1 Introduction (a remind)

Example. Evaluate time in which a surface of 1 atom will gain in photo-electric effect energy of 1 eV from the power source of 1 W from the distance of 1 m. We assume that light transmits in all directions equally and that the surface of single atom has area of approximately one square with its length of a side equal to $a = 1\text{Å}$. Energy necessary to invoke the photo-electric effect amounts 1 eV.

Solution.

This can be solved from proportion. Assuming that light transmits in all directions equally we can say that within $r = 1\text{m}$ from the source the surface of a sphere achieves 1 J of energy within 1 second (1 Wat = 1 J/1 s). So we are looking for the amount of energy which absorbs the surface of a square.

$$\frac{1\text{J}}{x} = \frac{4\pi r^2}{a^2}$$  \hspace{1cm} (1.1)

$$x = \frac{10^{-20}\text{m}^2 \cdot 1\text{J}}{4\pi r^2} = 10^{-21}\text{J}.$$  

To invoke the photo-electric effect one needs 1 eV = $10^{-19}\text{J}$, which is approx. 100-time more. Thus one can conclude, that after 100 s of light transmission for a metal plate the current will flow after approx. 100 s. While from experiment we know that the process is immediate ($t \approx 10^{-19}\text{s}$).

Example. Find wavelength for moving metal speck with velocity 1 cm/s which density equals $10\text{g/cm}^3$ and which radius equals 0.01 m.

Solution.

$$\lambda = \frac{h}{p}$$
$$p = m \cdot v$$
$$m = \frac{V \cdot d}{\frac{4}{3}\pi r^3}$$
2. Operators

Thus the wavelength is very short. We even don’t posses any physical apparatus with such distances.

\[ \begin{align*}
\lambda &= \frac{h}{4\pi r^2 dv} = \frac{3h}{4\pi r^2 dv} \approx \frac{3 \cdot 6.63 \cdot 10^{-34} \text{ J} \cdot \text{s}}{4 \cdot 3.14 \cdot 10^{-6} \text{ m}^3 \cdot 4 \text{ kg/m}^3 \cdot 10^{-2} \text{ m/s}} = \frac{19.89 \cdot 10^{-34} \text{ J} \cdot \text{s}}{12.56 \cdot 10^{-4}} = \\
&= 1.58 \cdot 10^{-30} \text{ m}
\end{align*} \]

2 Operators

Find components of the angular momentum operator.

Angular momentum is a vector: \( \vec{L} = \vec{r} \times \vec{p} \).

\[ \vec{L} = \begin{vmatrix}
\hat{i} & \hat{j} & \hat{k} \\
x & y & z \\
p_x & p_y & p_z
\end{vmatrix} = \hat{i}(yp_z - zp_y) + \hat{j}(zp_x - xp_z) + \hat{k}(xp_y - yp_x) = L_x\hat{i} + L_y\hat{j} + L_z\hat{k} \quad (2.1) \]

Thus, the below operator equations are valid

\[ \begin{align*}
\hat{L}_x &= \hat{y}\hat{p}_z - \hat{z}\hat{p}_y = y\left(-i\hbar \frac{\partial}{\partial z}\right) - z\left(-i\hbar \frac{\partial}{\partial y}\right) = -i\hbar \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y}\right) \\
\hat{L}_y &= \hat{z}\hat{p}_x - \hat{x}\hat{p}_z = -i\hbar \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z}\right) \\
\hat{L}_z &= \hat{x}\hat{p}_y - \hat{y}\hat{p}_x = -i\hbar \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x}\right) \quad (2.2)
\end{align*} \]

Find the \([\hat{L}_x, \hat{L}_y]\) commutator.

\[ \begin{align*}
[\hat{L}_x, \hat{L}_y] \varphi &= (\hat{L}_x\hat{L}_y - \hat{L}_y\hat{L}_x) \varphi = \hat{L}_x\hat{L}_y\varphi - \hat{L}_y\hat{L}_x\varphi = \\
&= \hat{L}_x(-i\hbar \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y}\right)) - \hat{L}_y\left(-i\hbar \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y}\right)\right) = \\
&= (-i\hbar)^2 \left( \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y}\right) \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y}\right) - \left(x \frac{\partial}{\partial z} - z \frac{\partial}{\partial x}\right) \left(x \frac{\partial}{\partial z} - z \frac{\partial}{\partial x}\right)\right) = \\
&= (-i\hbar)^2 \left[ y \frac{\partial}{\partial z} \left(z \frac{\partial}{\partial z}\right) + y \frac{\partial}{\partial z} \left(x \frac{\partial}{\partial z}\right) - z \frac{\partial}{\partial z} \left(x \frac{\partial}{\partial z}\right) + z \frac{\partial}{\partial z} \left(y \frac{\partial}{\partial z}\right) \right] + \\
&\quad + \left(y \frac{\partial}{\partial z} \left(x \frac{\partial}{\partial z}\right) + x \frac{\partial}{\partial z} \left(y \frac{\partial}{\partial z}\right) - z \frac{\partial}{\partial z} \left(y \frac{\partial}{\partial z}\right) \right) = (-i\hbar)^2 \left[ y \frac{\partial}{\partial z} \left(1 \frac{\partial}{\partial z} + z \frac{\partial}{\partial z}\right) + \\
&\quad - x \frac{\partial}{\partial z} \left(1 \frac{\partial}{\partial z} + y \frac{\partial}{\partial z}\right) \right] = (-i\hbar)^2 \left[ y \frac{\partial}{\partial z} \left(x \frac{\partial}{\partial z}\right) + x \frac{\partial}{\partial z} \left(y \frac{\partial}{\partial z}\right) - z \frac{\partial}{\partial z} \left(y \frac{\partial}{\partial z}\right) \right] = (-i\hbar)^2 \left( y \left(x \frac{\partial}{\partial z} - z \frac{\partial}{\partial z}\right) \varphi = -i\hbar \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial z}\right) \varphi = i\hbar\hat{L}_z\varphi \right)
\end{align*} \]

Therefore

\[ \begin{align*}
&= (-i\hbar)^2 \left( y \left(x \frac{\partial}{\partial z} - z \frac{\partial}{\partial z}\right) \varphi = (-i\hbar)^2 \left( y \left(x \frac{\partial}{\partial z} - z \frac{\partial}{\partial z}\right) \varphi = i\hbar\hat{L}_z\varphi \right)
\end{align*} \]
\[ [\hat{L}_x, \hat{L}_y] = i\hbar \hat{L}_z \] (2.4)

The above results can be easily memorized by the rule explained at the figure 1. One can find, for instance

\[ [\hat{L}_y, \hat{L}_z] = i\hbar \hat{L}_x \]
\[ [\hat{L}_z, \hat{L}_x] = i\hbar \hat{L}_y \]
\[ [\hat{L}_x, \hat{L}_z] = -i\hbar \hat{L}_y \] (2.5)

**Figure 1.** When the order of angular momentum operators in the commutator is clockwise then the resulting angular momentum operator is multiplied by \(+i\hbar\), otherwise it must be multiplied by \(-i\hbar\).

Check if the \(\hat{L}^2\) and \(\hat{L}_z\) operators commute each other.

\[
\begin{align*}
[\hat{L}^2, \hat{L}_z] &= \hat{L}^2 \hat{L}_z - \hat{L}_z \hat{L}^2 = (\hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2) \hat{L}_z - \hat{L}_z (\hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2) = \hat{L}_x \hat{L}_x \hat{L}_z + \\
&+ \hat{L}_y \hat{L}_y \hat{L}_z + \hat{L}_z^3 - \hat{L}_z \hat{L}_x \hat{L}_x - \hat{L}_z \hat{L}_y \hat{L}_y - \hat{L}_z^3 = \hat{L}_x \hat{L}_x \hat{L}_z - \hat{L}_y \hat{L}_x \hat{L}_x + \hat{L}_x \hat{L}_z \hat{L}_x + \\
&- \hat{L}_y \hat{L}_y \hat{L}_z - \hat{L}_y \hat{L}_y \hat{L}_z + \hat{L}_y \hat{L}_x \hat{L}_x + \hat{L}_y \hat{L}_z \hat{L}_x - \hat{L}_x \hat{L}_y \hat{L}_y - \hat{L}_x \hat{L}_z \hat{L}_y - \hat{L}_x \hat{L}_z \hat{L}_x - \hat{L}_y \hat{L}_z \hat{L}_y - \hat{L}_x \hat{L}_z \hat{L}_y = \hat{L}_x \hat{L}_x \hat{L}_z - \hat{L}_z \hat{L}_x \hat{L}_x - \hat{L}_y \hat{L}_y \hat{L}_z - \hat{L}_y \hat{L}_y \hat{L}_z + \\
&+ (\hat{L}_x \hat{L}_z - \hat{L}_z \hat{L}_x) \hat{L}_x + \hat{L}_y (\hat{L}_x \hat{L}_z - \hat{L}_z \hat{L}_x) + (\hat{L}_y \hat{L}_z - \hat{L}_z \hat{L}_y) \hat{L}_y = \hat{L}_x \hat{L}_x \hat{L}_z - \hat{L}_z \hat{L}_x \hat{L}_x - \hat{L}_y \hat{L}_y \hat{L}_z - \hat{L}_y \hat{L}_y \hat{L}_z \\
&+ [\hat{L}_x, \hat{L}_z] \hat{L}_x + [\hat{L}_y, \hat{L}_z] \hat{L}_y + [\hat{L}_z, \hat{L}_x] \hat{L}_y \hat{L}_z \hat{L}_y = \hat{L}_x (-i\hbar \hat{L}_y) + \hat{L}_y (-i\hbar \hat{L}_x) + \hat{L}_x (i\hbar \hat{L}_y) + \hat{L}_y (i\hbar \hat{L}_x) + \\
&+ (i\hbar \hat{L}_x) \hat{L}_y = -i\hbar \hat{L}_x \hat{L}_y - i\hbar \hat{L}_x \hat{L}_y + i\hbar \hat{L}_x \hat{L}_y + i\hbar \hat{L}_x \hat{L}_y = 0
\end{align*}
\] (2.6)

In a similar way one can prove that the \(\hat{L}_x\) and \(\hat{L}_y\) operators commute with the \(\hat{L}^2\) operator too.

The \(\hat{L}_+\) and \(\hat{L}_-\) operators have the following definitions

\[ \hat{L}_+ = \hat{L}_x + i\hat{L}_y \]
\[ \hat{L}_- = \hat{L}_x - i\hat{L}_y \] (2.7)

Find the commutator \([\hat{L}_+, \hat{L}_-]\).

\[
\begin{align*}
[\hat{L}_+, \hat{L}_-] &= \hat{L}_+ \hat{L}_- - \hat{L}_- \hat{L}_+ = (\hat{L}_x + i\hat{L}_y) (\hat{L}_x - i\hat{L}_y) - (\hat{L}_x - i\hat{L}_y) (\hat{L}_x + i\hat{L}_y) = \hat{L}_z^2 - i\hat{L}_x \hat{L}_y + \\
&+ i\hat{L}_y \hat{L}_x - i\hat{L}_z^2 - i\hat{L}_x \hat{L}_y + i\hat{L}_y \hat{L}_x + i\hat{L}_z^2 = -2i\hat{L}_x \hat{L}_y + 2i\hat{L}_y \hat{L}_x = -2i(\hat{L}_x \hat{L}_y - \hat{L}_y \hat{L}_x) = \\
&= -2i(\hat{L}_x, \hat{L}_y) = -2i(i\hbar \hat{L}_z) = 2\hbar \hat{L}_z
\end{align*}
\] (2.8)

Calculate the \([\hat{L}_z, \hat{L}_+]\) and \([\hat{L}_z, \hat{L}_-]\) commutators.

\[
\begin{align*}
[\hat{L}_z, \hat{L}_+] &= \hat{L}_z \hat{L}_+ - \hat{L}_+ \hat{L}_z = \hat{L}_z (\hat{L}_x + i\hat{L}_y) - (\hat{L}_x + i\hat{L}_y) \hat{L}_z = \hat{L}_z \hat{L}_x + i\hat{L}_z \hat{L}_y - \hat{L}_x \hat{L}_z - i\hat{L}_y \hat{L}_z = \\
&= (\hat{L}_z \hat{L}_x - \hat{L}_x \hat{L}_z) + i(\hat{L}_z \hat{L}_y - \hat{L}_y \hat{L}_z) = [\hat{L}_z, \hat{L}_x] + i[\hat{L}_z, \hat{L}_y] = i\hbar \hat{L}_y + i(-i\hbar \hat{L}_x) = \\
&= \hbar (\hat{L}_x + i\hat{L}_y) = \hbar \hat{L}_x
\end{align*}
\] (2.9)
\[
\begin{align*}
[\hat{L}_z, \hat{L}_-] &= \hat{L}_z \hat{L}_- - \hat{L}_- \hat{L}_z = \hat{L}_z (\hat{L}_x - i \hat{L}_y) - (\hat{L}_x - i \hat{L}_y) \hat{L}_z = \hat{L}_z \hat{L}_x - i \hat{L}_z \hat{L}_y - \hat{L}_x \hat{L}_z + i \hat{L}_y \hat{L}_z = \\
&= (\hat{L}_z \hat{L}_x - \hat{L}_x \hat{L}_z) - i (\hat{L}_z \hat{L}_y - \hat{L}_y \hat{L}_z) = [\hat{L}_z, \hat{L}_x] - i [\hat{L}_z, \hat{L}_y] = i \hbar \hat{L}_y - i (-i \hbar \hat{L}_x) = \\
&= -\hbar \hat{L}_x + i \hbar \hat{L}_y = -\hbar (\hat{L}_x - i \hat{L}_y) = -\hbar \hat{L}_-
\end{align*}
\] (2.10)

Find the result of acting of \( \hat{L}_z \) operator on an hydrogen atom orbital \( \varphi_{n\ell m} \).

We can utilize the commutator \([\hat{L}_z, \hat{L}_+] = \hbar \hat{L}_+ \). Thus

\[
\hat{L}_z \hat{L}_+ - \hat{L}_+ \hat{L}_z = \hbar \hat{L}_+
\] (2.11)

\[
\hat{L}_z \hat{L}_+ = \hat{L}_+ \hat{L}_z + \hbar \hat{L}_+
\] (2.12)

Moreover

\[
[\hat{L}_z, \hat{L}_+] \varphi_{n\ell m} = \hbar \hat{L}_+ \varphi_{n\ell m}
\] (2.13)

\[
\hat{L}_z \hat{L}_+ \varphi_{n\ell m} = \hat{L}_+ \hat{L}_z \varphi_{n\ell m} + \hbar \hat{L}_+ \varphi_{n\ell m}
\] (2.14)

\[
\hat{L}_z \varphi_{n\ell m} = m \hbar \varphi_{n\ell m}
\] (2.15)

where the \( m \) is an integer number. Thus

\[
\begin{align*}
\hat{L}_z \hat{L}_+ \varphi_{n\ell m} &= m \hbar \hat{L}_+ \varphi_{n\ell m} + \hbar \hat{L}_+ \varphi_{n\ell m} \\
\hat{L}_z (\hat{L}_+ \varphi_{n\ell m}) &= (m + 1) \hbar (\hat{L}_+ \varphi_{n\ell m})
\end{align*}
\] (2.16) (2.17)

So the function \( \hat{L}_+ \varphi_{n\ell m} \) is an eigenfunction of the \( \hat{L}_z \) operator with eigenvalue which is higher by \( \hbar \) in comparison to the \( \varphi_{n\ell m} \) function. One can say it corresponds to the function \( \varphi_{n\ell m+1} \). The \( \hat{L}_+ \) operator is called the raising operator. Analogously one can find the \( \hat{L}_- \) decreases the eigenvalue of \( \hat{L}_z \) operator by \( \hbar \) value and the \( \hat{L}_- \) operator is called the decreasing operator.

Example.
Check if the operator \( \hat{A} = x \) is hermitian.

Solution. The condition is now

\[
\int_{-\infty}^{\infty} \psi^*(x) x \phi(x) dx = \int_{-\infty}^{\infty} [x \psi(x)]^* \phi(x) dx
\]

Because

\[
\forall x \in \mathbb{R} \ [x \psi(x)]^* = x \psi^*(x)
\]

then both sides of the equation are equal and \( x \) is a hermitian operator.

Example.
Check if the operator \( \hat{A} = \frac{d}{dx} \) is hermitian.

\[
\int_{-\infty}^{\infty} \psi^*(x) \frac{d}{dx} \phi(x) dx = \int_{-\infty}^{\infty} \left[ \frac{d}{dx} \psi(x) \right]^* \phi(x) dx
\]

Left side
We must first calculate all necessary derivatives.

\[
\int_{-\infty}^{\infty} \psi^*(x) \frac{d}{dx} \phi(x) dx = \begin{cases} f(x) = \psi^*(x), f'(x) = \left[ \frac{d\psi(x)}{dx} \right]^* \\ g'(x) = \frac{d\phi(x)}{dx}, g(x) = \phi(x) \end{cases} = \psi^*(x) \phi(x) \bigg|_{-\infty}^{\infty} - \int_{-\infty}^{0} \left[ \frac{d\psi(x)}{dx} \right]^* \phi(x) dx = -\int_{-\infty}^{\infty} \left[ \frac{d\psi(x)}{dx} \right]^* \phi(x) dx
\]

what means that the $\frac{\partial}{\partial x}$ is not hermitian operator. It is easy to check now, that the $\hat{B} = i \frac{\partial}{\partial x}$ is a hermitian operator.

Figure 2. Spherical: $r, \theta, \varphi$, and cartesian: $x, y, z$, coordinates. The $\varphi$ is called azimuthal while the $\theta$ is called polar angle. $0 \geq \varphi < 2\pi, 0 < \theta \leq \pi, 0 \leq r < +\infty$.

\[
x = r \sin \theta \cos \varphi \\
y = r \sin \theta \sin \varphi \\
z = r \cos \theta
\]

(2.18)

\[
r = \sqrt{x^2 + y^2 + z^2} \\
\varphi = \arctan \frac{y}{x} \\
\theta = \arccos \frac{z}{\sqrt{x^2 + y^2 + z^2}}
\]

(2.19)

Find the $\frac{\partial}{\partial x}, \frac{\partial}{\partial y}$ and $\frac{\partial}{\partial z}$ operators in spherical coordinates.

The cartesian coordinates are in general functions of spherical coordinates.

\[
x = x(r, \theta, \varphi) \\
y = y(r, \theta, \varphi) \\
z = z(r, \theta, \varphi)
\]

Thus, one can utilize the implicit function’s differentiation

\[
\frac{\partial f(r, \theta, \varphi)}{\partial x} = \frac{\partial f}{\partial r} \frac{\partial r}{\partial x} + \frac{\partial f}{\partial \theta} \frac{\partial \theta}{\partial x} + \frac{\partial f}{\partial \varphi} \frac{\partial \varphi}{\partial x} \Rightarrow \frac{\partial}{\partial x} = \frac{\partial}{\partial x} \frac{\partial r}{\partial x} + \frac{\partial}{\partial x} \frac{\partial \theta}{\partial x} + \frac{\partial}{\partial x} \frac{\partial \varphi}{\partial x}
\]

We must first calculate all necessary derivatives
\[
\begin{align*}
\frac{\partial r}{\partial x} &= \frac{1}{2\sqrt{x^2 + y^2 + z^2}} \cdot 2x = \frac{x}{r} = \frac{r \sin \theta \cos \varphi}{r} = \sin \theta \cos \varphi \\
\frac{\partial r}{\partial y} &= \frac{1}{2\sqrt{x^2 + y^2 + z^2}} \cdot 2y = \sin \theta \sin \varphi \\
\frac{\partial r}{\partial z} &= \cos \theta \\
\frac{\partial \theta}{\partial x} &= -\frac{1}{\sqrt{1 - \left(\frac{z}{r}\right)^2}} \frac{\partial}{\partial x} \frac{z}{r} = \frac{1}{1 - \left(\frac{z}{r}\right)^2} \cdot \frac{z}{r} = \frac{z}{r} \\
\frac{\partial \theta}{\partial y} &= -\frac{1}{\sqrt{1 - \left(\frac{z}{r}\right)^2}} \frac{\partial}{\partial y} \frac{z}{r} = \frac{r}{\sqrt{r^2 - z^2}} \cdot \frac{z}{r} = \frac{z}{r} \\
\frac{\partial \theta}{\partial z} &= \frac{1}{\sin \theta} \frac{\cos \theta \sin \theta}{r} = \frac{1}{r} \cos \theta \sin \varphi \\
\frac{\partial \varphi}{\partial x} &= \frac{1}{1 + \left(\frac{z}{r}\right)^2} \cdot \frac{1}{x} = \frac{x}{x^2 + y^2} = \frac{x}{r^2 \sin^2 \theta} = \frac{\cos \varphi}{r \sin \theta} \\
\frac{\partial \varphi}{\partial y} &= \frac{1}{1 + \left(\frac{z}{r}\right)^2} \cdot \frac{1}{y} = \frac{x^2}{x^2 + y^2} = \frac{x}{r^2 \sin^2 \theta} = \frac{\cos \varphi}{r \sin \theta} \\
\frac{\partial \varphi}{\partial z} &= 0
\end{align*}
\]

Therefore

\[
\begin{align*}
\frac{\partial}{\partial x} &= \sin \theta \cos \varphi \frac{\partial}{\partial r} + \frac{1}{r} \cos \theta \cos \varphi \frac{\partial}{\partial \theta} - \frac{1}{r \sin \theta} \frac{\partial}{\partial \varphi} \\
\frac{\partial}{\partial y} &= \sin \theta \sin \varphi \frac{\partial}{\partial r} + \frac{1}{r} \cos \theta \sin \varphi \frac{\partial}{\partial \theta} + \frac{1}{r \sin \theta} \frac{\partial}{\partial \varphi} \\
\frac{\partial}{\partial z} &= \cos \theta \frac{\partial}{\partial r} - \frac{1}{r \sin \theta} \frac{\partial}{\partial \varphi}
\end{align*}
\]

Find the \(\hat{L}_z\) operator in spherical coordinates

\[
\hat{L}_z = -i\hbar \left( x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) = -i\hbar \left[ \sin \theta \cos \varphi \left( \sin \theta \sin \varphi \frac{\partial}{\partial r} + \frac{1}{r} \cos \theta \sin \varphi \frac{\partial}{\partial \theta} + \frac{1}{r \sin \theta} \frac{\partial}{\partial \varphi} \right) + \right. \\
- \sin \theta \sin \varphi \left( \sin \theta \cos \varphi \frac{\partial}{\partial r} + \frac{1}{r} \cos \theta \cos \varphi \frac{\partial}{\partial \theta} - \frac{1}{r \sin \theta} \frac{\partial}{\partial \varphi} \right) \right] = -i\hbar \left( r \sin^2 \theta \sin \varphi \cos \varphi \frac{\partial}{\partial r} + \\
+ \sin \theta \cos \theta \sin \varphi \cos \varphi \frac{\partial}{\partial \theta} + \cos^2 \theta \frac{\partial}{\partial \varphi} - r \sin^2 \theta \sin \varphi \cos \varphi \frac{\partial}{\partial r} - \sin \theta \cos \theta \sin \varphi \cos \varphi \frac{\partial}{\partial \theta} + \sin^2 \theta \frac{\partial}{\partial \varphi} \right)
\]
\[ = -i\hbar (\cos^2 \theta + \sin^2 \theta) \frac{\partial}{\partial \phi} = -i\hbar \frac{\partial}{\partial \phi} \] (2.20)

One can similarly obtain

\[ \hat{L}_x = -i\hbar \left( -\sin \varphi \frac{\partial}{\partial \theta} - \cot \theta \cos \varphi \frac{\partial}{\partial \varphi} \right) \]
\[ \hat{L}_y = -i\hbar \left( \cos \varphi \frac{\partial}{\partial \theta} - \cot \theta \sin \varphi \frac{\partial}{\partial \varphi} \right) \] (2.21)

Find the \( \hat{L}^2 \) in spherical coordinates.

\[ \hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 \] (2.22)

\[ \hat{L}_x^2 = \hat{L}_x \hat{L}_x = -i\hbar \left( -\sin \varphi \frac{\partial}{\partial \theta} - \cot \theta \cos \varphi \frac{\partial}{\partial \varphi} \right) \cdot \left( -i\hbar \left( -\sin \varphi \frac{\partial}{\partial \theta} - \cot \theta \cos \varphi \frac{\partial}{\partial \varphi} \right) \right) = \]
\[ = -\hbar^2 \left( \sin^2 \varphi \frac{\partial^2}{\partial \theta^2} + \sin \varphi \cos \varphi \frac{\partial^2}{\partial \theta^2} \left( \cot \theta \frac{\partial}{\partial \varphi} \right) + \cot \theta \cos \varphi \frac{\partial^2}{\partial \varphi^2} \left( \sin \varphi \frac{\partial}{\partial \varphi} \right) + \right) \]
\[ + \cot \theta \left( \cos \varphi \frac{\partial}{\partial \varphi} \left( \sin \varphi \frac{\partial}{\partial \varphi} \right) - \sin \varphi \frac{\partial}{\partial \varphi} \left( \cos \varphi \frac{\partial}{\partial \varphi} \right) \right) \]
\[ = -\hbar^2 \left( \frac{\partial^2}{\partial \theta^2} + \cot \theta \left( \cos \varphi \left( \cos \varphi \frac{\partial^2}{\partial \varphi^2} \right) + \sin \varphi \frac{\partial^2}{\partial \varphi^2} \right) - \sin \varphi \left( -\sin \varphi \frac{\partial}{\partial \theta} + \cos \varphi \frac{\partial^2}{\partial \varphi \partial \theta} \right) \right) + \]
\[ + \cot \theta \left( \cos \varphi \left( -\sin \varphi \frac{\partial}{\partial \varphi} + \cos \varphi \frac{\partial^2}{\partial \varphi^2} \right) + \sin \varphi \left( \cos \varphi \frac{\partial}{\partial \varphi} + \sin \varphi \frac{\partial^2}{\partial \varphi^2} \right) \right) + \frac{\partial^2}{\partial \varphi^2} \right) \]
\[ = -\hbar^2 \left( \frac{\partial^2}{\partial \theta^2} + \cot \theta \left( \cos \varphi \frac{\partial}{\partial \varphi} + \sin \varphi \frac{\partial^2}{\partial \varphi \partial \theta} + \sin^2 \varphi \frac{\partial}{\partial \varphi} + \sin \varphi \cos \varphi \frac{\partial^2}{\partial \varphi^2} \right) + \right) \]
\[ + \cot \theta \left( -\sin \varphi \frac{\partial}{\partial \varphi} + \cos^2 \varphi \frac{\partial^2}{\partial \varphi^2} + \sin \varphi \cos \varphi \frac{\partial}{\partial \varphi} + \sin^2 \varphi \frac{\partial^2}{\partial \varphi^2} \right) + \frac{\partial^2}{\partial \varphi^2} \right) \]
\[ = -\hbar^2 \left( \frac{\partial^2}{\partial \theta^2} + \cot \theta \frac{\partial}{\partial \theta} + \cot^2 \theta \frac{\partial^2}{\partial \varphi^2} + \frac{\partial^2}{\partial \varphi^2} \right) = -\hbar^2 \left( \frac{\partial^2}{\partial \theta^2} + \cot \theta \frac{\partial}{\partial \theta} + (1 + \cot^2 \theta) \frac{\partial^2}{\partial \varphi^2} \right) = \]

\[ = -\hbar^2 \left( \frac{\partial^2}{\partial \theta^2} + \cot \theta \frac{\partial}{\partial \theta} + \cot^2 \theta \frac{\partial^2}{\partial \varphi^2} + \frac{\partial^2}{\partial \varphi^2} \right) = -\hbar^2 \left( \frac{\partial^2}{\partial \theta^2} + \cot \theta \frac{\partial}{\partial \theta} + (1 + \cot^2 \theta) \frac{\partial^2}{\partial \varphi^2} \right) = \]
\[ = -\hbar^2 \left[ \frac{\partial^2}{\partial \theta^2} + \cot \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right] \] (2.26)

The formula for \( \hat{L}^2 \) could be rewritten into a different one, which is sometimes useful (for instance for hydrogen-atom model problem)

\[ \hat{L}^2 = -\hbar^2 \left[ \frac{\partial^2}{\partial \theta^2} + \cot \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right] = -\hbar^2 \left[ \frac{1}{\sin \theta} \left( \cos \theta \frac{\partial}{\partial \theta} + \sin \theta \frac{\partial^2}{\partial \theta^2} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right] = \] (2.27)

Sometimes the \( \hat{L}^2 \) operator is written in terms of \( \hat{L}_z \) operator

\[ \hat{L}^2 = -\frac{\hbar^2}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{\hat{L}_z^2}{\sin^2 \theta} \] (2.28)

Find the \( \nabla^2 \) in spherical coordinates.

