1s\beta}\rangle \langle\psi_{1s\beta}|$$

Comment: When you express the pure vector states of a mixture in terms of an arbitrary basis set $\{\phi_i\}$ you usually obtain cross term operators such as $|\phi_i\rangle\langle\phi_j|$. They are called *coherences* and act in a similar way to the projector operators: $(|\phi_i\rangle\langle\phi_j|) |\psi\rangle = |\phi_i\rangle\langle\phi_j|\psi\rangle$. We won't discuss their physical meaning, but if you are curious about it have a look the article *On the Physical Interpretation of Density Operators at the Atomic Scale: A Thorough Analysis of Some Simple Cases* by Juan C. Paniagua in *Concepts in Magnetic Resonance Part A*, Vol. **28A**(6) 384–409 (2006).

Solution of the exercise 1.8

$$\begin{aligned}
 a) \quad \hat{S}_x \Psi_{1S_{\pm}} &= \frac{1}{2} (\hat{S}_+ + \hat{S}_-) \frac{1}{\sqrt{2}} (\psi_{1S\alpha} \pm \psi_{1S\beta}) = \\
 &= \frac{1}{2\sqrt{2}} (0 \pm \psi_{1S\alpha} + \psi_{1S\beta} - 0) = \pm \frac{1}{2} \Psi_{1S_{\pm}}
 \end{aligned}$$

$$b) \quad \cancel{\hat{P} = \frac{1}{2} |\psi_{1S+}\rangle \langle \psi_{1S+}| + \frac{1}{2} |\psi_{1S-}\rangle \langle \psi_{1S-}|}$$

$$\hat{P} = \frac{1}{2} |\psi_{1S+}\rangle \langle \psi_{1S+}| + \frac{1}{2} |\psi_{1S-}\rangle \langle \psi_{1S-}| =$$

$$= \frac{1}{2} \frac{1}{2} |\psi_{1S\alpha} + \psi_{1S\beta}\rangle \langle \psi_{1S\alpha} + \psi_{1S\beta}| + \frac{1}{2} \frac{1}{2} |\psi_{1S\alpha} - \psi_{1S\beta}\rangle \langle \psi_{1S\alpha} - \psi_{1S\beta}| =$$

$$= \frac{1}{4} \left(|\psi_{1S\alpha}\rangle \langle \psi_{1S\alpha}| + |\psi_{1S\alpha}\rangle \langle \psi_{1S\beta}| + |\psi_{1S\beta}\rangle \langle \psi_{1S\alpha}| + |\psi_{1S\beta}\rangle \langle \psi_{1S\beta}| + \right. \\
 \left. + \quad \quad \quad - \quad \quad \quad - \quad \quad \quad + \quad \quad \quad \right) =$$

$$= \frac{1}{2} |\psi_{1S\alpha}\rangle \langle \psi_{1S\alpha}| + \frac{1}{2} |\psi_{1S\beta}\rangle \langle \psi_{1S\beta}|$$

Exercise 1.9

Indicate how could we prepare a hydrogen atom that emerged from an isotropic chamber in the pure state corresponding to the vector $\psi_{1s+} = (\psi_{1s\alpha} + \psi_{1s\beta}) / \sqrt{2}$. Which values could we obtain and with what probabilities when measuring S_z in that state? Which experiments should we perform to differentiate that pure state from the mixed state $\hat{\rho} = 0.5 |\psi_{1s\alpha}\rangle \langle\psi_{1s\alpha}| + 0.5 |\psi_{1s\beta}\rangle \langle\psi_{1s\beta}|$?

 This is the only way of describing a non-polarized spin-state.

Exercise 1.10

Show that the probability (or probability density) of obtaining a value 'a_i' in a measurement of an observable 'A' in a system that is in the state described by the density operator ρ is:

$$P_{\rho}(A = a_i) = \text{Tr} \left(\hat{P}_{a_i} \hat{\rho} \right) = \sum_{j=1}^{d_i} \langle \Phi_{ij} | \hat{\rho} | \Phi_{ij} \rangle$$

Solution of the exercise 1.9

Since ψ_{1s+} is univocally determined by the values $-\frac{1}{2}$ of the internal energy and $S_x = 1$ (exercise 1.8a) we could prepare it by measuring those 2 observables and selecting those 2 values.

Since $\psi_{1s+} = \frac{1}{\sqrt{2}} \psi_{1s\alpha} + \frac{1}{\sqrt{2}} \psi_{1s\beta}$ $P(S_z = \frac{1}{2}) = \left| \frac{1}{\sqrt{2}} \right|^2 = \frac{1}{2} = P(S_z = -\frac{1}{2})$

↑
coef. of $\psi_{1s\alpha}$

The same probabilities for S_z would be found in the mixed state $\hat{\rho}$, so we could not differentiate it from ψ_{1s+} by measuring only this observable. But by measuring S_x we would obtain $\frac{1}{2}$ with certainty for ψ_{1s+} and 50% of probability for $\pm \frac{1}{2}$ for $\hat{\rho}$ (exercise 1.8b)

Solution of the exercise 1.10 which is the same observable (see slide 49)

$$P_p(A=a_i) = \text{Tr}(\hat{P}_{a_i} \hat{\rho}) =$$

(slide 41) \rightarrow $= \text{Tr} \left(\sum_{j=1}^{d_i} |\Phi_{ij}\rangle \langle \Phi_{ij}| \hat{\rho} \right) = \sum_{j=1}^{d_i} \langle \Phi_{ij} | \hat{\rho} | \Phi_{ij} \rangle$

↑
(slide 53)

Quantum vs classical uncertainties

- A *mixed* state has **two kinds of uncertainty**: one has a **quantum** origin and the other is similar to that found in **classical** statistical mechanics.
- *Examples*: S_z can take the values $\pm 1/2$ with **equal probabilities** in the **pure** state $\psi_{1s+} = (\psi_{1s\alpha} + \psi_{1s\beta})/\sqrt{2}$ of a hydrogen atom (exercise 1.9), as well as in the **mixed** state $\hat{\rho} = 0.5 |\psi_{1s\alpha}\rangle \langle\psi_{1s\alpha}| + 0.5 |\psi_{1s\beta}\rangle \langle\psi_{1s\beta}|$, but in the former case we know which is the state vector (**quantum-type uncertainty in S_z**), while in the latter there are many states compatible with our (lack of) information about S_z : it could be that we have taken the atom from a chamber with many atoms, half of them in the pure state $\psi_{1s\alpha}$ and the other half in $\psi_{1s\beta}$ (**classic type uncertainty in S_z**), or (exercise 1.8) half in $\psi_{1s+} = (\psi_{1s\alpha} + \psi_{1s\beta})/\sqrt{2}$ and half in $\psi_{1s-} = (\psi_{1s\alpha} - \psi_{1s\beta})/\sqrt{2}$ (**classic + quantum type uncertainties**), or many other possibilities that lead to the same density operator. In fact, it can be shown that the density operator of that mixed state can be put as a uniform mixture of *every* possible spin state (see J. C. Paniagua, *Concepts in Magnetic Resonance Part A* **28A**, 384-409 (2006)).
- Recall that two pure states, such as $\psi_{1s\alpha}$ and $\psi_{1s+} = (\psi_{1s\alpha} + \psi_{1s\beta})/\sqrt{2}$, have the **same “degree” of information**: in the former we know E , L^2 , L_z and S_z , while in the latter we know E , L^2 , L_z and S_x .

Fourth postulate: *state collapse*

Lets consider a physical system that is, at time t , in the state described by the density operator $\hat{\rho}_t$. If we perform at that time an ideal measurement of an observable A that provides a set of values $\Delta = \Delta_d \cup \Delta_c$, Δ_d belonging to the discrete spectrum of \hat{A} and Δ_c belonging to the continuous one, then the system state changes to

$$\hat{\rho}_\Delta = \frac{\hat{P}_\Delta \hat{\rho}_t \hat{P}_\Delta}{\text{Tr}(\hat{P}_\Delta \hat{\rho}_t)}$$

where $\hat{P}_\Delta \equiv \sum_{a \in \Delta_d} \hat{P}_a + \int_{a \in \Delta_c} \hat{P}_a da$

Collapse of a pure state

- If the system was in a **pure state** Ψ :

$$\begin{aligned}
 \hat{\rho}_\Delta &= \frac{\hat{P}_\Delta |\Psi\rangle \langle \Psi| \hat{P}_\Delta}{\text{Tr} (\hat{P}_\Delta |\Psi\rangle \langle \Psi|)} \\
 &= \frac{|\hat{P}_\Delta \Psi\rangle \langle \hat{P}_\Delta \Psi|}{\langle \Psi | \hat{P}_\Delta | \Psi \rangle} \\
 &= \left| \frac{\hat{P}_\Delta \Psi}{\|\hat{P}_\Delta \Psi\|} \right\rangle \left\langle \frac{\hat{P}_\Delta \Psi}{\|\hat{P}_\Delta \Psi\|} \right|
 \end{aligned}$$

$$\Psi \rightarrow \frac{\hat{P}_\Delta \Psi}{\|\hat{P}_\Delta \Psi\|}$$

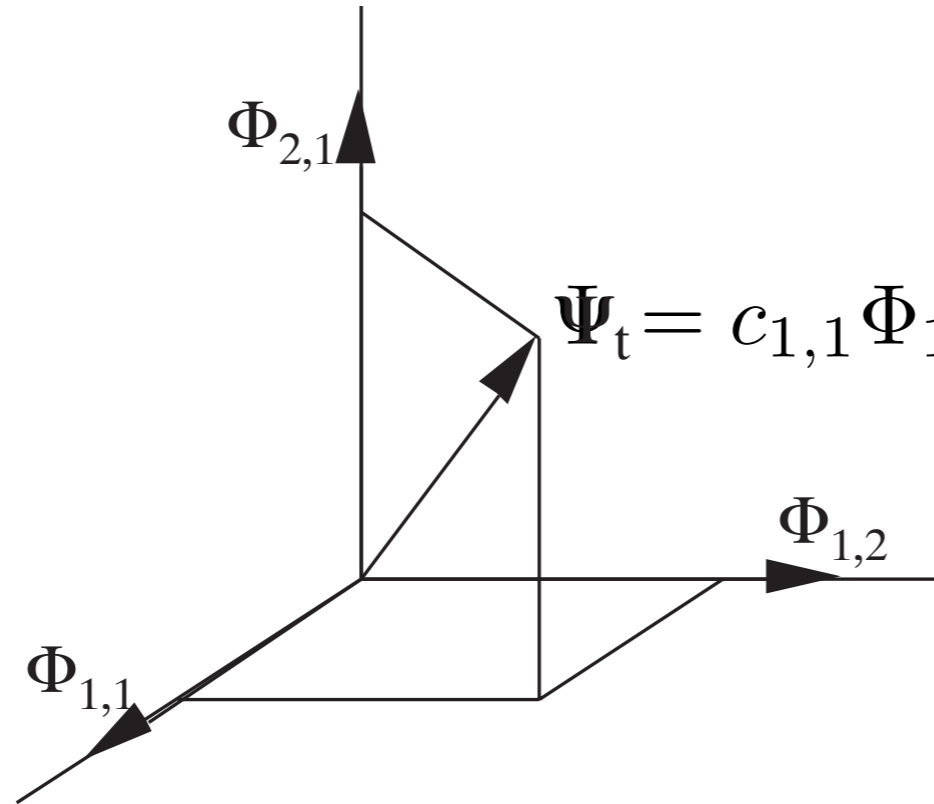
- The resulting state vector is the **normalized projection** of the previous state vector onto the subspace corresponding to the values obtained in the measurement.

