Operators in Quantum Mechanics

- Summary of operators in QM
- Eigenvalues and eigenfunctions
- Time and spin dependence
The material reviewed here is standard and can be found in any Quantum Mechanics textbook and in brief in several of the electronic structure calculations books.

Recommended reading material for these slides is given below:

- **Principles of Quantum Mechanics**, by R. Shankar
- **Introduction to Quantum Mechanics**, D. J. Griffiths
- **Quantum Mechanics**, B. H. Bransden and C.J. Joachain
- **Methods of Electronic-Structure Calculations**, M. Springborg
The Dirac Notation

For a given vector

\[
\begin{bmatrix}
  a_1 \\
  a_2 \\
  a_3 \\
  \vdots
\end{bmatrix}
\]

we call \( [a_1^* \ a_2^* \ a_3^* \ \cdots] \) the Hermitian adjoint or simply the adjoint.

A common notation used to indicate the Hermitian adjoint is to use the character “†” as a superscript

\[
\begin{bmatrix}
  a_1 \\
  a_2 \\
  a_3 \\
  \vdots
\end{bmatrix}^\dagger = [a_1^* \ a_2^* \ a_3^* \ \cdots]
\]

The “bra” (row vector) is the Hermitian adjoint of the “ket” (column vector) and vice versa.

The Hermitian adjoint of product of operators obeys the following:

\[
(\hat{A}\hat{B})^\dagger = \hat{B}^\dagger\hat{A}^\dagger
\]
To generalize linear algebra for quantum mechanics, we introduce Dirac’s “bra-ket” notation.

Bra-ket notation for functions and representing integrals (more specifically inner products): Note that each function is represented here using its values at some points (i.e. as a vector).

\[
\int g^*(x) f(x) \, dx \equiv \left[ g^*(x_1) \sqrt{\delta x} \quad g^*(x_2) \sqrt{\delta x} \quad g^*(x_3) \sqrt{\delta x} \quad \cdots \right]
\]

\[
\equiv \sum_n g^*(x_n) \sqrt{\delta x} f(x_n) \sqrt{\delta x}
\]

\[
\equiv \langle g(x) | f(x) \rangle
\]
We can represent a function using a complete orthonormal basis

\[ f(x) = \sum_n c_n \psi_n(x) \]

We can write the ‘bra’ and the ‘ket’ representations of the function as follows:

\[ \langle f(x) | \equiv \begin{bmatrix} c_1^* & c_2^* & c_3^* & \cdots \end{bmatrix} \quad | f(x) \rangle \equiv \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ \vdots \end{bmatrix} \]

We have simply changed the space to represent the function

We can now represent the integral \( \int |f(x)|^2 \, dx \) as follows:

\[
\int |f(x)|^2 \, dx \equiv \int f^*(x) f(x) \, dx \equiv \int \left[ \sum_n c_n^* \psi_n^*(x) \right] \left[ \sum_m c_m \psi_m(x) \right] \, dx \equiv \sum_{n,m} c_n^* c_m \delta_{nm} = \sum_n |c_n|^2 \\
\equiv \begin{bmatrix} c_1^* & c_2^* & c_3^* & \cdots \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ \vdots \end{bmatrix} = \langle f(x) | f(x) \rangle
\]
Expanding a function on an orthonormal basis

Similarly, if
\[ g(x) = \sum_n d_n \psi_n(x), \]
we can write:
\[
\int g^*(x) f(x) \, dx \equiv \begin{bmatrix} d_1^* & d_2^* & d_3^* & \cdots \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ \vdots \end{bmatrix} = (g(x) | f(x))
\]

Expansion coefficients in an orthonormal basis can be easily computed as follows:
\[
\int \psi_m^*(x) f(x) \, dx = \int \psi_m^*(x) \left( \sum_n c_n \psi_n(x) \right) \, dx = \sum_n c_n \langle \psi_m(x) | \psi_n(x) \rangle = c_m
\]
Thus we can write a function in its basis representation as:
\[
| f(x) \rangle = \sum_n c_n | \psi_n(x) \rangle = \sum_n | \psi_n(x) \rangle c_n
\]
\[
= \sum_n | \psi_n(x) \rangle \langle \psi_n(x) | f(x) \rangle
\]
The bra or ket always represents either the quantum mechanical state of the system (e.g. the wavefunction $\psi(x)$), or some state that the system could be in (such as one of the basis states $\psi_n(x)$).

The symbols we put inside the bra or ket should be enough to make it clear what state we are discussing in a given context.