\[ \nabla^2 = \Delta = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \] (2.29)

\[ \frac{\partial^2}{\partial x^2} = \frac{\partial}{\partial x} \frac{\partial}{\partial x} = \left( \sin \theta \cos \varphi \frac{\partial}{\partial r} + \frac{1}{r} \cos \theta \cos \varphi \frac{\partial}{\partial \theta} - \frac{1}{r \sin \theta} \frac{\partial}{\partial \varphi} \right) \left( \sin \theta \cos \varphi \frac{\partial}{\partial r} + \frac{1}{r} \cos \theta \cos \varphi \frac{\partial}{\partial \theta} - \frac{1}{r \sin \theta} \frac{\partial}{\partial \varphi} \right) = \sin \theta \cos \varphi \frac{\partial^2}{\partial r^2} + \sin \theta \cos \varphi \frac{\partial}{\partial r} \frac{\partial}{\partial \theta} \frac{\partial}{\partial \varphi} - \frac{1}{r} \sin \theta \sin \varphi \frac{\partial^2}{\partial \theta^2} - \frac{1}{r} \cos \theta \cos \varphi \frac{\partial}{\partial \theta} \frac{\partial}{\partial \varphi} + \frac{1}{r^2} \sin \theta \sin \varphi \frac{\partial}{\partial \varphi} \frac{\partial}{\partial \varphi} \frac{\partial}{\partial \varphi} \] (2.30)

\[ \frac{\partial^2}{\partial y^2} = \frac{\partial}{\partial y} \frac{\partial}{\partial y} = \left( \sin \theta \sin \varphi \frac{\partial}{\partial r} + \frac{1}{r} \cos \theta \sin \varphi \frac{\partial}{\partial \theta} + \frac{1}{r \sin \theta} \frac{\partial}{\partial \varphi} \right) \left( \sin \theta \sin \varphi \frac{\partial}{\partial r} + \frac{1}{r} \cos \theta \sin \varphi \frac{\partial}{\partial \theta} + \frac{1}{r \sin \theta} \frac{\partial}{\partial \varphi} \right) = \sin \theta \sin \varphi \frac{\partial^2}{\partial r^2} + \sin \theta \sin \varphi \frac{\partial}{\partial r} \frac{\partial}{\partial \theta} \frac{\partial}{\partial \varphi} - \frac{1}{r} \sin \theta \sin \varphi \frac{\partial^2}{\partial \theta^2} - \frac{1}{r} \cos \theta \sin \varphi \frac{\partial}{\partial \theta} \frac{\partial}{\partial \varphi} + \frac{1}{r^2} \sin \theta \sin \varphi \frac{\partial}{\partial \varphi} \frac{\partial}{\partial \varphi} \frac{\partial}{\partial \varphi} \] (2.31)

\[ \frac{\partial^2}{\partial z^2} = \frac{\partial}{\partial z} \frac{\partial}{\partial z} = \left( \cos \theta \frac{\partial}{\partial r} - \frac{\sin \theta}{r} \frac{\partial}{\partial \theta} - \frac{\sin \varphi}{r \sin \theta} \frac{\partial}{\partial \varphi} \right) \left( \cos \theta \frac{\partial}{\partial r} - \frac{\sin \theta}{r} \frac{\partial}{\partial \theta} - \frac{\sin \varphi}{r \sin \theta} \frac{\partial}{\partial \varphi} \right) = \cos^2 \theta \frac{\partial^2}{\partial r^2} - \cos \theta \sin \theta \frac{\partial}{\partial r} \frac{\partial}{\partial \theta} - \frac{1}{r} \sin \theta \frac{\partial}{\partial r} \frac{\partial}{\partial \varphi} + \frac{1}{r^2} \sin \theta \frac{\partial}{\partial \varphi} \frac{\partial}{\partial \varphi} \frac{\partial}{\partial \varphi} \] (2.32)

\[ \nabla^2 = \left( \sin^2 \theta \cos^2 \varphi + \sin^2 \theta \sin^2 \varphi + \cos^2 \theta \right) \frac{\partial^2}{\partial r^2} + \left( \sin \theta \cos \theta \sin^2 \varphi + \sin \theta \cos \theta \cos^2 \varphi - \sin \theta \cos \theta \right) \frac{\partial}{\partial \theta} \frac{1}{r} \frac{\partial}{\partial \theta} + \]
\begin{align}
&+ (\sin \phi \cos \phi - \sin \phi \cos \phi) \frac{\partial}{\partial r} \left( \frac{1}{r} \frac{\partial}{\partial \phi} \right) + \left( \frac{1}{r} \cos \theta \sin^2 \phi + \frac{1}{r} \cos \theta \cos^2 \phi \right) \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial r} \right) - \sin \theta \frac{\partial}{\partial \theta} \left( \cos \theta \frac{\partial}{\partial r} \right) + \\
&+ \frac{1}{r} \cos \theta \left( \cos^2 \phi + \sin^2 \phi \right) \frac{\partial}{\partial \theta} \left( \cos \theta \frac{\partial}{\partial \phi} \right) + \frac{1}{r^2} \sin \theta \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \phi} \right) + \left( \frac{1}{r^2} \sin \phi \cos \phi \cos \theta - \frac{1}{r^2} \sin \phi \cos \phi \cos \theta \right) .
\end{align}

\[ \cdot \frac{\partial}{\partial \theta} \left( \frac{1}{\sin \theta \frac{\partial}{\partial \phi}} \right) + \frac{1}{r} \cos \theta \frac{\partial}{\partial \phi} \left( \sin \phi \frac{\partial}{\partial r} \right) - \frac{1}{r} \sin \phi \frac{\partial}{\partial \phi} \left( \cos \phi \frac{\partial}{\partial r} \right) + \frac{1}{r^2} \cos \theta \frac{\partial}{\partial \theta} \left( \cos \theta \frac{\partial}{\partial \phi} \right) + \frac{1}{r^2} \sin \theta \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \phi} \right) + \\
- \frac{1}{r} \sin \theta \left( \frac{\partial}{\partial \theta} \right) + \cos \theta \frac{\partial^2}{\partial \theta \partial \phi} + \frac{1}{r^2} \cos \theta \left( - \sin \theta \frac{\partial}{\partial \theta} + \cos \theta \frac{\partial^2}{\partial \theta \partial \phi} \right) + \frac{1}{r^2} \sin \theta \left( \cos \theta \frac{\partial}{\partial \theta} + \sin \theta \frac{\partial^2}{\partial \theta \partial \phi} \right) + \\
+ \frac{1}{r} \cos \phi \left( \cos \phi \frac{\partial}{\partial \phi} + \sin \phi \frac{\partial^2}{\partial \phi \partial \theta} \right) - \frac{1}{r} \sin \phi \left( - \sin \phi \frac{\partial}{\partial \phi} + \cos \phi \frac{\partial^2}{\partial \phi \partial \theta} \right) + \frac{1}{r^2} \left( \cos \phi \left( - \sin \phi \frac{\partial}{\partial \phi} + \cos \phi \frac{\partial^2}{\partial \phi \partial \theta} \right) + \\
- \sin \phi \left( \frac{\partial^2}{\partial \phi \partial \theta} \right) + \sin \phi \left( - \sin \phi \frac{\partial}{\partial \phi} + \cos \phi \frac{\partial^2}{\partial \phi \partial \theta} \right) + \frac{1}{r^2} \left( \cos \phi \left( - \sin \phi \frac{\partial}{\partial \phi} + \cos \phi \frac{\partial^2}{\partial \phi \partial \theta} \right) + \\
+ \sin \phi \left( \cos \phi \frac{\partial}{\partial \phi} + \sin \phi \frac{\partial^2}{\partial \phi \partial \theta} \right) \right) = \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} + \frac{1}{r^2} \cot \theta \frac{\partial}{\partial \theta} + \frac{1}{r^2} \frac{\partial^2}{\partial \phi^2}.
\]

Sometimes there is another, equal, definition of Laplacian:

\[ \nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} + \frac{1}{r^2} \frac{\partial^2}{\partial \theta^2} + \frac{1}{r^2} \cot \theta \frac{\partial}{\partial \theta} + \frac{1}{r^2} \frac{\partial^2}{\partial \phi^2} = \frac{1}{r^2} \left( 2 \frac{\partial}{\partial r} + \frac{2}{r} \frac{\partial^2}{\partial r^2} \right) + \frac{1}{r^2} \sin^2 \theta \left( \cos \theta \frac{\partial}{\partial \theta} + \\
+ \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2} \frac{\partial^2}{\partial \phi^2}.
\]

And exploiting the \( \hat{L}^2 \) definition one can also say that

\[ \nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} - \frac{\hat{L}^2}{\hbar^2 r^2}, \quad \hat{H} = \frac{\hbar}{2m} \left( \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} - \frac{\hat{L}^2}{\hbar^2 r^2} \right) + V(r) \]

Show the Hamiltonian and the \( \hat{L}^2 \) operator commute each other. Also show that the commutation occurs between the Hamiltonian and the \( \hat{L}_z \) operators.

\[ [\hat{H}, \hat{L}^2] = \hat{H} \hat{L}^2 - \hat{L}^2 \hat{H} = \\
= \left[ - \frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} - \frac{\hat{L}^2}{\hbar^2 r^2} \right) + V(r) \right] \hat{L}^2 - \hat{L}^2 \left[ \frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} - \frac{\hat{L}^2}{\hbar^2 r^2} \right) + V(r) \right] = \\
= - \frac{\hbar^2}{2m} \frac{\partial^2}{\partial r^2} \hat{L}^2 - \frac{\hbar^2}{2m} \frac{\partial}{\partial r} \hat{L}^2 + \frac{1}{2mr^2} \hat{L}^4 + V(\hat{L}) \frac{\partial}{\partial r} \hat{L}^2 + \frac{\hbar^2}{2m} \frac{\partial^2}{\partial r^2} \hat{L}^2 + \frac{\hbar^2}{2m} \frac{\partial}{\partial r} \hat{L}^2 - \frac{1}{2mr^2} \hat{L}^4 - \hat{L}^2 V(\hat{r}) = 0 \]
The order of differentiation in above derivation remains unimportant because the $\hat{L}^2$ acts on only the terms containing the $\theta$ and $\varphi$ variables, while the $r$-depending terms remain independent.

\[
[\hat{H}, \hat{L}_z] = \hat{H} L_z - L_z \hat{H} = \\
\left[ -\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} - \frac{\hat{L}_z^2}{\hbar^2 r^2} \right) + V(r) \right] L_z - L_z \left[ -\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} - \frac{\hat{L}_z^2}{\hbar^2 r^2} \right) + V(r) \right] = \\
= \frac{i\hbar^3}{2m} \frac{\partial^2}{\partial \varphi^2} + \frac{i\hbar^3}{2m} \frac{\partial}{m r \partial \varphi} - \frac{i\hbar V(r)}{2r^2} \frac{\partial}{\partial \varphi} - \frac{i\hbar^3}{2m} \frac{\partial}{\partial \varphi} \frac{\partial^2}{\partial r^2} - \frac{i\hbar^3}{2m} \frac{\partial}{\partial \varphi} \frac{\partial}{r} + \frac{i\hbar}{2r^2} \frac{\partial}{\partial \varphi} L_z^2 + \\
+ i\hbar \frac{\partial}{\partial \varphi} V(r) = 0
\]

In the above derivation the order of derivatives doesn’t matter. Namely, the $\hat{L}_z$ acts on only the terms containing the $\varphi$ variables, while the other remain independent. Despite the fact the $\hat{L}_z^2$ operator contains the term differentiating functions with the $\varphi$ variables the derivative remains the same as in the case of the $\hat{L}_z$ operator. Moreover the $\hat{L}_z^2$ and the $\hat{L}_z$ commute each other. So we can interchange the order of derivatives and all terms above sum to zero.

Example. Prove that eigenvalues of hermitian operators are real numbers.

Solution

\[
\hat{A} \varphi = a \varphi \\
\hat{A}^* \varphi^* = a^* \varphi^*
\]

We multiply the first eqn. by $\varphi^*$ and the second by $\varphi$

\[
\varphi^* \hat{A} \varphi = \varphi^* a \varphi \\
\varphi \hat{A}^* \varphi^* = \varphi a^* \varphi^*
\]

and we integrate both equations and subtract both sides

\[
\int \varphi^* \hat{A} \varphi d\tau - \int \varphi \hat{A}^* \varphi^* d\tau = (a - a^*) \int \varphi^* \varphi d\tau
\]

The left side is equal to zero due to hermiticity of operator $\hat{A}$. The integral on the right must be equal to 1 due to normalization condition. Therefore

\[
a - a^* = 0 \\
a = a^*
\]

which is possible only when $a$ is a real number.

Example. Prove that if two eigenfunctions of the same hermitian operator have different eigenvalues then they must be orthogonal.

Solution

\[
\hat{A} \varphi_1 = a_1 \varphi_1 \\
\hat{A} \varphi_2 = a_2 \varphi_2 \\
a_1 \neq a_2
\]
So we can write down conjugated equations, for instance

\[ \hat{A}^* \phi_2^* = a_2^* \phi_2^* \]

We multiply the original equations by \( \phi_1^* \) and by \( \phi_2 \) respectively

\[ \phi_2^* \hat{A} \phi_1 = \phi_2^* a_1 \phi_1 \]
\[ \phi_1 \hat{A}^* \phi_2^* = \phi_1 a_2^* \phi_2^* \]

and we integrate both equations and subtract both sides

\[ \int \phi_2^* \hat{A} \phi_1 d\tau - \int \phi_1 \hat{A}^* \phi_2^* d\tau = (a_1 - a_2^*) \int \phi_2^* \phi_1 d\tau \]

Due to hermiticity of operator \( \hat{A} \) the left side of above equation equals 0, besides \( a_2 = a_2^* \) (see the previous example). Thus the right side must be equal to 0. Moreover, the condition says \( a_1 - a_2 \neq 0 \) which finally means that

\[ \int \phi_2^* \phi_1 d\tau = 0 \]

which is a condition of orthogonality.

1. Find the result of acting \( \nabla \) for a vector field \( \vec{A} = A_i \vec{i} + A_j \vec{j} + A_k \vec{k} \) in a scalar product (grad \( \vec{A} \)).
2. Find the result of acting \( \nabla \) for a vector field \( \vec{A} = A_i \vec{i} + A_j \vec{j} + A_k \vec{k} \) in a vector product (rot \( \vec{A} \)).
3. Find the \( \nabla^2 \) in scalar product.
4. Which of the operators below are linear.
   (a) \( \sqrt{\cdot} \)
   (b) \( \cdot^2 \)
   (c) \( \int d\tau \)
   (d) \( \frac{\partial}{\partial x} \)
   (e) \( \cdot \times \)
   (f) \( \sin(\cdot) \)

Caution. The operator \( \hat{A} \) is linear if it omits the following relation

\[ \hat{A}(C_1 \phi_1 + C_2 \phi_2) = C_1 \hat{A} \phi_1 + C_2 \hat{A} \phi_2 \]  \hspace{1cm} (2.38)

5. Prove that the following operators are hermitian
   (a) \( \cdot \times \)
   (b) \( -i\hbar \frac{\partial}{\partial x} \)

Caution. Operator \( \hat{A} \) is hermitian, if it obeys the relation

\[ \int_{-\infty}^{+\infty} \phi_1^* \hat{A} \phi_2 d\tau = \int_{-\infty}^{+\infty} \phi_2 (\hat{A} \phi_1)^* d\tau \]  \hspace{1cm} (2.39)

6. Find relations between cartesian and spherical coordinates.
7. Find the volume element \( d\tau = dxdydz \) in spherical coordinates.
8. Find \( \frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z} \) in spherical coordinates.
9. Find \( \hat{L}_z \) operator in spherical coordinates.
10. Find \( \frac{\partial}{\partial \phi} \) operator in cartesians.
3 Normalization

The Schrödinger equation is of linear type, which means that if $\Psi$ is its solution, then the $N\Psi$ is its solution too. We can choose the $N$ in this way that $\rho(r)$, which is defined as

$$\rho(r) = |\Psi(r)|^2 = |N\Psi(r)|^2 \tag{3.1}$$

will be equal exactly the density of probability that the particle will be in point $r$. The procedure is called the normalization.

How to find the $N$? We must use the condition for density of probability.

$$\int |\Psi(r)|^2 d^3r = 1 \tag{3.2}$$

which means that

$$1 = |N|^2 \int |\Psi(r)|^2 d^3r \tag{3.3}$$

and

$$N = \frac{1}{\sqrt{\int |\Psi(r)|^2 d^3r}} \tag{3.4}$$

In quantum theory we require that the functions must be normalizable, i.e. they must be integrable in square

$$\int |\Psi(r)|^2 d^3r < \infty \tag{3.5}$$

Example. Normalize the function $\exp(-ar)$ where $a > 0$ and $r = \sqrt{x^2 + y^2 + z^2}$.

$$N^{-2} = \int_{-\infty}^{+\infty} dx \int_{-\infty}^{+\infty} dy \int_{-\infty}^{+\infty} dz \exp(-a\sqrt{x^2 + y^2 + z^2}) \exp(-a\sqrt{x^2 + y^2 + z^2}) \tag{3.6}$$

In spherical coordinates

$$N^{-2} = \int_{0}^{2\pi} d\phi \int_{0}^{\pi} \sin \theta d\theta \int_{0}^{\infty} r^2 dr e^{-2ar} \tag{3.7}$$

First, let’s observe that

$$\int_{0}^{\infty} e^{-ar} dr = -\frac{1}{a} e^{-ar}\big|_{0}^{\infty} = \frac{1}{a} \tag{3.8}$$

and

$$\int_{0}^{\infty} re^{-ar} dr = -\frac{1}{a^2} \int_{0}^{\infty} e^{ar} dr \tag{3.9}$$

$$\int_{0}^{\infty} r^2 e^{-ar} dr = -\frac{1}{a^3} \int_{0}^{\infty} e^{ar} dr \tag{3.10}$$

Therefore

$$\int_{0}^{\infty} r^2 e^{-ar} dr = \frac{1}{a^3} \frac{1}{a} = \frac{1}{a^4} 2a = \frac{2}{a^3} \tag{3.11}$$

One can generalize the integral (will be usefull later on)

$$\int_{0}^{\infty} r^n e^{-ar} dr = \frac{n!}{a^{n+1}} \tag{3.12}$$
In our integral $\frac{1}{u_{1D6FC}} = 2\frac{1}{u_{1D44E}}$ and $\frac{1}{u_{1D45B}} = 2\frac{1}{u_{1D41}} - 2 = 4\frac{1}{u_{1D70B}}^2 \left(2\frac{1}{u_{1D44E}}\right)^3 = \frac{1}{u_{1D70B}}^3 \Rightarrow \frac{1}{u_{1D41}} = \frac{1}{u_{1D458}}^2 \sin\left(\frac{1}{u_{1D70B}}^2\right) \left(2\frac{1}{u_{1D45F}}\right)^3 = -\frac{1}{u_{1D458}}^2 \frac{1}{u_{1D41}}^2 (3.13)$

Example. Find the expectation value of $\hat{A}$ operator, where $\hat{A} = -\frac{1}{u_{1D450}}\hat{V}$, with function $\phi(r) = \sqrt{\frac{1}{u_{1D45F}}^2 e^{-ar}}$.

Average value of large amount of quantity $\hat{A}$’s observations performed for a given state which is described by a normalized function $\Psi$ is called the expectation value.

$\langle \hat{A} \rangle = \langle \psi | \hat{A} \psi \rangle$ (3.14)

Therefore

$\langle \hat{V} \rangle = \langle \phi(r) | \hat{V} \phi(r) \rangle = \int\sqrt{\frac{1}{u_{1D450}}^2 e^{-ar}} \sqrt{\frac{1}{u_{1D450}}^2 e^{-ar}} d^3r = \frac{-Z e^2 a^3}{\pi} \int \frac{1}{r} e^{-2ar} d^3r = \frac{-Ze^2 a^3}{\pi} \frac{1}{(2a)^2} = -Ze^2 a$ (3.15)

4 Harmonic oscillator

4.1 Classical approach

The harmonic oscillator is a point with mass $m$ which undergoes oscillations around the equilibrium point under the influence of harmonic force (restoring force) which is proportional to displacement $x$ and is pointed always to the equilibrium point. In one dimension

$F = -kx$ (4.1)

Moreover, recollecting the relation between force and potential energy

$F = -\frac{dV}{dx}$ (4.2)

and assuming that for the equilibrium the potential energy vanishes we are getting

$V = \frac{kx^2}{2}$ (4.3)

In classical approach the point’s trajectory we obtain as a solution of Newton’s equation

$m\frac{d^2x}{dt^2} = -kx \Rightarrow \frac{d^2x}{dt^2} = -\omega^2 x, \quad \omega = \sqrt{\frac{k}{m}}$ (4.4)

In general, the solutions are as follows

$x(t) = ae^{iot} + be^{-iwt}$ (4.5)

Moreover, assuming that

$x(0) = 0 \Leftrightarrow a + b = 0$ (4.6)

we are getting

$x(t) = a(e^{iwt} - e^{-iwt}) = A \sin(\omega t)$ (4.7)
where \( A = 2\pi a \) is harmonic oscillator’s amplitude. Therefore, the harmonic oscillator’s potential energy as a function of time is given by

\[
V(t) = \frac{1}{2} kA^2 \sin^2(\omega t) \tag{4.8}
\]

The kinetic energy we are finding by

\[
T = \frac{m v^2}{2} = \frac{m}{2} \left( \frac{dx}{dt} \right)^2 = \frac{1}{2} kA^2 \cos^2(\omega t) \tag{4.9}
\]

Thus, the total energy of harmonic oscillator equals

\[
E = T + V = \frac{kA^2}{2} \tag{4.10}
\]

and it can be of any value.

### 4.2 Quantum approach

In quantum methodology we need to know an appropriate operator, while we are taking classical definitions of kinetic and potential energies. Therefore the Schrödinger equations is as follows

\[
\left( -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{kx^2}{2} \right) \psi(x) = \left( -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{m\omega^2 x^2}{2} \right) \psi(x) = E \psi(x) \tag{4.11}
\]

The above equation can be rewritten in dimensionless coordinates

\[
\begin{array}{rcl}
\xi &=& \sqrt{\frac{m}{\hbar}} x \\
e &=& \frac{\sqrt{\frac{m}{\hbar}}}{\omega} t
\end{array} \tag{4.12}
\]

Calculating the kinetic-energy part of the Hamiltonian

\[
T = -\hbar^2 \frac{d^2}{dx^2} = -\hbar^2 \frac{d}{dx} \frac{d}{dx} + \frac{m\omega^2}{2} \sqrt{\frac{m}{\hbar}} \frac{d}{d\xi} \frac{d}{d\xi} = -\hbar^2 \frac{m\omega}{\hbar} \frac{d^2}{d\xi^2} \tag{4.13}
\]

one is getting in new coordinates

\[
\left( \frac{d^2}{d\xi^2} - \xi^2 \right) \psi = -2e\psi \tag{4.14}
\]

Let’s notice that

\[
\left( \frac{d}{d\xi} - \xi \right) \left( \frac{d}{d\xi} + \xi \right) \psi(\xi) = \frac{d^2}{d\xi^2} \psi(\xi) + \xi \frac{d}{d\xi} \psi(\xi) + \frac{d}{d\xi} \psi(\xi) = \left( \frac{d^2}{d\xi^2} - \xi^2 \right) \psi(\xi) + \psi(\xi) \tag{4.15}
\]

Thus

\[
\left( \frac{d}{d\xi} - \xi \right) \left( \frac{d}{d\xi} + \xi \right) \psi(\xi) = (-2e + 1)\psi(\xi) \tag{4.16}
\]

Analogously

\[
\left( \frac{d}{d\xi} + \xi \right) \left( \frac{d}{d\xi} - \xi \right) \psi(\xi) = (-2e - 1)\psi(\xi) \tag{4.17}
\]

Subtracting equation 4.17 from 4.16 one is getting
Let’s create a function

\[ \phi_1(\xi) = \left( \xi - \frac{d}{d\xi} \right) \phi_0(\xi) \]  \hspace{1cm} (4.19)

and let’s check what is the eigenvalue which obeys the equation 4.16

\[ \left( \frac{d}{d\xi} - \xi \right) \left( \frac{d}{d\xi} - \xi \right) \phi_1(\xi) = - \left( \frac{d}{d\xi} - \xi \right) \left( \frac{d}{d\xi} - \xi \right) \phi_0(\xi) \]

\[ = (-2\epsilon_0 - 1) \left( \xi - \frac{d}{d\xi} \right) \phi_0(\xi) = \]  \hspace{1cm} (4.20)

\[ = (-2\epsilon_0 - 1) \phi_1(\xi) = \]

\[ = (-2\epsilon_1 + 1) \phi_1(\xi) = \]

where

\[ \epsilon_1 = \epsilon_0 + 1 \]  \hspace{1cm} (4.21)

Now, let’s create a function

\[ \phi_{-1}(\xi) = \left( \xi + \frac{d}{d\xi} \right) \phi_0(\xi) \]  \hspace{1cm} (4.22)

and let’s check what is the eigenvalue which obeys the equation 4.17

\[ \left( \frac{d}{d\xi} + \xi \right) \left( \frac{d}{d\xi} + \xi \right) \phi_{-1}(\xi) = \left( \frac{d}{d\xi} + \xi \right) \left( \frac{d}{d\xi} + \xi \right) \phi_0(\xi) \]

\[ = (-2\epsilon_0 + 1) \left( \xi + \frac{d}{d\xi} \right) \phi_0(\xi) = \]  \hspace{1cm} (4.23)

\[ = (-2\epsilon_0 + 1) \phi_{-1}(\xi) = \]

\[ = (-2\epsilon_{-1} - 1) \phi_{-1}(\xi) = \]

where

\[ \epsilon_{-1} = \epsilon_0 - 1 \]  \hspace{1cm} (4.24)

Let’s notice that operator \( \xi - \frac{d}{d\xi} \) created state \( \phi_1 \) with energy \( \epsilon_1 \). In turn, operator \( \xi + \frac{d}{d\xi} \) acting on \( \phi_0 \) created state \( \phi_{-1} \) with energy \( \epsilon_0 - 1 \). The procedure can be repeated for functions \( \phi_1 \) and \( \phi_{-1} \) getting functions \( \phi_2 \) and \( \phi_{-2} \). In general repeating the same procedure \( v \) times we will get

\[
\begin{align*}
\phi_v(\xi) &= \left( \xi - \frac{d}{d\xi} \right)^v \phi_0(\xi) \\
\phi_{-v}(\xi) &= \left( \xi + \frac{d}{d\xi} \right)^v \phi_0(\xi)
\end{align*}
\]  \hspace{1cm} (4.25)

where \( v \in N \).

with eigenvalues

\[
\begin{align*}
\epsilon_v &= \epsilon_0 + v \\
\epsilon_{-v} &= \epsilon_0 - v
\end{align*}
\]  \hspace{1cm} (4.26)

\( \epsilon_v \) and \( \epsilon_{-v} \) correspond to energetical states of the oscillator. Energy of the oscillator is not bounded from above but its value can’t be too low. One can assume that
∀v ∈ \mathbb{N} : \epsilon_v > 0 \land \epsilon_{-v} = 0 \Rightarrow ∀v ∈ \mathbb{N} : \epsilon_{-v} = 0,

which in turn allows to derive \( \phi_0 \) from following condition

\[
\phi_{-1}(\xi) = 0 \Leftrightarrow \left( \xi + \frac{d}{d\xi} \right) \phi_0(\xi) = 0
\]

(4.28)

the solutions are as follows

\[
\phi_0(\xi) = e^{-\frac{\xi^2}{2}}
\]

(4.29)

Example.

Let’s find if the \( f(x) = e^{-\frac{x^2}{2}} \) is eigenfunction of operator \( \hat{a} = \left( \frac{d^2}{dx^2} - x^2 \right) \). If so, then find the appropriate eigenvalue.

Solution

\[
\hat{a} f(x) = \left( \frac{d^2}{dx^2} - x^2 \right) e^{-\frac{x^2}{2}} = -\frac{d}{dx} \left( x e^{-\frac{x^2}{2}} \right) - x^2 e^{-\frac{x^2}{2}} = -e^{-\frac{x^2}{2}} + x^2 e^{-\frac{x^2}{2}} - x^2 e^{-\frac{x^2}{2}} = -f(x)
\]

(4.30)

which means that function \( f(x) \) is eigenfunction of operator \( \hat{a} \) with eigenvalue \(-1\). Moreover, one can find that the \( \epsilon_0 = \frac{1}{2} \).

Therefore, the solutions might be written in following form

\[
\begin{align*}
\phi_v(\xi) &= \left( \xi - \frac{d}{d\xi} \right)^v e^{-\frac{\xi^2}{2}}, \quad v \in \mathbb{N} \cup \{0\}.
\end{align*}
\]

(4.31)

One can see that the functions \( \phi_v(\xi) \) are polynomials which contain only even or only odd powers of \( \xi \) multiplied by functions \( \phi_0 \).