Collapse in a 3D Hilbert space

$$\hat{A}\Phi_{1,1} = a_1\Phi_{1,1}$$

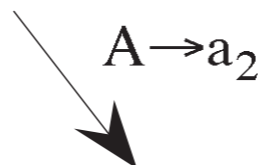
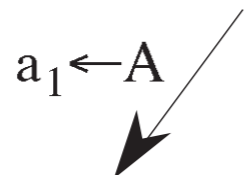
$$\hat{A}\Phi_{1,2} = a_1\Phi_{1,2}$$

$$\hat{A}\Phi_{2,1} = a_2\Phi_{2,1}$$

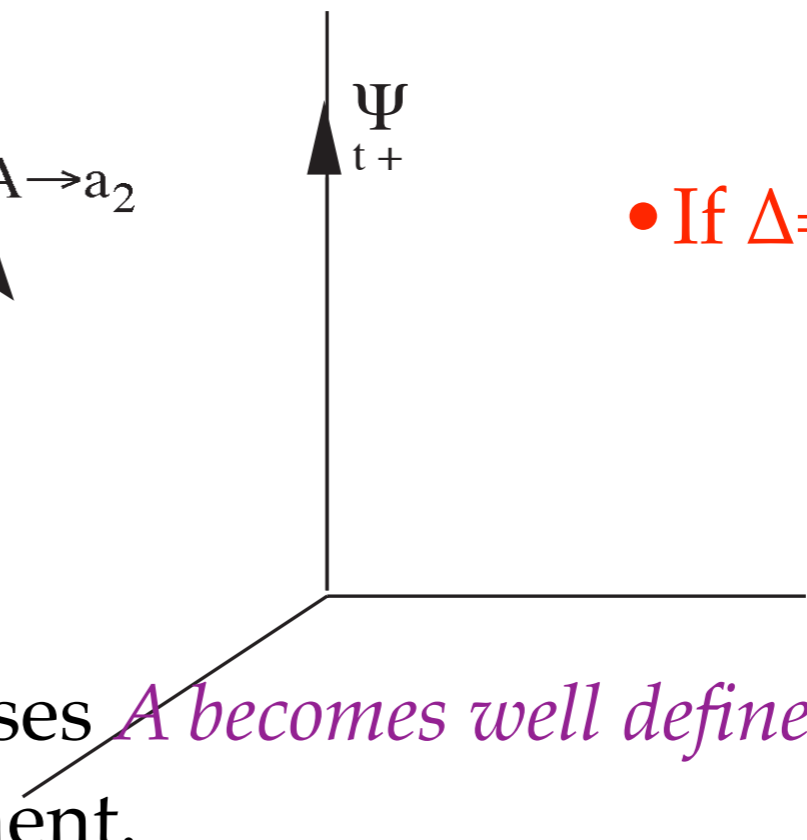
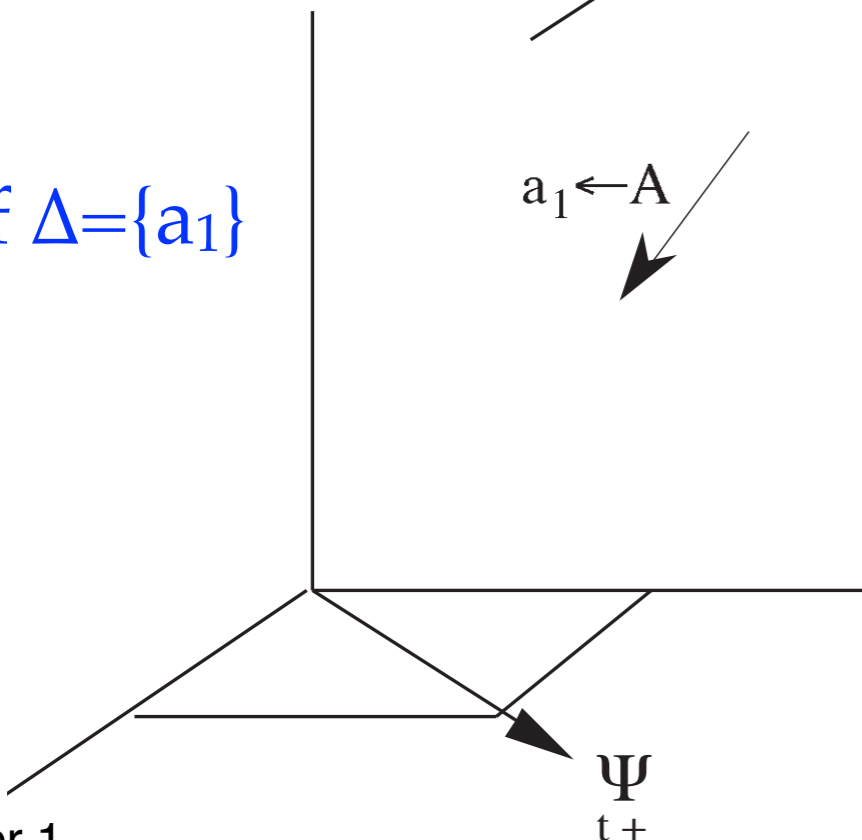


$$\Psi_t = c_{1,1}\Phi_{1,1} + c_{1,2}\Phi_{1,2} + c_{2,1}\Phi_{2,1}$$

• If $\Delta = \{a_1\}$



• If $\Delta = \{a_2\}$



In both cases *A becomes well defined* after the measurement.

Some remarks

- In general the states *changes* upon a measurement:

$$\hat{\rho}_\Delta = \frac{\hat{P}_\Delta \hat{\rho}_t \hat{P}_\Delta}{\text{Tr}(\hat{P}_\Delta \hat{\rho}_t)}$$

- The resulting density operator is the *normalized projection* of the previous density operator onto the subspace corresponding to the values obtained in the measurement:

- to apply the projected operator $\hat{P}_\Delta \hat{\rho} \hat{P}_\Delta$ to a vector Ψ is equivalent to applying the original operator $\hat{\rho}$ to the projected vector $\hat{P}_\Delta \Psi$ and then projecting again the resulting vector $\hat{\rho} \hat{P}_\Delta \Psi \rightarrow \hat{P}_\Delta \hat{\rho} \hat{P}_\Delta \Psi$.
- a new identical projection does not change the projected operator:

$$\hat{P}_\Delta \left(\hat{P}_\Delta \hat{\rho} \hat{P}_\Delta \right) \hat{P}_\Delta = \hat{P}_\Delta^2 \hat{\rho} \hat{P}_\Delta^2 = \hat{P}_\Delta \hat{\rho} \hat{P}_\Delta$$

- $\hat{\rho}_\Delta$ is normalized: $\text{Tr} \left(\hat{P}_\Delta \hat{\rho} \hat{P}_\Delta \right) = \text{Tr} \left(\hat{P}_\Delta \hat{P}_\Delta \hat{\rho} \right) = \text{Tr} \left(\hat{P}_\Delta \hat{\rho} \right)$

The measured observable becomes well defined

$$\hat{\rho}_{\Delta} = \frac{\hat{P}_{\Delta} \hat{\rho}_t \hat{P}_{\Delta}}{\text{Tr}(\hat{P}_{\Delta} \hat{\rho}_t)}$$

- The resulting state (not necessarily pure) has probability 1 for the provided values:

$$P_{\rho_{\Delta}}(A \in \Delta) = \text{Tr}(\hat{P}_{\Delta} \hat{\rho}_{\Delta}) = \text{Tr} \frac{\hat{P}_{\Delta}^2 \hat{\rho}_{\Delta} \hat{P}_{\Delta}}{\text{Tr}(\hat{P}_{\Delta} \hat{\rho}_{\Delta})} = 1$$

⇒ *A becomes defined within Δ .*

- This postulates states that *measurements are reproducible*, in the sense that a second measurement of A made immediately after the first one should give the same result.

Preparative measurements

- If a measurement provides a unique non-degenerate value the resulting state is $|a\rangle \equiv |\psi_a\rangle$ (no matter the system previous state):

$$\hat{\rho}_a = \frac{|a\rangle \langle a| \sum_{i=1}^m p_i |\Psi_i\rangle \langle \Psi_i| |a\rangle \langle a|}{\sum_{j=1}^{\infty} \langle \Phi_j | |a\rangle \langle a| \sum_{i=1}^m p_i |\Psi_i\rangle \langle \Psi_i| | \Phi_j \rangle}$$

$$\hat{\rho}_\Delta = \frac{\hat{P}_\Delta \hat{\rho}_t \hat{P}_\Delta}{\text{Tr}(\hat{P}_\Delta \hat{\rho}_t)}$$

Preparative measurements

- If a measurement provides **a unique non-degenerate value** the resulting state is $|a\rangle \equiv |\psi_a\rangle$ (no matter the system previous state):

$$\begin{aligned} \hat{\rho}_a &= \frac{|a\rangle \langle a| \sum_{i=1}^m p_i |\Psi_i\rangle \langle \Psi_i| |a\rangle \langle a|}{\sum_{j=1}^{\infty} \langle \Phi_j | |a\rangle \langle a| \sum_{i=1}^m p_i |\Psi_i\rangle \langle \Psi_i| | \Phi_j \rangle} \\ &= \frac{|a\rangle \langle a| \sum_{i=1}^m p_i |\langle \Psi_i | a \rangle|^2}{\sum_{i=1}^m p_i \underbrace{\sum_{j=1}^{\infty} \langle \Psi_i | | \Phi_j \rangle \langle \Phi_j | | a \rangle}_{\hat{1}}} = |a\rangle \langle a| \end{aligned}$$

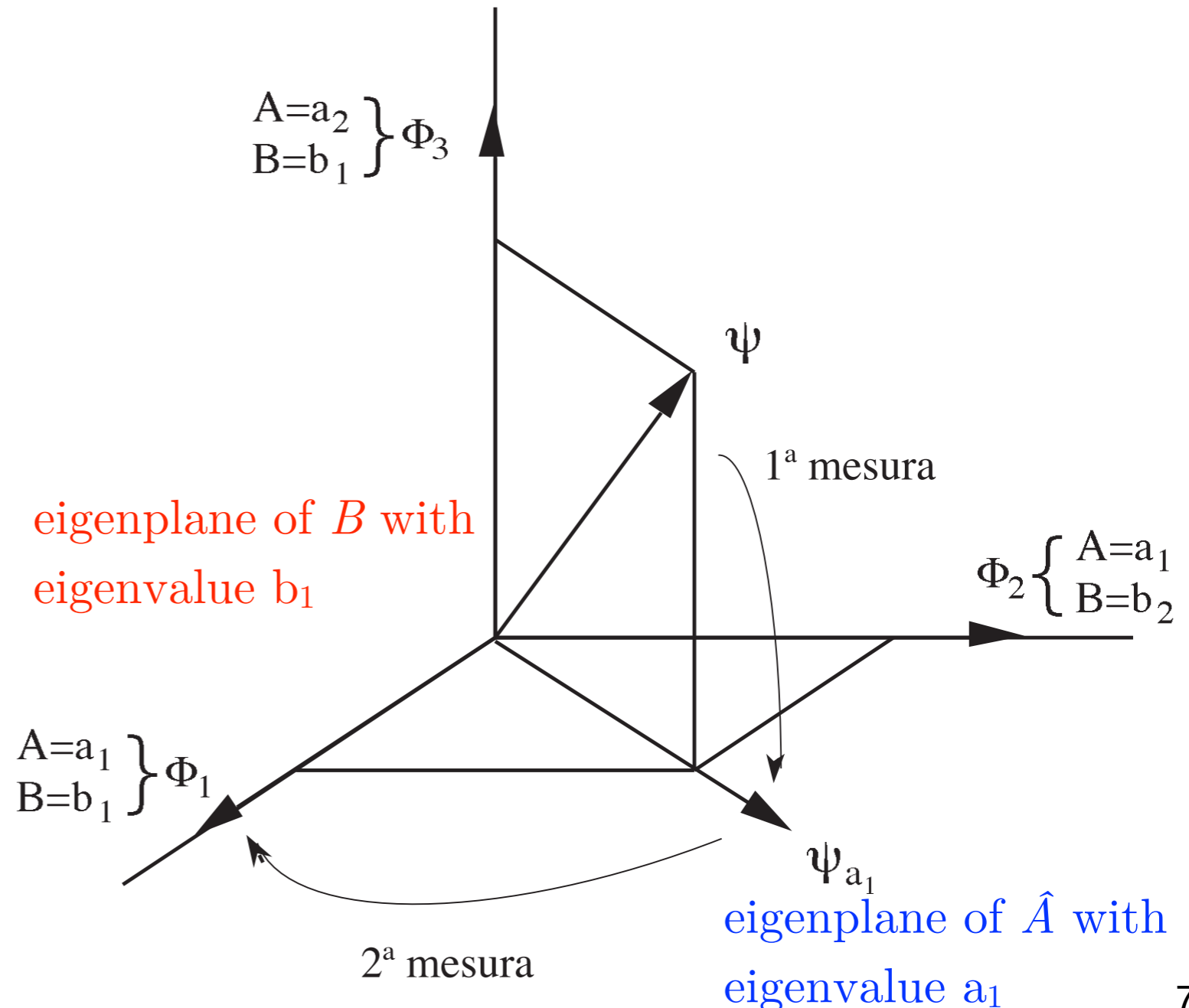
- If the measurement provides **a degenerate value** other compatible observables should be measured in order to prepare a pure state.

Compatibility \Leftrightarrow commutation

● **T10:** A and B compatible $\Leftrightarrow [\hat{A}, \hat{B}] = 0$

• \Leftarrow from **T5** (slide 37) there

exists a complete set of common eigenvectors, that can be chosen orthonormal. Let us express any state vector Ψ in that basis. A measurement of A with result a_i projects onto the corresponding eigenspace. If we then measure B the new projection must take place within that eigenspace, since Ψ_{a_i} has no components along axes orthogonal to it. Therefore a_i is preserved.



- **T10:** A and B compatible $\Leftrightarrow [\hat{A}, \hat{B}] = 0$

- \Rightarrow Let us assume that A and B are *compatible* observables. If we measure A and obtain a_i and then measure B and obtain b_k , A should retain its value a_i , which can be verified by measuring again A and repeating many times the whole experiment.
- If after obtaining a_i we always obtain b_k then the eigenspace of A with eigenvalue a_i must also be an eigenspace of B with eigenvalue b_k . Then any basis set of this eigenspace consists of common eigenvectors of A and B .
- If the measurement of B sometimes leads to b_k and sometimes leads to b_l then the eigenspace of A with eigenvalue a_i is contained in the direct sum of the eigenspaces of B with eigenvalues b_k and b_l respectively. By choosing in these eigenspaces of B basis vector pertaining to the eigenspace of A we obtain a basis set for this made of common eigenvectors of A and B . This can be repeated for every eigenvalue of A .
- According to **T5** this implies $[\hat{A}, \hat{B}] = 0$.

Incompatible observables

- If $[\hat{A}, \hat{B}] \neq 0$ there is not a basis set made of eigenstates of both operators, so that a measurement of B in an eigenstate of A may result in a collapsed state that is not an eigenstate of A .