A Hilbert space is a vector space analogous to the 3D geometrical space, with two important differences: (i) the space may have any number of dimensions, including an infinite number, and (ii) the inner product is in general complex. It is a suitable vector space for representing vectors that are linear in both addition and in multiplication by a constant.

Thus we are working with spaces that have inner product:

$$\langle f | g \rangle = (\langle g | f \rangle)^*$$

Such a relation leads $\langle f | f \rangle$ being real which is important to ensure a positive norm $\|f\| = \sqrt{\langle f | f \rangle}$ in these spaces.
An operator is an entity that changes one function into another, with the value of the new function at any point possibly being dependent on the values of the original function at any or all values of its argument.

Linear operators are linear both in addition of functions and in multiplication by a constant. Linear operators can be represented by matrices that can operate on the vectors in function space, and they obey the same algebra as matrices.

\[ |g\rangle = \hat{A} |f\rangle \]

If we regard the ket as a vector, we then regard the (linear) operator \( \hat{A} \) as a matrix.

In quantum mechanics linear operators are used as operators associated with measurable variables such as the Hamiltonian operator for energy, and the momentum operator for momentum, with the associated vectors that they are applied to representing quantum mechanical states.
We concentrate here on a general operator \( \hat{A} \) (but if you wish, think of \( \hat{A} \) being the Hamiltonian \( \hat{H} \)).

Operators commute when for each function \( f \), the following is true:

\[
\hat{A}\hat{B}f = \hat{B}\hat{A}f
\]

This can be formulated using the commutator \( [\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A} \). In general, we may choose to write this as:

\[
[\hat{A}, \hat{B}] = i\hat{C}
\]

where \( \hat{C} \) is usually referred to as the remainder of commutation.

For operators that commute the following is then true:

\[
[\hat{A}, \hat{B}] = 0
\]

You can verify that the following two operators don't commute:

\[
\hat{A}_1 f_1(x) = \frac{df_1(x)}{dx} \quad \hat{A}_2 f_2(x) = \cos[f_2(x)] + \pi + 4[f_2(x)]^2
\]
Consider $\hat{A}$ operating on the following $f$ as: $|g\rangle = \hat{A}|f\rangle$

Let us choose a representation basis for the two functions:

$$g(x) = \sum_n d_n \psi_n(x) \quad f(x) = \sum_n c_n \psi_n(x)$$

We can then write:

$$|g\rangle = \sum_i d_i |\psi_i\rangle = \hat{A} \sum_j c_j |\psi_j\rangle$$

From which we can see that: $d_i = \sum_h <\psi_i| \hat{A} |\psi_j> c_j$

Thus the matrix representation of our operator is: $A_{ij} = <\psi_i| \hat{A} |\psi_j>$ or explicitly:

$$A_{ij} = \int \psi_i^*(x) \hat{A} \psi_j(x) dx$$
In approximation methods, we often write the wave function in terms of a finite-dimensional basis:

The components of $|a>$ in the basis $e_i$, $i=1, 2,..,n$ are:

$$a_i = \langle e_i | a >$$

We can then write the ket $|a>$ as:

$$|a> = \sum_{i=1}^{n} a_i |e_i> = \sum_{i=1}^{n} \langle e_i | a > | e_i > = \left( \sum_{i=1}^{n} | e_i > < e_i | \right) | a >$$

We now identify the unit and projection operators as:

$$I = \left( \sum_{i=1}^{n} | e_i > < e_i | \right) = \sum_{i=1}^{n} \Lambda_i, \quad \Lambda_i = | e_i > < e_i |$$

How about an infinite-dimensional Hilbert space? We can generalize the above equations as shown next.
Assume that the countable set of basis kets $|e_i>$ becomes a continuous variable $|x>$ and the corresponding components of a ket $|a>$ become a continuous function of $x$:

$$a(x) = < x | a >$$

We can then write the ket $|a>$ as:

$$|a> = \int <x | a> |x> dx = \left( \int |x> <x | dx \right) |a>, \quad I = \int |x> <x | dx$$

Similarly, we can write inner products as:

$$<a | b> = \int <a | x> <x | b> dx = \int a^*(x)b(x)dx$$

Working in a different basis (w.g. Fourier space) is easy:

$$<a | b> = \int <a | k> <k | b> dk = \int a^*(k)\hat{b}(k)dk$$

For a general operator $A$, we can also write:

$$<a | A | b> = \int <a | x> <x | A | b> dx = \int a^*(x)Ab(x)dx$$
Unitary Operators

- A linear operator in a Hilbert space can be written as
  \[ \hat{A} = \sum_{i,j} A_{ij} |\psi_i\rangle \langle \psi_j| \]
  where \( \Psi_n \) is any complete basis in the space.