More general the functions

\[
H_v(\xi) = e^{\frac{\xi^2}{2}} \left( \xi - \frac{d}{d\xi} \right)^v e^{-\frac{\xi^2}{2}} = (-1)^v \frac{d^v e^{-\frac{\xi^2}{2}}}{d\xi^v}
\]

(4.32)

are called Hermite polynomials

The solutions for harmonic oscillators

\[
\psi_n(x) = N_n H_n \left( \frac{m \omega}{\hbar} x \right) e^{-\frac{m \omega x^2}{2\hbar}}
\]

(4.33)

while the eigenvalues

\[
E_n = \hbar \omega \left( n + \frac{1}{2} \right) = \hbar \nu \left( n + \frac{1}{2} \right)
\]

(4.34)

Some first Hermite polynomials (physical Hermite polynomials)

\[
\begin{align*}
H_0(\xi) &= 1 \\
H_1(\xi) &= 2\xi \\
H_2(\xi) &= 4\xi^2 - 2 \\
H_3(\xi) &= 8\xi^3 - 12\xi \\
H_4(\xi) &= 16\xi^4 - 48\xi^2 + 12
\end{align*}
\]

(4.35)
Some properties of Hermite polynomials

\[
\frac{d}{d\xi} H_n(\xi) = 2nH_{n-1}(\xi)
\]

(4.36)

\[
H_{n+1}(\xi) = 2\xi H_n(\xi) - 2nH_{n-1}(\xi)
\]

(4.37)

\[
\int_{-\infty}^{\infty} H_n(\xi) H_m(\xi) e^{-\xi^2} d\xi = \delta_{nm} 2^n n! \sqrt{\pi}
\]

(4.38)

**Task**

Let’s find normalization constant for harmonic oscillator’s eigenfunctions.

\[
1 = \langle \psi_n | \psi_n \rangle = \int_{-\infty}^{\infty} N_n H_n \left( \sqrt{\frac{m\omega}{\hbar}} \xi \right) e^{-\frac{m\omega}{\hbar} \xi^2} N_n H_n \left( \sqrt{\frac{m\omega}{\hbar}} \xi \right) e^{-\frac{m\omega}{\hbar} \xi^2} d\xi =
\]

(4.39)

\[
N_n = \left( \frac{2m\omega}{\hbar} \right)^{\frac{1}{4}} \frac{1}{2^n n!}
\]

(4.40)

Therefore, the normalized wavefunctions of harmonic oscillator are as follows

\[
\psi_n(\xi) = \left( \frac{2m\omega}{\hbar} \right)^{\frac{1}{4}} \frac{1}{2^n n!} H_n \left( \sqrt{\frac{m\omega}{\hbar}} \xi \right) e^{-\frac{m\omega}{\hbar} \xi^2}
\]

(4.41)

Let’s find an average value of displacement from equilibrium position of harmonic oscillator.

\[
\langle \xi \rangle = \int_{-\infty}^{\infty} \xi \psi_n^2(\xi) d\xi = \frac{N^2_n}{m\omega} \int_{-\infty}^{\infty} \xi H_n(\xi) H_n(\xi) e^{-\xi^2} d\xi = \frac{N^2_n}{m\omega} \int_{-\infty}^{\infty} H_n(\xi) \xi H_n(\xi) e^{-\xi^2} d\xi
\]

(4.42)

We know that

\[
\xi H_n(\xi) = \frac{1}{2} H_{n+1}(\xi) + nH_{n-1}(\xi)
\]

(4.43)

so

\[
\langle \xi \rangle = \frac{N^2_n}{m\omega} \left[ \frac{1}{2} \left( \int_{-\infty}^{\infty} H_n(\xi) H_{n+1}(\xi) e^{-\xi^2} d\xi + n \int_{-\infty}^{\infty} H_n(\xi) H_{n-1}(\xi) e^{-\xi^2} d\xi \right) \right] = 0
\]

(4.44)

**Task.** Let’s calculate average kinetic and potential energy of harmonic oscillator

\[
\hat{\mathcal{V}} = \frac{k\xi^2}{2}
\]

(4.45)

\[
\langle \xi^2 \rangle = \int_{-\infty}^{\infty} \xi^2 \psi_n^2(\xi) d\xi = \frac{N^2_n}{m\omega} \left( \frac{\hbar}{m\omega} \right)^{\frac{3}{4}} \int_{-\infty}^{\infty} \xi^2 H_n(\xi) H_n(\xi) e^{-\xi^2} d\xi = \frac{N^2_n}{m\omega} \left( \frac{\hbar}{m\omega} \right)^{\frac{3}{4}} \int_{-\infty}^{\infty} H_n(\xi) \xi H_n(\xi) e^{-\xi^2} d\xi =
\]

\[
= \frac{N^2_n}{m\omega} \left[ \frac{1}{4} \int_{-\infty}^{\infty} \sqrt{\frac{\hbar}{m\omega}} H_{n+1}(\xi) e^{-\xi^2} d\xi + n^2 \int_{-\infty}^{\infty} \sqrt{\frac{\hbar}{m\omega}} H_{n-1}(\xi) e^{-\xi^2} d\xi \right] =
\]
Moreover

\[
\left( \frac{N_n}{N_{n+1}} \right)^2 = \frac{2^{n+1}(n+1)!}{2^{2n}n!} = 2(n+1)
\]  \hspace{1cm} (4.47)

\[
\left( \frac{N_n}{N_{n-1}} \right)^2 = \frac{2^{n-1}(n-1)!}{2^{2n}n!} = \frac{1}{2n}
\]  \hspace{1cm} (4.48)

\[
\langle x^2 \rangle = \frac{\hbar}{2m\omega} \left( n + \frac{1}{2} \right)
\]  \hspace{1cm} (4.49)

We also remember that \( k = m\omega^2 \) which means that

\[
\langle \hat{V} \rangle = \frac{\hbar\omega}{2} \left( n + \frac{1}{2} \right) = \frac{E_n}{2}
\]  \hspace{1cm} (4.50)

And, because

\[ E_n = \langle \hat{V} \rangle + \langle \hat{T} \rangle \]  \hspace{1cm} (4.51)

thus, average value of kinetic energy

\[
\langle \hat{T} \rangle = \frac{E_n}{2}
\]  \hspace{1cm} (4.52)

**Task**

Let’s find average value of kinetic energy for harmonic oscillator directly from the definition

\[
\langle \hat{T} \rangle = \int_{-\infty}^{\infty} \psi_n(x) \hat{T} \psi_n(x) dx = \int_{-\infty}^{\infty} \psi_n(x) \left( -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \right) \psi_n(x) dx = \int_{-\infty}^{\infty} \psi_n(\xi) \left( -\frac{\hbar^2}{2m} \frac{d^2}{d\xi^2} + \frac{\hbar}{2\xi} \frac{d}{d\xi} \right) \psi_n(\xi) d\xi = -N^2 \left( \frac{\hbar\omega}{2} \right) \int_{-\infty}^{\infty} H_n(\xi) e^{-\frac{\xi^2}{2}} - \xi H_n(\xi) e^{-\frac{\xi^2}{2}} d\xi
\]  \hspace{1cm} (4.53)

Let’s notice, that

\[
\frac{d^2}{d\xi^2} N_n H_n(\xi) e^{-\frac{\xi^2}{2}} = N_n \frac{d}{d\xi} \left( H_n'(\xi) e^{-\frac{\xi^2}{2}} - \xi H_n(\xi) e^{-\frac{\xi^2}{2}} \right) = N_n \left( H_n''(\xi) e^{-\frac{\xi^2}{2}} - \xi H_n'(\xi) e^{-\frac{\xi^2}{2}} - H_n(\xi) e^{-\frac{\xi^2}{2}} - \xi H_n(\xi) e^{-\frac{\xi^2}{2}} + \xi^2 H_n(\xi) e^{-\frac{\xi^2}{2}} \right) = N_n \left( H_n'' - 2\xi H_n'(\xi) - H_n(\xi) + \xi^2 H_n(\xi) \right) \right) e^{-\frac{\xi^2}{2}}
\]  \hspace{1cm} (4.54)

And moreover let’s recollect that

\[
H_n'' - 2\xi H_n'(\xi) = -2nH_n(\xi)
\]  \hspace{1cm} (4.55)

Thus

\[
\hat{T} \psi_n(\xi) = -\frac{\hbar^2}{2m} \frac{m\omega}{\hbar} \left( \xi^2 - 2n - 1 \right) \psi_n(\xi) = -\frac{\hbar^2}{2m} \frac{m\omega}{\hbar} \left( \xi^2 - 2n \left( n + \frac{1}{2} \right) \right) \psi_n(\xi)
\]  \hspace{1cm} (4.56)

Therefore
\[
\langle T \rangle = \frac{\hbar^2 m \omega}{2 m} \left( 2 \left(n + \frac{1}{2}\right) - \langle \xi^2 \rangle \right)
\]  

(4.57)

Previously we found that \(\langle \xi^2 \rangle = \left(n + \frac{1}{2}\right)\), and

\[
\langle T \rangle = \frac{\hbar \omega}{2} \left(n + \frac{1}{2}\right) = \frac{\hbar \nu}{2} \left(n + \frac{1}{2}\right) = \frac{E_n}{2}
\]  

(4.58)

5 Rigid rotor

The linear rigid rotor model consists of two point masses located at fixed distances from their center of mass. The moment of inertia \(I\) of the diatomic molecule is equal to \(\mu R^2\), where \(\mu\) is the center of mass, while the \(R\) is the distance between the atoms. So it’s analogous to the moment of inertia of a single point.

In the case of a rigid rotor model the space is free of any field and thus the total energy corresponds only to the kinetic energy of the system.

5.1 Two-dimensional rigid rotor

Linear rigid rotor model is used to predict the rotational energy of diatomic molecules. We have two point masses \(m_1\) and \(m_2\) which reduced mass \(M = \frac{m_1 m_2}{m_1 + m_2}\). The two masses move in \(xy\) plane around a circle with constant radius \(R\) (from the center of their masses). Total kinetic energy equals \(E = \frac{p^2}{2M}\). The angular momentum related to rotation around \(z\) axis \(J_z = \pm R p\). Therefore

\[
E = \frac{p^2}{2M} = \frac{1}{2M} \left( \frac{J_z}{R} \right)^2 = \frac{J_z^2}{2I}
\]  

(5.1)

Further, using de Broglie’s relation

\[
\lambda = \frac{\hbar}{p} = \pm \frac{\hbar R}{J_z}
\]  

(5.2)

Moreover, when we consider a wave on a circle, we require it must be reproduced after every cycle, i.e. \(2\pi\)

\[
\lambda = \frac{2\pi R}{\tilde{m}}, \quad \tilde{m} = 1, 2, \ldots
\]  

(5.3)

\[
J_z = \pm \frac{h R \lambda}{\tilde{m}} = \pm \hbar R \frac{\tilde{m}}{2\pi R} = m \hbar, \quad m = \pm 1, \pm 2, \ldots
\]  

(5.4)

So, in this way we got energy quantized and the angular momentum also quantized

The Hamiltonian

\[
\hat{H} = \frac{\hat{p}^2}{2M} = -\frac{\hbar^2}{2M} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right)
\]  

(5.5)

In the rigid rotor model we require that the particle moves on a constant radius, therefore it’s simpler to go to spherical coordinates

\[
\hat{H} = -\frac{\hbar^2}{2M} \left( \frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} + \frac{1}{r^2} \frac{\partial^2}{\partial \phi^2} \right)
\]  

(5.6)

and claiming that \(r = R = \text{const}\) so that

\[
\hat{H} = \frac{\hbar^2}{2M} \frac{1}{R^2} \frac{\partial^2}{\partial \phi^2} = -\frac{\hbar}{2I} \frac{\partial^2}{\partial \phi^2}
\]  

(5.7)
So, when we know the Hamiltonian we can write the eigenproblem

\[ \frac{\partial^2}{\partial \phi^2} \Psi(\phi) = \frac{2IE}{\hbar^2} \Psi(\phi) \]  

(5.8)

It’s form is exactly the same like for a free particle problem, for which we know the exact solution. Thus

\[ \Psi(\phi) = \frac{e^{im\phi}}{\sqrt{2\pi}} \]  

(5.9)

where the \( m = \pm \frac{\sqrt{2IE}}{\hbar} \). The wavefunction is normalized for \( \phi \in [0, 2\pi] \).

Let’s apply the boundary condition

\[ \Psi(\phi + 2\pi) = \Psi(\phi) \]  

(5.10)

\[ \frac{e^{im(\phi+2\pi)}}{\sqrt{2\pi}} = \frac{e^{im\phi}}{\sqrt{2\pi}} \]  

(5.11)

\[ e^{2im\phi} = 1 \]  

(5.12)

Then, we can conclude that the \( m \) must be an integer. The \( m \) numbers either the wavefunctions and the relating energies

\[ E_m = \langle \Psi_m | \hat{H} | \Psi_m \rangle = \frac{m^2\hbar^2}{2I} \]  

(5.13)

It is well visible that for \( m \neq 0 \) the energetical levels are twice degenerated, i.e. for the wavefunctions \( \Psi_m \) and \( \Psi_{-m} \) the apropiate energies are equal \( E_m = E_{-m} \), but the values of angular momentum are different

\[ J_z \Psi_m = \hbar m \Psi_m \quad J_z \Psi_{-m} = -\hbar m \Psi_{-m} \]  

(5.14)

because the wavefunctions \( \Psi_m \) and \( \Psi_{-m} \) describe the same particles but moving in opposite directions.

### 5.2 Three-dimensional rigid rotor

Find eigenfunctions and eigenvalues of \( \hat{L}_z \) operator (\( \hat{L}_z = -i\hbar \frac{\partial}{\partial \phi} \)).

\[ \hat{L}_z \Phi(\phi) = L_z \Phi(\phi) \]

\[ -i\hbar \frac{\partial}{\partial \phi} = L_z \Phi(\phi) \]

\[ \frac{\partial}{\partial \phi} = \frac{i}{\hbar} L_z \Phi(\phi) \quad \Rightarrow \quad \Phi(\phi) = N e^{im\phi} \]

\[ \frac{\partial}{\partial \phi} = N i m e^{im\phi} = im\Phi(\phi) \]

\[ im = \frac{i}{\hbar} \quad \Rightarrow \quad L_z = \hbar m \]  

(5.15)

Due to periodicity of \( \Phi(\phi) \) function

\[ \Phi(\phi) = \Phi(\phi + 2\pi) \]

\[ N e^{im\phi} = N e^{i\phi(\phi+2\pi)} \]

\[ e^{im2\pi} = 1 \]
\[
\cos(2m\pi) + i \sin(2m\pi) = 1 \quad \Rightarrow \quad m = 0, \pm 1, \pm 2, \ldots 
\]

We can also find the normalization constant

\[
1 = \langle \Phi(\varphi) | \Phi(\varphi) \rangle = \int_0^{2\pi} |N|^2 e^{-im\varphi} e^{im\varphi} d\varphi = |N|^2 \int_0^{2\pi} d\varphi \quad \Rightarrow \quad N = \frac{1}{\sqrt{2\pi}}
\]

Thus, the eigenfunctions of the \( \hat{L}_z \) operator are the following

\[
\Phi_m(\varphi) = \frac{1}{\sqrt{2\pi}} e^{im\varphi}, \quad m = 0, \pm 1, \pm 2, \ldots
\]

Exercise. Show that the eigenfunctions of \( \hat{L}_z \) operator are orthogonal.

Exercise. Show that the \( \Phi_m(\varphi) \) functions satisfy the eigenproblem of \( \hat{L}_z \) operator.

Find eigenfunctions and eigenvalues of \( \hat{L}^2 \) operator.

The starting equation is the following

\[
\hat{L}^2 \Psi(\theta, \varphi) = L^2 \Psi(\theta, \varphi)
\]

Let’s consider first the eigenvalue, \( L^2 \), revealing from this equation. Classically the angular momentum \( \vec{L} = \vec{r} \times \vec{p} \) is a vector product. In SI units it is measured as \( [L] = kr^2 \). In quantum theory a component of angular momentum operator is measured in Planck constant’s units: \( L_z = mh \). \( [\hat{L}_z] = [\hat{h}] = [J \cdot s] = N \cdot m \cdot s = kg \cdot \pi \). Moreover, \( \hat{L}^2 = \sum_i \hat{L}_i^2 \), while \( i = x, y, z \), so eigenvalues of \( \hat{L}^2 \) operator should be expressed by \( \hbar^2 \). Additionally, the \( \hat{L}^2 \) commutes with each of components of the \( \hat{L} \) operator while the Hamiltonian can be partially expressed by the \( \hat{L}^2 \) operator which means the eigenvalues of the \( \hat{L}^2 \) should be real numbers. Most likely, the eigenvalues of \( \hat{L}^2 \) operator should be quantized, also because the eigenvalues of \( \hat{L}_z \) operator are quantized (by the \( m \) numbers). Moreover the \( \hat{L}^2 \) can be partially expressed by the \( \hat{L}_z \) operator. Therefore, it is justified to postulate that the eigenvalues of \( \hat{L}^2 \) operator should be considered as a product of \( \hbar^2 \) and some discrete number(s), here - \( \lambda \).

\[
\hat{L}^2 \Psi(\theta, \varphi) = \lambda \hbar^2 \Psi(\theta, \varphi)
\]

We also postulate that the wavefunction of two independent variables can be expressed by a product of independent functions of only one variable, say \( \Psi(\theta, \varphi) = \Theta_{\lambda,m}(\theta) \Phi_m(\varphi) \). Now we can try to solve the eigenproblem of the \( \hat{L}^2 \) operator.

\[
-h^2 \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right] \Theta_{\lambda,m}(\theta) \Phi_m(\varphi) = \lambda \hbar^2 \Theta_{\lambda,m}(\theta) \Phi_m(\varphi).
\]

Moreover

\[
\frac{\partial^2}{\partial \varphi^2} \Phi_m(\varphi) = \frac{\partial}{\partial \varphi} \left( im \frac{1}{\sqrt{2\pi}} e^{im\varphi} \right) = i^2 m^2 \left( \frac{1}{\sqrt{2\pi}} e^{im\varphi} \right) = m^2 \Phi_m(\varphi)
\]

\[
\left( \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) - \frac{m^2}{\sin^2 \theta} \right) \Theta_{\lambda,m}(\theta) \Phi_m(\varphi) = -\lambda \Theta_{\lambda,m}(\theta) \Phi_m(\varphi)
\]

\[
\left( \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) - \frac{m^2}{\sin^2 \theta} \right) \Theta_{\lambda,m}(\theta) = -\lambda \Theta_{\lambda,m}(\theta)
\]

\[
\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) \Theta_{\lambda,m}(\theta) + \left( \frac{\lambda}{\sin^2 \theta} \right) \Theta_{\lambda,m}(\theta) = 0
\]
\[
\frac{d^2 \Theta_{\lambda,m}(\theta)}{d \theta^2} + \frac{\cos \theta}{\sin \theta} \frac{d \Theta_{\lambda,m}(\theta)}{d \theta} + \left( \lambda - \frac{m^2}{\sin^2 \theta} \right) \Theta_{\lambda,m}(\theta) = 0
\]  
(5.20)

We substitute \( x = \cos \theta \) and \( \Theta_{\lambda,m}(\theta) = f_{\lambda,m}(x) \). \( 0 \leq \theta \leq \pi \Rightarrow -1 \leq x \leq 1 \). First we calculate derivatives

\[
\frac{d}{d \theta} \Theta_{\lambda,m}(\theta) = \frac{d f_{\lambda,m}(x)}{d x} \frac{d x}{d \theta} = - \sin \theta \frac{d f_{\lambda,m}(x)}{d x}
\]

\[
\frac{d^2}{d \theta^2} \Theta_{\lambda,m}(\theta) = \frac{d}{d \theta} \left( \frac{d}{d \theta} \Theta_{\lambda,m}(\theta) \right) = \frac{d}{d \theta} \left( - \sin \theta \frac{d f_{\lambda,m}(x)}{d x} \right) = - \cos \theta \frac{d}{d \theta} \frac{d f_{\lambda,m}(x)}{d x} - \sin \theta \frac{d}{d \theta} \frac{d f_{\lambda,m}(x)}{d x}
\]

\[
\begin{align*}
&= - \cos \theta \frac{d f_{\lambda,m}(x)}{d x} - \sin \theta \frac{d}{d x} \frac{d f_{\lambda,m}(x)}{d \theta} \\
&= - \cos \theta \frac{d f_{\lambda,m}(x)}{d x} + \sin^2 \theta \frac{d^2 f_{\lambda,m}(x)}{d x^2}
\end{align*}
\]  
(5.21)

Thus

\[
\begin{align*}
\sin^2 \theta \frac{d^2 f_{\lambda,m}(x)}{d x^2} & - \cos \theta \frac{d f_{\lambda,m}(x)}{d x} + \cos \theta \left( - \sin \theta \frac{d f_{\lambda,m}(x)}{d x} \right) + \left( \lambda - \frac{m^2}{1 - x^2} \right) f_{\lambda,m}(x) = 0 \\
(1 - x^2) f''_{\lambda,m}(x) - 2 x f'_{\lambda,m}(x) + \left( \lambda - \frac{m^2}{1 - x^2} \right) f_{\lambda,m}(x) &= 0
\end{align*}
\]  
(5.22)

or, skipping the indices

\[
(1 - x^2) f''(x) - 2 x f'(x) + \left( \lambda - \frac{m^2}{1 - x^2} \right) f(x) = 0
\]  
(5.23)

which is called the associated (general) Legendre’s equation. If \( m = 0 \) then it simplifies to so called Legendre’s equation.

\[
(1 - x^2) f''(x) - 2 x f'(x) + \lambda f(x) = 0
\]  
(5.24)

We start our considerations from solving first the simpler equation, i.e. from solving the Legendre’s equation. We will do this by power series method, i.e. by a method, where we postulate that the solution might be a general power series (Frobenius method), namely

\[
f = \sum_{k=0}^{+\infty} c_k x^k = c_0 + c_1 x + c_2 x^2 + c_3 x^3 + c_4 x^4 + \ldots
\]  
(5.25)

Thus, the problem comes down to find the \( c_k \) coefficients. To proceed further we calculate the derivatives

\[
f' = 0 + c_1 x^0 + 2 c_2 x^1 + 3 c_3 x^2 + 4 c_4 x^3 + \ldots = \sum_{k=1}^{+\infty} k c_k x^{k-1}
\]

\[
f'' = 0 + 0 + 2 c_2 + 6 c_3 x + 12 c_4 x^2 + \ldots = \sum_{k=2}^{+\infty} k(k-1) c_k x^{k-2}
\]

Let’s notice
Above all even coefficients can be expressed by which leads to a recurrence relation (one must discriminate the terms for even and for odd indices)

\[
L = \sum_{k=2}^{+\infty} k(k-1)c_k x^{k-2} = \sum_{k=0}^{+\infty} (k+2)(k+1)c_{k+2} x^k = R
\]

L: \( k = 2 \) \( \Rightarrow \) \((4 - 2)c_2 x^0 = 2c_2 \) R: \( k = 0 \) \( \Rightarrow \) \((0 + 2)(0 + 1)c_2 x^0 = 2c_2 \)

L: \( k = 3 \) \( \Rightarrow \) \((9 - 3)c_3 x^1 = 6c_3 x \) R: \( k = 1 \) \( \Rightarrow \) \((1 + 2)(1 + 1)c_3 x^1 = 6c_3 x \)

L: \( k = 4 \) \( \Rightarrow \) \((16 - 4)c_4 x^2 = 12c_4 x^2 \) R: \( k = 2 \) \( \Rightarrow \) \( 4 \cdot 3c_4 x^2 = 12c_4 x^2 \)

\[
\begin{align*}
L: & \ x_j^2 = \sum_{k=1}^{+\infty} 2k c_k x^k = \sum_{k=0}^{+\infty} 2k c_k x^k \\
(1 - x^2) f'' & = \sum_{k=2}^{+\infty} k(k-1)c_k x^{k-2} - \sum_{k=2}^{+\infty} k(k-1)c_k x^k = \sum_{k=0}^{+\infty} (k+2)(k+1)c_{k+2} x^k - \sum_{k=0}^{+\infty} k(k-1)c_k x^k \\
& = \sum_{k=0}^{+\infty} \left[ (k+2)(k+1)c_{k+2} - k(k-1)c_k \right] x^k
\end{align*}
\]

Plugging in

\[
(k + 2)(k + 1)c_{k+2} - k(k-1)c_k - 2kc_k + \lambda c_k = 0, \quad k \geq 0,
\]

which leads to a recurrence relation (one must discriminate the terms for even and for odd indices)

\[
\begin{align*}
c_{k+2} &= \frac{k(k-1) + 2k - \lambda}{(k + 2)(k + 1)} \ c_k = \frac{k(k+1) - \lambda}{(k + 2)(k + 1)} \ c_k \\
c_2 &= -\frac{2(2+1) - \lambda}{4 \cdot 3} c_0 = -\frac{2(2+1) - \lambda}{6!} c_0 \\
c_4 &= \frac{4(4+1) - \lambda}{6 \cdot 5} c_4 = (4(4+1) - \lambda)(2(2+1) - \lambda) c_0 \\
c_6 &= \frac{6(6+1) - \lambda}{6 \cdot 5} c_6 = (6(6+1) - \lambda)(2(2+1) - \lambda) c_0 \\
c_{2k} &= (-1)^{2k-2} \frac{[(2k - 2)(2k - 1) - \lambda][(2k - 4)(2k - 3) - \lambda][\ldots][(k + 2)(k + 3) - \lambda][k(k + 1) - \lambda]}{(2k)!} c_0 \\
c_3 &= \frac{3(3+1) - \lambda}{(3+2)(3+1)} c_3 = \frac{3(3+1) - \lambda}{5 \cdot 4} c_3 = (3(3+1) - \lambda)(2(2+1) - \lambda) c_3 \\
c_5 &= \frac{5(5+1) - \lambda}{(5+2)(5+1)} c_5 = \frac{5(5+1) - \lambda}{5 \cdot 4 \cdot 3} c_5 = (5(5+1) - \lambda)(2(2+1) - \lambda) c_5 \\
c_{2k+1} &= (-1)^{2k-1} \frac{[(2k(2k + 1) - \lambda][(2k(2k + 1) - \lambda)[\ldots][(k+2)(k+3) - \lambda][(k+1) - \lambda]}{(2k+1)!} c_1
\end{align*}
\]

Above all even coefficients can be expressed by \( c_0 \) and the odd coefficients can be written in terms of \( c_1 \). Therefore the general solution to Legendre’s equation, i.e. the series for \( f(x) \) can be written as

\[
\begin{align*}
f(x) &= c_0 f_1(x) + c_1 f_2(x) \\
f_1(x) &= 1 + \sum_{k=1}^{+\infty} (-1)^{(2k)} \frac{[(2k(2k + 1) - \lambda)((2k(2k + 1) - \lambda)[\ldots][(k+2)(k+3) - \lambda][k(k + 1) - \lambda]}{(2k)!} c_0 \\
f_2(x) &= \sum_{k=1}^{+\infty} (-1)^{(2k)} \frac{[(2k(2k + 1) - \lambda)((2k(2k + 1) - \lambda)[\ldots][(k+2)(k+3) - \lambda][k(k + 1) - \lambda]}{(2k)!} c_1 x^{2k}
\end{align*}
\]
\[ f_2(x) = x + \sum_{k=1}^{\infty} \frac{(-1)^k [2k(2k + 1) - \lambda][(2k - 2)(2k - 2 + 1) - \lambda] \cdots (\lambda - 2)}{(2k + 1)!} x^{2k+1} \]

with arbitrary constants \(c_0\) and \(c_1\).

Let’s examine the convergence of the power series function \(f = \sum_{k=0}^{\infty} c_k x^k\). If \(x = \pm 1\) then the series is \(f_a = \sum_{k=0}^{\infty} (-1)^k c_k\), which is unfortunately divergent. This reveals from the ratio test which can be done even for the recursion relation for the coefficients \(c_k\). This, in turn, means that the wave function, which should be normalized, diverges, which means it cannot be interpreted accordingly to Born and practically, the normalization integral on the domain \([-1, 1]\) is infinite, see figure below. If \(-1 < x < 1\) then one can perform a ratio test or apply the comparison test.

\[ \sum_{k=0}^{\infty} \left| \frac{c_{k+2}}{c_k} \right| x^{k+2} = 0 \quad \Rightarrow \quad k_{\text{max}}(k_{\text{max}} + 1) - \lambda = 0 \quad \Rightarrow \quad \lambda = k_{\text{max}}(k_{\text{max}} + 1) \quad (5.26) \]

We can name this \(k_{\text{max}}\) as \(l\) so that \(\lambda = l(l + 1)\). It’s obvious the \(l\) must be a positive integer. It is then clear that if only \(\lambda = l(l + 1)\) then the power series terminate.

Therefore

\[ \lambda = l(l + 1) \quad \Rightarrow \quad L^2 = l(l + 1)\hbar^2 \]

\[ \hat{L}^2 \Psi(\theta, \varphi) = l(l + 1)\hbar^2 \Psi(\theta, \varphi). \quad (5.27) \]

We can now rewrite the Legendre equation into the following

\[ (1 - x^2) f''(x) - 2 x f'(x) + l(l + 1) f(x) = 0 \quad (5.28) \]

or into the operator-like equation: \(\hat{T}(y) = \lambda y\) where \(\hat{T}(f) = (p f')'\) with \(p = x^2 - 1\) and \(\lambda = l(l + 1)\). We can rewrite the equations

\[ c_{k+2} = \frac{k(k + 1) - \lambda}{(k + 2)(k + 1)} c_k = -\frac{(l - k)(l + k + 1)}{(k + 1)(k + 2)} c_k \]

**Figure 3.** \(f = \sum_{k=0}^{\lambda=19} c_k x^k\) for arbitrary \(x \in [-1, 1]\) and arbitrary \(\lambda\), here equal to 3. Here \(c_0\) was chosen to be equal to 1 while the \(c_1\) was chosen to be equal to \(x\).
\[ c_2 = -\frac{\lambda}{1 \cdot 2} c_0 = -\frac{l(l + 1)}{2!} c_0 \]
\[ c_4 = -\frac{(l - 2)(l + 3)}{4 \cdot 3} c_2 = -\frac{(l - 2)(l + 1)(l + 3)}{4!} c_0 \]
\[ c_6 = -\frac{(l - 4)(l + 5)}{6 \cdot 5} c_4 = -\frac{(l - 4)(l - 2)(l + 1)(l + 3)(l + 5)}{6!} c_0 \]
\[ c_{2k} = (-1)^{k} \frac{(l - 2k - 2)(l - 2k - 4) \ldots (l + 1)(l + 3) \ldots (l + 2k - 1)}{(2k)!} c_0 \]
\[ c_3 = -\frac{(l - 1)(l + 2)}{2 \cdot 3} c_1 = -\frac{(l - 1)(l + 2)}{3!} c_1 \]
\[ c_5 = -\frac{(l - 3)(l + 4)}{4 \cdot 5} c_3 = -\frac{(l - 3)(l - 1)(l + 2)(l + 4)}{5!} c_1 \]
\[ c_7 = -\frac{(l - 5)(l + 6)}{6 \cdot 7} c_5 = -\frac{(l - 5)(l - 3)(l - 1)(l + 2)(l + 4)(l + 6)}{7!} c_1 \]
\[ c_{2k+1} = (-1)^{k} \frac{(l - 2k - 1)(l - 2k - 3) \ldots (l - 1)(l + 2)(l + 4) \ldots (l + 2k)}{(2k + 1)!} c_1 \]  \hspace{1cm} (5.29)

\[ \text{... series } \rightarrow \text{ polynomial} \]

Let’s note that (we choose some } n \text{ (positive integer or 0)) and for the highest } n

\[ (2n)! = 1 \cdot 2 \cdot 3 \cdot \ldots \cdot 2n = (2 \cdot 4 \cdot 6 \cdot \ldots \cdot 2n) \cdot (1 \cdot 3 \cdot 5 \cdot \ldots \cdot (2n - 1)) = \]
\[ = (1 \cdot 2) \cdot (2 \cdot 3) \cdot (3 \cdot 2) \cdot \ldots \cdot (2 \cdot n) \cdot (1 \cdot 3 \cdot 5 \cdot \ldots \cdot (2n - 1)) = \]
\[ = 2^n \cdot (1 \cdot 2 \cdot 3 \cdot \ldots \cdot n) \cdot (1 \cdot 3 \cdot 5 \cdot \ldots \cdot (2n - 1)) = \]
\[ = 2^n n! \cdot (1 \cdot 3 \cdot 5 \cdot \ldots \cdot (2n - 1)) \]
\[ c_n = \frac{(2n)!}{2^n(n!)^2} = \frac{1 \cdot 3 \cdot 5 \cdot \ldots \cdot (2n - 1)}{n!} \]
\[ c_s = -\frac{(s + 2)(s + 1)}{(n - s)(n + s + 1)} c_{s+2}, \quad s \leq n - 2. \quad \text{For } s = n - 2 \]
\[ c_{n-2} = -\frac{n(n - 1)}{2(2n - 1)} c_n = -\frac{n(n - 1)}{2(2n - 1)} \frac{(2n)!}{2^n(n!)^2} = -\frac{n(n - 1)2n(2n - 1)(2n - 2)}{2(2n - 1)2^n(n - 1)!(n - 1)(2n - 2)!} \]
\[ = -\frac{(2n - 2)!}{2^n(n - 1)!(n - 2)!} \]
\[ c_{n-4} = -\frac{(n - 2)(n - 3)}{4(2n - 3)} c_{n-2} = \frac{(2n - 4)!}{2^n(n - 4)!(n - 4)!} \]
\[ \ldots \]
\[ c_{n-2k} = (-1)^{k} \frac{(2n - 2k)!}{2^n k!(n - k)!(n - 2k)!}, \quad n - 2k \geq 0 \]

Thus we obtain

\[ P_n(x) = \sum_{k=0}^{N} (-1)^{k} \frac{(2n - 2k)!}{2^n k!(n - k)!(n - 2k)!} x^{n-2k} = (2n)! x^n - \frac{(2n - 2)!}{2^n 1!(n - 1)!(n - 2)!} x^{n-2} + \ldots, \]  \hspace{1cm} (5.30)

where } N = n/2 \text{ or } M = (n - 1)/2, \text{ whichever of these two is an integer. The above polynomials are called Legendre polynomials of degree } n. \text{ First Legendre polynomials are found below.}

It’s convenient to have some other form of the above formula for } n\text{-th Legendre polynomial. Let’s note that}

\[ \frac{d^n}{dx^n} x^{2n-2k} = (2n - 2k)(2n - 2k - 1)(2n - 2k - 2) \ldots (2n - 2k - (n - 1)) x^{2n-2k-n} = \]
= (2n − 2k)(2n − 2k − 1)(2n − 2k − 2) \ldots (n − 2k + 1) x^{n−2k} = \\
= \frac{(2n − 2k)(2n − 2k − 1) \ldots (n − 2k + 1)(n − 2k)(n − 2k − 1) \ldots 3 \cdot 2 \cdot 1}{(n − 2k)(n − 2k − 1) \ldots 3 \cdot 2 \cdot 1} x^{n−2k} = \\
= \frac{(2n − 2k)!}{(n − 2k)!} x^{n−2k} \quad (5.31)

Let’s remind the binomial theorem

\[(x + y)^n = \sum_{k=0}^{n} \binom{n}{k} x^{n−k} \quad \Rightarrow \quad (x + 1)^n = \sum_{k=0}^{n} \binom{n}{k} x^k\]

\[(x^2 − 1)^n = \sum_{k=0}^{n} (−1)^k \frac{n!}{k!(n−k)!} x^{2n−2k} \quad \Rightarrow \quad \frac{d}{dx}(x^2 − 1)^n = \frac{d}{dx} \sum_{k=0}^{n} (−1)^k \frac{n!}{k!(n−k)!} x^{2n−2k} \quad (5.32)\]

Therefore

\[P_n(x) = \frac{n^2}{2^n} \sum_{k=0}^{n/2} (−1)^k \frac{(2n − 2k)!}{2^k k!(n−k)!} x^{2n−2k} = \frac{n^2}{2^n} \sum_{k=0}^{n/2} (−1)^k \frac{1}{2^k k!(n−k)!} \frac{d^n}{dx^n} x^{2n−2k} = \]

\[= \frac{1}{2^n n!} \frac{d^n}{dx^n} \sum_{k=0}^{n} (−1)^k \frac{n!}{k!(n−k)!} x^{2n−2k} = \frac{1}{2^n n!} \frac{d^n}{dx^n}(x^2 − 1)^n \quad (5.33)\]

The formula above is called the Rodrigues’ formula.