Continuous spectra

- Position measurements: $\hat{P}_\Delta \equiv \int_{x \in \Delta} \hat{P}_x dx$

(non sharp limits that depend on the measurement device).

Exercise 1.11

- a)** The classical rotational energy of a two-particle rigid rotor with reduced mass μ , interparticle distance d and orbital angular momentum L is $H_{rot} = \frac{L^2}{2\mu d^2}$. Find its quantum rotational energies and their degeneracies. Write the spectral decomposition of the hamiltonian.
- b)** Write the spectral decomposition of the operator $\frac{\exp(-\widehat{H}_{rot}/kT)}{Z}$ and use the Boltzmann law to show that this is the density operator describing the rotational state of a two-particle rigid rotor taken from a gas of rotors at thermodynamic equilibrium at a temperature T : $\hat{\rho} = \frac{\exp(-\widehat{H}_{rot}/kT)}{Z}$
- c)** Which is the state of one of those rotors after measuring its energy with the result 0?
- d)** Which would be its state after measuring the energy with the result $1/\mu d^2$ a.u.?

Exercise 1.12

A beam of hydrogen atoms with energy E_1 passes through an Stern-Gerlach device with the magnetic field oriented along the z axis that filters the atoms with $S_z = 1/2$. These are then passed through a second Stern-Gerlach device with the magnetic field oriented along the x axis. The two resulting beams are redirected to a common trajectory and introduced into a third Stern-Gerlach device oriented along the z axis. Finally a detector screen registers the emerging atoms. Indicate what will register the screen

- a)** if we filter the atoms with $S_x = 1/2$ a.u. in the second device,
- b)** if we filter the atoms with $S_x = -1/2$ a.u. in the second device,
- c)** if we do not filter the atoms in the second device but we register their trajectories,
- d)** if we do not filter the atoms in the second device nor register their trajectories.

Solution of the exercise 1.11

a) $\hat{H}_{rot} = \frac{\hat{L}^2}{2\mu d^2}$ is a function of $\hat{L}^2 \Rightarrow$ the eigenfunctions of \hat{L}^2 are eigenfunctions of \hat{H}_{rot} : $\hat{L}^2 Y_{L,m} = L(L+1) Y_{L,m}$ $\left. \begin{array}{l} L=0, 1, 2, \dots \\ m=L, L-1, \dots, -L \end{array} \right\}$

$$\hat{H}_{rot} Y_{L,m} = \frac{L(L+1)}{2\mu d^2} Y_{L,m} \Rightarrow \boxed{E_{rot}(L) = \frac{L(L+1)}{2\mu d^2}, d_L = 2L+1}$$

(in a.u.)

(letter J is usually used instead of L)

$$\hat{H}_{rot} = \sum_{L=0}^{\infty} \underbrace{\frac{L(L+1)}{2\mu d^2}}_{E_L} \underbrace{\sum_{m=-L}^L |Y_{L,m}\rangle \langle Y_{L,m}|}_{\hat{P}_L}$$

b)

$$\frac{e^{-\frac{\hat{H}_{rot}}{kT}}}{\mathcal{Z}} = \sum_{L=0}^{\infty} \frac{e^{-\frac{E_L}{kT}}}{\mathcal{Z}} \sum_{m=-L}^L |Y_{L,m}\rangle \langle Y_{L,m}|$$

$$\hat{\rho} = \sum_{L=0}^{\infty} \sum_{m=-L}^L P_{L,m} |Y_{L,m}\rangle \langle Y_{L,m}| \quad \text{with } P_{L,m} = \frac{e^{-\frac{E_L}{kT}}}{\mathcal{Z}} = P_L \quad \left. \begin{array}{l} \Rightarrow \hat{\rho} = \frac{e^{-\frac{\hat{H}_{rot}}{kT}}}{\mathcal{Z}} \\ \text{(Boltzmann)} \end{array} \right\}$$

Solution of the exercise 1.11 (cont.)

$$c) \hat{\rho}_0 = \frac{\hat{P}_0 \hat{\rho} \hat{P}_0}{\text{Tr}(\hat{P}_0 \hat{\rho})} = \frac{|Y_{00}\rangle \langle Y_{00}| \sum_{L=0}^{\infty} \sum_{n=-L}^L P_L |Y_{Ln}\rangle \langle Y_{Ln}| |Y_{00}\rangle \langle Y_{00}|}{\text{Tr}(|Y_{00}\rangle \langle Y_{00}| \hat{\rho})} = \frac{P_0 |Y_{00}\rangle \langle Y_{00}|}{P_0}$$

$\langle Y_{00} | \hat{\rho} | Y_{00} \rangle = P_0$ (pure ground state)

$$d) \frac{1}{\mu d^2} = E_1$$

$$\hat{\rho}_1 = \frac{\hat{P}_1 \hat{\rho} \hat{P}_1}{\text{Tr}(\hat{P}_1 \hat{\rho})} = \frac{\sum_{n=-1}^1 |Y_{1n}\rangle \langle Y_{1n}| \hat{\rho} \sum_{n=-1}^1 |Y_{1n}\rangle \langle Y_{1n}|}{\sum_{n=-1}^1 \text{Tr}(|Y_{1n}\rangle \langle Y_{1n}| \hat{\rho})} = \frac{P_1 \sum_{n=-1}^1 |Y_{1n}\rangle \langle Y_{1n}|}{P_1 + P_1 + P_1}$$

$$= \frac{1}{3} |Y_{11}\rangle \langle Y_{11}| + \frac{1}{3} |Y_{10}\rangle \langle Y_{10}| + \frac{1}{3} |Y_{1-1}\rangle \langle Y_{1-1}|$$

Alternatively:

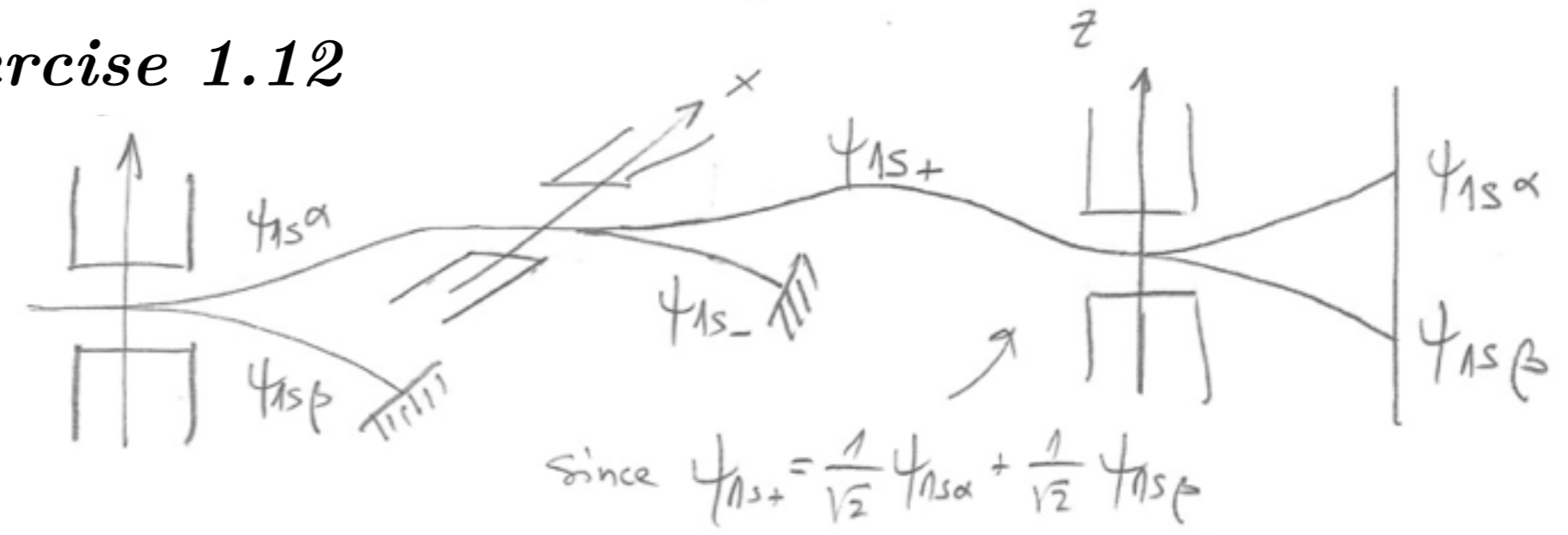
$$\hat{\rho}_1 = \frac{\hat{P}_1 \sum_{L=0}^{\infty} P_L \hat{P}_L \hat{P}_1}{\text{Tr}(\hat{P}_1 \sum_{L=0}^{\infty} P_L \hat{P}_L)} = \frac{\hat{P}_1 \hat{P}_1}{\text{Tr}(\hat{P}_1 \hat{P}_1)} = \frac{\hat{P}_1}{3}$$

$$\text{Tr} \sum_{n=-1}^1 |Y_{1n}\rangle \langle Y_{1n}| = \sum_{n=-1}^1 \langle Y_{1n} | Y_{1n} \rangle = 3$$

Solution of the exercise 1.12

a)

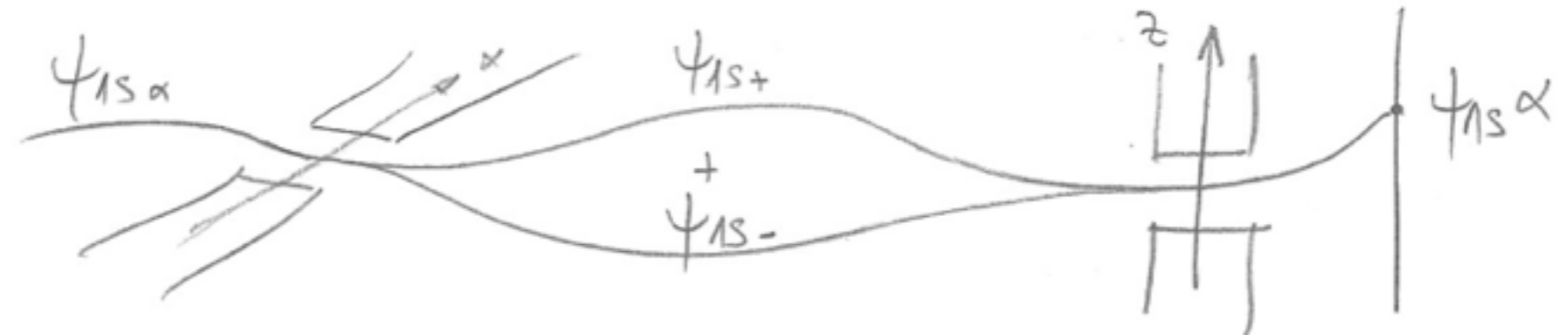
$$\rho = \frac{1}{2} |\psi_{1s\alpha}\rangle \langle \psi_{1s\alpha}| + \frac{1}{2} |\psi_{1s\beta}\rangle \langle \psi_{1s\beta}|$$



b) Same result if we filter $\psi_{1s-} = \frac{1}{\sqrt{2}} \psi_{1s\alpha} - \frac{1}{\sqrt{2}} \psi_{1s\beta}$

c) Same result (but double of detections), since the measurement of S_x projects onto ψ_{1s+} or ψ_{1s-} .

d) In this case no projection takes place (no measurement of S_x), so that the atoms entering the 3rd S-G device are all in the $\psi_{1s\alpha}$ internal state (the separation of the beams in the 2nd SG is not a measurement of S_x in there is no register of the path taken by each atom).



Fifth postulate: *free evolution*

A system prepared in a pure state remains in a pure state while no measurements are made on it. A vector representing the state of the system evolves during that time according to the (time dependent) Schrödinger equation:

$$i\hbar \frac{d\Psi_t}{dt} = \hat{H}(t) \Psi_t$$

(the hamiltonian can depend on t for non-isolated systems).