- The identity operator acting on a function leaves the function unchanged:
  \[ \hat{I} = \sum_{i} |\psi_i\rangle \langle \psi_i| \]

- The inverse operator, \( \hat{A}^{-1} \), if it exists, is that operator for which \( \hat{A}^{-1} \hat{A} = \hat{I} \)

- A unitary operator \( \hat{U} \) is an operator for which \( \hat{U}^{-1} = \hat{U}^\dagger \) or equivalently \( \hat{U}^\dagger \hat{U} = \hat{I} \)
  that is, its inverse is its Hermitian transpose (or adjoint).

- A unitary operator acting on a vector conserves the length of the vector. It can be used for coordinate transformations of vectors and operators:
  \[ |f_{\text{new}}\rangle = \hat{U} |f_{\text{old}}\rangle \quad \hat{A}_{\text{new}} = \hat{U} \hat{A}_{\text{old}} \hat{U}^\dagger \]

- A unitary operator conserves the inner product between two vectors (and the length of a vector):
  \[ \langle g_{\text{new}} | f_{\text{new}} \rangle = \langle g_{\text{old}} | f_{\text{old}} \rangle \]
Note that the Hermitian adjoint of a matrix is defined as:

\[
\begin{bmatrix}
  u_{11} & u_{12} & u_{13} & \cdots \\
  u_{21} & u_{22} & u_{23} & \cdots \\
  u_{31} & u_{32} & u_{33} & \cdots \\
  \vdots & \vdots & \vdots & \ddots
\end{bmatrix}^\dagger = 
\begin{bmatrix}
  u_{11}^* & u_{21}^* & u_{31}^* & \cdots \\
  u_{12}^* & u_{22}^* & u_{32}^* & \cdots \\
  u_{13}^* & u_{23}^* & u_{33}^* & \cdots \\
  \vdots & \vdots & \vdots & \ddots
\end{bmatrix}
\]

In matrix or operator multiplication with complex elements, we obtain

\[(\hat{A}\hat{B})^\dagger = \hat{B}^\dagger \hat{A}^\dagger\]

Also note that for matrix/vector multiplication:

\[(\hat{A}|\hat{h}\rangle)^\dagger = \langle \hat{h}|\hat{A}^\dagger\]

Using these identities, we can verify that:

\[
\langle g_{\text{new}} | f_{\text{new}} \rangle = \langle g_{\text{old}} | \hat{U}^\dagger \hat{U} | f_{\text{old}} \rangle = \langle g_{\text{old}} | \hat{U}^{-1} \hat{U} | f_{\text{old}} \rangle = \langle g_{\text{old}} | \hat{I} | f_{\text{old}} \rangle = \langle g_{\text{old}} | f_{\text{old}} \rangle
\]
Using unitary operators to change basis

Suppose that we have a vector (function) $|f_{\text{old}}\rangle$ that is represented, when we express it as an expansion on the functions $\psi_n$, as:

$$|f_{\text{old}}\rangle = \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ \vdots \end{bmatrix}$$

We want to represent $|f\rangle$ in a new set of basis functions $|\phi_i\rangle$:

You can show that the new representation is given as:

$$|f_{\text{new}}\rangle = \hat{U} |f_{\text{old}}\rangle$$

where the unitary operator $\hat{U}$ is defined as:

$$u_{ij} = \langle \phi_i | \psi_j \rangle$$

Note that $|f_{\text{old}}\rangle$ and $|f_{\text{new}}\rangle$ refer to the same vector. It is only the representation that has changed and not the vector itself.
Using unitary operators to change basis

- We need to show that $\hat{U}$ is indeed a unitary operator

$$
(\hat{U}^\dagger \hat{U})_{ij} = \sum_m u_{mi}^* u_{mj} = \sum_m \langle \phi_m | \psi_i \rangle^* \langle \phi_m | \psi_j \rangle \\
= \sum_m \langle \psi_i | \phi_m \rangle \langle \phi_m | \psi_j \rangle = \langle \psi_i | \left( \sum_m \phi_m \langle \phi_m | \right) \psi_j \rangle \\
= \langle \psi_i | \hat{I} | \psi_j \rangle = \langle \psi_i | \psi_j \rangle \\
= \delta_{ij}
$$