<table>
<thead>
<tr>
<th>n</th>
<th>(P_n(x))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>1</td>
<td>(x)</td>
</tr>
<tr>
<td>2</td>
<td>(\frac{1}{2}(3x^2 − 1))</td>
</tr>
<tr>
<td>3</td>
<td>(\frac{1}{2}(5x^3 − 3x))</td>
</tr>
<tr>
<td>4</td>
<td>(\frac{1}{8}(35x^4 − 30x^2 + 3))</td>
</tr>
<tr>
<td>5</td>
<td>(\frac{1}{16}(63x^5 − 70x^3 + 15x))</td>
</tr>
<tr>
<td>6</td>
<td>(\frac{1}{16}(231x^6 − 315x^4 + 105x^2 − 5))</td>
</tr>
<tr>
<td>7</td>
<td>(\frac{1}{16}(429x^7 − 693x^5 + 315x^3 − 35x))</td>
</tr>
<tr>
<td>8</td>
<td>(\frac{1}{128}(6435x^8 − 12012x^6 + 6930x^4 − 1260x^2 + 35))</td>
</tr>
</tbody>
</table>

**Figure 4.** First Legendre polynomials.

Lets check the orthogonality of Legendre polynomials, \(P_n(x)\) by using the Rodrigues formula. First let’s take an arbitrary function \(g(x)\) which is continous on the interval \(-1 \leq x \leq 1\) and let’s consider following integral

\[I = \int_{-1}^{1} g(x) P_n(x) dx \]

\[I = \frac{1}{2^n n!} \int_{-1}^{1} g(x) \frac{d^n}{dx^n}(x^2 − 1)^n dx = \frac{1}{2^n n!} \int_{-1}^{1} g(x) \left[ \frac{d^{n−1}}{dx^{n−1}}(x^2 − 1)^n \right] dx \quad (5.34)\]

Integrating the \(I\) by parts
\[
\int uv' \, dx = uv - \int vu' \, dx, \quad \text{or} \quad \int udv = uv - \int vdu
\]

\[
u(x) = g(x) \implies du(x) = g'(x) \, dx
\]

\[
v'(x) = \frac{d^n}{dx^n}(x^2 - 1), \quad \implies \quad v(x) = \frac{d^{n-1}}{dx^{n-1}}(x^2 - 1) = d \left[ \frac{d^{n-1}}{dx^{n-1}}(x^2 - 1)^n \right]
\]

\[
I = \frac{1}{2^n n!} \left\{ \left[ g(x) \frac{d^{n-1}}{dx^{n-1}}(x^2 - 1)^n \right]_{-1}^{1} - \int_{-1}^{1} g'(x) \frac{d^{n-1}}{dx^{n-1}}(x^2 - 1)^n \, dx \right\} = 0 - \frac{1}{2^n n!} \left\{ \left[ g(x) \frac{d^{n-2}}{dx^{n-2}}(x^2 - 1)^n \right]_{-1}^{1} - \int_{-1}^{1} g''(x) \frac{d^{n-2}}{dx^{n-2}}(x^2 - 1)^n \, dx \right\} = \frac{1}{2^n n!} \int_{-1}^{1} g''(x) \frac{d^{n-2}}{dx^{n-2}}(x^2 - 1)^n \, dx
\]

... after n partial integrations

\[
I = \frac{1}{2^n n!} \int_{-1}^{1} g(x) P_n(x) \, dx = \frac{(-1)^n}{2^n n!} \int_{-1}^{1} (x^2 - 1)^n \frac{d^n}{dx^n} g(x) \, dx
\]

Let’s now utilize the final equality by replacing the g(x) function into the \( P_m(x) \) Legendre polynomial

\[
\int_{-1}^{1} P_m(x) P_n(x) \, dx = \frac{(-1)^n}{2^n n!} \int_{-1}^{1} (x^2 - 1)^n \frac{d^n}{dx^n} \left[ \frac{1}{2^{m+n} m! n!} \frac{d^m}{dx^m}(x^2 - 1)^m \right] \, dx
\]

- case 1. \( m \neq n \). Moreover, let \( m < n \).

In this case the degree of polynomial \((x^2 - 1)^m\) is \(2m < m + n\) so that \(\frac{d^{m+n}}{dx^{m+n}}(x^2 - 1)^m = 0\). Therefore

\[
\int_{-1}^{1} P_m(x) P_n(x) \, dx = \frac{(-1)^n}{2^n n!} \int_{-1}^{1} (x^2 - 1)^n \frac{d^n}{dx^n}(x^2 - 1)^m \, dx = 0
\]

The order of polynomials under the integral can be opposite so that for any \( P_n \) and any \( P_m \) if only \( m \neq n \) the integral equals 0. This means the Legendre polynomials are orthogonal.

- case 2. \( m = n \).

First, let’s notice that \( \frac{d^{2n}}{dx^{2n}} (x^2 - 1)^n = (2n)! \). Thus

\[
\int_{-1}^{1} P_n(x) P_n(x) \, dx = \frac{(-1)^n(2n)!}{2^n n!} \int_{-1}^{1} (x^2 - 1)^n \, dx = \frac{(-1)^n 2^n (2n) (2n + 1)}{2^n n!} \frac{2^n (2n) (2n + 1)}{(2n + 1)} = \frac{2}{2n + 1}
\]

Thus the normalized Legendre equations are given by the following Rodrigues formula

\[
NP_n(x) = \frac{2}{2n + 1} \frac{d}{dx^n} (x^2 - 1)^n \quad (5.35)
\]

In general

\[
\int_{-1}^{1} P_m(x) P_n(x) \, dx = \frac{2}{2n + 1} \delta_{nm} \quad (5.36)
\]
The Legendre polynomials are solutions of Legendre’s equation. Let’s come back to the associated (general) Legendre’s equation

\[(1 - x^2) f''(x) - 2x f'(x) + \left(l(l + 1) - \frac{m^2}{1 - x^2}\right) f(x) = 0, \quad m \neq 0\]

Let’s recall Leibnitz’s formula for differentiating products of functions

\[
\left(\frac{d}{dx}\right)^n (f \cdot g) = \sum_{s=0}^{n} \binom{n}{s} \frac{d^{n-s}}{dx^{n-s}} g \frac{d^s}{dx^s} f
\]

and let’s apply it to the Legendre’s (the non-associated) equation which can be written in this form too:

\[
\frac{d}{dx} \left[ (1 - x^2) P_l(x) \right] + l(l + 1) P_l(x) = 0,
\]

so let’s differentiate this equation \(m\) times

\[
\sum_{s=0}^{m+1} \frac{(m + 1)!}{(m + 1 - s)!s!} \frac{d^{m+1-s}}{dx^{m+1-s}} (1 - x^2) \frac{d^{s+1}}{dx^{s+1}} P_l(x) + l(l + 1) \frac{d^m}{dx^m} P_l(x) = 0
\]

Let’s have a look at the differentiation of the \(1 - x^2\) term

\[
\frac{d}{dx} (1 - x^2) = -2x, \quad \frac{d^2}{dx^2} (1 - x^2) = -2, \quad \frac{d^3}{dx^3} (1 - x^2) = 0
\]

It reveals that the nonzero terms are present for only \(s = m + 1, s = m\) and \(s = m - 1\). Thus

\[
\sum_{s=\{m+1,m,m-1\}} \frac{(m + 1)!}{(m + 1 - s)!s!} \frac{d^{m+1-s}}{dx^{m+1-s}} (1 - x^2) \frac{d^{s+1}}{dx^{s+1}} P_l(x) + l(l + 1) \frac{d^m}{dx^m} P_l(x) =
\]

\[
= (1 - x^2) \frac{d^{m+2}}{dx^{m+2}} P_l(x) - \frac{(m + 1)!}{m!} 2x \frac{d^{m+1}}{dx^{m+1}} P_l(x) - 2 \frac{(m + 1)!}{2!(m - 1)!} \frac{d^m}{dx^m} P_l(x) + l(l + 1) \frac{d^m}{dx^m} P_l(x) = 0 \quad (5.37)
\]

Let

\[
u(x) = \frac{d^m}{dx^m} P_l(x)
\]

Then the Legendre’s equation can be rewritten into the following form

\[(1 - x^2)u'' - 2(m + 1)xu' + [l(l + 1) - 2m(m + 1)]u = 0\]

Let’s define

\[v(x) = (1 - x^2)^{m/2} u(x)\]

\[u(x) = (1 - x^2)^{-m/2} v(x)\]

\[
\left( (1 - x^2)^{-m/2} \right)' = -\frac{1}{\sqrt{(1 - x^2)^m}} \frac{1}{2 \sqrt{(1 - x^2)^m}} m (1 - x^2)^{m-1} (-2x) = \frac{mx(1 - x^2)^{m-1}}{(1 - x^2)^m \sqrt{(1 - x^2)^m}} =\]

\[
= \frac{mx}{1 - x^2} (1 - x^2)^{-m/2}
\]

\[u'(x) = (1 - x^2)^{-m/2} \left( v' + \frac{mx}{1 - x^2} v \right)\]


\[ u''(x) = \left[ (1 - x^2)^{-m/2} u' \right]' + \left[ (1 - x^2)^{-m/2} \frac{mx}{1 - x^2} \right]' = \frac{mx}{1 - x^2} (1 - x^2)^{-m/2} u' + (1 - x^2)^{-m/2} u'' + \]

\[ + \frac{mx}{1 - x^2} (1 - x^2)^{-m/2} \frac{mx}{1 - x^2} (1 - x^2)^{-m/2} v + (1 - x^2)^{-m/2} \left[ \frac{mx}{1 - x^2} v \right]' = \]

\[ = (1 - x^2)^{-m/2} \left[ \frac{mx}{1 - x^2} u' + u'' + \frac{m^2 x^2}{(1 - x^2)^2} v + \frac{m}{1 - x^2} v + \frac{2m x^2}{(1 - x^2)^2} v \right] = \]

\[ = (1 - x^2)^{-m/2} \left[ u'' + \frac{2mx}{1 - x^2} u' + \frac{m}{1 - x^2} v + \frac{m(m + 2)x^2}{(1 - x^2)^2} v \right] \]

Plugging the function \( u \) and its derivatives and dividing by \( (1 - x^2)^{-m/2} \)

\[ (1 - x^2) u'' + 2mx u' + Mv + \frac{m(m + 2)x^2}{(1 - x^2)} v - 2(m + 1)x v - 2(m + 1)x \frac{mx}{1 - x^2} v + [l(l + 1) - 2m(m + 1)] v = \]

\[ = (1 - x^2) u'' - 2x v' + l(l + 1) v + mv - m(m + 1) v + \frac{m(m + 2)x^2}{(1 - x^2)} - \frac{2m(m + 1)x^2}{1 - x^2} v = \]

\[ = (1 - x^2) u'' - 2x v' + l(l + 1) v - m^2 v - \frac{m^2 x^2}{1 - x^2} v = (1 - x^2) u'' - 2x v' + \left[ l(l + 1) - \frac{m^2}{1 - x^2} \right] v = 0 \]  \( \text{(5.40)} \)

The above equation stands for the associated (general) Legendre’s equation. Thus, its solutions are (the so called associated Legendre functions)

\[ P_n^m(x) = (-1)^m (1 - x^2)^{m/2} \frac{d^m}{dx^m} P_l(x) \]  \( \text{(5.41)} \)

We consider a particle with mass \( M \) moving around a sphere, while the origin will be in the middle of the sphere. Analogously to the two-dimensionall rigid rotor, the Hamiltonian will contain only the kinetic energy part, and for the system we impose a constrain that the radius \( R \) is constant. So, we will go to spherical coordinates to freeze the radius.

\[ \hat{H} = -\frac{\hbar^2}{2M} \left( \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right) \]  \( \text{(5.42)} \)

and in our case (the constant radius) \( r = R = \text{const.} \)

\[ \hat{H} = -\frac{\hbar^2}{2I} \left( \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right) = \frac{\hat{J}^2}{2I} \]  \( \text{(5.43)} \)

So, now we apply the hamiltonian in our Schrödinger equation

\[ \left( \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right) \Psi(\theta, \phi) = -\frac{2I E}{\hbar^2} \Psi(\theta, \phi) \]  \( \text{(5.44)} \)

Now, like in the case of two-dimensional paricle in a box model, we assume our solution in the following form

\[ \Psi(\theta, \phi) = \Theta(\theta) \Phi(\phi) \]  \( \text{(5.45)} \)

Now we can separate the variables and get the following equation

\[ \frac{1}{\Phi} \frac{d^2}{d\phi^2} \Phi = -\sin \theta \frac{d}{d\theta} \sin \theta \frac{d}{d\theta} - \frac{2I E}{\hbar^2} \sin^2 \theta \]  \( \text{(5.46)} \)

So, the two sides of the same equation depend on different variables, and they are equal only if they are equal the same constant. We assume the constant \(-m^2\). Therefore
\[
\frac{d^2}{d\phi^2} \Phi = -m^2 \Phi \tag{5.47}
\]
\[
\left( \sin \theta \frac{d}{d\theta} \sin \theta \frac{d}{d\theta} + \frac{2I E}{\hbar^2} \sin^2 \theta + m^2 \right) \Theta = 0 \tag{5.48}
\]
\[
\Phi_m(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi} \quad m = 0, \pm 1, \pm 2, \ldots \tag{5.49}
\]

Solutions of the second equation are well known in mathematics, but physical sense have only those functions for which the \( \frac{2I E}{\hbar^2} = l(l + 1) \), where \( l = 0, 1, 2, \ldots \). Therefore
\[
E_l = \frac{\hbar^2}{2I} l(l + 1) \tag{5.50}
\]

From the solutions for the functions \( \Theta(\theta) \) one may conclude they depend on either \( m \) and \( l \). The solutions one can find in many books on mathematics. They have the following form
\[
\Theta_l^m(\theta) = N_l^m P_l^{|m|}(\cos \theta) \tag{5.51}
\]
where the \( N_l^m \) is a normalization constant
\[
N_l^m = \frac{\sqrt{2l + 1 (l - |m|)!}}{2 (l + |m|)!} \tag{5.52}
\]
while the \( P_l^m \) are so called the associated Legendre polynomials
\[
P_l^m(x) = (-1)^m (1 - x^2)^{\frac{m}{2}} \frac{d^m}{dx^m} P_l(x) \quad m \geq 0 \tag{5.53}
\]
\[
P_l^{-m}(x) = \frac{(-1)^m (l - m)!}{(l + m)!} P_l^m(x) \quad m < 0 \tag{5.54}
\]

where the \( P_n(x) \) is so called Legendre function (given by the Rodrigues’ formula)
\[
P_n(x) = \frac{1}{2n!} \frac{d^n}{dx^n} (x^2 - 1)^n, \quad n = 0, 1, \ldots \tag{5.55}
\]

Legendre functions are solutions to Legendre’s differential equation:
\[
\frac{d}{dx} \left( (1 - x^2) \frac{d}{dx} P_n(x) \right) + n(n + 1) P_n(x) = 0 \tag{5.56}
\]

The Legendre differential equation may be solved using the standard power series method. The solutions for \( n = 0, 1, 2, \ldots \) (with the normalization \( P_n(1) = 1 \)) form a polynomial sequence of orthogonal polynomials called the Legendre polynomials. Each Legendre polynomial \( P_n(x) \) is an \( n \)-th degree polynomial.

The associated Legendre polynomials are determined at the \([-1, 1]\) bracket. When we change the variable for \( x = \cos \theta \) then we get the bracket for \( \theta \in [0, \pi] \).

So, the \( P_l^m(x) \) are nonzero functions only for \( |m| \leq l \).

The final solutions for the rigid rotor are as follows
\[
Y_l^m(\theta, \phi) = \frac{N_l^m}{\sqrt{2\pi}} P_l^{|m|}(\cos \theta)e^{im\phi}
\]
The Legendre function is given by the following formula

\[ P^m_l(x) = \binom{l}{m} x^m \begin{cases} \cos \theta & \text{for } m \leq 0 \\ \sin \theta & \text{for } m > 0 \end{cases} \]

Solution

End the energies

\[ E = \frac{\hbar^2}{2I}(l + 1) \]  

(5.57)

where the \( l = 0, 1, 2, \ldots \) and \( m = -l, -l + 1, -l + 2, \ldots, 0, 1, 2, \ldots, l - 1, l \).

<table>
<thead>
<tr>
<th>l</th>
<th>m</th>
<th>( P^m_l(x) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>( P^0_0(x) = 0 )</td>
</tr>
<tr>
<td>1</td>
<td>-1</td>
<td>( P^{-1}_1(x) = -\frac{1}{2} P^1_1(x) )</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>( P^0_1(x) = x )</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>( P^1_1(x) = (1 - x^2)^{1/2} )</td>
</tr>
<tr>
<td>2</td>
<td>-2</td>
<td>( P^{-2}_2(x) = \frac{1}{24} P^2_2(x) )</td>
</tr>
<tr>
<td>2</td>
<td>-1</td>
<td>( P^{-1}_2(x) = -\frac{1}{6} P^1_2(x) )</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>( P^0_2(x) = \frac{1}{2}(3x^2 - 1) )</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>( P^1_2(x) = 3(1 - x^2)^{1/2} x )</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>( P^2_2(x) = 3(1 - x^2)^{3/2} )</td>
</tr>
</tbody>
</table>

Table 1. Some first associated Legendre polynomials

<table>
<thead>
<tr>
<th>l</th>
<th>m</th>
<th>( Y^m_l(\theta, \phi) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>( Y^0_0(\theta, \phi) = \frac{1}{2\sqrt{\pi}} )</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>( \frac{1}{2\sqrt{\pi}} )</td>
</tr>
<tr>
<td>1</td>
<td>( \pm 1 )</td>
<td>( \frac{3}{2\sqrt{\pi}} \sin \theta e^{\pm i \phi} )</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>( \frac{1}{4\sqrt{\pi}} (3 \cos^2 \theta - 1) )</td>
</tr>
<tr>
<td>2</td>
<td>( \pm 1 )</td>
<td>( \frac{3}{2\sqrt{\pi}} \sin \theta \cos \theta e^{\pm i \phi} )</td>
</tr>
<tr>
<td>2</td>
<td>( \pm 2 )</td>
<td>( \frac{15}{16\sqrt{\pi}} \sin^2 \theta e^{\pm 2i \phi} )</td>
</tr>
</tbody>
</table>

Because the energy of rigid rotor depends on only \( l \) it means, that the energy levels are \( l(l + 1) \)-times degenerated. The \( l \) is sometimes called the rotational quantum number.

Find Legendre polynomials and associated Legendre polynomials for \( r \) and \( s = 0, 1, 2, 3 \).

Solution

Legendre function is given by the following formula

\[ P^r_l(x) = \frac{1}{2^r r!} \frac{d^r}{dx^r} (x^2 - 1)^r \quad r = 0, 1, 2, \ldots \]  

(5.58)

while the associated Legendre function is given by the following formula

\[ P^s_r(x) = (1 - x^2)^{s/2} \frac{d^s}{dx^s} P^r_l(x) \quad s = 0, 1, 2, \ldots, r \]  

(5.59)

\[ P^0_0(x) = \frac{1}{2^0 0!} (x^2 - 1)^0 = 1 \]

\[ P^1_1(x) = \frac{1}{2^1 1!} \frac{d}{dx} (x^2 - 1)^1 = \frac{1}{2} \cdot 2x = x \]
\[ P_2(x) = \frac{1}{2^2 2!} \frac{d^2}{dx^2} (x^2 - 1)^2 = \frac{1}{8} \frac{d^2}{dx^2} (x^4 - 2x^2 + 1) = \frac{1}{8} \frac{d}{dx} (4x^3 - 4x) = \frac{1}{2} (3x^2 - 1) \]

\[ P_3(x) = \frac{1}{2^3 3!} \frac{d^3}{dx^3} (x^2 - 1)^3 = \frac{1}{8 \cdot 6} \frac{d^3}{dx^3} (x^6 - 3x^4 + 3x^2 - 1) = \frac{1}{8 \cdot 6} \frac{d^2}{dx^2} (6x^5 - 12x^3 + 6x) = \]

\[ = \frac{1}{8} \frac{d^2}{dx^2} (x^5 - 2x^3 + x) = \frac{1}{8} \frac{d}{dx} (5x^4 - 6x^2 + 1) = \frac{1}{8} (20x^3 - 12x) = \frac{1}{2} (5x^3 - 3x) \]

\[ P_4(x) = \frac{1}{8} (35x^4 - 30x^2 + 3) \]

\[ P_5(x) = \frac{1}{8} (63x^5 - 70x^3 + 15x) \]

\[ P_6(x) = \frac{1}{16} (231x^6 - 315x^4 + 105x^2 - 5) \]

\[ P_0^1(x) = (1 - x^2)^0 \frac{d^0}{dx^0} P_0(x) = P_0(x) = 1 \]

\[ P_1^1(x) = (1 - x^2)^{1/2} \frac{d^0}{dx^0} P_1(x) = x \]

\[ P_2^1(x) = -(1 - x^2)^{1/2} \frac{d}{dx} P_1(x) = -(1 - x^2)^{1/2} \]

\[ P_1^2(x) = P_2(x) = x \]

\[ P_2^2(x) = (1 - x^2)^{1/2} \frac{d}{dx} P_2(x) = (1 - x^2)^{1/2} \frac{d}{dx} \frac{1}{2} 6x = 3x(1 - x^2)^{1/2} \]

\[ P_3^2(x) = (1 - x^2)^{1} \frac{d^2}{dx^2} P_2(x) = (1 - x^2)^{1} \frac{d^2}{dx} \frac{3}{2} x = 3(1 - x^2) \]

\[ P_0^3(x) = (1 - x^2)^0 \frac{d^0}{dx^0} P_3(x) = P_3(x) = \frac{1}{2} (5x^3 - 3x) \]

\[ P_1^3(x) = -(1 - x^2)^{1/2} \frac{d}{dx} P_3(x) = -(1 - x^2)^{1/2} \frac{d}{dx} \frac{1}{2} (15x^2 - 3) = -\frac{3}{2} (1 - x^2)^{1/2} (5x^3 - 1) \]

\[ P_2^3(x) = (1 - x^2)^{1} \frac{d^2}{dx^2} P_3(x) = (1 - x^2)^{1} \frac{d^2}{dx} \frac{1}{2} (15x^2 - 3) = (1 - x^2) 15x = 15(-x^3 + x) \]

\[ P_3^3(x) = (1 - x^2)^{3/2} \frac{d^3}{dx^3} P_3(x) = (1 - x^2)^{3/2} \frac{d^3}{dx^3} \frac{1}{2} (15x^2 - 3) = 15(1 - x^2)^{3/2} \]

\[ P_4^0(x) = P_4(x) = \frac{1}{8} (35x^4 - 30x^2 + 3) \]

\[ P_1^4(x) = \frac{1}{2} x(3 - 7x^2)(1 - x^2)^{1/2} \]

\[ P_2^4(x) = \frac{15}{2} (7x^2 - 1)(1 - x^2) \]

\[ P_3^4(x) = -105x(1 - x^2)^{3/2} \]

\[ P_4^4(x) = 105(1 - x^2)^2 \]

\[ P_5^0(x) = P_5(x) = \frac{1}{8} x(63x^4 - 70x^2 + 15) \]

\[ P_1^5(x) = -\frac{1}{8} (1 - x^2)^{1/2} (315x^4 - 210x^2 + 15) \]

\[ P_2^5(x) = \frac{1}{8} (1 - x^2)(1260x^3 - 420x) = \frac{1}{2} (1 - x^2)(315x^3 - 105x) \]

\[ P_3^5(x) = \frac{1}{8} (1 - x^2)(3465x^4 - 1890x^2 + 210) \]
Figure 5. First unnormalized associated Legendre functions, \( P_l^m(x) \), for \( m = 1 \) and for \( m = 2 \). For \( m = 0 \): \( P_0^0(x) = P_0(x) \)

For \( s > r \) the associated Legendre polynomial equals zero. Associated polynomials for \( x = \cos \theta \) are the unnormalized \( \Theta(\theta) \) functions of the rigid rotor and of hydrogen atom models.

Find spherical harmonic functions for \( \ell = 0, 1, 2 \).

Solution

Spherical harmonic function is given by the following formula:

\[
Y_{\ell}^{m}(\theta, \varphi) = \Theta_{\ell}^{[m]}(\theta) \Phi_{m}(\varphi)
\]  

(5.60)

where

\[
\Theta_{\ell}^{[m]}(\theta) = N_{\ell|m} P_{\ell}^{[m]}(\cos \theta)
\]  

(5.61)

\[
N_{\ell|m} = \frac{\left[2\ell + 1 (\ell - |m|)\right]}{2} \frac{1}{(\ell + |m|)!}
\]  

(5.62)

\[
\Phi_{m}(\varphi) = \frac{1}{\sqrt{2\pi}} e^{im\varphi}
\]  

(5.63)

while the \( P_{\ell}^{[m]} \) stands for the associated Legendre polynomial.

- For \( \ell = 0, m = 0 \)

\[
N_{0,0} = \frac{1}{\sqrt{2}} \cdot 1 = \frac{1}{\sqrt{2}}
\]

\[
\Theta_{0}^{0} = \frac{1}{\sqrt{2}} \cdot 1 = \frac{1}{\sqrt{2}}
\]

\[
Y_{0}^{0} = \frac{1}{\sqrt{2\pi}} \cdot \frac{1}{\sqrt{4\pi}} = \frac{1}{\sqrt{4\pi}}
\]

- For \( \ell = 1, |m| = 0, 1 \)

\[
N_{1,0} = \frac{3}{2} \left(\frac{1}{1!}\right)^{\frac{1}{2}} = \frac{3}{2} \quad N_{1,1} = \frac{3}{2} \left(\frac{2}{2!}\right)^{\frac{1}{2}} = \sqrt{3}
\]
\[ \Theta_0(\theta) = \sqrt{\frac{3}{2}} \cos \theta, \quad \Theta_1(\theta) = \sqrt{3} \left( 1 - \cos^2 \theta \right)^{1/2} = \sqrt{3} \sin \theta \]

\[ Y_1^0 = \sqrt{\frac{3}{2}} \frac{1}{\sqrt{2\pi}} = \sqrt{\frac{3}{4\pi}} \cos \theta, \quad Y_1^1 = \sqrt{\frac{3}{8\pi}} \sin \theta e^{i\varphi}, \quad Y_1^{-1} = \sqrt{\frac{3}{8\pi}} \sin \theta e^{-i\varphi} \]

- For \( l = 2, |m| = 0, 1, 2 \)

\[ N_{2,0} = \left[ \frac{5}{2} \right]_{\frac{1}{2}} \frac{1}{\sqrt{2}}, \quad N_{2,1} = \left[ \frac{5}{2} \frac{3}{2} \right]_{\frac{1}{2}} \frac{1}{\sqrt{15}}, \quad N_{2,2} = \left[ \frac{5}{2} \frac{4}{2} \right]_{\frac{1}{2}} = \sqrt{60}, \]

\[ \Theta_0(\theta) = \sqrt{\frac{5}{8}} (3 \cos^2 \theta - 1), \quad \Theta_1(\theta) = 3\sqrt{15} \cos \theta \sin \theta, \quad \Theta_2(\theta) = 6\sqrt{15} \sin^2 \theta \]

\[ Y_2^0 = \sqrt{\frac{5}{16\pi}} (3 \cos^2 \theta - 1), \quad Y_2^1 = \sqrt{\frac{15}{8\pi}} \sin \theta \cos \theta e^{i\varphi}, \quad Y_2^2 = \sqrt{\frac{15}{32\pi}} \sin^2 \theta e^{2i\varphi}, \]

\[ Y_2^{-1} = \sqrt{\frac{15}{8\pi}} \sin \theta \cos \theta e^{-i\varphi}, \quad Y_2^{-2} = \sqrt{\frac{15}{32\pi}} \sin^2 \theta e^{-2i\varphi}. \]

### 6 Hydrogen atom

Find the Laguerre and associated Laguerre polynomials for \( r \) and \( s \) equal up to 3.

The Laguerre polynomial (unassociated) is given by the following generating function

\[ L_r(x) = e^x \frac{d^r}{dx^r} (x^r e^{-x}), \quad (6.1) \]

while the associated (generalized) Laguerre polynomial is given by the following generating function

\[ L^*_r(x) = (-1)^r \frac{d^r}{dx^r} L_{r+s}(x) \quad (6.2) \]

\[ L_0(x) = e^x x^0 e^{-x} = 1 \]

\[ L_1(x) = e^x \frac{d}{dx} (xe^{-x}) = e^x (e^{-x} - xe^{-x}) = -x + 1 \]

\[ L_2(x) = e^x \frac{d^2}{dx^2} (x^2 e^{-x}) = e^x \frac{d}{dx} \left( 2xe^{-x} - x^2 e^{-x} \right) = e^x \left( 2e^{-x} - 2xe^{-x} - 2xe^{-x} + x^2 e^{-x} \right) = \]

\[ = x^2 - 4x + 2 \]

\[ L_3(x) = e^x \frac{d^3}{dx^3} (x^3 e^{-x}) = e^x \frac{d^2}{dx^2} \left( 3x^2 e^{-x} - x^3 e^{-x} \right) = \]

\[ = e^x \frac{d}{dx} \left( 6xe^{-x} - 3x^2 e^{-x} - 3x^2 e^{-x} + x^3 e^{-x} \right) = \]

\[ = e^x \left( 6e^{-x} - 6xe^{-x} - 12xe^{-x} + 6x^2 e^{-x} + 3x^2 e^{-x} - x^3 e^{-x} \right) = -x^3 + 9x^2 - 18x + 6 \]

\[ L_4(x) = x^4 - 16x^3 + 72x^2 - 96x + 24 \]

\[ L_5(x) = -x^5 + 25x^4 - 200x^3 + 600x^2 - 600x + 120 \]

\[ L_6(x) = x^6 - 36x^5 + 450x^4 - 2400x^3 + 5400x^2 - 4320x + 720 \]
polynomials the Laguerre’s polynomials are also orthogonal over Soinine polynomials) are solutions of the following equation:

\[ \frac{d^2u}{dx^2} + \frac{1}{x} \frac{du}{dx} + \left( \frac{\alpha}{x} - \frac{\ell (\ell + 1)}{x^2} \right) u = 0 \]

stands for a non-negative integer while the \( \alpha \) stands for order of the polynomial. Associated Laguerre polynomials (or, rarely, Sonine polynomials) are solutions of the following equation:

\[ x \frac{d^2y}{dx^2} + (1 - x) \frac{dy}{dx} + ry(x) = 0, \]

where the \( r \) stands for degree of the polynomial while the \( s \) stands for order of the polynomial. Within the definitions of associated Laguerre’s polynomials

\( r \)

stands for degree of the polynomial while the \( s \) stands for order of the polynomial. Associated Laguerre’s polynomials are also orthogonal over \([0, \infty)\) but with respect to the \( e^{-x} \) function:

\[ \int_0^\infty x^a e^{-x} L_n^{(a)}(x) L_m^{(a)}(x) dx = \frac{\Gamma(n + a + 1)}{n!} \delta_{n,m} \]

Find the normalized radial wave functions up to \( n \) equal to 3.