Free evolution of expected values

$$\frac{d \langle \Psi_t | \hat{A}(t) \Psi_t \rangle}{d t} = \left\langle \frac{d \Psi_t}{d t} | \hat{A}(t) \Psi_t \right\rangle + \left\langle \Psi_t | \left(\frac{d \hat{A}(t)}{d t} \right) \Psi_t \right\rangle + \left\langle \Psi_t | \hat{A}(t) \frac{d \Psi_t}{d t} \right\rangle$$

$$i\hbar \frac{d \langle \Psi_t | \hat{A}(t) \Psi_t \rangle}{d t} = \langle \Psi_t | [\hat{A}(t), \hat{H}(t)] \Psi_t \rangle + i\hbar \left\langle \Psi_t | \left(\frac{d \hat{A}(t)}{d t} \right) \Psi_t \right\rangle$$

Constants of motion: constant expected values *in any state*.

$$[\hat{A}(t), \hat{H}(t)] + i\hbar (d \hat{A}(t) / dt) = 0$$

Time evolution operator

$$\Psi(t) = \hat{U}(t, t_0) \Psi(t_0) \quad i\hbar \frac{d\hat{U}(t, t_0)}{dt} = \hat{H}(t) \hat{U}(t, t_0)$$

- **Time-independent** hamiltonian: $\hat{U}(t, t_0) = e^{-i(t-t_0)\hat{H}/\hbar}$

(Cohen eq. (61) p. 174)

- *Stationary states:*

$$\hat{H}\Phi_k(t_0) = E_k\Phi_k(t_0) \quad \Rightarrow$$

$$\Phi_k(t) = e^{-i(t-t_0)\hat{H}/\hbar}\Phi_k(t_0) = e^{-i(t-t_0)E_k/\hbar}\Phi_k(t_0)$$

- *nothing changes with time in a stationary state:*

$$\begin{aligned} \langle \Phi_k(t) | \hat{A} \Phi_k(t) \rangle &= \langle e^{-i(t-t_0)E_k/\hbar}\Phi_k(t_0) | \hat{A} e^{-i(t-t_0)E_k/\hbar}\Phi_k(t_0) \rangle \\ &= e^{i(t-t_0)E_k/\hbar} e^{-i(t-t_0)E_k/\hbar} \langle \Phi_k(t_0) | \hat{A} \Phi_k(t_0) \rangle \\ &= \langle \Phi_k(t_0) | \hat{A} \Phi_k(t_0) \rangle \end{aligned}$$

Time evolution operator

- *Non-stationary states:*

$$\Psi(t_0) = \sum_k c_k \Phi_k(t_0) \quad \Rightarrow$$

$$\Psi(t) = e^{-i(t-t_0)\hat{H}/\hbar} \sum_k c_k \Phi_k(t_0) = \sum_k c_k e^{-i(t-t_0)E_k/\hbar} \Phi_k(t_0)$$

- *Example:* for a hydrogen atom in the initial state $\Psi(t_0) = \frac{1}{2}\phi_{1s} + \frac{\sqrt{3}}{2}\phi_{2p_0}$

$$\Psi(t) = \frac{1}{2} e^{-i(t-t_0)E_1/\hbar} \phi_{1s} + \frac{\sqrt{3}}{2} e^{-i(t-t_0)E_2/\hbar} \phi_{2p_0}$$

$$\text{in a. u.: } \Psi(t) = \frac{1}{2} e^{i(t-t_0)/2} \phi_{1s} + \frac{\sqrt{3}}{2} e^{i(t-t_0)/8} \phi_{2p_0} \quad \langle x \rangle = ?$$

- **T11:** $\hat{U}(t, t_0)$ is *unitary*: $\left(\hat{U}(t, t_0)\right)^{-1} = \left(\hat{U}(t, t_0)\right)^\dagger$

- trivial for time-independent hamiltonians

Unitary operators

- **Unitary operators** preserve scalar products and, in particular, norms (probability conservation):

$$\begin{aligned}
 \langle \Phi(t) | \Psi(t) \rangle &= \left\langle \hat{U}(t, t_0) \Phi(t_0) \middle| \hat{U}(t, t_0) \Psi(t_0) \right\rangle \\
 &= \left\langle \hat{U}^\dagger(t, t_0) \hat{U}(t, t_0) \Phi(t_0) \middle| \Psi(t_0) \right\rangle \\
 &= \langle \Phi(t_0) | \Psi(t_0) \rangle
 \end{aligned}$$

- Parallelism with complex numbers:

Complex numbers	Linear operators
real: $z^* = z$	self-adjoint (hermitian): $\hat{A}^\dagger = \hat{A}$
α real $\Rightarrow e^{i\alpha} = 1; (e^{i\alpha})^* = (e^{i\alpha})^{-1} = e^{-i\alpha}$	\hat{A} self-adjoint $\Rightarrow e^{i\hat{A}}$ unitary; $(e^{i\hat{A}})^\dagger = (e^{i\hat{A}})^{-1} = e^{-i\hat{A}}$
phase: $ z = 1; z^* = z^{-1}$	unitary: $\hat{A}^\dagger = \hat{A}^{-1}$
$\langle \Phi z \Psi \rangle = \langle z^* \Phi \Psi \rangle$	$\langle \Phi \hat{A} \Psi \rangle = \langle \hat{A}^\dagger \Phi \Psi \rangle$

Exercise 1.13

A sample of sparkling water is put in an NMR spectrometer for obtaining its ^{13}C spectrum. The interaction hamiltonian of a nuclear spin with an applied static field $\vec{B}_0 = B_0 \vec{u}_z$ is $\hat{H} = -\hat{\vec{\mu}} \cdot \vec{B}_0 = -\gamma \hat{I}_z B_0 = \omega \hat{I}_z$, where $\omega = -\gamma B_0$, γ is the gyromagnetic ratio of the nuclide and I_z is its spin angular momentum z -component.

a) Obtain the energies of the stationary spin-states of a ^{13}C nucleus of the sample (the I quantum number of this nuclide is $1/2$). You can neglect the interactions between the ^{13}C spin and other particles of the sample (their main effects are included in γ).

b) Write the time evolution operator for the spin states of ^{13}C .

c) If a ^{13}C nucleus were in the pure state $\psi_+ = (1/\sqrt{2})(\alpha + \beta)$ at $t=0$, which would be its state vector as a function of time t ? Calculate $\langle I_x \rangle$, $\langle I_y \rangle$ and $\langle I_z \rangle$ as functions of t . What kind of motion undergoes the vector $\langle \vec{I} \rangle$? Compare it with the classical precession motion.

d) For the initial state considered in **c)** what are the state vectors at $t=2\pi/\omega$ and $t=4\pi/\omega$? Note that the state vector comes back to its initial value after 2 turns of $\langle \vec{I} \rangle$.

Results: a) $\pm \hbar\omega/2$; b) $\hat{U}(t, 0) = e^{-i\frac{\omega \hat{I}_z}{\hbar} t}$; c) $\frac{1}{\sqrt{2}} (e^{-i\frac{\omega}{2} t} \alpha + e^{i\frac{\omega}{2} t} \beta)$;
 $\langle I_x \rangle = \frac{\hbar}{2} \cos \omega t$; $\langle I_y \rangle = \frac{\hbar}{2} \sin \omega t$; $\langle I_z \rangle = 0$; d) $-\psi_+(0)$; $\psi_+(0)$.

Solution of the exercise 1.13

a) $\hat{H} = \omega \hat{I}_z$, $\omega = -\gamma B_0$, $\hat{I}_z g_m = m g_m$ $\xrightarrow{m=1/2} g_{1/2} \equiv \alpha$
 $\xrightarrow{m=-1/2} g_{-1/2} \equiv \beta$
 (in a.u. $\hbar=1$)

b) $\hat{U}(t) = e^{-i\frac{\hat{H}}{\hbar}t} = e^{-i\omega I_z t}$
 (in a.u.)

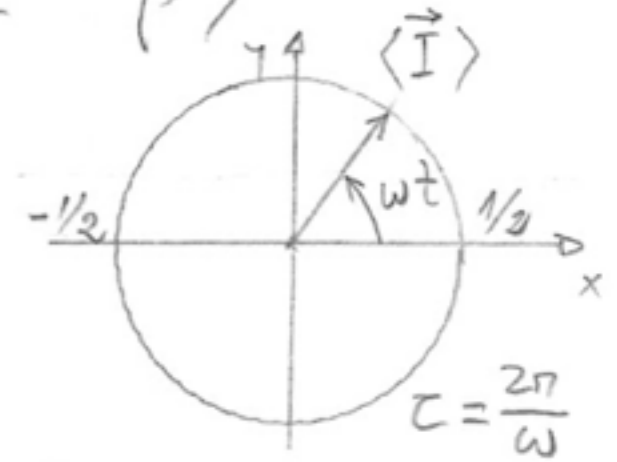
c) $\psi_+(0) = \frac{1}{\sqrt{2}}(\alpha + \beta) \Rightarrow \psi_+(t) = \frac{1}{\sqrt{2}} e^{-i\omega \hat{I}_z t} (\alpha + \beta) = \frac{1}{\sqrt{2}} (e^{-i\frac{\omega}{2}t} \alpha + e^{i\frac{\omega}{2}t} \beta)$

$\langle I_x \rangle_t = \langle \psi_+(t) | \frac{1}{2}(\hat{I}_+ + \hat{I}_-) \psi_+(t) \rangle = \frac{1}{4} \langle e^{-i\frac{\omega}{2}t} \alpha + e^{i\frac{\omega}{2}t} \beta | e^{i\frac{\omega}{2}t} \alpha + e^{-i\frac{\omega}{2}t} \beta \rangle$

$= \frac{1}{4} (e^{i\omega t} \langle \alpha | \alpha \rangle + e^{-i\omega t} \langle \beta | \beta \rangle) = \frac{1}{2} \cos \omega t$

$\langle I_y \rangle_t = \langle \psi_+(t) | \frac{1}{2i}(\hat{I}_+ - \hat{I}_-) \psi_+(t) \rangle = \frac{1}{4i} (e^{i\omega t} - e^{-i\omega t}) = \frac{1}{2} \sin \omega t$

$\langle I_z \rangle_t = \langle \psi_+(t) | \hat{I}_z \psi_+(t) \rangle = \frac{1}{2} \langle e^{-i\frac{\omega}{2}t} \alpha + e^{i\frac{\omega}{2}t} \beta | e^{-i\frac{\omega}{2}t} \frac{1}{2} \alpha + e^{i\frac{\omega}{2}t} (-\frac{1}{2}) \beta \rangle = 0$
 (constant of motion!)



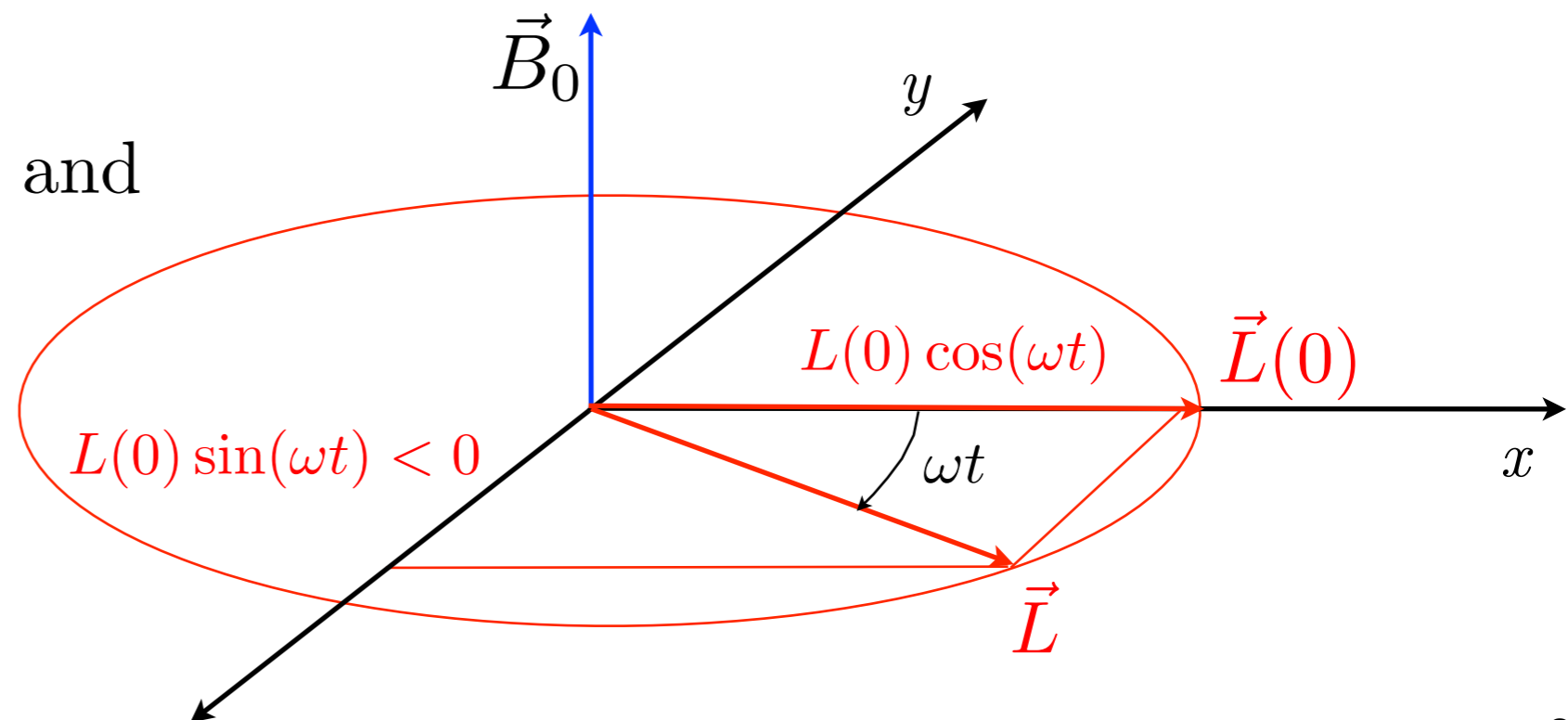
d) $\psi_+(\frac{2\pi}{\omega}) = \frac{1}{\sqrt{2}} (e^{-i\pi} \alpha + e^{i\pi} \beta) = -\psi_+(0)$

$\psi_+(\frac{4\pi}{\omega}) = \frac{1}{\sqrt{2}} (e^{-i2\pi} \alpha + e^{i2\pi} \beta) = \psi_+(0)$ (after 2 turns, as can be verified by interference experiments)