- We can similarly transform operators using unitary operators. Using representations of the arbitrary vectors $f$ and $g$ in the old and new bases, we can write:

$$
\langle g_{\text{new}} | \hat{A}_{\text{new}} | f_{\text{new}} \rangle = \langle g_{\text{old}} | \hat{U}^\dagger \hat{A}_{\text{new}} \hat{U} | f_{\text{old}} \rangle
$$

- We can then conclude that: $\hat{A}_{\text{old}} = \hat{U}^\dagger \hat{A}_{\text{new}} \hat{U}$ from which we can then show:

$$
\hat{U} \hat{A}_{\text{old}} \hat{U}^\dagger = (\hat{U} \hat{U}^\dagger) \hat{A}_{\text{new}} (\hat{U}^\dagger \hat{U}) = \hat{A}_{\text{new}}
$$
Let us consider the quantum mechanical state of a particle $\psi$ expanded on the complete orthonormal basis $\psi_n$:

$$|\psi\rangle = \sum_n a_n |\psi_n\rangle \quad \text{with} \quad \sum_n |a_n|^2 = 1$$

Thus if the particle is to be conserved then the sum $\sum_n |a_n|^2$ needs to be retained as the quantum mechanical system evolves (e.g. in time). This sum is just the square of the length of the vector $\psi$.

Hence a unitary operator, which conserves length, will be an appropriate operator for describing changes in that system that conserve the particle.

As an example, it can be shown that the time-evolution operator $\exp(-i\hat{H}t/\hbar)$ when the Hamiltonian does not change with time is unitary!
**Hermitian operators**: A Hermitian operator is one for which \( \hat{M}^\dagger = \hat{M} \)

or equivalently in terms of matrix components \( M_{ij} = M_{ji}^* \)

Let us consider the following calculation \( \langle g | \hat{M} | f \rangle \). Since this is a scalar,

\[
(\langle g | \hat{M} | f \rangle)^\dagger = (\langle g | \hat{M} | f \rangle)^*
\]

from which we can write:

\[
(\langle g | \hat{M} | f \rangle)^* = (\langle g | \hat{M} | f \rangle)^\dagger = [\langle g | (\hat{M} | f \rangle)]^\dagger
\]

(\text{using } (AB)^\dagger = B^\dagger A^\dagger. )

\[
= (\hat{M} | f \rangle)^\dagger (\langle g |)^\dagger = (| f \rangle)^\dagger \hat{M}^\dagger (\langle g |)^\dagger
\]

\[
= \langle f | \hat{M}^\dagger | g \rangle
\]

Using the Hermiticity of \( \hat{M} \), we conclude that:

\[
\langle f | \hat{M} | g \rangle = (\langle g | \hat{M} | f \rangle)^*
\]

Equivalently, for functions of a spatial variable,

\[
\int g^* (x) \hat{M} f (x) \, dx = \int \{ \hat{M} g (x) \}^* f (x) \, dx
\]
Is the derivative operator linear?

\[ \hat{A}_1 f_1(x) = \frac{df_1(x)}{dx} \]

\[ \hat{A}_1 (c_1 f_1 + c_2 f_2) = \frac{d}{dx} (c_1 f_1 + c_2 f_2) \]

\[ = c_1 \frac{d}{dx} f_1 + c_2 \frac{d}{dx} f_2 \]

\[ = c_1 \hat{A}_1 f_1 + c_2 \hat{A}_1 f_2. \]

How about Hermitian?

\[ \langle f_1 | \hat{A}_1 | f_2 \rangle = \int_a^b f_1^*(x) \frac{d}{dx} f_2(x) \, dx \]

\[ = [f_1^*(x) f_2(x)]_a^b - \int_a^b \left[ \frac{d}{dx} f_1^*(x) \right] f_2(x) \, dx \]

\[ = -\int_a^b f_2(x) \frac{d}{dx} f_1^*(x) \, dx \]

\[ = -\left[ \int_a^b f_2^*(x) \frac{d}{dx} f_1(x) \, dx \right]^* \]

\[ = -\langle f_2 | \hat{A}_1 | f_1 \rangle^*. \]
The eigenfunctions of Hermitian operators are orthonormal and the eigenvalues are real. Indeed consider two eigenvectors as follows:

\[ \hat{A} f_n = a_n f_n \]
\[ \hat{A} f_m = a_m f_m \]