The normalized radial wave functions are given by the following formula

\[ R_n(r) = \sqrt{\frac{2}{na_0}} \frac{(n - l - 1)!}{2(n + l)!} e^{-r/na_0} \left( \frac{2r}{na_0} \right)^l L_{n-l-1}^{2l+1} \left( \frac{2r}{na_0} \right) \]
where \( L \) stands for the associated Laguerre polynomial and the big square root is the normalization factor.

\[
R_{1,0}(r) = \sqrt{\left( \frac{2}{a_0} \right)^3 \frac{0!}{2 \cdot 1 \cdot 1}} e^{-r/a_0} \cdot 1 \cdot L_0^1 \left( \frac{2r}{a_0} \right) = 2a_0^{-3/2} e^{-r/a_0} \cdot 1 = 2a_0^{-3/2} e^{-r/a_0}
\]

\[
R_{2,0}(r) = \sqrt{\left( \frac{2}{2a_0} \right)^3 \frac{1!}{4 \cdot 2}} e^{-r/2a_0} \cdot 1 \cdot L_1^1 \left( \frac{2r}{2a_0} \right) = a_0^{-3/2} \frac{1}{2 \cdot 2\sqrt{2}} e^{-r/2a_0} \left( 4 - 2 \frac{r}{a_0} \right) = \frac{1}{\sqrt{2}} a_0^{-3/2} \left( 1 - \frac{r}{2a_0} \right) e^{-r/2a_0}
\]

\[
R_{2,1}(r) = \sqrt{\left( \frac{2}{2a_0} \right)^3 \frac{0!}{2 \cdot 2 \left[(3!)^2 \right]}} e^{-r/2a_0} \cdot 1 \cdot L_2^1 \left( \frac{2r}{2a_0} \right) = a_0^{-3/2} \sqrt{\frac{1}{3!}} \left[ 3 \left( \frac{2r}{3a_0} \right)^2 - 18 \frac{2r}{3a_0} + 18 \right] e^{-r/3a_0} = \frac{2}{27\sqrt{6}} a_0^{-3/2} \left( 1 - \frac{2r}{3a_0} + \frac{2r^2}{27a_0^2} \right) e^{-r/3a_0}
\]

\[
R_{3,0}(r) = \frac{8}{27\sqrt{6}} a_0^{-5/2} \left( r - \frac{r^2}{6a_0} \right) e^{-r/3a_0}
\]

\[
R_{3,1}(r) = \frac{4}{81\sqrt{30}} a_0^{-7/2} r^2 e^{-r/3a_0}
\]

(6.7)

Find first hydrogen atom orbitals taking into account the calculated spherical harmonics and radial wave functions.

The normalized hydrogen atom orbitals are given by the following formula

\[
\Psi_{nlm}(r, \theta, \varphi) = Y_{lm}^n(\theta, \varphi) \cdot R_{nl}(r), \quad \begin{cases} n = 1, 2, \ldots, \\ l = 0, 1, \ldots, n-1, \\ m = -l, -l+1, \ldots, l-1, l \end{cases} \tag{6.8}
\]

\[
\Psi_{100}(r, \theta, \varphi) = Y_{10}^0(\theta, \varphi) \cdot R_{10}(r) = \frac{1}{\sqrt{4\pi}} a_0^{-3/2} e^{-r/a_0} = \frac{1}{\sqrt{\pi} a_0^3} e^{-r/a_0}
\]

\[
\Psi_{200}(r, \theta, \varphi) = Y_{20}^0(\theta, \varphi) \cdot R_{20}(r) = \frac{1}{\sqrt{4\pi}} a_0^{-3/2} \left( 1 - \frac{r}{2a_0} \right) e^{-r/2a_0}
\]

\[
\Psi_{210}(r, \theta, \varphi) = Y_{11}^0(\theta, \varphi) \cdot R_{21}(r) = \sqrt{\frac{3}{4\pi}} \cos \theta \frac{1}{2\sqrt{6}} a_0^{-5/2} r e^{-r/2a_0}
\]

\[
\Psi_{21\pm 1}(r, \theta, \varphi) = Y_{11}^{\pm 1}(\theta, \varphi) \cdot R_{21}(r) = \sqrt{\frac{3}{8\pi}} \sin \theta \frac{1}{2\sqrt{6}} a_0^{-5/2} r e^{-r/2a_0}
\]

- 36 -
Find the $3d_{x^2 - y^2}$ and $3d_{xy}$ orbitals of hydrogen atom taking into account the $3d_2$ and the $3d_{-2}$ functions.

Solution

The $3d_2$ and the $3d_{-2}$ functions could be given by the following (simplified here) formulas

$$\psi_{3d_2} = \sqrt{\frac{3}{2}} N_{3d} e^{-r^2/3} \sin^2 \theta e^{2i\varphi}$$

$$\psi_{3d_{-2}} = \sqrt{\frac{3}{2}} N_{3d} e^{-r^2/3} \sin^2 \theta e^{-2i\varphi}$$

The $3d_{x^2 - y^2}$ and the $3d_{xy}$ are appropriate linear combinations of the $3d_2$ and the $3d_{-2}$ functions:

$$\psi_{3d_{x^2 - y^2}} = \frac{1}{\sqrt{2}} (\psi_{3d_2} + \psi_{3d_{-2}}) = \frac{1}{\sqrt{2}} \sqrt{\frac{3}{2}} N_{3d} e^{-r^2/3} \sin^2 \theta (e^{2i\varphi} + e^{-2i\varphi}) =$$

$$= \sqrt{\frac{3}{2}} N_{3d} e^{-r^2/3} \sin^2 \theta 2 \cos 2\varphi = \sqrt{3} N_{3d} e^{-r^2/3} \sin^2 \theta (\cos^2 \varphi - \sin^2 \varphi) =$$

$$= \sqrt{3} N_{3d} e^{-r^2/3} (x^2 - y^2)$$
Figure 8. Radial densities of probability: $r^2 R_{n,l}^2(r)$. It was drawn assuming the $a_0$ was equal to 1.

\[
\psi_{3d_{xy}} = -\frac{i}{\sqrt{2}}(\psi_{3d_2} - \psi_{3d_{-2}}) = -\frac{i}{\sqrt{2}}\sqrt{\frac{5}{2}}N_{3d} e^{-r/\sqrt{3}} r^2 \sin^2 \theta 2i \sin 2\varphi =
\]
\[
= 2\sqrt{3}N_{3d} e^{-r/\sqrt{3}} (r \sin \theta \sin \varphi)(r \sin \theta \cos \varphi) = 2\sqrt{3}N_{3d} e^{-r/\sqrt{3}} xy
\]  

(6.12)

Find the result of acting of $\hat{L}_z$ operator on the $2p_x$ and the $2p_y$ functions of hydrogen atom.

Solution

The $2p_x$ and the $2p_y$ functions could be written in the following manner

\[
\psi_{2p_x} = N_{2p} e^{-r^2/2} r \sin \theta \cos \varphi
\]  

(6.13)

\[
\psi_{2p_y} = N_{2p} e^{-r^2/2} r \sin \theta \sin \varphi
\]  

(6.14)

\[
\hat{L}_z \psi_{2p_x} = -ih \frac{\partial}{\partial \varphi} (N_{2p} e^{-r^2/2} r \sin \theta \cos \varphi) = ihN_{2p} e^{-r^2/2} r \sin \theta \sin \varphi = i\hbar \psi_{2p_y}
\]  

(6.15)

\[
\hat{L}_z \psi_{2p_y} = -ih \frac{\partial}{\partial \varphi} = -i\hbar \psi_{2p_x}
\]  

(6.16)

The functions $\psi_{2p_x}$ and $\psi_{2p_y}$ are not eigenfunctions of the $\hat{L}_z$ operator. This is because they’re the linear combinations of the $\psi_{2p_{-1}}$ and the $\psi_{2p_1}$ orbitals, which are eigenfunctions of the $\hat{L}_z$ operator with different eigenvalues.
Looking at the results above it can be easy noticed that the $\psi_{2p_1}$ and the $\psi_{2p_2}$ are the eigenfunctions of the $L^2$ operator. Thus, the real $\psi_{2p_1}$ and $\psi_{2p_2}$ functions should not be taken into account whenever the magnetic field influence on the atom is being considered, while in the case of energy change considerations, the real functions should be valid (the Hamiltonian can be written on the basis of the $L^2$ operator).

**Example:** Find an average distance between electron and nucleus in state $|100\rangle$.

$$\langle r \rangle = \langle 100| r |100 \rangle = \int_0^{2\pi} \int_0^\pi (\sin \theta |Y_{00}(\theta, \varphi))|^2 d\theta d\varphi \int_0^{\infty} r^3 |R_{10}(r)|^2 dr = \frac{4Z^3}{a_0^3} \int_0^{\infty} r^3 e^{-2Zr/a_0} dr$$

(6.17)

We know how to calculate the latter integrals, thus

$$\langle r \rangle = \frac{4Z^3}{a_0^3} \frac{3l^4}{(2Z)^4} = \frac{3a_0}{2Z}$$

(6.18)

One can derive more general dependence of the distance for a given $\Psi_{nlm}$ state

$$\langle r \rangle_{nl} = n^2 \left[ 1 + \frac{1}{2} \left( 1 - \frac{l(l+1)}{n^2} \right) \right]$$

(6.19)

**Example** Find an average value of electron’s velocity being in ground state of hydrogen atom.

$$\langle \dot{r} \rangle = \frac{\mu v^2}{2}$$

(6.20)

Thus

$$\langle \dot{r} \rangle = \sqrt{\frac{2\langle \dot{T} \rangle}{\mu}}$$

(6.21)

This means we first need to calculate the average value of kinetic energy of electron living in ground state.

$$\langle \dot{T} \rangle = \frac{\hbar^2}{2\mu} (\Delta) = -\frac{\hbar^2}{2\mu} \int \Psi_{100}^* \Delta \Psi_{100} d^3r =$$

$$= -\frac{\hbar^2}{2\mu} \frac{1}{(a_0)^3} \int_0^{2\pi} d\varphi \int_0^\pi \sin \theta d\theta \int_0^{\infty} r^2 e^{-Zr/a_0} \left( \frac{d}{dr} \frac{d^2}{dr^2} \right) e^{-Zr/a_0} dr =$$

$$= \frac{2\hbar^2}{\mu} \left( \frac{Z}{a_0} \right)^4 \int_0^{\infty} \left( 2r - \frac{Z}{a_0} r^2 \right) e^{-2Zr/a_0} dr =$$

$$= \frac{2\hbar^2}{\mu} \left( \frac{Z}{a_0} \right)^4 \left( \frac{a_0}{a_0^2} - 2 \frac{Z}{a_0} \left( \frac{a_0}{2Z} \right)^3 \right) =$$

$$= \frac{2\hbar^2}{\mu} \left( \frac{Z}{a_0} \right)^4 \left( \frac{a_0}{2Z} \right)^2 = \frac{\hbar^2 Z^2}{2\mu a_0^2}$$

(6.22)

Thus

$$v = \sqrt{\frac{2\hbar^2 Z^2}{\mu 2\mu a_0^2}} = \frac{Z \hbar}{\mu a_0}$$

(6.23)

In atomic units $v = Z$. But in atomic units the speed of light $c = 137$. which in turn means that for heavy atoms (with relatively large $Z$) the velocity is relatively large and the relativistic effects play important role.
7 Hybridisation

Find hybridised atomic orbitals of carbon atom of methane molecule.

Solution

![Figure 9. Methane molecule. $t_1$ lays down in z axis, while the $t_2$ lays down in yz plane.](image)

![Figure 10. 4 $\sigma$ molecular bonding orbitals of methane molecule. Created from carbon hybridised $t_i$, $i = 1, \ldots, 4$ atomic orbitals and atomic 2s orbitals of hydrogens](image)

We know from experiments that methane molecule is very symmetric, i.e. it is a tetrahedral molecule with 4 equivalent C-H bonds. Its electronic structure is described by four molecular orbitals (MOs) resulting from the overlap of the valence orbitals on C and H. Hence, it’s justified to think that the four equivalent C-H bonds reveals from some kind of change of carbon atom’s atomic orbitals after which the 4 molecular orbitals remain equivalent. This in turn means we observe a hybridization of carbon orbitals in case of methane molecule.

We are looking for four hybrid orbitals (from four atomic orbitals):

$$t_i = a_i 2s + b_i 2p_x + c_i 2p_y + d_i 2p_z, \quad i = 1, 2, 3, 4$$

(7.1)

Due to orthogonality of hybrid orbitals we can write down following conditions

$$a_i a_j + b_i b_j + c_i c_j + d_i d_j = 0, \quad i = 1, \ldots, 4, \quad j = 1, \ldots, 4.$$  

(7.2)

Normalization condition equation

$$a_i^2 + b_i^2 + c_i^2 + d_i^2 = 1, \quad i = 1, \ldots, 4$$

(7.3)

Moreover we can assume the $a_i$ coefficient for orbital $s$ is greater then zero. We can also utilize information that the contribution of each atomic orbital into all hybridised orbitals’ set remains the same, i.e. that the sum of all coefficients’s squares for a given atomic orbital and in case of each hybridised orbital equals 1, i.e.

$$a_1^2 + a_2^2 + a_3^2 + a_4^2 = 1$$

$$b_1^2 + b_2^2 + b_3^2 + b_4^2 = 1$$

$$c_1^2 + c_2^2 + c_3^2 + c_4^2 = 1$$

$$d_1^2 + d_2^2 + d_3^2 + d_4^2 = 1$$

(7.4)

In case of methane molecule, all bonds are identical, hence

$$a_1 = a_2 = a_3 = a_4 = a \quad \Rightarrow \quad 4a^2 = 1 \quad \Rightarrow \quad a = \frac{1}{2}$$
We must orientate arbitrary orbital along some axis, to reduce the number of variables. Let’s arrange \( t_1 \) along \( z \) axis (in positive direction) so that

\[
b_1 = c_1 = 0; \quad d_1 > 0
\]

From normalization condition it reveals that \( a_1^2 + d_1^2 = 1 \implies d_1 = \frac{1}{4} \quad \Rightarrow \quad d_1 = \frac{\sqrt{3}}{4} \).

The second hybridised orbital we can arrange in some cartesian plane (we can always do this because two hybridised orbitals will certainly be layed down within some plane), so let’s arrange it within the \( yz \) plane so that the \( y \) will be positive. Hence \( b_2 = 0 \) and \( c_2 > 0 \).

Normalization condition for \( t_2 \) orbital

\[
a_2^2 + b_2^2 + c_2^2 + d_2^2 = 1
\]

Orthogonality of \( t_1 \) and \( t_2 \) orbitals

\[
\left( \frac{1}{2} \right)^2 + 0 + c_2^2 + d_2^2 = 1
\]

The negative sign tells of that the angle between \( t_1 \) and \( t_2 \) is greater then 90°. Continuing and applying the normalization condition for \( t_2 \)

\[
\frac{1}{4} + c_2^2 + \frac{1}{12} = 1 \quad \Rightarrow \quad c_2^2 = \frac{2}{3} \quad \Rightarrow \quad c_2 = \frac{\sqrt{2}}{3}
\]

The \( t_3 \) orbital must be layed down somewhere about the \( yz \) plane, because all C-H bonds of methane molecule are equivalent. Utilizing the orthogonality of \( t_1 \) and \( t_3 \) orbitals

\[
\frac{1}{2} \cdot \frac{1}{2} + 0 \cdot b_3 + 0 \cdot c_3 + \frac{\sqrt{3}}{2} \cdot d_3 = 0 \quad \Rightarrow \quad d_3 = \frac{-1}{2\sqrt{3}}
\]

Similarly, orthogonality of \( t_4 \) and \( t_1 \) orbitals is written by the following equation

\[
\frac{1}{2} \cdot \frac{1}{2} + 0 \cdot b_4 + 0 \cdot c_4 + \frac{\sqrt{3}}{2} \cdot d_4 = 0 \quad \Rightarrow \quad d_4 = \frac{-1}{2\sqrt{3}}
\]

Orthogonality of \( t_3 \) and \( t_2 \): 

\[
\frac{1}{2} \cdot \frac{1}{2} + b_3 \cdot 0 + c_3 \cdot \sqrt{\frac{2}{3}} \left( \frac{-1}{2\sqrt{3}} \right) \left( \frac{-1}{2\sqrt{3}} \right) = c_3 = \frac{-1}{\sqrt{6}}
\]

Orthogonality of \( t_4 \) and \( t_2 \): 

\[
\frac{1}{2} \cdot \frac{1}{2} + b_4 \cdot 0 + c_4 \cdot \sqrt{\frac{2}{3}} \left( \frac{-1}{2\sqrt{3}} \right) \left( \frac{-1}{2\sqrt{3}} \right) = c_4 = \frac{-1}{\sqrt{6}}
\]
\[ \frac{1}{2} \cdot \frac{1}{2} + b_4 \cdot 0 + c_4 \cdot \sqrt{\frac{2}{3}} + \left( -\frac{1}{2} \frac{1}{2\sqrt{3}} \right) \cdot \left( -\frac{1}{2} \frac{1}{2\sqrt{3}} \right) \]

\[ c_4 = c_3 = -\frac{1}{\sqrt{6}} \]

Orthogonality of \( t_3 \) and \( t_4 \):

\[ \frac{1}{2} \cdot \frac{1}{2} + b_3 \cdot b_4 + \frac{1}{6} + \frac{1}{12} = 0 \implies b_3 \cdot b_4 = -\frac{1}{2} \]

And normalization condition for both \( t_3 \) and \( t_4 \):

\[ a_3^2 + b_3^2 + c_3^2 + c_4^2 = 1 \]
\[ \frac{1}{4} + b_3^2 + \frac{1}{6} + \frac{1}{12} = 1 \]

\[ b_3^2 = \frac{12}{12} - \frac{3}{12} - \frac{2}{12} - \frac{1}{12} = \frac{1}{2} \]

\[ b_3^2 b_4 = -\frac{1}{2} b_3 \]

\[ \frac{1}{2} b_4 = -\frac{1}{2} b_3 \]

\[ b_4 = -b_3 \]

Hence \( b_3 = \frac{1}{\sqrt{2}} \), \( b_4 = -\frac{1}{\sqrt{2}} \) or vice versa. Which depends on whether we arrange \( t_3 \) orbital above the yz plane or below this plane. Let's collect all the results in a table.

<table>
<thead>
<tr>
<th></th>
<th>( a_i )</th>
<th>( b_i )</th>
<th>( c_i )</th>
<th>( d_i )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( t_1 )</td>
<td>( \frac{1}{2} )</td>
<td>0</td>
<td>0</td>
<td>( \frac{1}{2\sqrt{2}} )</td>
</tr>
<tr>
<td>( t_2 )</td>
<td>( \frac{1}{2} )</td>
<td>0</td>
<td>( \frac{1}{\sqrt{3}} )</td>
<td>( -\frac{1}{2\sqrt{3}} )</td>
</tr>
<tr>
<td>( t_3 )</td>
<td>( \frac{1}{2} )</td>
<td>( \frac{1}{\sqrt{6}} )</td>
<td>( \frac{1}{\sqrt{6}} )</td>
<td>( -\frac{1}{\sqrt{3}} )</td>
</tr>
<tr>
<td>( t_4 )</td>
<td>( \frac{1}{2} )</td>
<td>( -\frac{1}{\sqrt{2}} )</td>
<td>( -\frac{1}{\sqrt{6}} )</td>
<td>( -\frac{1}{\sqrt{3}} )</td>
</tr>
</tbody>
</table>

**Table 2.** One possible representation of hybridised orbitals of methane molecule.

The angle between hybridised orbitals can be found from definition of scalar product of two vectors, hence

\[ \cos \theta_{ij} = \frac{b_i b_j + c_i c_j + d_i d_j}{\sqrt{b_i^2 + c_i^2 + d_i^2} \cdot \sqrt{b_j^2 + c_j^2 + d_j^2}} = \frac{a_i a_j}{\sqrt{1 - a_i^2} \cdot \sqrt{1 - a_j^2}} \quad i = 1, \ldots, 4 \quad j = 1, \ldots, 4 \]

and for any pair of hybridised orbitals: \( \cos \theta_{ij} = -\frac{1}{3} \implies \theta = 109^\circ 28' \).

If we arrange one (first one) hybridised orbital in some other direction (relative to xyz axis) we can achieve some other, equivalent, set of coefficients for the hybridised orbitals. In general - there is infinite number of solutions. One of the most easy to remember sets can be found below.

---
Find hybridised orbitals of ammonia molecule (NH$_3$).

Solution

One hybridised orbital (say $t_1$) describes a free electron pair of nitrogen atom, the three others ($t_2$, $t_3$, $t_4$), describing three N-H bonds should be equivalent. In the case of this molecule the situation is similar to the situation in CH$_4$ molecule, where the C-H bonds were created from the 2p$_x$, 2p$_y$ and 2p$_z$ orbitals of carbon atom and the s orbitals of hydrogen atoms. What is different in NH$_3$ molecule is that instead of four hydrogens we have only three while there is an additional free pair orbital presence. So we assume there should be 4 hybridised orbitals presence out of which one (the $t_1$) will be a „special” one designed for holding the free pair of electrons of nitrogen.

$$a_2 = a_3 = a_4 = a$$

All four orbitals should be similar but one of them will be a little different due to the fact that it holds a free electron pair. We thus require

$$a_1^2 + a_2^2 + a_3^2 + a_4^2 = 1$$

From the two equations above it reveals that

$$a_1 = \sqrt{1 - 3a^2} \quad \Rightarrow \quad a_1 = \sqrt{1 - 3a^2} \quad (7.5)$$

Notice that the $a$ remains unknown. We can arrange the $t_1$ of the free electron pair along the positive z axis, so that $b_1 = c_1 = 0, \quad d_1 > 0$.

From normalization condition for the $t_1$:

$$a_1^2 + d_1^2 = 1$$

$$1 - 3a^2 + d_1^2 = 1 \quad \Rightarrow \quad d_1 = a\sqrt{3}$$

The $t_2$ orbital could be arranged in yz plane, so that the y remains positive, and then $b_2 = 0, \quad c_2 > 0$.

From orthogonality of $t_1$ and $t_2$:

$$a\sqrt{1 - 3a^2} + 0 + 0 \cdot c_2 + a\sqrt{3} \cdot d_2 = 0$$

The $a$ must not be zero. Otherwise, the $t_1$ of the free electron pair would be pure 2p$_z$. So the equation above we can divide by $a$, and

$$\sqrt{1 - 3a^2} = -\sqrt{3}d_2 \quad \Rightarrow \quad d_2 = -\sqrt{\frac{1}{3} - a^2}$$

Because the $d_2$ is negative we can conclude that the angle between $t_1$ and $t_2$ is greater then 90°. And from the normalization condition for $t_2$ orbital we can find $c_2$

$$a^2 + c_2^2 + \frac{1}{3} - a^2 = 1 \quad \Rightarrow \quad c_2 = \sqrt{\frac{2}{3}}$$
Orthogonality of \( t_3 \) and \( t_4 \) with orbital \( t_1 \) leads to identical \( d_3 \) and \( d_4 \):

\[
\begin{align*}
    a_3a_1 + b_3b_1 + c_3c_1 + d_3d_1 &= 0 \\
    a\sqrt{1 - 3a^2} + 0 + 0 + d_3a\sqrt{3} = 0 \\
    d_2 = d_3 = d_4 &= -\sqrt{\frac{1}{3} - a^2}
\end{align*}
\]

Orthogonality of \( t_3 \) and \( t_4 \) with orbital \( t_2 \) leads to identical \( c_3 \) and \( c_4 \):

\[
\begin{align*}
    a_2 + 0 + c_3\sqrt{23} + \frac{1}{3} - a^2 &= 0 \\
    c_3 = c_4 &= -\frac{1}{\sqrt{6}}
\end{align*}
\]

Orthogonality of \( t_3 \) and \( t_4 \):

\[
\begin{align*}
    a^2 + b_3b_4 + \frac{1}{6} + \frac{1}{3} - a^2 &= 0 \\
    b_3b_4 &= -\frac{1}{2},
\end{align*}
\]

and normalization condition for \( t_3 \) and for \( t_4 \) leads to

\[
b_3^2 = b_4^2 = \frac{1}{2}. \tag{7.6}
\]

Hence, \( b_3 = \frac{1}{\sqrt{2}} \), \( b_4 = -\frac{1}{\sqrt{2}} \) or vice versa.

And the orbitals can be shown in a table

<table>
<thead>
<tr>
<th></th>
<th>( a_i )</th>
<th>( b_i )</th>
<th>( c_i )</th>
<th>( d_i )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( t_1 )</td>
<td>( \sqrt{1 - 3a^2} )</td>
<td>0</td>
<td>0</td>
<td>( a\sqrt{3} )</td>
</tr>
<tr>
<td>( t_2 )</td>
<td>( a )</td>
<td>0</td>
<td>( \sqrt{\frac{2}{3}} )</td>
<td>( -\sqrt{\frac{1}{3} - a^2} )</td>
</tr>
<tr>
<td>( t_3 )</td>
<td>( a )</td>
<td>( \frac{1}{\sqrt{2}} )</td>
<td>( -\frac{1}{\sqrt{6}} )</td>
<td>( -\sqrt{\frac{1}{3} - a^2} )</td>
</tr>
<tr>
<td>( t_4 )</td>
<td>( a )</td>
<td>( \frac{1}{\sqrt{2}} )</td>
<td>( -\frac{1}{\sqrt{6}} )</td>
<td>( -\sqrt{\frac{1}{3} - a^2} )</td>
</tr>
</tbody>
</table>

Table 4. Representation of hybridised orbitals of ammonia molecule. \( t_1 \) represents free electron pair.

Unknown coefficient \( a \) can be determined from experimental data, for instance if one knows that the angle between N-H bonds (for instance between \( t_3 \) and \( t_4 \)) equals 107.3\(^\circ\) then

\[
\cos \theta_{34} = -0.2974 = -\frac{a^2}{1 - a^2} \quad \Rightarrow \quad a = 0.47876
\]

The overall hybridisation in ammonia molecule is of \( sp^3 \) type, i.e. it’s a combination of 2s and 3 p-type orbitals of nitrogen. However independently the hybridized \( tt \) orbitals can have different contribution of \( s \) and \( p \) functions. For instance for the orbital \( t_3 \):

- contribution from 2s orbital: \( a^2 \)
- contribution from 2p\(_x\) orbital: \( \frac{1}{2} \)
7. Hybridisation

- contribution from 2p\(_x\) orbital: \(\frac{1}{6}\)
- contribution from 2p\(_z\) orbital: \(\frac{1}{3} - a^2\)

So that the character of the t\(_3\) orbital can be expressed as \(s^a p^{1-a^2} = sp^{\frac{1-a^2}{a^2}} = sp^{3.36}\). The coefficient \(\frac{1-a^2}{a^2}\) (it can be noninteger) says on how many the contribution of p orbital in a given hybridised orbital is larger then the contribution of s orbital. Hence, a single t\(_i\) orbital can be described as, for instance, sp\(^4\) or sp\(^5\).

Find hybridised orbitals of ethylene molecule (C\(_2\)H\(_4\)).

Solution

Ethylene molecule is the simplest example of a double bond organic molecule.

![Ethylene molecule](image1)

**Figure 12.** Ethylene molecule. Pure 2p orbital, perpendicular to the plane of the molecule (say it is the 2p\(_x\) orbital) doesn’t change at all in the hybridisation process. Two such (atomic) orbitals create 2 \(\pi\) (molecular) orbitals: one is bonding and one is antibonding.

The 2p\(_x\) remains unchanged, so we assume \(t_1 = 2p_x\), hence \(d_1 = 1, a_1 = b_1 = c_1 = 0\). The three other hybridised orbitals create bonds with hydrogens (\(t_2\) and \(t_3\)) while the \(t_4\) will create bond with the second carbon atom. Therefore:

\[
\begin{align*}
a_2 &= a_3 = a \\
a_2^2 + a_2^2 + a_3^2 + a_4^2 &= 1 \\
a_2^2 + a_2^2 + a_4^2 &= 1 \quad \Rightarrow \quad a_4 = \sqrt{1 - 2a^2}
\end{align*}
\]

Moreover, the \(t_1\) entirely consists of only the 2p\(_x\) of carbon atom. Therefore

\[
\begin{align*}
d_1^2 + d_2^2 + d_3^2 + d_4^2 &= 1 \\
d_1 = 1 \quad \Rightarrow \quad d_2 = d_3 = d_4 = 0
\end{align*}
\]

Let’s arrange the \(t_4\) orbital along positive x axis. Then it reveals that \(4 = 0, b_4 > 0\). Normalization of \(t_4\):

\[
a_4^2 + b_4^2 + c_4^2 + d_4^2 = 1 - 2a^2 + b_4^2 + 0 + 0 = 1 \quad \Rightarrow \quad b_4 = a\sqrt{2}
\]

Orthogonality of \(t_2\) and \(t_4\) (and the same - of \(t_3\) and \(t_4\)) leads to calculation of \(b_2\) (and \(b_3\)):

\[
a\sqrt{1 - 2a^2} + b_2a\sqrt{2} = 0
\]
\[ b_2 = -\sqrt{\frac{1}{2} - a^2} = b_3 \]

Normalization condition for \( t_2 \) allows for calculation of \( c_2 \), while the normalization condition for \( t_3 \) allows for calculation of \( c_3 \). Of course \( c_2 > 0 \) and \( c_3 < 0 \) which reveals from the arrangement of orbitals in coordinate system (\( t_2 \) goes in positive z direction).

\[ a_2^2 + b_2^2 + c_2^2 + d_2^2 = a^2 + \frac{1}{2} - a^2 + c_2^2 = 1 \Rightarrow c_2 = \frac{1}{\sqrt{2}} = -c_3 \]

We can represent the results in a table.

<table>
<thead>
<tr>
<th>( t )</th>
<th>( a_i )</th>
<th>( b_i )</th>
<th>( c_i )</th>
<th>( d_i )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( t_1 )</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>( t_2 )</td>
<td>( a )</td>
<td>( -\sqrt{\frac{1}{2} - a^2} )</td>
<td>( \frac{1}{\sqrt{2}} )</td>
<td>0</td>
</tr>
<tr>
<td>( t_3 )</td>
<td>( a )</td>
<td>( -\sqrt{\frac{1}{2} - a^2} )</td>
<td>( -\frac{1}{\sqrt{2}} )</td>
<td>0</td>
</tr>
<tr>
<td>( t_4 )</td>
<td>( \sqrt{1 - 2a^2} )</td>
<td>( a\sqrt{2} )</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 5. Representation of hybridised orbitals of carbon atom in ethylene molecule. \( t_4 \) entirely is engaged in the creation of \( \pi \) orbital in ethylene molecule and it is a pure \( 2p_z \) atomic orbital.