Classical precession motion of a magnetic moment under a static magnetic field

$$\left. \begin{aligned} d\vec{L}/dt = \vec{\tau} = \vec{\mu} \times \vec{B}_0 \\ \vec{\mu} = \gamma \vec{L} \end{aligned} \right\} \begin{aligned} d\vec{L}/dt = \vec{L} \times \gamma \vec{B}_0 \text{ is } \perp \text{ to } \vec{L} \text{ and } \vec{B}_0 \\ \vec{B}_0 \text{ static} \Rightarrow \vec{L} \text{ rotates about } \vec{B}_0 \\ \text{with angular velocity } \omega = -\gamma B_0 \\ \text{(see } J. \text{ Chem. Ed. } \mathbf{73}, 310 \text{ (1996))} \end{aligned}$$

For $\vec{L}(0) = L(0)\vec{u}_x$ and $\gamma > 0$ ($\omega < 0$):



Evolution of mixed states

$$\hat{\rho}_t = \sum_i p_i |\psi_i(t)\rangle \langle \psi_i(t)| = \sum_i p_i |\hat{U}(t, t_0) \psi_i(t_0)\rangle \langle \hat{U}(t, t_0) \psi_i(t_0)|$$

$$\hat{\rho}_t = \hat{U}(t, t_0) \hat{\rho}_{t_0} \hat{U}^\dagger(t, t_0)$$

- By taking the derivative with respect to t and using $i\hbar \frac{d\hat{U}(t, t_0)}{dt} = \hat{H}(t) \hat{U}(t, t_0)$ and $(\hat{A}\hat{B})^\dagger = \hat{B}^\dagger \hat{A}^\dagger$:

Liouville - von Neumann eqn.
 (\equiv Schrödinger eqn.)

$$i\hbar \frac{d\hat{\rho}_t}{dt} = [\hat{H}(t), \hat{\rho}_t]$$

- An equilibrium macroscopic state does not evolve: $\hat{\rho} = \frac{\exp(-\hat{H}/kT)}{Z}$

Exercise 1.14

- a)** Write the spectral decomposition of the density operator describing the spin state of any ^{13}C nucleus of a sparkling water sample at thermodynamic equilibrium in an NMR spectrometer of static magnetic field B_0 at a temperature T (see the previous exercise).
- b)** Calculate the expected value of I_x , I_y and I_z for a ^{13}C nucleus of the sample.
- c)** Use the gyromagnetic ratio of the ^{13}C nuclide ($\gamma = 6,728 \times 10^7 \text{ T}^{-1}\text{s}^{-1}$) to calculate $\hbar\omega/(2kT)$ for $B_0=10\text{T}$ and $T = 300\text{K}$, and justify the “high temperature” approximation: $\exp(\hbar\omega/(2kT)) \approx 1 + \hbar\omega/(2kT)$. Use it to justify the Curie law: $M \propto 1/T$, where M is the macroscopic magnetization of the sample (magnetic moment per unit volume: $\vec{M} = N\gamma \langle \vec{I} \rangle$).
- d)** Use the high temperature approximation to write the density operator as $\frac{1}{2}(\hat{1} - \frac{\omega}{kT}\hat{I}_z)$.

How does this operator evolve with time?

- e)** A $\pi/2$ radio-frequency pulse over the y axis changes the equilibrium density operator to $\frac{1}{2}(\hat{1} - \frac{\omega}{kT}\hat{I}_x)$. How does this evolve with time? Calculate the magnetization after the pulse as a function of time. Compare it with the classical precession motion of a magnetic moment under a static magnetic field. *Hint:* use the following equation, that can be proved by Taylor expanding the exponential and trigonometric functions in the left and right hand sides:
$$e^{i\theta\hat{I}_z/\hbar}\hat{I}_xe^{-i\theta\hat{I}_z/\hbar} = \hat{I}_x \cos \theta - \hat{I}_y \sin \theta$$

Results: a) $\rho = \frac{1}{Z} \left(e^{-\frac{\omega\hbar}{2kT}} |\alpha\rangle \langle\alpha| + e^{\frac{\omega\hbar}{2kT}} |\beta\rangle \langle\beta| \right)$; b) $\langle I_x \rangle = \langle I_y \rangle = 0$; $\langle I_z \rangle = \frac{\hbar}{2} \tanh \frac{-\omega\hbar}{2kT}$; c) $\frac{\omega\hbar}{2kT} \approx 8 \times 10^{-6}$; $M_z \approx \frac{N\gamma^2 B_0 \hbar^2}{4kT}$; d) $\hat{\rho}(t) = \hat{\rho}(0)$; e) $\hat{\rho}(t) = \frac{1}{2} \left(\hat{1} - \frac{\omega}{kT} (\hat{I}_x \cos \omega t + \hat{I}_y \sin \omega t) \right)$; $\langle I_x \rangle = -\frac{\omega\hbar^2}{4kT} \cos \omega t$; $\langle I_y \rangle = -\frac{\omega\hbar^2}{4kT} \sin \omega t$; $\langle I_z \rangle = 0$

Solution of the exercise 1.14

a)

$$\hat{\rho} = \frac{1}{Z} e^{-\frac{\hat{H}}{kT}} \quad ; \quad \hat{H} = \omega \hat{I}_z = \frac{\omega \hbar}{2} |\alpha\rangle\langle\alpha| - \frac{\omega \hbar}{2} |\beta\rangle\langle\beta|$$

$$\hat{\rho} = \frac{1}{Z} e^{-\frac{\omega \hbar}{2kT}} |\alpha\rangle\langle\alpha| + \frac{1}{Z} e^{+\frac{\omega \hbar}{2kT}} |\beta\rangle\langle\beta| \quad (\text{also from Boltzmann law})$$

b)

$$\langle I_x \rangle_{\rho} = \text{Tr}(\hat{I}_x \hat{\rho}) = \frac{1}{Z} e^{-\frac{\omega \hbar}{2kT}} \text{Tr}(\hat{I}_x |\alpha\rangle\langle\alpha|) + \frac{1}{Z} e^{\frac{\omega \hbar}{2kT}} \text{Tr}(\hat{I}_x |\beta\rangle\langle\beta|) = 0$$

$$\langle I_y \rangle_{\rho} = \text{Tr}(\hat{I}_y \hat{\rho}) = 0 \quad \langle \alpha | \frac{1}{2} (\hat{I}_+ + \hat{I}_-) | \alpha \rangle = \frac{\hbar}{2} \langle \alpha | \beta \rangle = 0$$

$\frac{1}{2i} (\hat{I}_+ - \hat{I}_-)$

$$\langle I_z \rangle_{\rho} = \text{Tr}(\hat{I}_z \hat{\rho}) = \frac{1}{Z} e^{-\frac{\omega \hbar}{2kT}} \langle \alpha | \hat{I}_z | \alpha \rangle + \frac{1}{Z} e^{\frac{\omega \hbar}{2kT}} \langle \beta | \hat{I}_z | \beta \rangle = \frac{\hbar}{2} \frac{e^{-\frac{\omega \hbar}{2kT}} - e^{\frac{\omega \hbar}{2kT}}}{e^{-\frac{\omega \hbar}{2kT}} + e^{\frac{\omega \hbar}{2kT}}} = \frac{\hbar}{2} \text{danh}\left(-\frac{\omega \hbar}{2kT}\right)$$

c)

$$\frac{\hbar \omega}{2kT} \approx \frac{1 \times 10^{-34} \times 7 \times 10^7 \times 10}{2 \times 1.4 \times 10^{-23} \times 300} \approx 8 \times 10^{-6}$$

$$\langle I_z \rangle_{\rho} \approx \frac{\hbar}{2} \frac{1 - \frac{\omega \hbar}{2kT} - (1 + \frac{\omega \hbar}{2kT})}{1 - \frac{\omega \hbar}{2kT} + 1 + \frac{\omega \hbar}{2kT}} = -\frac{\omega \hbar^2}{4kT} \Rightarrow M_z = -\frac{N \gamma \omega \hbar^2}{4kT} = \frac{N \gamma^2 B_0 \hbar^2}{4kT}$$

**Solution of the
exercise 1.14 (cont.)**

d)
$$\hat{\rho} = \frac{1}{2} \left(\left(1 - \frac{\omega \hbar}{2kT}\right) |\alpha\rangle\langle\alpha| + \left(1 + \frac{\omega \hbar}{2kT}\right) |\beta\rangle\langle\beta| \right) =$$

$$= \frac{1}{2} (|\alpha\rangle\langle\alpha| + |\beta\rangle\langle\beta|) - \frac{1}{2} \frac{\omega}{kT} \left(\frac{\hbar}{2} |\alpha\rangle\langle\alpha| - \frac{\hbar}{2} |\beta\rangle\langle\beta| \right) = \frac{1}{2} \left(\hat{1} - \frac{\omega}{kT} \hat{I}_z \right)$$

$$\hat{\rho}(t) = \hat{U}(t) \hat{\rho}(0) \hat{U}^\dagger(t) = e^{-i \frac{\omega \hat{I}_z t}{\hbar}} \hat{\rho}(0) e^{i \frac{\omega \hat{I}_z t}{\hbar}} = \hat{\rho}(0) \quad (\text{equilibrium!})$$

e)
$$\hat{\rho}(t) = e^{-i \frac{\omega \hat{I}_z t}{\hbar}} \frac{1}{2} \left(\hat{1} - \frac{\omega}{kT} \hat{I}_x \right) e^{i \frac{\omega \hat{I}_z t}{\hbar}} = \frac{1}{2} \left(\hat{1} - \frac{\omega}{kT} (\hat{I}_x \cos \omega t + \hat{I}_y \sin \omega t) \right)$$

$$\langle I_x \rangle = \text{Tr}(\hat{I}_x \hat{\rho}) = -\frac{\omega}{2kT} (\cos \omega t \text{Tr}(\hat{I}_x^2) + \sin \omega t \text{Tr}(\hat{I}_x \hat{I}_y))$$

$$\begin{aligned} \text{Tr}(\hat{I}_x \hat{I}_y) &= \langle \alpha | \hat{I}_x \hat{I}_y | \alpha \rangle + \langle \beta | \hat{I}_x \hat{I}_y | \beta \rangle = \langle \frac{\hat{I}_+ + \hat{I}_-}{2} \alpha | \frac{\hat{I}_+ - \hat{I}_-}{2i} \alpha \rangle + \langle \frac{\hat{I}_+ + \hat{I}_-}{2} \beta | \frac{\hat{I}_+ - \hat{I}_-}{2i} \beta \rangle \\ &= \langle \frac{\hbar}{2} \beta | \frac{-\hbar}{2i} \beta \rangle + \langle \frac{\hbar}{2} \alpha | \frac{\hbar}{2i} \alpha \rangle = 0 \end{aligned}$$

$$\text{Tr}(\hat{I}_x^2) = \text{Tr}\left(\frac{\hbar^2}{4} \hat{1}\right) = \frac{\hbar^2}{2} \Rightarrow \langle I_x \rangle = -\frac{\omega \hbar^2}{4kT} \cos \omega t$$

$$\langle I_y \rangle = \text{Tr}(\hat{I}_y \hat{\rho}) = -\frac{\omega \hbar^2}{4kT} \sin \omega t, \quad \langle I_z \rangle = 0$$

Time evolution pictures

Alternative statements of the evolution postulate:

Heisenberg vs Schrödinger pictures $\langle \Psi_H | \hat{A}_H(t) \Psi_H \rangle = \langle \Psi_S(t) | \hat{A}_S(t) \Psi_S(t) \rangle$

$$\begin{aligned} \Psi_H &\equiv \hat{U}^\dagger(t, t_0) \Psi_S(t) & \hat{A}_H(t) &= \hat{U}^\dagger(t, t_0) \hat{A}_S(t) \hat{U}(t, t_0) \\ &= \Psi_S(t_0) \end{aligned}$$

$$i\hbar \frac{d\hat{A}_H(t)}{dt} = \left[\hat{A}_H(t), \hat{H}_H(t) \right] + i\hbar \left(\frac{d\hat{A}_S(t)}{dt} \right)_H$$

- Constants of motion: $d\hat{A}_H(t)/dt = 0$
- $m d\hat{x}_H/dt = \hat{p}_H$, Newton law, electromagnetic radiation, ...
- For a mixed state: $\langle A \rangle(t) = \text{Tr}\{\hat{A}_S \hat{\rho}_S(t)\} = \text{Tr}\{\hat{A}_S \hat{U}(t, t_0) \hat{\rho}_S(t_0) \hat{U}^\dagger(t, t_0)\}$
 $= \text{Tr}\{\hat{U}^\dagger(t, t_0) \hat{A}_S \hat{U}(t, t_0) \hat{\rho}_S(t_0)\} = \text{Tr}\{\hat{A}_H(t) \hat{\rho}_H\}$
- *Interaction picture*: $\hat{H}(t) = \hat{H}_0 + \hat{H}'(t)$ $\Psi_D(t) = \exp(i(t-t_0)\hat{H}_0/\hbar) \Psi_S(t)$

Spin precession in Heisenberg picture

Exercise 1.15

a) Obtain the operators as functions of time for the three cartesian components of the nuclear spin angular momentum of a ^{13}C nucleus under a static magnetic field in the Heisenberg picture (see exercise 1.14).

b) Calculate the expected values of those three angular momentum components for the state $\psi_+ = (1/\sqrt{2})(\alpha + \beta)$ and verify that they coincide with those obtained in exercise 1.13 for the Schrödinger picture.