From these equations we can write the following:

\[ \langle f_m | \hat{A} | f_n \rangle = \langle f_m | \hat{A} | f_n \rangle = \langle f_m | a_n f_n \rangle = a_n \langle f_m | f_n \rangle \]
\[ \langle f_m | \hat{A} | f_n \rangle = \langle f_n | \hat{A} | f_m \rangle^* = \langle f_n | \hat{A} | f_m \rangle^* = \langle f_n | a_m f_m \rangle^* = a_m^* \langle f_n | f_m \rangle^* = a_m^* \langle f_m | f_n \rangle. \]

Combination of the two equations leads to

\[ (a_n - a_m^*) \langle f_m | f_n \rangle = 0 \]

For \( n = m \), we conclude that the eigenvalue \( a_n \) is real:

For \( n \neq m \)

\[ \langle f_m | f_n \rangle = 0 \quad \text{for} \quad a_m \neq a_n. \]

Finally with normalization of the eigenvectors:

\[ \langle f_m | f_n \rangle = \delta_{n,m} \]
When working with the Hamiltonian, we have often more than one eigenvector corresponding to the same eigenvalue.

For example, for the H-atom, the two $2s$ and six $2p$ states (including spin) have all the same energy.

In the general case, any linear combination of these will also be an eigenfunction, e.g. the $2s\sigma$, $2p_x\sigma$, $(2p_x+2p_y)\sigma$ and $(2p_x+2p_y+2p_z)\sigma$ (with $\sigma$ being either the $\alpha$ or $\beta$ spin-function) forms a set of eight functions that are also eigenfunctions of the Hamiltonian. These eigenfunctions are not orthogonal but can be made orthogonal (for example by using the Gram-Schmidt algorithm).

So in general we can assume that we have a set of eigenvectors such that:

$$\langle f_m | f_n \rangle = 0 \quad \text{for} \quad m \neq n.$$

Or with normalization of the eigenvectors:

$$\langle f_m | f_n \rangle = \delta_{n,m}$$
The eigenfunctions of a bounded Hermitian operator form a complete set: Thus for any function \( g \), we can approximate it in terms of the eigenvectors as follows:

\[
g = \sum_n c_n f_n.
\]

For example, the H-atom eigenfunctions can be used to expand any function with arguments the three spatial coordinates and two spin variables \((+1/2, -1/2)\).

To obtain the coefficients \( c_n \), we use a projection approach as follows:

\[
\langle f_m | g \rangle = \sum_n c_n \langle f_m | f_n \rangle \quad \Rightarrow \quad c_m = \langle f_m | g \rangle
\]

**Hermitian operators and measurable quantities**: Physically measurable quantities in quantum mechanics can be represented by Hermitian operators.
Consider two commuting linear Hermitian operators: 

\[ [\hat{A}, \hat{B}] = 0. \]

It can be shown that they both share a common set of eigenvectors, i.e.

\[
\hat{A} f_n = a_n f_n \\
\hat{B} f_n = b_n f_n.
\]

To prove this, define the following operators:

\[
\hat{C}_+ = \hat{A} + i\hat{B} \\
\hat{C}_- = \hat{A} - i\hat{B}.
\]

These operators are each others adjoint, indeed:

\[
\langle f_1|\hat{C}_+|f_2 \rangle = \langle f_1|\hat{A} + i\hat{B}|f_2 \rangle = \langle f_1|\hat{A}|f_2 \rangle + i\langle f_1|\hat{B}|f_2 \rangle \\
= \langle f_2|\hat{A}|f_1 \rangle^* + i\langle f_2|\hat{B}|f_1 \rangle^* = \langle f_2|\hat{A}|f_1 \rangle^* - \langle f_2|i\hat{B}|f_1 \rangle^* \\
= \langle f_2|\hat{A} - i\hat{B}|f_1 \rangle^* = \langle f_2|\hat{C}_-|f_1 \rangle^*.
\]

Also \( C_+ \) and \( C_- \) commute:
C_+ and C_- commute:

\[
\left[ \hat{C}_+, \hat{C}_- \right] = [\hat{A} + i\hat{B}, \hat{A} - i\hat{B}] = (\hat{A} + i\hat{B})(\hat{A} - i\hat{B}) - (\hat{A} - i\hat{B})(\hat{A} + i\hat{B}) \\
= \hat{A}\hat{A} + i\hat{B}\hat{A} - i\hat{A}\hat{B} - \hat{B}\hat{B} + i\hat{B}\hat{A} - i\hat{A}\hat{B} \\
= 2i[\hat{B}, \hat{A}] = 0.
\]

Can be shown that the eigenfunctions of \( \hat{C}_+ \) and \( \hat{C}_- \) form a complete set.