In the table above the \( a \) parameter remains unknown. However, the angle between C-H bonds equals \( 112^\circ \) as it reveals from experiments. Hence

\[ \cos \theta_{23} = \cos 112^\circ = -\frac{a^2}{1 - a^2} \Rightarrow a^2 = 0.320 \Rightarrow a = 0.565 \]

Thus we are able to find the final hybridised orbitals of carbon atom in ethylene molecule.

<table>
<thead>
<tr>
<th>( t )</th>
<th>( a_i )</th>
<th>( b_i )</th>
<th>( c_i )</th>
<th>( d_i )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( t_1 )</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>( t_2 )</td>
<td>( \frac{1}{\sqrt{3}} )</td>
<td>( \frac{1}{\sqrt{6}} )</td>
<td>( \frac{1}{\sqrt{2}} )</td>
<td>0</td>
</tr>
<tr>
<td>( t_3 )</td>
<td>( \frac{1}{\sqrt{3}} )</td>
<td>( -\frac{1}{\sqrt{6}} )</td>
<td>( -\frac{1}{\sqrt{2}} )</td>
<td>0</td>
</tr>
<tr>
<td>( t_4 )</td>
<td>( \frac{1}{\sqrt{3}} )</td>
<td>( \frac{1}{\sqrt{3}} )</td>
<td>( \frac{2}{\sqrt{3}} )</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 6. Final representation of hybridised orbitals of carbon atom in ethylene molecule.

Table 7. Another possible representation of hybridised orbitals of methane molecule.

Hence, for instance the \( t_4 \) orbital can be written as: \( t_3 = \phi_3 = 0.565 \cdot 2s - 0.424 \cdot 2p_x - 0.707 \cdot 2p_y \).

If we assume that 3 hybridised orbitals remain equivalent and will create equivalent molecular bonds (for each carbon atom: 2 C-H sigma bonds + 1 C-C sigma bond) in ethylene molecule then the hybridised orbitals of carbon atom in ethylene molecule would be defined as in the right table above.

Find hybridised orbitals of acetylene molecule \((\text{C}_2\text{H}_2)\).

Solution

Acetylene molecule is the simplest example of a triple bond organic molecule.
Let’s arrange $t_3$ hybridised orbital which will create the C-H bond, as well as $t_4$ hybridised orbital for the C-C bond along the $z$ axis. While the pure p orbitals (say $2p_x$ and $2p_y$ orbitals) will correspond to $t_1$ and $t_2$ hybridised orbitals, respectively. The pure $2p_x$ and $2p_y$ orbitals will create two $\pi$ orbitals (2 bonding and two antibonding molecular orbitals). Therefore

\[
a_1 = c_1 = d_1 = 0, b_1 = 1
\]
\[
a_2 = b_2 = d_2 = 0, c_2 = 1
\]
\[
b_3 = b_3 = b_4 = 0
\]
\[
c_1 = c_3 = c_4 = 0
\]

Let’s denote $a_3 = a$, then

\[
a_3^2 + a_4^2 = 1
\]
\[
a_4 = \sqrt{1 - a^2}
\]

Moreover if $t_3$ lays down at the positive x axis then $d_3 > 0$. From normalization condition for $t_3$ we can calculate $d_3$

\[
a_3^2 + b_3^2 + c_3^2 + d_3^2 = a^2 + 0 + 0 + d_3^2 = 1 \quad \Rightarrow \quad d_3 = \sqrt{1 - a^2}
\]

$t_4$ orbital, on the other hand, should have $d_4 < 0$

\[
1 - a^2 + 0 + 0 + d_4^2 = 1 \quad \Rightarrow \quad d_4 = -a
\]

We can present the orbitals in a table

It is worth noticing we cannot determine the $a$ parameter utilizing the information that the angle between bonds equals 180°, because we already assumed that the $t_3$ and $t_4$ orbitals lay down at the $z$ axis. We could only say that the orbitals are equally valuable, i.e. that $a = \frac{1}{\sqrt{2}}$. Hence

\[
t_3 = \frac{1}{\sqrt{2}} (\phi_{2s} + \phi_{2p_z})
\]
### Table 8. Representation of hybridised orbitals of carbon atom in acetylene molecule.

<table>
<thead>
<tr>
<th></th>
<th>$a_i$</th>
<th>$b_i$</th>
<th>$c_i$</th>
<th>$d_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$t_1$</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$t_2$</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>$t_3$</td>
<td>$a$</td>
<td>0</td>
<td>0</td>
<td>$\sqrt{1 - a^2}$</td>
</tr>
<tr>
<td>$t_4$</td>
<td>$\sqrt{1 - a^2}$</td>
<td>0</td>
<td>0</td>
<td>$-a$</td>
</tr>
</tbody>
</table>

$t_3$ and $t_4$ are entirely engaged in creation of $\pi$ orbitals in acetylene molecule and they have a pure $2p_x$ and $2p_y$ nature, respectively.

$$t_4 = \frac{1}{\sqrt{2}} \left( \phi_{2s} - \phi_{2p_z} \right)$$

Find hybridised orbitals for metal ion in square planar complex molecule.

**Solution**

In case of a square planar complex we choose the following atomic orbitals of metal ion: $3d_{x^2-y^2}$, $4s$, $4p_x$, $4p_y$ (the choice of atomic orbitals is generally dictated by the rules of group theory which systematically orders the dependencies between symmetry of molecules and the wave functions). Hence this type of hybridisation is called dsp$^3$. This is very symmetric type of hybridisation and can be related to the order of axis in cartesian system.

![Figure 16. Order of square-planar hybridised orbitals in cartesian system.](image)

![Figure 17. Orientation of chosen atomic orbitals in cartesian system.](image)

Thus the hybridized orbitals will be defined in following:

$$t_i = a_i 4s + b_i 4p_x + c_i 4p_y + f_i 3d_{x^2-y^2}$$

Contribution of 4s orbital to all hybridised orbitals is the same, hence

$$a_1 a_2 = a_3 = a_4 = a$$

$$4a^2 = 1 \Rightarrow a = \frac{1}{2}$$

(normalization condition)

(7.7)

The $p_x$ orbital gives equal contribution to $t_1$ and to $t_2$, hence

$$b_1^2 = b_2^2$$

$$b_3 = b_4 = 0$$
\[ b_1^2 + b_2^2 = 1 \]
\[ 2b_1^2 = 1 \Rightarrow b_1 = \frac{1}{\sqrt{2}}, \quad b_2 = -\frac{1}{\sqrt{2}} \]

As far as the \( p_y \) is concerned we proceed in the same manner

\[ c_1 = c_2 = 0 \]
\[ c_3^2 = c_4^2 \]
\[ c_3 = \frac{1}{\sqrt{2}} \Rightarrow c_4 = -\frac{1}{\sqrt{2}} \]

Additionaly, after having a look at the shape of the \( 3d_{x^2-y^2} \) orbital we can conclude that

\[ f_1 = f_2 > 0 \]
\[ f_3 = f_4 < 0 \]
\[ f_1^2 = f_2^2 = f_3^2 = f_4^2 \]
\[ f_1^2 + f_2^2 + f_3^2 + f_4^2 = 1 \]
\[ f_1 = f_2 = \frac{1}{2}, \quad f_3 = f_4 = -\frac{1}{2} \]

The hybridized orbitals were shown in a table below

<table>
<thead>
<tr>
<th>( t_1 )</th>
<th>( a_1 )</th>
<th>( b_1 )</th>
<th>( c_1 )</th>
<th>( f_1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \frac{1}{2} )</td>
<td>( \frac{1}{2} )</td>
<td>( 0 )</td>
<td>( \frac{1}{2} )</td>
<td></td>
</tr>
<tr>
<td>( \frac{1}{2} )</td>
<td>( -\frac{1}{2} )</td>
<td>( 0 )</td>
<td>( \frac{1}{2} )</td>
<td></td>
</tr>
<tr>
<td>( \frac{1}{2} )</td>
<td>( 0 )</td>
<td>( \frac{1}{\sqrt{2}} )</td>
<td>( -\frac{1}{2} )</td>
<td></td>
</tr>
<tr>
<td>( \frac{1}{2} )</td>
<td>( 0 )</td>
<td>(-\frac{1}{\sqrt{2}} )</td>
<td>( -\frac{1}{2} )</td>
<td></td>
</tr>
</tbody>
</table>

**Table 9.** Representation of hybridised orbitals of metal ion in a square planar complex molecule. The hybridization type is called \( dsp^2 \).

Find hybridised orbitals for metal ion in octahedral complex molecule.

**Solution**

**Figure 18.** Order of hybridised orbitals of metal ion of octahedral complex in cartesian system.

**Figure 19.** Orientation of chosen atomic orbitals of metal ion in cartesian system.
In case of an octahedral complex we choose the following atomic orbitals of metal ion: $3d_{x^2-y^2}$, $3d_{z^2}$, $4s$, $4p_x$, $4p_y$, $4p_z$. Hence this type of hybridisation is called $d^2sp^3$.

Definition of hybridized orbitals:

$$t_i = a_i 4s + b_i 4p_x + c_i 4p_y + d_i 4p_z + f_i 3d_{x^2-y^2} + g_i 3d_{z^2} \quad i = 1, 2 \ldots, 6$$

Contribution of $4s$ orbital to all hybridised orbitals is the same, hence

$$\sum_i a_i^2 = 1$$

$$a_1 = a_2 = a_3 = a_4 = a_5 = a_6 = \frac{1}{\sqrt{6}}$$

$4p_x$ orbital contributes only to $t_1$ and to $t_2$. Moreover, $b_1 > 0$ and $b_2 < 0$. Thus it reveals that

$$b_3 = b_4 = b_5 = b_6 = 0$$

$$b_1 = \frac{1}{\sqrt{2}} \quad b_2 = -\frac{1}{\sqrt{2}}$$

$$c_1 = c_2 = c_3 = c_6 = 0$$

$$c_3 = \frac{1}{\sqrt{2}} \quad c_4 = -\frac{1}{\sqrt{2}}$$

$$d_1 = d_2 = d_3 = d_4 = 0$$

$$d_5 = \frac{1}{\sqrt{2}} \quad d_6 = -\frac{1}{\sqrt{2}}$$

$3d_{x^2-y^2}$ orbital contributes to only $t_1$, $t_2$, $t_3$, $t_4$ orbitals:

$$f_1 = f_2 = \frac{1}{2}$$

$$f_3 = f_4 = -\frac{1}{2}$$

$$f_5 = f_6 = 0$$

Contribution of $3d_{z^2}$ orbital can be calculated from the normalization condition for hybridized orbitals.

$$a_i^2 + b_i^2 + c_i^2 + d_i^2 + f_i^2 + g_i^2 = 1$$

$$g_i^2 = 1 - a_i^2 - b_i^2 - c_i^2 - d_i^2 - f_i^2 - g_i^2 =$$

$$= 1 - \frac{1}{6} - \frac{1}{2} - 0 - \frac{1}{4} = \frac{1}{12}, \quad i = 1, 2, 3, 4$$

$$g_i < 0, \quad \text{(from contribution of negative torus)}$$

$$g_i = -\frac{1}{\sqrt{12}}$$

$$g_i^2 = 1 - \frac{1}{6} - \frac{1}{2} = \frac{1}{3}, \quad i = 5, 6$$

$$g_i = \frac{1}{\sqrt{3}}, \quad i = 5, 6$$
Table 10. Representation of hybridised orbitals of metal ion in a square planar complex molecule. The hybridization type is called d²sp³.

The coefficients were shown in a table below.

Find hybridised orbitals for metal ion in trigonal bipyramidal complex molecule.

Solution

Figure 20. Order of hybridised orbitals of metal ion of trigonal bipyramidal complex in cartesian system.

Figure 21. Orientation of chosen atomic orbitals of metal ion in cartesian system.

In this case following orbitals are used: 3d₂z, 4s, 4pₓ, 4pᵧ, 4p₂. Hence this type of hybridisation is called dsp³. An example is PCl₅ molecule.

Definition of hybridized orbitals:

\[ t_i = a_i 4s + b_i 4p_x + c_i 4p_y + d_i 4p_z + f_i 3d_{z^2} \quad i = 1, 2, \ldots, 5. \]

Contribution of 4s orbital to all hybridised orbitals is the same, hence

\[ \sum_{i} a_i^2 = 1 \]

\[ a_1 = a_2 = a_3 = a_4 = a_5 = \frac{1}{\sqrt{5}}. \]

4p₂ orbital contributes only to \( t_4 \) and to \( t_5 \) hybridised orbitals.
\[ d_1 = d_2 = d_3 = 0 \]
\[ d_4 = \frac{1}{\sqrt{2}}, \quad d_5 = -\frac{1}{\sqrt{2}} \]

From the arrangement of orbitals in the cartesian system it reveals that

\[
\begin{align*}
    b_1 &= 0 \\
    b_2 &> 0 \\
    b_3 &= -b_2 \\
    c_1 &> 0 \\
    c_2 &= c_3 \\
    c_2 &< 0, \quad c_3 < 0
\end{align*}
\]

4p\(_x\) and 4p\(_y\) orbitals don't contribute to \(t_4\) and to \(t_5\) orbitals, therefore

\[
\begin{align*}
    b_4 &= b_5 = c_4 = c_5 = 0 \\
    \sum_{i=1}^{5} b_i^2 &= 1 \\
    b_2^2 + b_3^2 &= 1 \\
    2b_2^2 &= 1 \quad \Rightarrow \quad b_2 = \frac{1}{\sqrt{2}}, \quad b_3 = -\frac{1}{\sqrt{2}}
\end{align*}
\]

Contribution of 3d\(_{2z}\) orbital to \(t_4\) and to \(t_5\) remains identical, hence

\[
\begin{align*}
    f_4^2 &= f_5^2 \\
    f_4 &= f_5 > 0 \quad \text{(same sign of function in } z \text{ direction).}
\end{align*}
\]

From normalization condition for \(t_4\)

\[
\begin{align*}
    a_4^2 + b_4^2 + c_4^2 + d_4^2 + f_4^2 &= 1 \\
    \frac{1}{5} + 0 + 0 + \frac{1}{2} + f_4^2 &= 1 \\
    f_4 &= \sqrt{\frac{3}{10}} = f_5
\end{align*}
\]

Of course, contribution of 3d\(_{2z}\) orbital to \(t_1\) and to \(t_2\) as well as to \(t_3\) orbitals remains also identical, i.e.

\[
\begin{align*}
    f_1^2 &= f_2^2 = f_3^2 = 1 \quad (7.8)
\end{align*}
\]

Moreover

\[
\begin{align*}
    &f_i < 0, \quad i = 1, 2, 3 \\
    \sum_{i=1}^{5} f_i^2 &= 1
\end{align*}
\]
\[ 3f_1^2 + 2 \frac{3}{10} = 1 \]
\[ f_1 = f_2 = f_3 = -\sqrt{\frac{2}{15}} \quad (7.9) \]

\( c_2 \) coefficient can be found from normalization equation for \( t_2 \) orbital and in the same way we can find the \( c_3 \):

\[ a_2^2 + b_2^2 + c_2^2 + d_2^2 + f_2^2 = 1 \]
\[ \frac{1}{5} + \frac{1}{2} + c_2^2 + 0 + \frac{2}{15} = 1 \]
\[ c_2 = \frac{1}{\sqrt{6}} \]
\[ c_3 = c_2 \]

We still need the \( c_1 \) coefficient, which can be found from the equation for the sum of contributions of each atomic orbital to all hybridized orbitals, i.e.:

\[ \sum_{i=1}^{5} c_i^2 = 1 \]
\[ c_1^2 + \frac{1}{6} + \frac{1}{6} + 0 + 0 = 1 \]
\[ c_1 = \sqrt{\frac{2}{3}} \]

The coefficients were shown in a table below.

<table>
<thead>
<tr>
<th>( t_i )</th>
<th>( a_i )</th>
<th>( b_i )</th>
<th>( c_i )</th>
<th>( d_i )</th>
<th>( f_i )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( t_1 )</td>
<td>( \frac{1}{\sqrt{5}} )</td>
<td>0</td>
<td>( \sqrt{\frac{2}{3}} )</td>
<td>0</td>
<td>( -\sqrt{\frac{2}{15}} )</td>
</tr>
<tr>
<td>( t_2 )</td>
<td>( \frac{1}{\sqrt{3}} )</td>
<td>( \frac{1}{\sqrt{2}} )</td>
<td>( \frac{1}{\sqrt{6}} )</td>
<td>0</td>
<td>( -\sqrt{\frac{2}{15}} )</td>
</tr>
<tr>
<td>( t_3 )</td>
<td>( \frac{1}{\sqrt{3}} )</td>
<td>( -\frac{1}{\sqrt{2}} )</td>
<td>( \frac{1}{\sqrt{6}} )</td>
<td>0</td>
<td>( -\sqrt{\frac{2}{15}} )</td>
</tr>
<tr>
<td>( t_4 )</td>
<td>( \frac{1}{\sqrt{5}} )</td>
<td>0</td>
<td>0</td>
<td>( \frac{1}{\sqrt{2}} )</td>
<td>( \sqrt{\frac{3}{10}} )</td>
</tr>
<tr>
<td>( t_5 )</td>
<td>( \frac{1}{\sqrt{5}} )</td>
<td>0</td>
<td>0</td>
<td>( -\frac{1}{\sqrt{2}} )</td>
<td>( \sqrt{\frac{3}{10}} )</td>
</tr>
</tbody>
</table>

**Table 11.** Representation of hybridized orbitals of metal ion in a trigonal bipyramidal complex molecule. The hybridization type is called dsp\(^3\).

**8 Hückel method**

In Hückel methods for atoms \( p \) and \( q \) we denote:

1. \( S_{pq} = \delta_{pq} \), \( \delta_{pq} \) = Cronecker delta
2. \( H_{pp} = \alpha \),
3. \( H_{pq} = \beta \), for two adjacent atoms,
4. \( H_{pq} = 0 \), for two nonadjacent atoms.
Find molecular orbitals, $\pi$-electron densities and bond orders for following molecules:

1. ethylene,
2. allyl group (cation, anion, radical),
3. 1,3-butadiene,
4. pentadienyl radical,
5. cyclopropenyl anion,
6. cyclobutadiene.

**Solution**

1. Ethylene.

![Ethylene molecule and numbering of atoms](image1)

**Figure 22.** Ethylene molecule and numbering of atoms.

<table>
<thead>
<tr>
<th>Atoms</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$\alpha - \epsilon$</td>
<td>$\beta$</td>
</tr>
<tr>
<td>2</td>
<td>$\beta$</td>
<td>$\alpha - \epsilon$</td>
</tr>
</tbody>
</table>

$\begin{vmatrix} x & 1 \\ 1 & x \end{vmatrix} = x^2 - 1 = 0 \quad \Rightarrow \quad x_1 = -1, \ x_2 = +1$

Thus

$x_1 = -1 \quad \Rightarrow \quad \frac{\alpha - \epsilon_1}{\beta} = -1, \quad \epsilon_1 = \alpha + \beta$

$x_2 = +1 \quad \Rightarrow \quad \epsilon_2 = \alpha - \beta$

The two energies correspond to two molecular orbitals

$\psi_1 = c_{11}\phi_1 + c_{12}\phi_2$

$\psi_2 = c_{21}\phi_1 + c_{22}\phi_2$

The atomic orbitals: $\phi_1$ and $\phi_2$ correspond to atomic $2p_z$ orbitals (from which the $\pi$ orbitals are created). The $c_{11}, c_{12}, c_{21}, c_{22}$ coefficients can be found solving the secular equations. First, plugging $\epsilon_1 = -1$ we can find the $c_{11}$ and $c_{12}$

$[H_{pq} - \epsilon S_{pq}] [c_{1q}] = 0 = \begin{bmatrix} \alpha - c_1 \\ \beta \end{bmatrix} \begin{bmatrix} c_{11} \\ c_{12} \end{bmatrix} = \begin{bmatrix} -\beta \\ -\beta \end{bmatrix} \begin{bmatrix} c_{11} \\ c_{12} \end{bmatrix} = -\beta \begin{bmatrix} 1 & -1 \\ -1 & 1 \end{bmatrix} \begin{bmatrix} c_{11} \\ c_{12} \end{bmatrix} = 0$
Hence \( c_{11} = c_{12} \). From normalization condition

\[
c_{11}^2 + c_{12}^2 = 1 \quad \Rightarrow \quad c_{11} = c_{12} = \frac{1}{\sqrt{2}}
\]

Caution. \( c_{11} = -\frac{1}{\sqrt{2}} \) gives us the same orbital but with different sign.

Plugging the \( c_2 = 1 \) we can, in turn, find the \( c_{21} \) and \( c_{22} \)

\[
\begin{bmatrix}
\alpha - e_2 & \beta \\
\beta & \alpha - e_2
\end{bmatrix}
\begin{bmatrix}
c_{21} \\
c_{22}
\end{bmatrix}
= \begin{bmatrix}
\beta \\
\beta
\end{bmatrix}
\begin{bmatrix}
c_{11} \\
c_{12}
\end{bmatrix}
= \beta
\begin{bmatrix}
1 & 1 \\
1 & 1
\end{bmatrix}
\begin{bmatrix}
c_{11} \\
c_{12}
\end{bmatrix}
= 0
\]

Hence, \( c_{21} = -c_{22} \). And utilizing the normalization condition

\[
c_{21}^2 + c_{22}^2 = 1 \quad \Rightarrow \quad c_{21} = \frac{1}{\sqrt{2}}, \quad c_{22} = -\frac{1}{\sqrt{2}}
\]

Therefore, the molecular orbitals

\[
\psi_1 = \frac{1}{\sqrt{2}} (\phi_1 + \phi_2)
\]

\[
\psi_2 = \frac{1}{\sqrt{2}} (\phi_1 - \phi_2)
\]

It’s convenient to represent the results in a table

**Table 12.** \( \pi \) orbitals’ coefficients (of \( i \)-th orbital), corresponding energies \((\epsilon_i)\) and occupation numbers \((n_i)\).

<table>
<thead>
<tr>
<th>( i )</th>
<th>( \epsilon_i )</th>
<th>( x_i )</th>
<th>( n_i )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( \alpha - \beta )</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>( \alpha + \beta )</td>
<td>-1</td>
<td>0</td>
</tr>
</tbody>
</table>

\( \pi \)-electron energy: \( E = 2 (\alpha + \beta) \) (\( \beta \) is negative and the two electrons occupy the \( \psi_2 \) orbital, for which the energy is lower (by \( 2\beta \) in comparison to energy of \( \psi_1 \) orbital)).

\( \pi \)-electron bond order is given by following formula

\[
p_{ab} = \sum_i n_i c_{ia} c_{ib}
\]

(8.1)

where \( n_i \) stands for the number of electrons occupying \( i \)-th molecular orbital, and the coefficients stand for the coefficients standing by the atomic p orbitals found for each molecular orbital. Bond orders characterize the strength of p-electron bond between two atoms so it can be calculated for each bond in \( \pi \)-bond molecules.

In ethylene molecule \( p_{12} = 2 \frac{1}{\sqrt{2} \sqrt{2}} = 1 \).

p-electron electron density on \( a \)-th atom is given by following formula
Hückel method

\[ q_a = \sum_i n_i c_{ia}^2 \]  

(8.2)

where the notation remains the same as in the case of bond orders.

In ethylene molecule the electron densities

\[ q_1 = 2 \left( \frac{1}{\sqrt{2}} \right)^2 = q_2 \]  

(8.3)

2. Allyl group (cation, radical anion)

\[ \begin{array}{c}
\text{Figure 24. Allyl radical and numbering of atoms.}
\end{array} \]

\[ \begin{array}{c}
\text{Figure 25. Molecular orbitals' energy levels of allyl cation, radical and anion.}
\end{array} \]

The secular determinant:

\[
\begin{bmatrix}
x & 1 & 0 \\
1 & x & 1 \\
0 & 1 & x
\end{bmatrix}
- \begin{bmatrix}
1 & 1 \\
x & 1 \\
0 & x
\end{bmatrix}
= x \begin{bmatrix}
x^2 - 1 \\
x \\
1
\end{bmatrix}
- \begin{bmatrix}
1 & 1 \\
x & 1 \\
0 & x
\end{bmatrix}
= x(x^2 - 1) - x = x^3 - 2x
\Rightarrow
x_1 = -\sqrt{2}, \ x_2 = 0, \ x_3 = \sqrt{2}
\]

Thus

\[ x = \frac{\alpha - \epsilon}{\beta}, \quad \Rightarrow \quad \epsilon = \alpha - x\beta \]

\[ e_1 = \alpha + \sqrt{2}\beta \]

\[ e_2 = \alpha \]

\[ e_3 = \alpha - \sqrt{2}\beta \]

Secular equation

\[
\begin{bmatrix}
x & 1 & 0 \\
1 & x & 1 \\
0 & 1 & x
\end{bmatrix}
\begin{bmatrix}
c_{pq}
\end{bmatrix}
= 0
\]

For \( e_2 \) (for \( x_1 = -\sqrt{2} \))
8. Hückel method

\[
\begin{align*}
&\begin{align*}
  c_{11}x_1 + c_{12} + 0 = 0 \\
  c_{11} + c_{12}x_1 + c_{13} = 0 \\
  0 + c_{12} + c_{13}x_1 = 0
\end{align*}

\Rightarrow \begin{align*}
  c_{12} &= \sqrt{2}c_{11} \\
  c_{11} &= -\sqrt{2}\left(\sqrt{2}c_{11}\right) + c_{13} = 0
\Rightarrow c_{13} = c_{11}
\end{align*}
\]

Normalization condition

\[
\begin{align*}
  c_{11}^2 + c_{12}^2 + c_{13}^2 &= 1 \\
  c_{11}^2 + 2c_{11}^2 + c_{11}^2 &= 1 \\
  c_{11} &= \frac{1}{2} = c_{13}, \quad c_{12} = \frac{1}{2}\sqrt{2} = \frac{1}{\sqrt{2}}
\end{align*}
\]

Therefore

\[
\Psi_1 = \frac{1}{2} \left( \phi_1 + \sqrt{2}\phi_2 + \phi_3 \right)
\]

For \( e_2 \) (for \( x_2 = 0 \))

\[
\begin{align*}
&\begin{align*}
  c_{21}x_2 + c_{22} &= 0 \\
  c_{21} + c_{22}x_2 + c_{23} &= 0 \\
  c_{22} + c_{23}x_2 &= 0
\end{align*}
\]

\Rightarrow \begin{align*}
  c_{22} &= 0 \\
  c_{21} &= -c_{23} \\
  c_{22} &= 0
\end{align*}
\]

Normalization condition

\[
\begin{align*}
  c_{21}^2 + c_{22}^2 + c_{23}^2 &= 1 
\Rightarrow c_{21} = \frac{1}{\sqrt{2}}, \quad c_{23} = -\frac{1}{\sqrt{2}}
\end{align*}
\]

Hence

\[
\Psi_2 = \frac{1}{\sqrt{2}} (\phi_1 - \phi_3)
\]

For \( e_3 \) (i.e. for \( x_3 = \sqrt{2} \))

\[
\begin{align*}
&\begin{align*}
  c_{31}x_3 + c_{32} &= 0 \\
  c_{31} + c_{32}x_3 + c_{33} &= 0 \\
  c_{32} + c_{33}x_3 &= 0
\end{align*}
\]

\Rightarrow \begin{align*}
  \sqrt{2}c_{31} + c_{32} &= 0 \\
  c_{31} + \sqrt{2}c_{32} + c_{33} &= 0 \\
  c_{32} + \sqrt{2}c_{33} &= 0
\Rightarrow \begin{align*}
  c_{32} &= -\sqrt{2}c_{31} \\
  c_{32} &= -\sqrt{2}c_{33}
\Rightarrow c_{33} = c_{31}
\end{align*}
\]

Normalization condition

\[
\begin{align*}
  c_{31}^2 + 2c_{31}^2 + c_{31}^2 &= 1 
\Rightarrow c_{31} = \frac{1}{2} = c_{33}, \quad c_{32} = -\frac{1}{\sqrt{2}}
\end{align*}
\]

Hence
Table 13. \( \pi \) orbitals' coefficients (of \( i \)-th orbital), corresponding energies (\( \epsilon_i \)) and occupation numbers (here for radical molecule) (\( n_i \)).

<table>
<thead>
<tr>
<th>( i )</th>
<th>( \epsilon_i )</th>
<th>( x_i )</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>( \alpha - \sqrt{2} \beta )</td>
<td>( \sqrt{2} )</td>
<td>( \frac{1}{2} )</td>
<td>( \frac{1}{2} )</td>
<td>( \frac{1}{2} )</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>( \alpha )</td>
<td>( 0 )</td>
<td>( \frac{1}{2} \sqrt{2} )</td>
<td>( 0 )</td>
<td>( \frac{1}{2} \sqrt{2} )</td>
<td>1</td>
</tr>
<tr>
<td>1</td>
<td>( \alpha + \sqrt{2} \beta )</td>
<td>( -\sqrt{2} )</td>
<td>( \frac{1}{2} )</td>
<td>( \frac{1}{2} )</td>
<td>( \frac{1}{2} )</td>
<td>2</td>
</tr>
</tbody>
</table>

\[ \Psi_3 = \frac{1}{2} (\phi_1 - \sqrt{2} \phi_2 + \phi_3) \]

\( \pi \)-electron bond orders (\( p_{pq} \)) and electron densities (\( q \)).

<table>
<thead>
<tr>
<th>radical</th>
<th>cation</th>
<th>anion</th>
</tr>
</thead>
<tbody>
<tr>
<td>( p_{12} = 2 \frac{1}{2} \frac{1}{\sqrt{2}} + 1 \frac{1}{\sqrt{2}} \cdot 0 = \frac{1}{\sqrt{2}} = p_{23} )</td>
<td>( p_{12} = 2 \frac{1}{2} \frac{1}{\sqrt{2}} = \frac{1}{\sqrt{2}} = p_{23} )</td>
<td>( p_{12} = 2 \frac{1}{2} \frac{1}{\sqrt{2}} + 2 \frac{1}{\sqrt{2}} \cdot 0 = \frac{1}{\sqrt{2}} = p_{23} )</td>
</tr>
<tr>
<td>( q_1 = 2 \left( \frac{1}{2} \right)^2 + 1 \left( \frac{1}{\sqrt{2}} \right)^2 = 1 )</td>
<td>( q_1 = 2 \left( \frac{1}{2} \right)^2 = \frac{1}{2} )</td>
<td>( q_1 = 2 \left( \frac{1}{2} \right)^2 + 2 \left( \frac{1}{\sqrt{2}} \right)^2 = 1.5 )</td>
</tr>
<tr>
<td>( q_2 = 2 \left( \frac{1}{\sqrt{2}} \right)^2 + 1 \cdot 0^2 = 1 )</td>
<td>( q_2 = 2 \left( \frac{1}{\sqrt{2}} \right)^2 = 1 )</td>
<td>( q_2 = 2 \left( \frac{1}{\sqrt{2}} \right)^2 + 2 \cdot 0^2 = 1 )</td>
</tr>
<tr>
<td>( q_3 = 2 \left( \frac{1}{2} \right)^2 + 1 \left( -\frac{1}{\sqrt{2}} \right)^2 = 1 )</td>
<td>( q_3 = 2 \left( \frac{1}{2} \right)^2 = \frac{1}{2} )</td>
<td>( q_3 = 2 \left( \frac{1}{2} \right)^2 + 2 \left( -\frac{1}{\sqrt{2}} \right)^2 = 1.5 )</td>
</tr>
</tbody>
</table>

3. cis-1,3-butadiene and trans-1,3-butadiene

Figure 26. cis- and trans-1,3-butadiene molecule and numbering of atoms.