Hint: You can use the equation given in exercise 1.14 together with:

$$e^{i\theta\hat{I}_z/\hbar}\hat{I}_ye^{-i\theta\hat{I}_z/\hbar} = \hat{I}_y \cos \theta + \hat{I}_x \sin \theta$$

Solution of the exercise 1.15

$$- a) (\hat{I}_x)_H(t) = \hat{U}^\dagger(t) (\hat{I}_x)_S \hat{U}(t) = e^{i\omega \hat{I}_z t} (\hat{I}_x)_0 e^{-i\omega \hat{I}_z t} = (\hat{I}_x)_0 \cos \omega t - (\hat{I}_y)_0 \sin \omega t$$

$$(\hat{I}_y)_H(t) = (\hat{I}_y)_0 \cos \omega t + (\hat{I}_x)_0 \sin \omega t$$

$$(\hat{I}_z)_H(t) = e^{i\omega \hat{I}_z t} (\hat{I}_z)_0 e^{-i\omega \hat{I}_z t} = (\hat{I}_z)_0 \quad (\text{constant of motion})$$

$$- b) \langle I_x \rangle_{\psi_+} = \langle \frac{1}{\sqrt{2}}(\alpha + \beta) | (\hat{I}_x)_0 \frac{1}{\sqrt{2}}(\alpha + \beta) \rangle \cos \omega t - \langle \frac{1}{\sqrt{2}}(\alpha + \beta) | (\hat{I}_y)_0 \frac{1}{\sqrt{2}}(\alpha + \beta) \rangle \sin \omega t$$

$$= \frac{1}{2} \left(\langle \alpha + \beta | \frac{1}{2}(\alpha + \beta) \rangle \cos \omega t - \langle \alpha + \beta | \frac{1}{2i}(\alpha - \beta) \rangle \sin \omega t \right) = \frac{1}{2} \cos \omega t$$

$$\langle I_y \rangle_{\psi_+} = 0 + \frac{1}{2} \sin \omega t$$

$$\langle I_z \rangle_{\psi_+} = \langle (\hat{I}_z)_0 \rangle_{\psi_+} = 0$$

\hat{v}_x_H is the time derivative of \hat{x}_H

Exercise 1.16

Show that:

(a) If $[\hat{A}_S, \hat{B}_S] = \hat{C}_S$ then $[\hat{A}_H, \hat{B}_H] = \hat{C}_H$.

(b) For a particle that moves along the x axis with hamiltonian $\hat{H} = \frac{1}{2m}\hat{p}^2 + V(\hat{x})$,

$$m \frac{d\hat{x}_H}{dt} = \hat{p}_H$$

Is x a constant of motion?

Solution of the exercise 1.16

a) $[\hat{A}_S, \hat{B}_S] = \hat{C}_S$

$$[\hat{A}_H, \hat{B}_H] = (\hat{U}^\dagger \hat{A}_S \hat{U}) (\hat{U}^\dagger \hat{B}_S \hat{U}) - (\hat{U}^\dagger \hat{B}_S \hat{U}) (\hat{U}^\dagger \hat{A}_S \hat{U}) =$$

$$= \hat{U}^\dagger (\hat{A}_S \hat{B}_S - \hat{B}_S \hat{A}_S) \hat{U} = \hat{U}^\dagger \hat{C}_S \hat{U} = \hat{C}_H$$

b) $\hat{H} = \frac{1}{2m} \hat{p}^2 + V(\hat{x})$ is time-independent in the Schrödinger picture

$\Rightarrow \hat{U}(t, 0) = e^{-it\hat{H}}$ (we have taken $t_0 = 0$ and $t = 1$ (a.u.)).

Time-evolution in the Heisenberg picture (slide 1-86):

$$i \frac{d\hat{X}_H(t)}{dt} = [\hat{X}_H(t), \hat{H}_H(t)] + i \underbrace{\left(\frac{d\hat{X}_S(t)}{dt} \right)}_0_H$$

$$[\hat{X}_S, \hat{H}_S] = [\hat{X}, \frac{1}{2m} \hat{p}^2 + V(\hat{x})] = \frac{1}{2m} [\hat{X}, \hat{p}^2] + [\hat{X}, V(\hat{x})] = \frac{i}{m} \hat{p}_S$$

(all Schröd.)

(ex 1.2.f) $\rightarrow \hat{p} [\hat{x}, \hat{p}] + [\hat{x}, \hat{p}] \hat{p} = 2\hat{p}i \rightarrow = 0$ (slide 1-45)

\Rightarrow according to a) $[\hat{X}_H, \hat{H}_H] = \frac{i}{m} \hat{p}_H \Rightarrow \frac{d\hat{X}_H(t)}{dt} = \frac{\hat{p}_H}{m} \neq 0$

$\Rightarrow x$ is not a constant of motion.

Sixth postulate: *compound systems*

*The Hilbert space associated to a system made of **two or more parts** is the direct product of the Hilbert spaces associated to each part.*

*If two of these parts are **identical** particles the state vectors of the compound system (including spin observables) must be symmetric or antisymmetric with respect to the exchange of the labels of those particles depending on their spin quantum number being integer or half-odd.*

Notes:

- The 2nd part of the postulate is a theorem in relativistic quantum field theory (*Spin–statistics theorem*).
- For compound particles (nuclei, atoms, etc.) the term “spin” refers to “total angular momentum”.

Direct, tensorial or Kronecker product of two spaces

$$\mathcal{H}_1 \times \mathcal{H}_2 \rightarrow \mathcal{H}_1 \otimes \mathcal{H}_2$$

$(\psi(1), \phi(2)) \rightarrow \psi(1) \otimes \phi(2) \equiv |\psi(1)\phi(2)\rangle$ is bilinear and

if $\{\psi_i(1)\}$ and $\{\phi_j(2)\}$ are basis of \mathcal{H}_1 and \mathcal{H}_2 then

$\{\psi_i(1) \otimes \phi_j(2)\}$ is a basis of $\mathcal{H}_1 \otimes \mathcal{H}_2$:

$$\Psi(1, 2) = \sum_{ij} c_{ij} \psi_i(1) \otimes \phi_j(2) \quad (\text{so that } \text{Dim}(\mathcal{H}_1 \otimes \mathcal{H}_2) = \text{Dim}(\mathcal{H}_1) \times \text{Dim}(\mathcal{H}_2))$$

$$\text{and } \langle \psi(1) \otimes \phi(2) | \psi'(1) \otimes \phi'(2) \rangle = \langle \psi(1) | \psi'(1) \rangle \langle \phi(2) | \phi'(2) \rangle$$

Direct product of operators:

$$\{\hat{A}(1) \otimes \hat{B}(2)\} \psi(1) \otimes \phi(2) = \{\hat{A}(1) \psi(1)\} \otimes \{\hat{B}(2) \phi(2)\}$$

$$\hat{C}(1, 2) = \sum_{ij} c_{ij} \hat{A}_i(1) \otimes \hat{B}_j(2)$$

$$\hat{\hat{A}}(1) \equiv \hat{A}(1) \otimes \hat{1}(2) \quad \hat{\hat{B}}(2) \equiv \hat{1}(1) \otimes \hat{B}(2) \quad [\hat{A}(1), \hat{B}(2)] = 0$$

Separable operators

$$\hat{A}(1) \psi_i(1) = a_i \psi_i(1) \quad \text{y} \quad \hat{B}(2) \phi_j(2) = b_j \phi_j(2)$$

$$\{\hat{A}(1) + \hat{B}(2)\} \psi_i(1) \otimes \phi_j(2) = (a_i + b_j) \psi_i(1) \otimes \phi_j(2)$$

- *Examples:*

- **three-dimensional harmonic oscillator of force constants k_x , k_y and k_z :**

$$\hat{H}(\hat{p}^2, \hat{\vec{r}}) = \hat{H}_{k_x}(\hat{p}_x^2, \hat{x}) + \hat{H}_{k_y}(\hat{p}_y^2, \hat{y}) + \hat{H}_{k_z}(\hat{p}_z^2, \hat{z}) \quad \Psi = \psi_{k_x, n_x} \otimes \psi_{k_y, n_y} \otimes \psi_{k_z, n_z}$$

- **particle in a three-dimensional potential box of sides a , b and c :**

$$\hat{H}_{abc}(\hat{p}^2, \hat{\vec{r}}) = \hat{H}_a(\hat{p}_x^2, \hat{x}) + \hat{H}_b(\hat{p}_y^2, \hat{y}) + \hat{H}_c(\hat{p}_z^2, \hat{z}) \Rightarrow \Psi = \psi_{a, n_x} \otimes \psi_{b, n_y} \otimes \psi_{c, n_z}$$

- **hydrogen atom without spin-orbit interaction:**

$$\hat{H}(\hat{p}^2, \hat{\vec{r}}, \hat{\vec{S}}) = \hat{H}(\hat{p}^2, \hat{\vec{r}}) + \hat{0}(\hat{\vec{S}}) \Rightarrow \psi_{nlmm_s} = \phi_{nlm} \otimes g_{m_s}$$

- **independent particle model for a poly-electronic system (orbital approximation):** $\hat{H}(1, \dots, N) \approx \hat{f}(1) + \dots + \hat{f}(N) \Rightarrow \Psi(1, \dots, N) \approx \hat{\mathcal{A}}\{\psi_1(1) \otimes \dots \otimes \psi_N(N)\}$

Entangled vs non-entangled states

- *Non-entangled* states: $\Psi(1, 2) = \psi(1) \otimes \phi(2)$

$$\langle \psi(1) \otimes \phi(2) | \hat{A}(1) \otimes \hat{1}(2) | \psi(1) \otimes \phi(2) \rangle = \langle \psi(1) | \hat{A}(1) | \psi(1) \rangle$$

$$\langle \psi(1) \otimes \phi(2) | \hat{A}(1) \otimes \hat{B}(2) | \psi(1) \otimes \phi(2) \rangle = \langle \psi(1) | \hat{A}(1) | \psi(1) \rangle \langle \phi(2) | \hat{B}(2) | \phi(2) \rangle$$

- *Entangled* states: $\Psi(1, 2) = \sum_{ij} c_{ij} \psi_i(1) \otimes \phi_j(2)$ (orthonormal basis sets)

$$\langle A(1) \rangle_{\Psi(1,2)} = \langle \sum_{ij} c_{ij} \psi_i(1) \otimes \phi_j(2) | \hat{A}(1) \otimes \hat{1}(2) | \sum_{kl} c_{kl} \psi_k(1) \otimes \phi_l(2) \rangle =$$

$$\sum_j \langle \sum_i c_{ij} \psi_i(1) | \hat{A}(1) | \sum_k c_{kj} \psi_k(1) \rangle = \sum_j \langle \psi'_j(1) | \hat{A}(1) | \psi'_j(1) \rangle$$

$$\psi'_j(1) \equiv \sum_i c_{ij} \psi_i(1) \quad \psi''_j(1) \equiv \psi'_j(1) / \{ \sum_i |c_{ij}|^2 \}^{1/2} \quad p_j = \sum_i |c_{ij}|^2$$


$$\langle A(1) \rangle_{\Psi(1,2)} = \sum_j p_j \langle \psi''_j(1) | \hat{A}(1) | \psi''_j(1) \rangle$$

(the state describing particle 1 is a mixed one)

Entanglement

Let's have a system with two particles in an *entangled* state, and let express it in a basis set $\{\psi_i(1) \otimes \phi_j(2)\}$ where the $\psi_i(1)$ are orthonormal eigenvectors of $A(1)$: $\Psi(1, 2) = \sum_{ij} c_{ij} \psi_i(1) \otimes \phi_j(2)$

Lets assume that its free evolution leads to a large separation distance between the two particles, so *they no longer interact*. If we measure $A(1)$ in particle 1 and we obtain the non-degenerate value a_k with eigenvector ψ_k the system changes to the *non-entangled* state:

$$|\psi_k(1)\rangle \langle \psi_k(1)| \sum_{ij} c_{ij} \psi_i(1) \otimes \phi_j(2) = \psi_k(1) \otimes \sum_j c_{kj} \phi_j(2)$$


The new state of particle 2 depends on the result obtained for 1, and the state change of 2 is produced *simultaneously* with the change occurred in 1, no matter the distance between them!!! (*non-locality*).

$s_z(i)$ in singlet and triplet spin-states

The symbol \otimes is usually omitted in quantum physics or chemistry books.

Exercise 1.17

Two particles with $s = 1/2$ are in the spin state described by the state vector $\Psi_S = (1/\sqrt{2}) \{ \alpha(1)\beta(2) - \beta(1)\alpha(2) \}$ (*singlet* state). After the particles separate without interacting with any other system we measure s_z in the first one and obtain the result $1/2$ a.u.

a) In which state will be left the second particle? Is this state dependent on the result of the measurement performed on the first particle? Is Ψ_S an entangled state?

b) Answer the same questions as in **a)** for the initial *triplet* state $\Psi_{T_1} = \alpha(1)\alpha(2)$.

c) Answer the same questions as in **a)** for the initial *triplet* state $\Psi_{T_0} = (1/\sqrt{2}) \{ \alpha(1)\beta(2) + \beta(1)\alpha(2) \}$?

d) What do we know about $s_z(1)$, $s_z(2)$ and $s_z(1)s_z(2)$ –this *joint observable* informs about the relative orientation of the two $s_z(i)$ – in the initial states considered in **a)**, **b)**, **c)** and in the state with density operator $\hat{\rho} = 0.5 |\Psi_S\rangle \langle \Psi_S| + 0.5 |\Psi_{T_0}\rangle \langle \Psi_{T_0}|$?