Let us consider the eigenfunctions of \( \hat{C}_+ \):

\[
\hat{C}_+ g_n = c_n g_n
\]

Since \( c_n \) is a constant, we can write:

\[
\langle f_2 | \hat{C}_- - c_n^* | f_1 \rangle^* = \langle f_1 | \hat{C}_+ - c_n | f_2 \rangle = \langle f_1 | (\hat{C}_+ - c_n) f_2 \rangle \\
= \langle (\hat{C}_- - c_n^*) f_2 | f_1 \rangle^*.
\]

In the first 2 expressions above, insert

\[
f_1 = g_n \\
f_2 = (\hat{C}_- - c_n^*) g_n
\]
We thus obtain the following:

\[
((\hat{C}_- - c_n^*) g_n | \hat{C}_- - c_n^* | g_n)^* = \langle g_n | (\hat{C}_+ - c_n)(\hat{C}_- - c_n^*) g_n \rangle \\
= \langle g_n | (\hat{C}_+ - c_n)(\hat{C}_- - c_n^*) | g_n \rangle
\]

Since \( \hat{C}_+ \) and \( \hat{C}_- \) commute, so does \( \hat{C}_+ - c_n \) and \( \hat{C}_- - c_n^* \). So from the eq. above we can write:

\[
((\hat{C}_- - c_n^*) g_n | \hat{C}_- - c_n^* | g_n)^* = \langle g_n | (\hat{C}_- - c_n^*)(\hat{C}_+ - c_n) | g_n \rangle.
\]

The rhs vanishes because \( \hat{C}_+ g_n = c_n g_n \). Thus \( \hat{C}_- g_n = c_n^* g_n \).

So \( \hat{C}_+ \) and \( \hat{C}_- \) share the same eigenvectors but their eigenvalues are the complex of each other

\[
\hat{C}_+ g_n = (\hat{A} + i\hat{B}) g_n = c_n g_n \\
\hat{C}_- g_n = (\hat{A} - i\hat{B}) g_n = c_n^* g_n
\]
Commuting operators share the same eigenvectors

- The sum and the difference of these two eqs gives the following:

\[ \hat{A}g_n = \frac{1}{2} [c_n + c_n^*]g_n \]
\[ \hat{B}g_n = \frac{1}{2i} [c_n - c_n^*]g_n \]

- Thus there is the same complete set of eigenfunctions for both \( A \) and \( B \) operators.

The eigenvalues are given from above as

\[ \frac{1}{2} [c_n + c_n^*] \]

and

\[ \frac{1}{2i} [c_n - c_n^*] \]
Where one will encounter commuting operators?

- A common place where commuting operators come to place is when one of them is the Hamiltonian and the other a symmetry operator:

- Consider for example one of the symmetry operations for the benzyne molecule: A $60^\circ$ rotation around the six-fold axis:

![Diagram of benzyne molecule]

- The symmetry operator and the Hamiltonian $H$ commute, i.e. we don’t have to modify the electronic coordinates when we rotate by $60^\circ$!

- We thus attribute to each eigenfunction of $H$ not only an energy but also a label that describes how it transforms under the symmetry operator.
When the symmetry operator \( \hat{O} \) is a mirror operation or an inversion, we use the symbols \( g \) (symmetric) and \( u \) (anti-symmetric) wrt to the symmetry operation.

- \( g \) or \( u \) tells us whether the eigenvalue \( o \) of \( \hat{O} \) is +1 or -1.

\[
\hat{O} \Psi = o \Psi
\]

- For the 60° rotation in the benzyne molecule, the eigenvalue will not be +1 or -1 but like in any symmetry operation the following holds:

\[
|o| = 1
\]

- Note that symmetry operators are not Hermitian – but usually the operators that are commuting with \( H \) are Hermitian.

- The commutation of \( H \) with another operator is important in the H-atom. Here the quantum number \( n \) describes the eigenvalues of \( H \), whereas \( l \) and \( m \) describe the eigenvalues of the operators \( L^2 \) (angular momentum) and of its z-component \( (L_z) \).

- Similarly for the spin operators \( \hat{s}^2 \) and \( \hat{s}_z \), with eigenvalues \( s \) and \( m_s \).
The commutator operator is used often in QM: $A f(x,y) = f(y,x)$

Note that we are interested in operators that operate on discrete functions (spin variables) and continuous functions.