The secular determinant

\[
\begin{vmatrix}
1 & 1 & 0 & 0 \\
1 & x & 1 & 0 \\
0 & 1 & x & 1 \\
0 & 0 & 1 & x \\
\end{vmatrix}
= x \begin{vmatrix} x & 1 & 0 \end{vmatrix} - \frac{1}{1} \begin{vmatrix} 1 & 1 & 0 \end{vmatrix} = x \begin{vmatrix} x & x \end{vmatrix} - \frac{1}{x} \begin{vmatrix} 1 & 1 \end{vmatrix} \frac{x}{1} \begin{vmatrix} 1 \end{vmatrix} = \]

- 58 -
\[
\begin{align*}
8. \text{Hückel method} & \\
\text{For other coefficients, the calculations go in the same manner. Below are the final results.} \\
\text{Secular equation for } x_1 = -\sqrt{(3 + \sqrt{5})/2} \approx 1.618 \\
\begin{cases}
 c_{11}x_1 + c_{12} + 0 + 0 = 0 \\
 c_{11} + c_{12}x_1 + c_{13} + 0 = 0 \\
 0 + c_{12} + c_{13}x_1 + c_{14} = 0 \\
 0 + 0 + c_{13} + c_{14}x_1 = 0
\end{cases} \\
\Rightarrow \begin{cases}
 c_{12} = -x_1c_{11} \\
 c_{13} = (x_1^2 - 1)c_{11} \\
 c_{14} = -\frac{1}{x_1}c_{13} = \left(\frac{1}{x_1} - x_1\right)c_{11}
\end{cases}
\end{align*}
\]

Normalization condition

\[
\begin{align*}
 c_{11}^2 + c_{12}^2 + c_{13}^2 + c_{14}^2 &= 1 \\
 c_{11}^2 + x_1^2c_{11}^2 + (x_1^2 - 1)^2c_{11}^2 + \left(\frac{1}{x_1} - x_1\right)^2c_{11}^2 &= 1 \\
 c_{11}^2 \left(1 + x_1^2 + x_1^4 - 2x_1^2 + 1 + \frac{1}{x_1^2} - 2\frac{1}{x_1}x_1 + x_1^2\right) &= 1 \\
\Rightarrow c_{11} &= \sqrt{\frac{1}{x_1^4 + \frac{1}{x_1^2}}} \approx 0.372
\end{align*}
\]

And

\[
\begin{align*}
c_{12} &= -\sqrt{\frac{x_1^4}{x_1^6 + 1}} \approx 0.601, \quad c_{13} \approx 0.601, \quad c_{14} \approx 0.372
\end{align*}
\]

For other coefficients, the calculations go in the same manner. Below are the final results.

\[
\begin{align*}
e_1 &= a + 1.618 \beta \quad \Rightarrow \quad \psi_1 = 0.372 \phi_1 + 0.601 \phi_2 + 0.601 \phi_3 + 0.372 \phi_4 \\
e_2 &= a + 0.618 \beta \quad \Rightarrow \quad \psi_2 = 0.601 \phi_1 + 0.372 \phi_2 - 0.372 \phi_3 - 0.601 \phi_4 \\
e_3 &= a - 0.618 \beta \quad \Rightarrow \quad \psi_2 = 0.601 \phi_1 - 0.372 \phi_2 - 0.372 \phi_3 + 0.601 \phi_4 \\
e_4 &= a - 1.618 \beta \quad \Rightarrow \quad \psi_2 = 0.372 \phi_1 - 0.601 \phi_2 + 0.601 \phi_3 - 0.372 \phi_4
\end{align*}
\]
Table 14. $\pi$ orbitals’ coefficients (of $i$-th orbital), corresponding energies ($\epsilon_i$) and occupation numbers ($n_i$).

<table>
<thead>
<tr>
<th>1</th>
<th>$\epsilon_i$</th>
<th>$\chi_i$</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>$n_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>$\alpha - 1.618 \cdot \beta$</td>
<td>1.618</td>
<td>0.372</td>
<td>-0.601</td>
<td>0.601</td>
<td>-0.372</td>
</tr>
<tr>
<td>3</td>
<td>$\alpha - 0.618 \cdot \beta$</td>
<td>0.618</td>
<td>0.601</td>
<td>-0.371</td>
<td>-0.371</td>
<td>0.602</td>
</tr>
<tr>
<td>2</td>
<td>$\alpha + 0.618 \cdot \beta$</td>
<td>-0.618</td>
<td>0.601</td>
<td>0.371</td>
<td>-0.371</td>
<td>-0.602</td>
</tr>
<tr>
<td>1</td>
<td>$\alpha + 1.618 \cdot \beta$</td>
<td>-1.618</td>
<td>0.372</td>
<td>0.601</td>
<td>0.601</td>
<td>0.372</td>
</tr>
</tbody>
</table>

$\pi$-electron bond orders ($p_{pq}$) and electron densities ($q$).

\[
p_{12} = 2 \cdot 0.372 \cdot 0.601 + 2 \cdot 0.601 \cdot 0.372 = 0.894
\]
\[
p_{23} = 2 \cdot 0.601 \cdot 0.601 + 2 \cdot 0.372 \cdot (-0.372) = 0.447
\]
\[
p_{34} = p_{12}
\]
\[
q_1 = 2 \cdot (0.371)^2 + 2 \cdot (0.602)^2 = 1
\]
\[
q_2 = 2 \cdot (0.602)^2 + 2 \cdot (0.371)^2 = 1
\]
\[
q_3 = 2 \cdot (0.602)^2 + 2 \cdot (-0.371)^2 = 1
\]
\[
q_4 = 2 \cdot (0.371)^2 + 2 \cdot (-0.602)^2 = 1
\]

At picture below (see figure 28) the bond orders are depicted along with the numbers of atoms. Bond between atoms C$_1$ and C$_2$ as well as bond between C$_3$ and C$_4$ are significantly shorter then the single bond between atoms C$_2$ and C$_3$.

Let’s nonsider a singly-excited singlet state of butadiene, see fig. 29. The Hückel method is not capable of handling excited states and can not handle spin of molecules. However, one can examine how the bond orders and the electron densities change when the occupation numbers change, which is actually happening when the exciation is being considered.

Figure 28. Bond orders (and numbers of atoms) of butadiene molecule.

Figure 29. Molecular $\pi$-orbitals’ energy levels of singly-excited 1,3-butadiene molecule.

The electron densities in Hückel method don’t change at all, because from the densities are calculated for atoms (recollect the formula representing electron density). Let’s calculate the bond orders for excited-state butadiene.

\[
p_{12}^* = 2 \cdot 0.372 \cdot 0.601 + 1 \cdot 0.601 \cdot 0.372 + 1 \cdot 0.601 \cdot (-0.372) = 0.447
\]
\[
p_{23}^* = 2 \cdot 0.601 \cdot 0.601 + 1 \cdot 0.372 \cdot (-0.372) + 1 \cdot (-0.372) \cdot (-0.372) = 0.725
\]
\[
p_{34}^* = 2 \cdot 0.372 \cdot 0.601 + 1 \cdot (-0.372) \cdot (-0.601) + 1 \cdot (-0.372) \cdot 0.601 = 0.447 = p_{12}
\]

It reveals that while in the case of ground state of butadiene molecule, the double bonds C$_1$–C$_2$ and C$_3$–C$_4$ are much shorter then the longer single C$_2$–C$_3$ bond, in the case of singly-excited butadiene molecule the C$_1$–C$_2$
and the C₃–C₄ bonds are much longer than the C₂–C₃ bond. Likely, in the singly-excited butadiene molecule
the double bond is located between C₂ and C₃ atoms, while the C₁–C₂ and C₃–C₄ seems to be single. Hence
the singly-excited butadiene molecule could be represented as a biradical structure, see fig. 30. Such a structure
explains the chemical properties of butadiene molecule which, for instance, can react with bromine while the
product is a 1,4-bromobutadiene, i.e. the radical atoms of butadiene molecule (number 1 and 4) react with bromine.

Figure 30. Structures of butadiene in ground state and biradical butadiene (singly-excited state of butadiene).

4. Pentadienyl radical

Figure 31. Pentadienyl mesomers and atoms’ numbering.

![Diagram](image)

The secular determinant

\[
\begin{vmatrix}
1 & x & 1 & 0 & 0 & 0 \\
2 & 1 & x & 1 & 0 & 0 \\
3 & 0 & 1 & x & 1 & 0 \\
4 & 0 & 0 & 1 & x & 1 \\
5 & 0 & 0 & 0 & 1 & x \\
\end{vmatrix} = x \left( x \begin{vmatrix} 1 & x & 1 \\ 1 & x & 1 \\ 1 & x & 1 \end{vmatrix} - \frac{1}{x} \begin{vmatrix} 1 & 1 & 0 \\ 1 & 1 & 0 \\ 1 & 1 & 0 \end{vmatrix} \right) = x \left( x^4 - 3x^2 + 3 \right) - x = 0
\]

\[
x_1 = 0, \quad x^4 - 4x^2 + 3 = 0, \quad x^2 = y, \quad \Rightarrow \quad y^2 - 4y + 3 = 0
\]

Thus (we will change order of xs, i.e. for from the lowest to the highest)

\[
x = \frac{\alpha - \epsilon}{\beta}, \quad \Rightarrow \quad \epsilon = \alpha - x\beta
\]
\[ e_1 = \alpha + \sqrt{3} \beta, \quad e_2 = \alpha + \beta, \quad e_3 = \alpha, \quad e_4 = \alpha - \beta, \quad e_5 = \alpha - \sqrt{3} \beta. \]

\(\beta\) is negative and hence \(e_1 < e_2 < e_3 < e_4 < e_5\).

Secular equation for \(e_1\) (\(x_1 = -\sqrt{3}\))

\[ \begin{bmatrix}
  H_{11} - e & H_{12} & H_{13} & H_{14} & H_{15} \\
  H_{21} & H_{22} - e & H_{23} & H_{24} & H_{25} \\
  H_{31} & H_{32} & H_{33} - e & H_{34} & H_{35} \\
  H_{41} & H_{42} & H_{43} & H_{44} - e & H_{45} \\
  H_{51} & H_{52} & H_{53} & H_{54} & H_{55} - e
\end{bmatrix}
\begin{bmatrix}
  c_{11} \\
  c_{12} \\
  c_{13} \\
  c_{14} \\
  c_{15}
\end{bmatrix} =
\begin{bmatrix}
  a - e & \beta & 0 & 0 & 0 \\
  \beta & a - e & \beta & 0 & 0 \\
  0 & \beta & a - e & \beta & 0 \\
  0 & 0 & \beta & a - e & \beta \\
  0 & 0 & 0 & \beta & a - e
\end{bmatrix}
\begin{bmatrix}
  c_{11} \\
  c_{12} \\
  c_{13} \\
  c_{14} \\
  c_{15}
\end{bmatrix} =
\begin{bmatrix}
  c_{11} x_1 + c_{12} + 0 + 0 + 0 = 0 \\
  c_{11} + c_{12} x_1 + c_{13} + 0 + 0 = 0 \\
  0 + c_{12} + c_{13} x_1 + c_{14} + 0 = 0 \\
  0 + 0 + c_{13} + c_{14} x_1 + c_{15} = 0 \\
  0 + 0 + 0 + c_{14} + c_{15} x_1 = 0
\end{bmatrix} \Rightarrow
\begin{bmatrix}
  c_{12} = -x_1 c_{11} \quad c_{13} = (x_1^2 - 1) c_{11} \quad c_{14} = x_1 (2 - x_1^2) c_{11} \quad c_{15} = (x_1^4 - 3x_1^2 + 1) c_{11}
\end{bmatrix}
\]

Normalization condition

\[ c_{11}^2 + c_{12}^2 + c_{13}^2 + c_{14}^2 + c_{15}^2 = 1 \]
\[ c_{11}^2 = \frac{1}{\sqrt{x_1^8 - 5x_1^6 + 8x_1^4 + 3x_1^2 + 3}} = \frac{1}{\sqrt{3^4 - 5 \cdot 3^3 + 8 \cdot 3^2 + 3 \cdot 3 + 3}} = \frac{1}{\sqrt{30}} \]
\[ c_{12} = -x_1 c_{11} = \frac{1}{\sqrt{10}}, \quad c_{13} = 2c_{11} = \frac{2}{\sqrt{30}}, \quad c_{14} = \frac{1}{\sqrt{30}} = c_{12}, \quad c_{15} = \frac{1}{\sqrt{30}} = c_{11} \]

The same equations can be applied for finding coefficients of four other \(\pi\) orbitals.

\[ x_2 = -1, \quad c_{21} = \frac{1}{\sqrt{10}}, \quad c_{22} = -x_2 c_{21} = -\frac{1}{\sqrt{10}} = -c_{21}, \quad c_{23} = (x_2^2 - 1) c_{21} = 0, \]
\[ c_{24} = x_2 (2 - x_2^2) c_{21} = -\frac{1}{\sqrt{10}} = -c_{21}, \quad c_{25} = (x_2^4 - 3x_2^2 + 1) c_{21} = -\frac{1}{\sqrt{10}} = -c_{21}. \]
\[ x_3 = 0, \quad c_{31} = c_{35} = \frac{1}{\sqrt{3}}, \quad c_{33} = -c_{31} = -\frac{1}{\sqrt{3}}, \quad c_{32} = c_{34} = 0. \]
\[ x_4 = 1, \quad c_{41} = c_{44} = \frac{1}{\sqrt{10}}, \quad c_{42} = c_{45} = -\frac{1}{\sqrt{10}}, \quad c_{43} = 0. \]
\[ x_5 = \sqrt{3}, \quad c_{51} = c_{55} = \frac{1}{\sqrt{30}}, \quad c_{52} = c_{54} = -\frac{1}{\sqrt{30}}, \quad c_{53} = \frac{2}{\sqrt{30}} = 2c_{51}. \]

\(\pi\)-electron bond orders and densities.

\[ p_{12} = 2 \cdot \frac{1}{\sqrt{30}} \cdot \frac{1}{\sqrt{10}} + 2 \cdot \frac{1}{\sqrt{30}} \left( -\frac{1}{\sqrt{10}} \right) + 1 \cdot \frac{1}{\sqrt{3}} \cdot 0 = \frac{2 - 2\sqrt{3} - 100}{\sqrt{300}} \approx 0.493 \]
8. Hückel method

Table 15. \( \pi \) orbitals’ coefficients (of \( i \)-th orbital), corresponding energies (\( \epsilon \)) and occupation numbers (\( n_i \)).

<table>
<thead>
<tr>
<th></th>
<th>( \epsilon_i )</th>
<th>( x_i )</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>( \alpha - \sqrt{3} \beta )</td>
<td>( \sqrt{3} )</td>
<td>( \sqrt{10} )</td>
<td>( \sqrt{30} )</td>
<td>( -1 )</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>( \alpha - \beta )</td>
<td>1</td>
<td>( \sqrt{10} )</td>
<td>( \sqrt{30} )</td>
<td>( -1 )</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>( \alpha )</td>
<td>0</td>
<td>( \sqrt{3} )</td>
<td>( \sqrt{10} )</td>
<td>( -1 )</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>( \alpha + \beta )</td>
<td>-1</td>
<td>( \sqrt{10} )</td>
<td>( \sqrt{30} )</td>
<td>( -1 )</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>1</td>
<td>( \alpha + \sqrt{3} \beta )</td>
<td>( -\sqrt{3} )</td>
<td>( \sqrt{10} )</td>
<td>( \sqrt{30} )</td>
<td>( 0 )</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>2</td>
</tr>
</tbody>
</table>

\[ p_{23} = 2 \frac{1}{\sqrt{10}} \frac{2}{\sqrt{30}} + 0 + 1 \cdot 0 = \frac{4}{\sqrt{300}} \approx 0.231 \]

\[ p_{34} = 2 \frac{1}{\sqrt{30}} \frac{1}{\sqrt{10}} + 0 + 0 = \frac{4}{\sqrt{300}} \approx 0.231 \]

\[ p_{45} = 2 \left( \frac{1}{\sqrt{10}} \right) \left( \frac{1}{\sqrt{30}} \right) + 2 \left( -\frac{1}{\sqrt{10}} \right) \left( -\frac{1}{\sqrt{10}} \right) + 0 = \frac{2 + 2\sqrt{3}}{\sqrt{300}} \approx 0.315 \]

\[ q_1 = 2 \left( \frac{1}{2} \right)^2 + 1 \left( \frac{1}{\sqrt{2}} \right)^2 = 1 \]

\[ q_2 = 2 \left( \frac{1}{\sqrt{2}} \right)^2 + 1 \cdot 0^2 = 1 \]

\[ q_3 = 2 \left( \frac{1}{2} \right)^2 + 1 \left( -\frac{1}{\sqrt{2}} \right)^2 = 1 \]

5. Cyclopropenyl anion

![Figure 33. Cyclopropenyl mesomers and atoms’ numbering.](image)

![Figure 34. Molecular orbitals’ energy levels of cyclopropenyl molecule.](image)

The secular determinant

<table>
<thead>
<tr>
<th>atoms</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

\[ x^3 - 3x + 2 = 0 \]
$x_1 = 1, \quad \Rightarrow \quad (x^3 - 3x + 2) : (x - 1) = x^2 + x - 2 \quad \Rightarrow \quad x_2 = -2, \quad x_3 = 1.$

Thus (changing the order of $x$s)

$$x = \frac{\alpha - \epsilon}{\beta}, \quad \Rightarrow \quad \epsilon = \alpha - x\beta \quad \Rightarrow \quad \epsilon_1 = \alpha + 2\beta, \quad \epsilon_2 = \epsilon_3 = \alpha - \beta$$

6. Cyclobutadiene

![Cyclobutadiene mesomers and atoms' numbering.](image)

Figure 35. Cyclobutadiene mesomers and atoms' numbering.

## 9 Variational procedure

Particle in one-dimensional box of width $L$. Find the expectation value of hamiltonian for the following trial function:

$$\Psi(x) = Nx(l - x)$$

Check, if the variational principle is satisfied.

### Solution

First we must normalize the function

$$N^{-2} = \int_0^L (x(L - x))^2 dx = \int_0^L (x^4 - 2Lx^3 + L^2x^2) dx = \left[ \frac{1}{5}x^5 - \frac{2L}{4}x^4 + \frac{L^2}{3}x^3 \right]_0^L$$

$$= \frac{1}{5}L^5 - \frac{1}{2}L^5 + \frac{1}{3}L^5 = \frac{L^5}{30}$$

thus

$$N = \sqrt{\frac{30}{L^5}}$$

As in the variational methods, we must calculate the mean energy
\[ e = \langle \hat{H} \rangle = -\frac{\hbar^2}{2mL^2} \int_0^L (Lx - x^2) \frac{d^2}{dx^2} (Lx - x^2) \, dx = 2\frac{\hbar^2}{2mL^2} \int_0^L (Lx - x^2) \, dx = \frac{\hbar^2}{mL} \left( \frac{1}{2}L^3 - \frac{1}{3}L^3 \right) = \frac{\hbar^2}{mL^3} \cdot 6 = \frac{5\hbar^2}{mL^2} \]

while the exact energy is following

\[ E = \frac{\hbar^2}{2mL^2} = \frac{4.935\hbar^2}{mL^2} \]

and it reveals that the variational rule is fulfilled, i.e. \( E < e \).

Example. Let’s consider a hydrogen-like atom. By means of variational method find the \( c \) parameter present in trial function \( \phi(r; c) = e^{-cr} \).

Solution

First, we must normalize the trial function. We already did this is one of previous examples:

\[ N = \sqrt{\frac{c^3}{\pi}} \]

We must determine the expectaion value of Hamiltonian for the hydrogen-like atom and for our normalized trial function

\[ \langle \phi | \hat{H} | \phi \rangle = -\frac{\hbar^2}{2\mu} \langle \phi | \Delta | \phi \rangle - \frac{Ze^2}{4\pi\epsilon} \langle \phi | \frac{1}{r} | \phi \rangle \]

\[ \langle \phi | \frac{1}{r} | \phi \rangle = \frac{c^3}{\pi} \int_0^\infty \frac{1}{r} e^{-2cr} r^2 \, dr = 4c^3 \left( \frac{1}{2c} \right)^2 = c \]

\[ \langle \phi | \Delta | \phi \rangle = \frac{c^3}{\pi} \int_0^\infty r^2 e^{-cr} \frac{1}{r^2} d\frac{dr}{2\pi} r^2 e^{-cr} \, dr = 4c^3 \int_0^\infty e^{-cr} (c^2 r^2 e^{-cr} - 2ce^{-cr}) \, dr \]

\[ = 4c^3 \int_0^\infty (c^2 r^2 - 2cr) e^{-2cr} \, dr = 4c^3 \left( c^2 \left( \frac{2!}{(2c)^3} - 2c \frac{1!}{(2c)^2} \right) \right) = 4c^3 \left( -\frac{1}{4c} \right) = -c^2 \]

Thus

\[ e(c) = \frac{\hbar^2}{2\mu} e^2 - \frac{Ze^2}{4\pi\epsilon} c \]

We are looking for the minimum of function \( e(c) \)

\[ \frac{d}{dc} e(c) = 0 = \frac{\hbar^2}{\mu} c - \frac{Ze^2}{4\pi\epsilon} \]

Thus

\[ c = \frac{Ze^2 \mu}{4\pi \epsilon \hbar^2} = \frac{Z}{a_0} \]

We actually got the optimal function which corresponds to the wave function of hydrogen atom for its ground state

\[ \phi = \frac{1}{\sqrt{\pi}} \left( \frac{Z}{a_0} \right) e^{-Zr/a_0} \]

This is a typical scenario for variational procedure operating for a family of functions which contains an exact solution among its components, namely the variational method will find this function from among the pool of functions.
Example. Let’s consider a hydrogen-like atom. By means of variational method find the $c$ parameter present in
trial function $\phi(r; c) = e^{-cr^2}$.

Solution

First, we must normalize the trial function.

\[ N^{-2} = \int e^{-2cr^2} d^3r = 4\pi \int_0^\infty r^2 e^{-2cr^2} dr \]

To calculate this integral, let’s first calculate the following integral

\[ I = \int_{-\infty}^{+\infty} e^{-ax^2} dx \]

It’s convenient to calculate the square of $I$

\[ I^2 = \int_{-\infty}^{+\infty} e^{-ax^2} dx \int_{-\infty}^{+\infty} e^{-ay^2} dy = \int_{-\infty}^{+\infty} e^{-a(x^2+y^2)} dx dy \]

Let’s continue in polar coordinates

\[
\begin{align*}
\rho &= \sqrt{x^2 + y^2} \\
\phi &= \tan^{-1} \left( \frac{y}{x} \right)
\end{align*}
\]

Jacobian:

\[
\begin{vmatrix}
\frac{\partial x}{\partial \rho} & \frac{\partial x}{\partial \phi} \\
\frac{\partial y}{\partial \rho} & \frac{\partial y}{\partial \phi}
\end{vmatrix} = \begin{vmatrix} \cos \phi & -\rho \sin \phi \\ \sin \phi & \rho \cos \phi \end{vmatrix} = \rho \cos^2 \phi + \rho \sin^2 \phi = \rho
\]

Therefore

\[
I^2 = \int_0^{2\pi} d\phi \int_0^{+\infty} r e^{-ar^2} dr = 2\pi \int_0^{+\infty} e^{-ar^2} dr = \left\{ \begin{array}{l}
t = e^{-ar^2}, \frac{dt}{dr} = e^{-ar^2}(-2ar) \Rightarrow dt = -2are^{-ar^2} dr \\
r = 0 \Rightarrow t = 1, r = +\infty \Rightarrow t = 0
\end{array} \right\}
\]

\[
= 2\pi \int_1^0 \frac{dt}{-2at e^{-at^2}} = \frac{\pi}{a} \int_0^1 dt = \frac{\pi}{a}
\]

And, because

\[ \forall x \in \mathbb{R} \quad e^{-ax^2} > 0 \]

\[ I = \int_{-\infty}^{+\infty} e^{-ax^2} dx = \sqrt{\frac{\pi}{a}} \]

Automatically, because the function under integral is even

\[ \int_0^{+\infty} e^{-ax^2} dx = \frac{1}{2} \sqrt{\frac{\pi}{a}} \]

Now, it’s easy to calculate similar integrals

\[
\int_0^{+\infty} xe^{-ax^2} dx = \left\{ \begin{array}{l}
t = e^{-ax^2}, \frac{dt}{dx} = e^{-ax^2}(-2ax) \Rightarrow dt = -2axe^{-ax^2} dx \\
x = 0 \Rightarrow t = 1, x = +\infty \Rightarrow t = 0
\end{array} \right\} = \frac{1}{2a} \int_0^1 dt = \frac{1}{2a}
\]

Let’s notice that

\[ \frac{d}{da} \int_0^{+\infty} e^{-ax^2} dx = -\int_0^{+\infty} x^2 e^{-ax^2} dx = -\frac{1}{4} \sqrt{\frac{\pi}{a^3}} \]
and
\[
\frac{d}{da} \int_0^{\infty} x e^{-ax^2} dx = -\int_0^{\infty} x^3 e^{-ax^2} dx = -\frac{1}{2a^2}
\]
In general, such integrals (with even and odd \(n\) in power of \(x\)) one can calculate accordingly to the formulas
\[
\int_0^{\infty} x^{2n} e^{-ax^2} dx = \frac{\sqrt{\pi}}{2} \left( -\frac{d}{da} \right)^n \frac{1}{\sqrt{a}} = \frac{(2n)!}{2^{n+1}n!a^{n+1/2}}
\]
\[
\int_0^{\infty} x^{2n+1} e^{-ax^2} dx = \frac{1}{2} \left( -\frac{d}{da} \right)^n \frac{1}{a} = \frac{n!}{2a^{n+1}}
\]
Going back to calculation of normalization constant
\[
N^{-2} = 4\pi \int_0^{\infty} r^2 e^{-ar^2} dr = -4\pi \frac{d}{da} \int_0^{\infty} e^{-ar^2} dr = -2\pi \frac{d}{da} \sqrt{\frac{\pi}{a}} = \left( \frac{\pi}{a} \right)^{3/2}
\]
\[
N = \left( \frac{2c}{\pi} \right)^{3/2}
\]
Now we must calculate the expectation value of the Hamiltonian with the normalized trial function
\[
\langle \phi | \hat{H} | \phi \rangle = -\frac{h^2}{2\mu} \langle \phi | \Delta | \phi \rangle - \frac{Ze^2}{4\pi\epsilon} \langle \phi | \frac{1}{r} | \phi \rangle
\]
\[
\langle \phi | \frac{1}{r} | \phi \rangle = \left( \frac{2c}{\pi} \right)^{3/2} \int_0^{2\pi} d\phi \int_0^{\pi} \sin \theta d\theta \int_0^{\infty} r^2 e^{-2cr^2} dr = \left( \frac{2c}{\pi} \right)^{3/2} \int_0^{\infty} r e^{-2cr^2} dr
\]
we substitute \(s = r^2\) and \(ds = 2rdr\):
\[
\langle \phi | \frac{1}{r} | \phi \rangle = \left( \frac{2c}{\pi} \right)^{3/2} \int_0^{\infty} e^{-2cs} ds = \left( \frac{2c}{\pi} \right)^{3/2} 2\pi \frac{1}{2c} = 2\sqrt{\frac{2c}{\pi}}
\]
\[
\langle \phi | \Delta | \phi \rangle = \left( \frac{2c}{\pi} \right)^{3/2} 4\pi \int_0^{\infty} r^2 e^{-cr^2} \frac{d}{dr} \frac{1}{r} \frac{d}{dr} e^{-cr^2} dr = \left( \frac{2c}{\pi} \right)^{3/2} 4\pi \int_0^{\infty} e^{-cr^2} 2c \left( 2c r^4 - 3r^2 \right) e^{-cr^2} dr =
\]
\[
= \left( \frac{2c}{\pi} \right)^{3/2} 4\pi 2c \left( \int_0^{\infty} 2c r^4 e^{-2cr^2} dr - \int_0^{\infty} 3r^2 e^{-2cr^2} dr \right) =
\]
\[
= \left( \frac{2c}{\pi} \right)^{3/2} 4\pi 2c \left( 2c \frac{3}{2} \sqrt{\frac{\pi}{(2c)^3}} - \frac{3}{2} \frac{1}{2} \sqrt{\frac{\pi}{(2c)^3}} \right) = - \left( \frac{2c}{\pi} \right)^{3/2} 4\pi 2c \frac{3}{8} \sqrt{\frac{\pi}{(2c)^3}} = -3c
\]
Energy functional
\[
\epsilon[\phi(c)] = \frac{3h^2}{2\mu} c - 2 \frac{Ze^2}{4\pi\epsilon} \sqrt{\frac{2c}{\pi}}
\]
\[
\frac{d}{dc} \epsilon[\phi(c)] = 0 = \frac{3h^2}{2\mu} - \frac{Ze^2 \sqrt{2}}{4\pi\epsilon \sqrt{\pi} c}
\]
\[
\sqrt{c} = \frac{2\sqrt{2} Z}{3\sqrt{\pi} \frac{e^2 \mu}{4\pi \epsilon h^2}} \Rightarrow c = \frac{8 Z^2}{9\pi a_0^1}
\]
In atomic units for \(Z = 1\) (hydrogen atom)
Example. By means of variational method find energy of the ground state of helium atom. As a trial function take

$$\Psi(r_1, r_2; c) = \frac{(cZ)^3}{\pi} e^{-Zcr_1} e^{-Zcr_2}$$

where \( Z \) stands for the nucleus charge (\( Z=2 \)) while the \( r_i \) stands for the distance of \( i \)-th electron from the origin, and \( c \) stands for variational parameter. Apply atomic units.