Results: **a)** $\beta(2)$, yes, yes; **b)** $\alpha(2)$, no, no; **c)** $\beta(2)$, yes, yes; **d)** in Ψ_S , Ψ_{T_0} and $\hat{\rho}$ we know that $s_z(1)s_z(2) = -1/4$ with certainty, but $s_z(1)$ and $s_z(2)$ are completely indeterminate (in $\hat{\rho}$ neither we know S^2); in Ψ_{T_1} we know $s_z(1)$, $s_z(2)$ and $s_z(1)s_z(2)$ with certainty.

Solution of the exercise 1.17

- a) $\Psi_S = \frac{1}{\sqrt{2}} \{ \alpha(1)\beta(2) - \beta(1)\alpha(2) \}$ (singlet: $S=0, M_S=0$)

$S_z(1) \rightarrow \frac{1}{2}$ a.u. $\Rightarrow \Psi_S$ changes to

$$\Psi_{\text{after}} = N \hat{P}_{S_z(1)=\frac{1}{2}} \Psi_S = N |\alpha(1)\rangle \langle \alpha(1) | \frac{1}{\sqrt{2}} \{ \alpha(1)\beta(2) - \beta(1)\alpha(2) \} =$$

$$= N |\alpha(1)\rangle \frac{1}{\sqrt{2}} |\beta(2)\rangle = \alpha(1)\beta(2) \text{ non-entangled state (2 in } \beta)$$

If $S_z(1) \rightarrow -\frac{1}{2}$ a.u. $\Rightarrow \Psi_{\text{after}} = \beta(1)\alpha(2) \Rightarrow$ the result of the measurement performed in 1 determines the state acquired by 2
 $\Rightarrow \Psi_S$ is an entangled state

- b) $\Psi_{T_1} = \alpha(1)\alpha(2)$ is an eigenstate of $S_z(1)$ with eigenvalue $\frac{1}{2}$ a.u.

\Rightarrow a measurement of $S_z(1)$ will give $\frac{1}{2}$ with certainty, and the state of 2 is α independently of $S_z(1)$ being measured or not.

$\Rightarrow \Psi_{T_1}$ is not an entangled state.

Solution of the exercise 1.17 (cont.)

- c) $\Psi_{T_0} = \frac{1}{\sqrt{2}} \{ \alpha(1) \beta(2) + \beta(1) \alpha(2) \}$: the same as in a)

- d) In Ψ_S and Ψ_{T_0} we have no information about $S_z(1)$ and $S_z(2)$, but we know $S_z(1) S_z(2) = -\frac{1}{4}$ with certainty, since

$$\hat{S}_z(1) \hat{S}_z(2) \frac{1}{\sqrt{2}} \{ \alpha(1) \beta(2) \pm \beta(1) \alpha(2) \} = \frac{1}{\sqrt{2}} \left\{ -\frac{1}{4} \alpha(1) \beta(2) \pm (-\frac{1}{4}) \beta(1) \alpha(2) \right\}$$

$$= -\frac{1}{4} \frac{1}{\sqrt{2}} \{ \alpha(1) \beta(2) \pm \beta(1) \alpha(2) \}$$

The same for $\hat{p} = 0,5 | \Psi_S \rangle \langle \Psi_S | + 0,5 | \Psi_{T_0} \rangle \langle \Psi_{T_0} |$, since it's a mixture of those.

In Ψ_{T_1} the 3 observables are well determined, since it is an eigenvector of them (with eigenvalues $\frac{1}{2}$, $\frac{1}{2}$ and $-\frac{1}{4}$).

Notes: Ψ_S , Ψ_{T_0} and \hat{p} have the same information about $S_z(1)$, $S_z(2)$ and $S_z(1) S_z(2)$, but the 2 former have well defined S^2 and the latter ~~is~~ doesn't.

Ψ_{T_1} has more information than Ψ_{T_0} (or Ψ_S) for the observables we have considered, but the reverse happens to the x components (ex 1.17)

$s_x(i)$ in singlet and triplet spin-states

Exercise 1.18

Two particles with $s = 1/2$ are in one of the spin states described by the state vectors $\Psi_{T_0/S} = (1/\sqrt{2})\{\alpha(1)\beta(2) \pm \beta(1)\alpha(2)\}$.

a) Show that $\Psi_{T_0} = (1/\sqrt{2})\{p(1)p(2) - m(1)m(2)\}$ and $\Psi_S = (1/\sqrt{2})\{m(1)p(2) - p(1)m(2)\}$, where $p/m(i) = (1/\sqrt{2})\{\alpha(i) \pm \beta(i)\}$ are eigenvectors of $s_x(i)$ (see exercise 1.8). What do we know about $s_x(1)$, $s_x(2)$ and $s_x(1)s_x(2)$ in $\Psi_{T_0/S}$?

b) Put $\Psi_{T_1} = \alpha(1)\alpha(2)$ in terms of $p/m(i)$. What do we know about $s_x(1)$, $s_x(2)$ and $s_x(1)s_x(2)$ in Ψ_{T_1} ?

c) Calculate the probability of obtaining the result 1/2 a.u. in a measurement of $s_x(1)$ and 1/4 a.u. in a measurement of $s_x(1)s_x(2)$ in the mixed state considered in point *d)* of the preceding exercise. What do we know about those observables in this mixed state?

Results: **a)** $s_x(1)$ and $s_x(2)$ are completely indeterminate but we know with certainty that $s_x(1)s_x(2) = 1/4$ a.u. for Ψ_{T_0} and $-1/4$ a.u. for Ψ_S ; **b)** $s_x(1)$, $s_x(2)$ and $s_x(1)s_x(2)$ are completely indeterminate; **c)** $s_x(1)$, $s_x(2)$ and $s_x(1)s_x(2)$ are completely indeterminate.

$$\Psi_{T_1} = \alpha(1)\alpha(2): s_z(1) // s_z(2); \quad \Psi_{T_0} = (1/\sqrt{2})\{\alpha(1)\beta(2) + \beta(1)\alpha(2)\}: s_x(1) // s_x(2).$$

Solution of the exercise 1.18

$$\Psi_{T_0/S} = \frac{1}{\sqrt{2}} \begin{pmatrix} \alpha & \beta \\ \beta & \alpha \end{pmatrix} \quad \left. \begin{array}{l} p = \frac{1}{\sqrt{2}}(\alpha + \beta) \\ m = \frac{1}{\sqrt{2}}(\alpha - \beta) \end{array} \right\} \begin{array}{l} + \rightarrow \alpha = \frac{1}{\sqrt{2}}(p + m) \\ - \rightarrow \beta = \frac{1}{\sqrt{2}}(p - m) \end{array}$$

a)

$$\begin{aligned} \overline{\Psi}_{T_0} &= \frac{1}{\sqrt{2}} \frac{1}{2} \left\{ (p+m)(p-m) + (p-m)(p+m) \right\} = \frac{1}{2\sqrt{2}} (pp - pm + mp - mm + pp + pm - mp - mm) \\ &= \frac{1}{\sqrt{2}} (pp - mm) \end{aligned}$$

$$\overline{\Psi}_S = \frac{1}{\sqrt{2}} \frac{1}{2} \left\{ pp - pm + mp - mm - (pp + pm - mp - mm) \right\} = \frac{1}{\sqrt{2}} (mp - pm)$$

$$P(S_x(i) \rightarrow \frac{1}{2}) = P(S_x(i) \rightarrow -\frac{1}{2}) = \left(\frac{1}{\sqrt{2}}\right)^2 = \frac{1}{2} \quad \text{in both, } \overline{\Psi}_{T_0} \text{ and } \overline{\Psi}_S$$

$$P_{T_0}(S_x(1)S_x(2) \rightarrow \frac{1}{4}) = \left(\frac{1}{\sqrt{2}}\right)^2 + \left(\frac{1}{\sqrt{2}}\right)^2 = 1 \quad \Rightarrow S_x(i) \text{ indeterminate but parallel}$$

$$P_S(S_x(1)S_x(2) \rightarrow -\frac{1}{4}) = \left(\frac{1}{\sqrt{2}}\right)^2 + \left(\frac{1}{\sqrt{2}}\right)^2 = 1 \quad \Rightarrow S_x(i) \text{ " " anti "}$$

Solution of the exercise 1.18 (cont.)

$$b) \hat{\mathbb{I}}_{T_1} = \alpha \alpha = \frac{1}{2} (p+m)(p+m) = \frac{1}{2} (pp + pm + mp + mm)$$

$$P(S_x(1) \rightarrow \frac{1}{2}) = \left(\frac{1}{2}\right)^2 + \left(\frac{1}{2}\right)^2 = \frac{1}{2} = P(S_x(1) \rightarrow -\frac{1}{2}) = P(S_x(2) \rightarrow \frac{1}{2}) = P(S_x(2) \rightarrow -\frac{1}{2}) =$$

$$P(S_x(1)S_x(2) \rightarrow \frac{1}{4}) = P(S_x(1)S_x(2) \rightarrow -\frac{1}{4}) \Rightarrow S_x(1), S_x(2) \text{ and } S_x(1)S_x(2) \text{ are completely indeterminate.}$$

$$c) \hat{\rho} = 0,5 |\mathbb{I}_S\rangle\langle\mathbb{I}_S| + 0,5 |\mathbb{I}_{T_0}\rangle\langle\mathbb{I}_{T_0}|$$

$S_x(1)$ and $S_x(2)$ are completely indeterminate because they are so in \mathbb{I}_S and in \mathbb{I}_{T_0}

$S_x(1)S_x(2)$ is completely indeterminate because the states with values $-\frac{1}{4}$ and $+\frac{1}{4}$ have equal weights in the mixture.

Teleportation

Exercise 1.19

Alice wants to teleport to Bob the spin-quantum-state of a spin-1/2 particle: $\psi_1(1) = c_\alpha\alpha(1) + c_\beta\beta(1)$, where c_α and c_β are any complex numbers satisfying $|c_\alpha|^2 + |c_\beta|^2 = 1$. She produces a pair of particles in the singlet state

$$\Psi_{23}(2, 3) = \frac{1}{\sqrt{2}} \{ \alpha(2)\beta(3) - \beta(2)\alpha(3) \}$$

- (a) What is the state vector $\Psi(1, 2, 3)$ describing the three particles if particle 1 is not entangled with particle 2 nor particle 3? (1 could be identical to 2 and/or 3, but far enough from them to be considered distinguishable).
- (b) She keeps particle 2 and sends particle 3 to Bob (avoiding interactions with other particles). Then she measures the total spin of particles 1 and 2 (S_{12}^2) and obtains the result 0, so that $\Psi(1, 2, 3)$ is projected onto the singlet state

$$\Psi_{12}(1, 2) = \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

What is the state describing the three particles after the measurement?
Has she succeeded in teleporting the state of particle 1 to particle 3?

Solution of the exercise 1.19

a) There is no entanglement between 1 and the pair 2-3 \Rightarrow

$$\Psi(1,2,3) = \psi_1(1) \otimes \Psi_{23}(2,3) = \frac{1}{\sqrt{2}} \left\{ c_\alpha \alpha(1) \alpha(2) \beta(3) - c_\alpha \alpha(1) \beta(2) \alpha(3) + c_\beta \beta(1) \alpha(2) \beta(3) - c_\beta \beta(1) \beta(2) \alpha(3) \right\}$$

b) $\Psi_{\text{after}}(1,2,3) = |\Psi_{12}(1,2)\rangle \langle \Psi_{12}(1,2)| \Psi(1,2,3)\rangle N =$ ← normalization constant

$$= N \frac{1}{2} |\alpha(1)\beta(2) - \beta(1)\alpha(2)\rangle \langle \alpha(1)\beta(2) - \beta(1)\alpha(2)| \frac{1}{\sqrt{2}} \left\{ c_\alpha \alpha(1) \alpha(2) \beta(3) - c_\alpha \alpha(1) \beta(2) \alpha(3) + c_\beta \beta(1) \alpha(2) \beta(3) - c_\beta \beta(1) \beta(2) \alpha(3) \right\}$$