For example, let us consider the function that we operate to be the wavefunction $\Psi$ of a single electron. In position representation it depends on three position coordinates and one spin coordinate. Often each position coordinate may take any value between $-\infty$ and $+\infty$, whereas the spin coordinate can only take the two values $-1/2$ and $+1/2$. 
Recall the definitions of the mean and the variance of a measurable quantity associated with a Hermitian operator \( \hat{A} \) when the state of the system is \( |f> \):

\[
\bar{A} = \langle A \rangle = \langle f | \hat{A} | f \rangle \quad \quad \Delta \hat{A} = \hat{A} - \bar{A}
\]

We examine the variance of \( A \) (expectation value of \( (\Delta \hat{A})^2 \)). Let \( |f> = \sum_i c_i |\psi_i> \):

\[
\langle (\Delta \hat{A})^2 \rangle = \left( \sum_i c_i^* \langle \psi_i | \right) (\hat{A} - \bar{A})^2 \left( \sum_j c_j |\psi_j> \right)
\]

\[
= \left( \sum_i c_i^* \langle \psi_i | \right) (\hat{A} - \bar{A}) \left( \sum_j c_j (A_j - \bar{A}) |\psi_j> \right)
\]

\[
= \left( \sum_i c_i^* \langle \psi_i | \right) \left( \sum_j c_j (A_j - \bar{A})^2 |\psi_j> \right)
\]

\[
= \sum_i |c_i|^2 (A_i - \bar{A})^2
\]

Recall that \( |c_i|^2 \) are the probabilities for the system to be found on measurement to be on state \( i \).
The quantity \((A_i - \bar{A})^2\) represents the squared deviation of the value of the quantity \(A\) from its average value. We then define:

\[
(\Delta A)^2 = \langle (\Delta \hat{A})^2 \rangle = \langle (\hat{A} - \bar{A})^2 \rangle = \langle f | (\hat{A} - \bar{A})^2 | f \rangle
\]

This is the mean squared deviation we will find for the quantity \(A\) on repeatedly measuring the system prepared in state \(|f\rangle\).

The square root of the variance (std) gives a well-defined measure of the width of a distribution.

Let us now consider another quantity \(B\) associated with the Hermitian operator \(\hat{B}\). As before, we can write:

\[
\bar{B} = \langle B \rangle = \langle f | \hat{B} | f \rangle \quad \quad (\Delta B)^2 = \langle (\Delta \hat{B})^2 \rangle = \langle (\hat{B} - \bar{B})^2 \rangle = \langle f | (\hat{B} - \bar{B})^2 | f \rangle
\]

We can now calculate the uncertainty in the measurements of \(A\) and \(B\) when the system is in the state \(|f\rangle\).

N. Zabaras (1/30/2012)
Define the following function: $$G(\alpha) = \langle (\alpha \Delta \hat{A} - i \Delta \hat{B}) f | (\alpha \Delta \hat{A} - i \Delta \hat{B}) f \rangle \geq 0$$

Using Hermiticity of the operators, we can see that:

$$G(\alpha) = \langle f | (\alpha \Delta \hat{A} - i \Delta \hat{B})^\dagger (\alpha \Delta \hat{A} - i \Delta \hat{B}) | f \rangle$$

$$= \langle f | (\alpha \Delta ^{\hat{A}} + i \Delta ^{\hat{B}})^\dagger (\alpha \Delta ^{\hat{A}} - i \Delta ^{\hat{B}}) | f \rangle$$

$$= \langle f | (\alpha \Delta ^{\hat{A}} + i \Delta ^{\hat{B}})(\alpha \Delta ^{\hat{A}} - i \Delta ^{\hat{B}}) | f \rangle$$

$$= \langle f | \alpha^2 (\Delta ^{\hat{A}})^2 + (\Delta ^{\hat{B}})^2 - i\alpha (\Delta ^{\hat{A}} \Delta ^{\hat{B}} - \Delta ^{\hat{B}} \Delta ^{\hat{A}}) | f \rangle$$

$$= \langle f | \alpha^2 (\Delta ^{\hat{A}})^2 + (\Delta ^{\hat{B}})^2 - i\alpha [\Delta ^{\hat{A}}, \Delta ^{\hat{B}}] | f \rangle$$

$$= \langle f | \alpha^2 (\Delta ^{\hat{A}})^2 + (\Delta ^{\hat{B}})^2 + \alpha \hat{C} | f \rangle$$

$$= \alpha^2 (\Delta A)^2 + (\Delta B)^2 + \alpha \bar{C}$$

$$= (\Delta A)^2 \left[ \alpha + \frac{\bar{C}}{2(\Delta A)^2} \right]^2 + (\Delta B)^2 - \frac{(\bar{C})^2}{4(\Delta A)^2} \geq 0$$
Uncertainty Principle

- The last equation:

\[ G(\alpha) = (\Delta A)^2 \left[ \alpha + \frac{C}{2(\Delta A)^2} \right]^2 + (\Delta B)^2 - \frac{(C)^2}{4(\Delta A)^2} \geq 0 \]

needs to be true for any \( \alpha \), thus for

\[ \alpha = -\frac{C}{2(\Delta A)^2} \]

- We can finally conclude that:

\[ \frac{(\Delta A)^2}{(\Delta B)^2} \geq \frac{(C)^2}{4} \]

- This is the uncertainty principle. It tells us the relative minimum size of the uncertainties in two quantities if we perform a measurement.