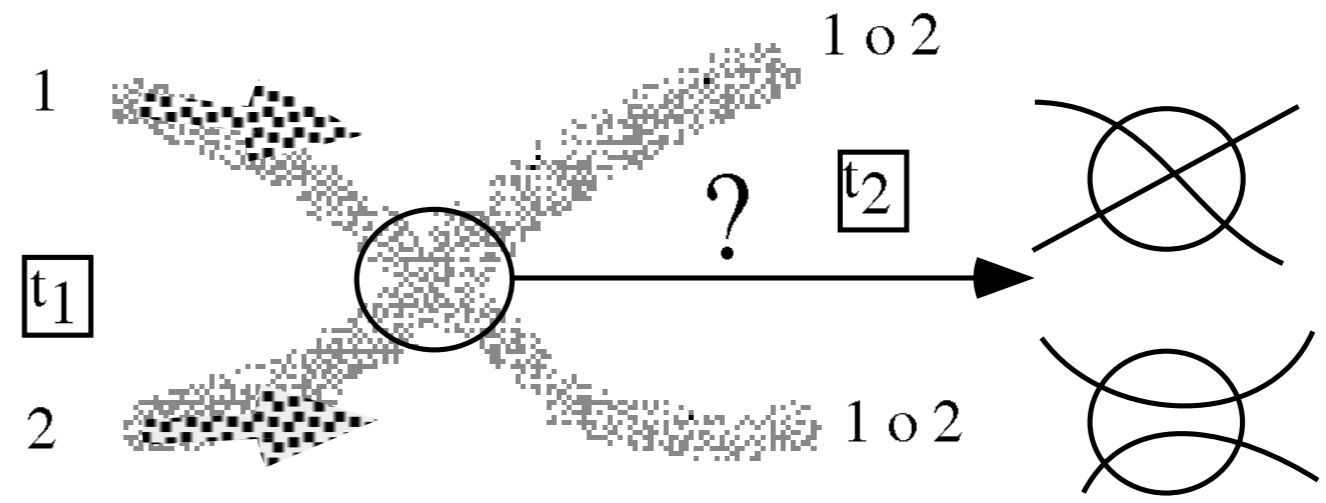
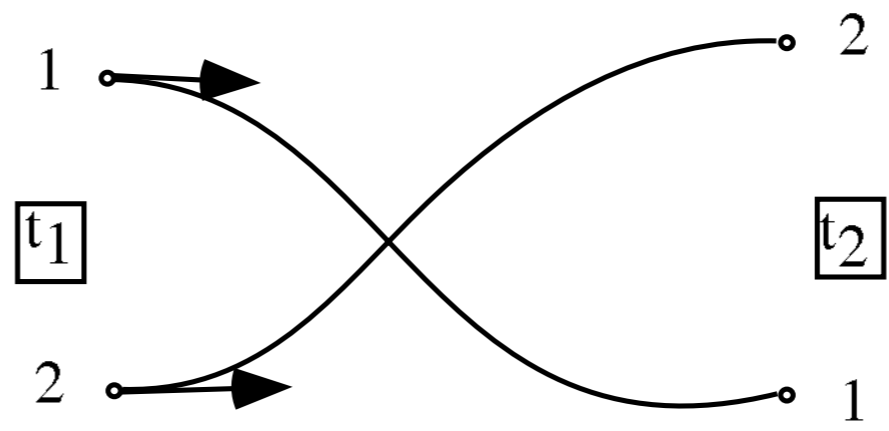
$$= \frac{1}{\sqrt{2}} |\alpha(1)\beta(2) - \beta(1)\alpha(2)\rangle \underbrace{\frac{N}{2} | -c_\alpha \alpha(3) - c_\beta \beta(3) \rangle}_{= \psi_1(3)} \Rightarrow \text{particle 3 acquires the original state of particle 1 (except for an irrelevant change of sign)} \Rightarrow \text{singos!}$$

(N must be 2, since $|c_\alpha|^2 + |c_\beta|^2 = 1$)

Identical particles

Let us consider a system composed of N identical particles

- Distinguishable according to classical mechanics (trajectories)
- *Indistinguishable* according to quantum mechanics (except for very separated particles)



Identical bosons

The state vector of a system containing identical *bosons* (particles with *integer* spin quantum number) must be *symmetric* with respect to the exchange of any two of those particles.

The Hilbert space $\mathcal{H} = \mathcal{H}_1(1) \otimes \dots \mathcal{H}_1(N)$.

has a *symmetric* subspace $\mathcal{H}_1^{\otimes N} \equiv \mathcal{H}_1(1) \otimes^s \dots \mathcal{H}_1(N)$

with a basis set $|(\psi_k \dots \psi_n)_+\rangle \equiv \psi_k(1) \otimes^s \dots \psi_n(N)$
 $= (1/\sqrt{N!}) \sum_{\alpha=1}^{N!} \hat{P}_\alpha \{\psi_k(1) \otimes \dots \psi_n(N)\}$

where $\{\psi_i\}$ is a basis set of \square_i (permutations are applied to the indices of the N one-particle states)

Identical fermions

The state vector of a system containing identical *fermions* (particles with *half-odd* spin quantum number) must be *antisymmetric* with respect to the exchange of any two of those particles.

The antisymmetric vectors

$$\begin{aligned} |(\psi_i(1) \cdots \psi_l(N))_-\rangle &= \psi_i(1) \otimes^a \cdots \psi_l(N) \\ &= \frac{1}{\sqrt{N!}} \sum_{\alpha=1}^{N!} (-1)^{\pi_\alpha} \widehat{P}_\alpha \{ \psi_i(1) \otimes^a \cdots \psi_l(N) \} \\ &= \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_i(1) \cdots \psi_i(N) \\ \cdots \cdots \cdots \\ \psi_l(1) \cdots \psi_l(N) \end{vmatrix} \end{aligned}$$

form a basis set of the *antisymmetric* subspace: $\mathcal{H}_1^{\otimes^a N} \equiv \mathcal{H}_1(1) \otimes^a \cdots \mathcal{H}_1(N)$ (π_α is the number of *transpositions* or *inversions* leading from the *main permutation* to P_α ; the *parity* of P_α is the parity of π_α).

3 identical particles

Examples:

- An **antisymmetrized** direct product of 3 mono-**fermionic** states (every next permutation is obtained from the previous one by exchanging the 2 indicated mono-fermionic states, hence the sign alternation):

$$\begin{aligned}
 |(\psi_i(1)\psi_j(2)\psi_k(3))_-\rangle = \frac{1}{\sqrt{3!}} \left\{ \right. & \left. \begin{aligned} & |\psi_i(1) \overbrace{\psi_j(2)\psi_k(3)}\rangle - |\overbrace{\psi_i(1)\psi_k(2)}\psi_j(3)\rangle \\ & + |\psi_k(1) \overbrace{\psi_i(2)\psi_j(3)}\rangle - |\overbrace{\psi_k(1)\psi_j(2)}\psi_i(3)\rangle \\ & + |\psi_j(1) \overbrace{\psi_k(2)\psi_i(3)}\rangle - |\psi_j(1)\psi_i(2)\psi_k(3)\rangle \end{aligned} \right\}
 \end{aligned}$$

- An **symmetrized** direct product of 3 mono-**bosonic** states

$$\begin{aligned}
 |(\psi_i(1)\psi_j(2)\psi_k(3))_+\rangle = \frac{1}{\sqrt{3!}} \{ & |\psi_i(1)\psi_j(2)\psi_k(3)\rangle + |\psi_i(1)\psi_k(2)\psi_j(3)\rangle \\ & + |\psi_k(1)\psi_i(2)\psi_j(3)\rangle + |\psi_k(1)\psi_j(2)\psi_i(3)\rangle \\ & + |\psi_j(1)\psi_k(2)\psi_i(3)\rangle + |\psi_j(1)\psi_i(2)\psi_k(3)\rangle \}
 \end{aligned}$$

Non-interacting bi-electronic states

- He $1s^2$ (closed-shell singlet: $S^2 = 0$):

$$\begin{aligned}
 \left| (\psi_{1s\alpha}(1)\psi_{1s\beta}(2))_- \right\rangle &= \frac{1}{\sqrt{2}} \{ |\psi_{1s\alpha}(1)\psi_{1s\beta}(2)\rangle - |\psi_{1s\beta}(1)\psi_{1s\alpha}(2)\rangle \} \\
 &= \frac{1}{\sqrt{2}} \{ |\phi_{1s}(1)\rangle |\alpha(1)\rangle |\phi_{1s}(2)\rangle |\beta(2)\rangle - |\phi_{1s}(1)\rangle |\beta(1)\rangle |\phi_{1s}(2)\rangle |\alpha(2)\rangle \} \\
 &= |\phi_{1s}(1)\rangle |\phi_{1s}(2)\rangle \frac{1}{\sqrt{2}} \{ |\alpha(1)\rangle |\beta(2)\rangle - |\beta(1)\rangle |\alpha(2)\rangle \}
 \end{aligned}$$

- He $1s2s$ open-shell singlet:

$$\begin{aligned}
 \frac{1}{\sqrt{2}} \left(\left| (\psi_{1s\alpha}(1)\psi_{2s\beta}(2))_- \right\rangle - \left| (\psi_{1s\beta}(1)\psi_{2s\alpha}(2))_- \right\rangle \right) &= \dots \\
 &= \frac{1}{\sqrt{2}} \{ |\phi_{1s}(1)\rangle |\phi_{2s}(2)\rangle + |\phi_{2s}(1)\rangle |\phi_{1s}(2)\rangle \} \frac{1}{\sqrt{2}} \{ |\alpha(1)\rangle |\beta(2)\rangle - |\beta(1)\rangle |\alpha(2)\rangle \}
 \end{aligned}$$

Identical particles may be distinguishable

The 6th postulate applies to *any* pair of identical particles, whether or not they interact. Should we then antisymmetrize the state vector of a *polyelectronic* system with respect to *every* electron of the universe?

- Not necessary for electrons that are far enough (H_2 for $R \rightarrow \infty$)
- except for joint measurements on entangled states!

Molecular vector states have to be (anti)symmetrized with respect to the interchange of *identical nuclei* *only if these occupy positions that can be interchanged by means of proper rotations or low-barrier conformational changes* (H_2 , CH_4 , $\text{CH}_3\text{C}_6\text{H}_5$, but not in CH_2ClBr , except if bond breaking is possible).

Polyelectronic systems

$\hat{A} \equiv \frac{1}{N!} \sum_{\alpha} (-1)^{\pi_{\alpha}} \hat{\mathcal{P}}_{\alpha}$ is a **projection** operator (*antisymmetrizer*)

$$\begin{aligned} \Psi = |(\psi_1 \cdots \psi_N)_-\rangle &= \frac{1}{\sqrt{N!}} \sum_{\alpha} (-1)^{\pi_{\alpha}} \hat{\mathcal{P}}_{\alpha} \{ \psi_1(1) \otimes \cdots \psi_N(N) \} \\ &= \sqrt{N!} \hat{A} \{ \psi_1(1) \otimes \cdots \psi_N(N) \} \end{aligned}$$

- If $\psi_1, \cdots, \psi_N, \psi'_1, \cdots, \psi'_N$ are orthonormal, then

$$\begin{aligned} \langle \Psi | \Psi' \rangle &= \langle \sqrt{N!} \hat{A} \{ \psi_1 \cdots \psi_N \} | \sqrt{N!} \hat{A} \{ \psi'_1 \cdots \psi'_N \} \rangle \\ &= \sum_{\alpha=1}^{N!} (-1)^{\pi_{\alpha}} \langle \psi_1 \cdots \psi_N | \hat{\mathcal{P}}_{\alpha} (\psi'_1 \cdots \psi'_N) \rangle \\ &= \begin{cases} 1 & \text{si } \psi_i = \psi'_i \quad \forall i \\ 0 & \text{otherwise} \end{cases} \end{aligned}$$

Slater-Condon rules

$\Psi = |(\psi_1 \dots \psi_a \dots \psi_b \dots \psi_N)_-\rangle$ *reference state vector (HF, DFT-KS, ...)*

$\Psi_a^r = |(\psi_1 \dots \psi_r \dots \psi_b \dots \psi_N)_-\rangle$ *monosubstituted state vector*

$\Psi_{ab}^{rs} = |(\psi_1 \dots \psi_r \dots \psi_s \dots \psi_N)_-\rangle$ *disubstituted state vector*

$$\langle \Psi | \hat{F} | \Psi \rangle = \sum_{a=1}^N \langle \psi_a | \hat{f} | \psi_a \rangle \quad \hat{F}(1, \dots, N) = \sum_{i=1}^N \hat{f}(i) ,$$

$$\langle \Psi | \hat{F} | \Psi_a^r \rangle = \langle \psi_a | \hat{f} | \psi_r \rangle \quad \hat{G}(1, \dots, N) = \sum_{i=1}^N \sum_{j>i}^N \hat{g}(i, j)$$

$$\langle \Psi | \hat{F} | \Psi_{ab}^{rs} \rangle = 0$$

...

$$\langle \Psi | \hat{G} | \Psi \rangle = \sum_{a=1}^N \sum_{b>a}^N \langle \psi_a \psi_b || \psi_a \psi_b \rangle$$

$$\langle \Psi | \hat{G} | \Psi_a^r \rangle = \sum_{b=1}^N \langle \psi_a \psi_b || \psi_r \psi_b \rangle$$

$$\langle \Psi | \hat{G} | \Psi_{ab}^{rs} \rangle = \langle \psi_a \psi_b || \psi_r \psi_s \rangle$$

$$\langle \Psi | \hat{G} | \Psi_{abc}^{rst} \rangle = 0$$

$$\langle \psi_a \psi_b || \psi_r \psi_s \rangle \equiv \langle \psi_a \psi_b | \hat{g}(1, 2) | \psi_r \psi_s \rangle - \langle \psi_a \psi_b | \hat{g}(1, 2) | \psi_s \psi_r \rangle$$

Hartree-Fock energy

For the state $\Psi = |(\psi_1 \dots \psi_a \dots \psi_b \dots \psi_N)_-\rangle$ with $\psi = \varphi \otimes g$

$$\hat{H} = \sum_i^N \hat{h}(i) + \sum_{j>i}^N \widehat{r_{ij}^{-1}}$$

$$\langle \Psi | \hat{H} | \Psi \rangle = \sum_{a=1}^{N_\alpha} h_{aa} + \sum_{a=1}^{N_\beta} h_{aa} + \sum_{a=1}^{N_\alpha} \sum_{b>a}^{N_\alpha} J_{ab} - K_{ab} + \sum_{a=1}^{N_\beta} \sum_{b>a}^{N_\beta} J_{ab} - K_{ab} + \sum_{a=1}^{N_\alpha} \sum_{b=1}^{N_\beta} J_{ab}$$