- Only if the operators associated with the two quantities commute (and hence give \( C = 0 \)) is it possible for there to be no width to the distribution of results for both quantities.
Let us consider the commutator of the momentum and position operators:

\[ [\hat{p}, \hat{x}]|f\rangle = -i\hbar \left( \frac{d}{dx} x - x \frac{d}{dx} \right)|f\rangle \]

\[ = -i\hbar \left\{ \frac{d}{dx} (x|f\rangle) - x \frac{d}{dx} |f\rangle \right\} \]

\[ = -i\hbar \left| f\rangle + x \frac{d}{dx} |f\rangle - x \frac{d}{dx} |f\rangle \right| \]

\[ = -i\hbar |f\rangle \]

Since \(|f\rangle\) is arbitrary, we conclude that: \[ [\hat{p}, \hat{x}] = -i\hbar \], i.e. \[ \hat{C} = -\hbar \]

Thus our uncertainty principle, \( \frac{(\Delta A)^2}{4} \frac{(\Delta B)^2}{(\bar{C})^2} \geq \frac{(\bar{C})^2}{4} \) becomes:

\[ (\Delta p_x)^2 (\Delta x)^2 \geq \frac{\hbar^2}{4} \]

\[ \Rightarrow \Delta p_x \Delta x \geq \frac{\hbar}{2} \]

The more precise the position of the wave is, the less precise its wavelength (\( \lambda = h/p \)) and vice-versa.
Let us start with the time-dependent Schrödinger equation:

\[ \hat{H} \Psi_0 = i\hbar \frac{\partial \Psi_0}{\partial t} \]

Note that \( \Psi_0 \) depends on time \( (t) \) and on all other (position and spin) coordinates \( (\vec{x}) \).

Let’s write the time-dependent solution using separation of variables

\[ \Psi_0(\vec{x}, t) = \Psi(\vec{x})A(t) \]

Inserting into the Schrödinger equation leads to the following:

\[ \hat{H}[\Psi(\vec{x})A(t)] = i\hbar \frac{\partial \Psi(\vec{x})A(t)}{\partial t} \]

From which we can conclude that

\[ \frac{\hat{H} \Psi(\vec{x})}{\Psi(\vec{x})} = i\hbar \frac{\partial A(t)}{A(t)} \]
The two sides are identical for all $\vec{x}$ and $t$, so we can set them equal to a constant $E$

$$\frac{\hat{H}\psi(\vec{x})}{\psi(\vec{x})} = i\hbar \frac{\partial A(t)}{\partial t} = E$$

This leads to

$$i\hbar \frac{\partial A(t)}{\partial t} = E \cdot A(t)$$

From which (taking the integration constant as 1) we conclude:

$$A(t) = \exp \left[ -i \frac{Et}{\hbar} \right]$$

The other equation is of course the time-independent Schrödinger equation

$$\hat{H}\psi = E\psi$$
Spin Dependence

- Note that in the non-relativistic case, \( \hat{H} \) contains no explicit spin dependence.

- However for a system of \( N \) particles, we have \( N \)-position vectors and \( N \)-spin variables, thus:

\[
\Psi(\vec{x}) = \Psi(\vec{r}_1, \vec{r}_2, \vec{r}_3, \ldots, \vec{r}_N, \sigma_1, \sigma_2, \sigma_3, \ldots, \sigma_N) \equiv \Psi(\vec{r}, \vec{\sigma})
\]

- In this case, we can assume that \( \Psi(\vec{r}, \vec{\sigma}) \) can be written as a product of position and spin-dependent functions as follows:

\[
\Psi(\vec{r}, \vec{\sigma}) = \psi(\vec{r})\Theta(\vec{\sigma})
\]

- Upon insertion of this equation in \( \hat{H}\Psi = E\Psi \), we note that the spin part is cancelled out (\( \hat{H} \) does not contain a spin part)