A hint

$$\int_{R_3} \int_{R_5} \frac{e^{-\rho r_1} e^{-\rho r_2}}{r_{12}} \, d^3r_1 \, d^3r_2 = \frac{20\pi^2}{\beta^5}$$

Solution

The Hamiltonian of helium atom

$$\hat{H} = \hat{T}_1 + \hat{T}_2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}$$

The wavefunction is normalized so we must look for the value of energy functional

$$\epsilon[\Psi] = \langle \Psi | \hat{H} | \Psi \rangle = \langle \Psi | \hat{T}_1 | \Psi \rangle + \langle \Psi | \hat{T}_2 | \Psi \rangle + \langle \Psi | - \frac{Z}{r_1} | \Psi \rangle + \langle \Psi | - \frac{Z}{r_2} | \Psi \rangle + \langle \Psi | \frac{1}{r_{12}} | \Psi \rangle$$

$$\langle \Psi | \hat{T}_1 | \Psi \rangle = -\frac{1}{2} \langle \Psi | \hat{\Delta} | \Psi \rangle = -\frac{1}{2} \frac{(cZ)^6}{\pi^2} \int_{R^3} e^{-2Zcr_2} d^3r_2 \int_{R^3} e^{-Zcr_1} \Delta e^{-Zcr_1} d^3r_1 =$$

$$= -\frac{1}{2} \frac{(cZ)^6}{\pi^2} \int_0^{2\pi} d\phi \int_0^\pi \sin \theta \, d\theta \int_0^\infty r_2^2 e^{-2Zcr_2} \, dr_2 \int_{R^3} e^{-Zcr_1} \Delta e^{-Zcr_1} d^3r_1 =$$

$$= -\frac{1}{2} \frac{(cZ)^6}{\pi^2} \frac{4\pi}{(2Zc)^3} \int_0^{2\pi} d\phi \int_0^\pi \sin \theta \, d\theta \int_0^\infty r_2^2 e^{-2Zcr_2} \, dr_2 \int_0^\infty \left( \frac{1}{r_1^2} \frac{d}{dr_1} \frac{1}{r_1} \right) e^{-Zcr_1} \, dr_1 =$$

$$= -\frac{1}{2} \frac{(cZ)^3}{\pi} 2 \left( \frac{cZ}{(2Zc)^3} - Z \frac{1}{(2Zc)^2} \right) = \frac{1}{2} (cZ)^2$$

$$\langle \Psi | \hat{T}_2 | \Psi \rangle = \frac{1}{2} (cZ)^2$$

$$\langle \Psi | - \frac{Z}{r_1} | \Psi \rangle = - \frac{(cZ)^6}{\pi^2} \int_{R^3} e^{-Zcr_1} e^{-Zcr_2} \frac{Z}{r_1} e^{-Zcr_1} e^{-Zcr_2} d^3r_1 d^3r_2 =$$

$$= - \frac{(cZ)^6}{\pi^2} \int_0^{2\pi} d\phi \int_0^\pi \sin \theta \, d\theta \int_0^\infty r_2^2 e^{-2Zcr_2} \, dr_2 \int_{R^3} e^{-Zcr_1} \frac{Z}{r_1} e^{-Zcr_1} d^3r_1 =$$

$$= - \frac{(cZ)^6}{\pi^2} \frac{4\pi}{(2Zc)^3} \int_0^{2\pi} d\phi \int_0^\pi \sin \theta \, d\theta \int_0^\infty r_2^2 e^{-Zcr_1} \frac{Z}{r_1} e^{-Zcr_1} d^3r_1 =$$

$$= - \frac{(cZ)^3}{\pi} 2 \int_0^\infty r_1 e^{-2Zcr_1} \, dr_1 = -4 (cZ)^3 Z \frac{1!}{(2Zc)^2} = -c Z^2$$

$$\langle \Psi | - \frac{Z}{r_2} | \Psi \rangle = -c Z^2$$
We still need to calculate the two-electron integral

\[
\langle \Psi | \frac{1}{r_{12}} | \Psi \rangle = \frac{(cZ)^6}{\pi^2} \int_{R_1} \int_{R_2} e^{-Zcr_1} e^{-Zcr_2} \frac{Z}{r_{12}} e^{-Zcr_1} e^{-Zcr_2} d^3r_1 d^3r_2 = \\
= \frac{(cZ)^6}{\pi^2} \int_{R_1} \int_{R_2} e^{-2Zcr_1} \frac{Z}{r_{12}} e^{-2Zcr_1} d^3r_1 d^3r_2 = \\
= \frac{(cZ)^6}{\pi^2} (2\pi^2)^2 = \frac{5}{8} cZ
\]

Finally

\[
\epsilon(c) = \frac{1}{2} (cZ)^2 + \frac{1}{2} (cZ)^2 - cZ^2 - cZ^2 + \frac{5}{8} cZ = Z^2 c^2 + \left( \frac{5}{8} - 2Z \right) Zc
\]

\[
\frac{d}{dc} \epsilon(c) = 0 = 2Z^2 c + \left( \frac{5}{8} - 2Z \right) Z
\]

\[
c_{opt} = 1 - \frac{5}{16Z}
\]

For helium atom $Z = 2$, $c_{opt} = 1 - \frac{5}{32} = \frac{27}{32} = \frac{3^3}{25}$. Inserting the $c_{opt}$ into the energy expression

\[
\epsilon(c_{opt}) = 2^2 \frac{3^6}{2^0} + \left( \frac{5}{8} - 2 \cdot 2 \right) \frac{21^3}{25} = \frac{3^6}{28} + (10 - 2^5) \frac{3^3}{28} = - \frac{3^6}{28} \cong -2.84766
\]

More accurate energy of helium atom equals $E_0 = -2.903724$. Thus our results is encumbered with \(-2.903724 \div (-2.84766)\). 100% \(\pm 2\%\) error.

Example. By means of variational method find energy of the ground state of helium atom. As a trial function take the following product of two gaussian functions

\[
\Psi(r_1, r_2; c) = e^{-Zcr_1^2} e^{-Zcr_2^2}
\]

This is a case where the two gaussian functions are all centered at the same origin, i.e. at nucleus of helium atom. And in such case the two-electron integrals can be called one-center. In case where two orbitals come from two atoms there are two origins and in this case the two-electron integrals are called two-center. Of course, despite the fact we have two electrons only the integrals can be three-center or four-center.

Let’s start from evaluation of necessary integrals. Below: $S$ stands for so called overlap integral, i.e. a dot product of two functions of only one electron, $T$ stands for the kinetic energy integral of one electron, $V$ stands for potential energy integral of interaction of electron with the nucleus (in case where there are more centers one should take into account a sum of such integrals), and $g$ stands for two-electron one-center integral, i.e. for the interaction of two electrons while the functions are the functions of the same helium atom.

\[
S(a) = \int e^{-ar^2} e^{-ar^2} d^3r = \int_{-\infty}^{+\infty} e^{-2ax^2} dx \int_{-\infty}^{+\infty} e^{-2ay^2} dy \int_{-\infty}^{+\infty} e^{-2az^2} dz = \left( \frac{\pi}{2a} \right)^{\frac{3}{2}}
\]

\[
T(a) = \int e^{-ar^2} \left( -\frac{1}{2} \Delta \right) e^{-ar^2} d^3r = \frac{1}{2} \int e^{-ar^2} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) e^{-ar^2} d^3r =
\]

\[
= -\frac{1}{2} \left( \int e^{-ax^2} e^{-ax^2} \frac{\partial^2}{\partial x^2} e^{-ax^2} d^3r + \int e^{-ay^2} \frac{\partial^2}{\partial y^2} e^{-ay^2} d^3r + \int e^{-az^2} \frac{\partial^2}{\partial z^2} e^{-az^2} d^3r \right) =
\]

\[
= -\frac{3}{2} \pi \frac{\pi}{2a} 2a \int_{-\infty}^{+\infty} (2ax^2 - 1)e^{-2ax^2} dx = -\frac{3}{2} \pi \left( 2a \int_{-\infty}^{+\infty} x^2 e^{-2ax^2} dx - \int_{-\infty}^{+\infty} e^{-2ax^2} dx \right) =
\]
Example. Apply Ritz method to following trial function

\[ \Phi = c_1 \varphi_1 + c_2 \varphi_2 + c_3 \varphi_3 \]

where the basis functions \{ \varphi_1, \varphi_2, \varphi_3 \} are normalized and are not orthogonal, while the \{c_1, c_2, c_3\} stand for variational coefficients.

Solution.

The energy functional

\[ e = \int \int \Phi^* \dot{\Phi} d\tau d\sigma = \frac{A}{B} \]

where the integration goes over the space (d\tau) and over the spin (d\sigma) coordinates.

\[ A = \int \int \Phi^* \dot{\Phi} d\tau d\sigma = \int \int (c_1 \varphi_1 + c_2 \varphi_2 + c_3 \varphi_3) \dot{\Phi} (c_1 \varphi_1 + c_2 \varphi_2 + c_3 \varphi_3) d\tau d\sigma = \]

\[ = c_1^2 \int \int \varphi_1^* \dot{\varphi}_1 d\tau d\sigma + c_2 c_1 \int \int \varphi_2^* \dot{\varphi}_2 d\tau d\sigma + c_3 c_1 \int \int \varphi_3^* \dot{\varphi}_3 d\tau d\sigma + \]

\[ + c_2 c_1 \int \int \varphi_2^* \dot{\varphi}_1 d\tau d\sigma + c_2^2 \int \int \varphi_2^* \dot{\varphi}_2 d\tau d\sigma + c_3 c_2 \int \int \varphi_3^* \dot{\varphi}_2 d\tau d\sigma + \]

\[ + c_3 c_1 \int \int \varphi_3^* \dot{\varphi}_1 d\tau d\sigma + c_3 c_2 \int \int \varphi_3^* \dot{\varphi}_2 d\tau d\sigma + c_3^2 \int \int \varphi_3^* \dot{\varphi}_3 d\tau d\sigma = \]

\[ = \sum_{i=1}^{3} \sum_{j=1}^{3} c_i c_j \int \varphi_i^* \dot{\varphi}_j d\tau d\sigma = \sum_{i=1}^{3} \sum_{j=1}^{3} c_i c_j H_{ij} = \sum_{i=1}^{3} c_i \left( \sum_{j=1}^{3} c_j H_{ij} \right) \]

\[ B = \int \int \Phi \dot{\Phi} d\tau d\sigma = \sum_{i=1}^{3} \sum_{j=1}^{3} c_i c_j \int \varphi_i^* \varphi_j d\tau d\sigma = \sum_{i=1}^{3} \sum_{j=1}^{3} c_i c_j S_{ij} \]

In the equations above \( H_{ij} = H_{ji} \) due to hermiticity of \( \dot{\Phi} \) operator.

Accordingly to the variational procedures

\[ \frac{de}{dc_i} = 0 \]
\[
d\frac{A}{dc_i} B = \frac{dA}{dc_i} (AB^{-1}) = \frac{dA}{dc_i} B^{-1} + A \left( -\frac{1}{B^2} \right) \frac{dB}{dc_i} = \frac{dA}{dc_i} \frac{1}{B} - \frac{A}{B^2} \frac{dB}{dc_i} = 0
\]

\[
d\frac{A}{dc_i} - e \frac{dB}{dc_i} = 0
\]

\[
d\frac{A}{dc_1} = 2c_1H_{11} + c_2H_{12} + c_3H_{13} + c_2H_{21} + c_3H_{31} = 2 \sum_{j=1}^{3} c_j H_{ij}
\]

\[
d\frac{B}{dc_1} = 2 \sum_{j=1}^{3} c_j S_{1j}
\]

And

\[
d\frac{A}{dc_1} - e \frac{dB}{dc_1} = 2 \sum_{j=1}^{3} c_j H_{1j} - e 2 \sum_{j=1}^{3} c_j S_{1j} = 0
\]

\[
\sum_{j=1}^{3} c_j (H_{1j} - e S_{1j}) = 0
\]

Thus, for \( \{c_1, c_2, c_3\} \) we get system of 3 secular equations

\[
\sum_{j=1}^{3} c_j (H_{ij} - e S_{ij}) = 0, \quad i = 1, 2, 3
\]

The system of equations has one trivial solution: \( c_j = 0, \quad j = 1, 2, 3 \), or nontrivial which can be written in matrix form

\[
det \left| H_{ij} - e S_{ij} \right| = 0, \quad i = 1, 2, 3
\]

i.e.

\[
det \begin{pmatrix} H_{11} - e S_{11} & H_{12} - e S_{12} & H_{13} - e S_{13} \\ H_{21} - e S_{21} & H_{22} - e S_{22} & H_{23} - e S_{23} \\ H_{31} - e S_{31} & H_{32} - e S_{32} & H_{33} - e S_{33} \end{pmatrix} = 0
\]

The solution of the equation above comprises 3 \( e \) while for each \( e \) one is getting one set of coefficients \( c_j, \quad j = 1, 2, 3 \). So the \( e \) they stand for the roots of system of secular equations. If the basis (i.e. the functions \( \{\varphi_1, \varphi_2, \varphi_3\} \)) are orthogonal then the problem comes down to a simpler one because the \( S \) matrix becomes identity and then

\[
det \left| H_{ij} - e I \right| = 0, \quad i = 1, 2, 3
\]

i.e. in the matrix form

\[
det \begin{pmatrix} H_{11} - e & H_{12} & H_{13} \\ H_{21} & H_{22} - e & H_{23} \\ H_{31} & H_{32} & H_{33} - e \end{pmatrix} = 0
\]

which can be solved also by means of numerical methods of diagonalization of matrix \( H \): Jacobi, Householder, LR, QR, Lanczos, Davidson and other. For larger systems this is practically the only way to find the roots of the system of equations. The matrix \( H \) is the energy matrix and the \( H_{ij} \) elements stand for the appropriate energy integrals. Thus the roots of the system of secular equations stand for the eigenvalues. The eigenvetors \( \{c_j\}, \quad j = 1, 2, ..., n \) (collected into the column vector \( e \)) can be found from the following equation
(\(H - \epsilon I\)) \(\epsilon = 0\).

If the numerical diagonalization process is utilized then the eigenvectors corresponding to eigenvalues found are automatically computed too, without any necessity of additional calculations. That is why the orthogonization process is practically done before the computation of matrix \(H\) and its further diagonalization.

10 Rayleigh-Schrödinger perturbation theory

We divide the Hamiltonian into two parts

\[ \hat{H} = \hat{H}_0 + \lambda \hat{V} \]  \hspace{1cm} (10.1)

where the eigenvectors of \(\hat{H}_0\) are known and here they’re denoted as \(\Psi_k^{(0)}\), while the \(\hat{V}\) is scaled by parameter \(\lambda\) so that the size of perturbation \(\hat{V}\) can be adjusted so that the \(E_k^{(0)}\) and \(\Psi_k^{(1)}\) can be only subtly changed. Practically one assumes that the \(\hat{V}\) is not large in comparison to \(\hat{H}_0\). We don’t know dependence of eigen functions and eigenvalues from the parameter \(\lambda\) but we can expand them as Taylor series of this parameter

\[ \Psi_k = \Psi_k^{(0)} + \lambda \Psi_k^{(1)} + \lambda^2 \Psi_k^{(2)} + \cdots = \sum_{i=0}^{\infty} \lambda^i \Psi_k^{(i)} \]  \hspace{1cm} (10.2)

\[ E_k = E_k^{(0)} + \lambda E_k^{(1)} + \lambda^2 E_k^{(2)} + \cdots = \sum_{i=0}^{\infty} \lambda^i E_k^{(i)} \]  \hspace{1cm} (10.3)

where

\[
\begin{cases}
\Psi_k^{(i)} = \frac{1}{i!} \frac{\partial^i \Psi_k}{\partial \lambda^i} \\
E_k^{(i)} = \frac{1}{i!} \frac{\partial^i E_k}{\partial \lambda^i}
\end{cases}
\]  \hspace{1cm} (10.4)

We expect to solve the following equation (the eigen problem)

\[ \hat{H} \Psi_k = E_k \Psi_k \]  \hspace{1cm} (10.5)

Substituting the series into the Schrödinger eqn.

\[ (\hat{H}_0 + \lambda \hat{V}) \left( \sum_{0}^{\infty} \lambda^i \Psi_k^{(i)} \right) = \left( \sum_{0}^{\infty} \lambda^i E_k^{(i)} \right) \left( \sum_{0}^{\infty} \lambda^i \Psi_k^{(i)} \right) \]  \hspace{1cm} (10.6)

The \(\lambda\) parameter can assume any value which means that the eqn. above is satisfied if only the expressions standing by same powers of \(\lambda\) are equal

\[
\begin{align*}
\hat{H}_0 \Psi_k^{(0)} &= E_k^{(0)} \Psi_k^{(0)} \\
\hat{H}_0 \Psi_k^{(1)} + \hat{V} \Psi_k^{(0)} &= E_k^{(0)} \Psi_k^{(1)} + E_k^{(1)} \Psi_k^{(0)} \\
\hat{H}_0 \Psi_k^{(2)} + \hat{V} \Psi_k^{(1)} &= E_k^{(0)} \Psi_k^{(2)} + E_k^{(1)} \Psi_k^{(1)} + E_k^{(2)} \Psi_k^{(0)} \\
&= \cdots
\end{align*}
\]  \hspace{1cm} (10.7)

In general formula for \(n\)-th order equation is following
Multiplying from the left by $\Psi^{(0)}_k$ and integrating one is getting (due to the fact that the $\hat{H}_0$ is hermitian and due to the orthonormality of states, i.e. $(\langle \Psi^{(0)}_k | \Psi^{(n)}_k \rangle) = \delta_{0,n}$)

the first term:

$$\langle \Psi^{(0)}_k | \hat{H}_0 | \Psi^{(n)}_k \rangle = \langle \hat{H}_0 \Psi^{(0)}_k | \Psi^{(n)}_k \rangle = E^{(0)}_k \langle \Psi^{(0)}_k | \Psi^{(n)}_k \rangle = 0$$

the right side:

$$\langle \Psi^{(0)}_k | \sum_0^n E^{(i)}_k \Psi^{(n-i)}_k \rangle = \sum_0^{n-1} E^{(i)}_k \langle \Psi^{(0)}_k | \Psi^{(n-i)}_k \rangle + E^{(n)}_k \langle \Psi^{(0)}_k | \Psi^{(0)}_k \rangle = E^{(n)}_k$$

End thus the $n$-th improvement to the energy equals

$$E^{(n)}_k = \langle \Psi^{(0)}_k | \hat{V} | \Psi^{(n-1)}_k \rangle$$

In particular the 1-st improvement to the energy equals ($n = 1$)

$$E^{(1)}_k = \langle \Psi^{(0)}_k | \hat{V} | \Psi^{(0)}_k \rangle$$

10.1 Second improvement to the energy

The 2-nd improvement to the energy equals

$$E^{(2)}_k = \langle \Psi^{(0)}_k | \hat{V} | \Psi^{(1)}_k \rangle$$

which means we need the 1-st improvement to the function, i.e. $\Psi^{(1)}_k$

We proceed in the following manner. The first-order improvement to $\Psi_k$ which is the eigenfunction of $\hat{H}$ we define as a linear combination of complete set of eigenfunctions of unperturbed state

$$\Psi^{(0)}_k(\lambda) = \sum_{i=0; \neq k} c_k^{(0)}(\lambda) \Psi^{(0)}_i$$

The problem comes down to derivation of $c_{ik}$ and then the improvements to energies of $(n+1)$-order.

We submit the $\Psi^{(n)}_k$ into the 1-st order perturbation equation i.e. into the

$$(\hat{H}_0 - E^{(0)}_k) \Psi^{(1)}_k = (E^{(1)}_k - \hat{V}) \Psi^{(0)}_k$$

getting

$$\sum_{i=0; \neq k} c^{(1)}_k (\hat{H}_0 - E^{(0)}_k) \Psi^{(0)}_i = \sum_{i=0; \neq k} c^{(1)}_k (E^{(0)}_i - E^{(0)}_k) \Psi^{(0)}_i = (E^{(1)}_k - \hat{V}) \Psi^{(0)}_k$$

Then multiplying from left by $\Psi^{(0)}_m, m \neq k$ and integrating one is achieving (on the left side)

$$\sum_{i=0; \neq k} c^{(1)}_k (\Psi^{(0)}_i | (E^{(0)}_i - E^{(0)}_k) | \Psi^{(0)}_i) = \sum_{i=0; \neq k} c^{(1)}_k (E^{(0)}_i - E^{(0)}_k) \Psi^{(0)}_i | \Psi^{(0)}_i) = c^{(1)}_m (E^{(0)}_m - E^{(0)}_k)$$
Improvement to the function, we propose that

\[ \langle \Psi_m^{(0)} | (E_k^{(1)} - \hat{V}) | \Psi_k^{(0)} \rangle = E_k^{(1)} \langle \Psi_m^{(0)} | \Psi_k^{(0)} \rangle - \langle \Psi_m^{(0)} | \hat{V} | \Psi_k^{(0)} \rangle = 0 - \langle \Psi_m^{(0)} | \hat{V} | \Psi_k^{(0)} \rangle \]  

(10.18)

due to the fact that \( \langle \Psi_m^{(0)} | \Psi_k^{(0)} \rangle = \delta_{mk} \).

Therefore, the coefficients

\[ c_m^{(1)} = \frac{\langle \Psi_m^{(0)} | \hat{V} | \Psi_k^{(0)} \rangle}{E_k^{(0)} - E_m^{(0)}} \]  

(10.19)

and the first improvement to the wavefunction

\[ \Psi_k^{(1)} = \sum_{n \neq k} \frac{\langle \Psi_n^{(0)} | \hat{V} | \Psi_k^{(0)} \rangle}{E_k^{(0)} - E_n^{(0)}} \Psi_n^{(0)} \]  

(10.20)

Thus one can one derive the 2-nd improvement to the energy

\[ E_k^{(2)} = \sum_{n \neq k} \frac{\langle \Psi_n^{(0)} | \hat{V} | \Psi_k^{(0)} \rangle \langle \Psi_k^{(0)} | \hat{V} | \Psi_n^{(0)} \rangle}{E_k^{(0)} - E_n^{(0)}} = \frac{\langle \Psi_n^{(0)} | \hat{V} | \Psi_k^{(0)} \rangle^2}{E_k^{(0)} - E_n^{(0)}} \]  

(10.21)

### 10.2 Third improvement to the energy/Second improvement to the function

Accordingly to previously derived equation, the 3-rd improvement to the energy equals

\[ E_k^{(3)} = \langle \Psi_k^{(2)} | \hat{V} | \Psi_k^{(2)} \rangle \]  

(10.22)

Which means we need first the \( \Psi_k^{(2)} \), i.e. the second improvement to the function. Analogously to the 1-st order improvement to the function, we propose that

\[ \Psi_k^{(2)} = \sum_{n \neq k} d_{nk} \Psi_n^{(0)} \]  

(10.23)

Submitting this function into the following equation

\[ (\hat{H}_0 - E_k^{(0)})\Psi_k^{(2)} + \hat{V}\Psi_k^{(1)} = E_k^{(1)}\Psi_k^{(1)} + E_k^{(2)}\Psi_k^{(0)} \]  

(10.24)

and recollecting that \( \hat{H}_0 \Psi_n^{(0)} = E_n^{(0)} \Psi_n^{(0)} \), one is getting

\[ (\hat{H}_0 - E_k^{(0)})\Psi_k^{(2)} + \hat{V}\Psi_k^{(1)} = \sum_{n \neq k} d_{nk}(\hat{H}_0 - E_k^{(0)})\Psi_n^{(0)} + \hat{V}\Psi_k^{(1)} = \sum_{n \neq k} d_{nk}(E_n^{(0)} - E_k^{(0)})\Psi_n^{(0)} \]  

= \( E_k^{(1)} - \hat{V} \)\Psi_k^{(1)} + E_k^{(2)}\Psi_k^{(0)} \]  

(10.25)

Left and right sides of the equation above we will multiply by \( \Psi_m^{(0)} \) and will integrate

1. Left side (first term). For \( m \neq k \)

\[ \sum_{n \neq k} d_{nk} \langle \Psi_m^{(0)} | (E_n^{(0)} - E_k^{(0)}) | \Psi_n^{(0)} \rangle = \sum_{n \neq k} d_{nk} (E_n^{(0)} - E_k^{(0)}) \langle \Psi_m^{(0)} | \Psi_n^{(0)} \rangle = d_{mk} (E_m^{(0)} - E_k^{(0)}) \]  

(10.26)
2. Right side (second term). For \( m \neq k \)

\[
\langle \Psi_m^{(0)} | (E_k^{(1)} - \hat{V}) | \Psi_k^{(1)} \rangle = \langle \Psi_m^{(0)} | E_k^{(1)} - \hat{V} \rangle \sum_{n \neq k} \frac{\langle \Psi_k^{(0)} | \hat{V} | \Psi_n^{(0)} \rangle}{E_k^{(0)} - E_n^{(0)}} = 
\]

\[
= \sum_{n \neq k} \frac{\langle \Psi_m^{(0)} | (E_k^{(1)} - \hat{V}) V_{kn} | \Psi_n^{(0)} \rangle}{E_k^{(0)} - E_n^{(0)}} = 
\]

\[
= \sum_{n \neq k} \frac{\langle \Psi_m^{(0)} | E_k^{(1)} V_{kn} | \Psi_n^{(0)} \rangle}{E_k^{(0)} - E_n^{(0)}} - \sum_{n \neq k} \frac{\langle \Psi_m^{(0)} | \hat{V} V_{kn} | \Psi_n^{(0)} \rangle}{E_k^{(0)} - E_n^{(0)}} = 
\]

\[
= \sum_{n \neq k} \frac{E_k^{(1)} V_{kn}}{E_k^{(0)} - E_m^{(0)}} - \sum_{n \neq k} \frac{V_{kn}}{E_k^{(0)} - E_n^{(0)}} \langle \Psi_m^{(0)} | \hat{V} | \Psi_n^{(0)} \rangle = 
\]

\[
= \frac{E_k^{(1)} V_{km}}{E_k^{(0)} - E_m^{(0)}} \cdot 1 - \sum_{n \neq k} \frac{V_{km} V_{mn}}{E_k^{(0)} - E_n^{(0)}} 
\]

(10.27)

3. Right side (third term). For \( m \neq k \)

\[
\langle \Psi_m^{(0)} | E_k^{(2)} | \Psi_k^{(0)} \rangle = E_k^{(2)} \langle \Psi_m^{(0)} | \Psi_k^{(0)} \rangle = E_k^{(2)} \cdot 0 = 0 
\]

(10.28)

Thus, one can define the coefficients \( d_{nk} \) standing in the definition of \( \Psi_k^{(2)} \), eqn. no 10.23

\[
d_{mk}(E_m^{(0)} - E_k^{(0)}) = \frac{E_k^{(1)} V_{km}}{E_k^{(0)} - E_m^{(0)}} - \sum_{n \neq k} \frac{V_{kn} V_{mn}}{E_k^{(0)} - E_n^{(0)}}
\]

\[
d_{mk} = \frac{1}{E_k^{(0)} - E_m^{(0)}} \left[ \sum_{n \neq k} \frac{V_{kn} V_{mn}}{E_k^{(0)} - E_n^{(0)}} - \frac{V_{kk}}{E_k^{(0)} - E_m^{(0)}} \right]^2 = 
\]

(10.29)

Definitions of \( \Psi_k^{(2)} \) and \( E_k^{(3)} \) become now the following

\[
\Psi_k^{(2)} = \sum_{n \neq k} \sum_{l \neq k} \frac{V_{lk} V_{nl}}{(E_k^{(0)} - E_m^{(0)})(E_k^{(0)} - E_l^{(0)})} - V_{kk} \sum_{n \neq k} \frac{V_{nk}}{(E_k^{(0)} - E_n^{(0)})^2} \Psi_n^{(0)} 
\]

(10.30)

\[
E_k^{(3)} = \sum_{n \neq k} \sum_{l \neq k} \frac{V_{kn} V_{lk} V_{nl}}{(E_k^{(0)} - E_n^{(0)})(E_k^{(0)} - E_l^{(0)})} - V_{kk} \sum_{n \neq k} \frac{V_{nk}^2}{(E_k^{(0)} - E_n^{(0)})^2} 
\]

(10.31)

10.2.0.1 Example 1. No-dimensionless nucleus. Find the first-order improvement to the energy of ground state hydrogen atom related to the fact that the nucleus has dimension (is not dimensionless, as we have assumed all the time). We assume the proton can be represented by an oval with radius \( R \ll a_0 \).

Solvation

From electrostatics (… look into your lecture notes)
of interaction of an electron with a point nucleus.

Rayleigh-Schrödinger perturbation theory

ions (mion is a particle which has same charge and spin as electron, but its mass is 200 times larger) the improvement from unperturbed energy (energy for unperturbed state). However, this improvement becomes important for cases of high levels (2s and 2p) in hydrogen atom where we see that for the ground state the first improvement to the energy is only 9 orders of magnitude lower than the unperturbed energy.

Finite radius of nucleus is one of the factors causing splitting of energy levels (2s and 2p) from hydrogen atom which is called the Lamba splitting. Function 2p vanishes at the nucleus and its finite radius doesn’t influence so much the energy change as in the case of function 2s. The main factor influencing the Lamba splitting are the radiation effects which can be estimated on the basis of quantum electrodynamics.

\[
\Psi_{100} = \frac{1}{\sqrt{\pi}} \frac{1}{a_0^{1/2}} e^{-r/a_0}
\]

Thus

\[
E_0^{(1)} = \int \Psi_{100} \hat{V} \Psi_{100} d\tau = \frac{1}{\pi a_0^2} \int_0^{2\pi} d\phi \int_0^\pi \sin \theta d\theta \int_0^\infty r^2 \hat{V} e^{-2r/a_0} dr = \frac{4}{a_0^2} \frac{e^2}{2R^2} \int_0^R r^4 e^{-2r/a_0} dr - \frac{3e^2}{2R} \int_0^R r^2 e^{-2r/a_0} dr + e^2 \int_0^R r e^{-2r/a_0} dr = \frac{4e^2}{a_0^2} \left[ \frac{R^2}{10} - \frac{R^2}{2} + \frac{R^2}{2} \right] = \frac{2R^2e^2}{5a_0^3}
\]

Proton’s radius equals (in the ball park) \( R = 1.64 \cdot 10^{-10} a_0 \), which means that in atomic units

\[
E_0^{(1)} = 1.08 \cdot 10^{-10} = 2.16 \cdot 10^{-10} E_0
\]
10.2.0.2 Example 2. Relativistic effect  

Non-relativistic kinetic energy operator has the following form: 
\[ \hat{T} = \frac{\mathbf{p}^2}{2\mu} \]

It can be assumed the relativistic first improvement to this operator is the following: 
\[ \hat{H}_r = -\frac{1}{2\mu c^2} \frac{\mathbf{p}^2}{c^2} \]  

where \( c \) is the speed of light. Find improvement to the kinetic energy of electron of hydrogen atom using the first-order perturbation theory.

Kinetic energy operator is hermitian, thus

\[
\langle \Psi_{100} | \hat{H}_r | \Psi_{100} \rangle = \langle 100 | \hat{H}_r | 100 \rangle = -\frac{1}{2\mu c^2} \langle 100 | \hat{T}^2 | 100 \rangle = -\frac{1}{2\mu c^2} \langle \hat{T} \Psi_{100} | \hat{T} \Psi_{100} \rangle
\]  

(10.40)

Remembering the definition of the unperturbed Hamiltonian:

\[ \hat{T} = \hat{H} - \hat{\mathcal{V}} \]

(10.41)

one is getting

\[
\langle \hat{T} \Psi_{100} | \hat{T} \Psi_{100} \rangle = \langle (\hat{H} - \hat{\mathcal{V}}) \Psi_{100} | (\hat{H} - \hat{\mathcal{V}}) \Psi_{100} \rangle = \langle \hat{H} \Psi_{100} | \hat{H} \Psi_{100} \rangle + \langle \hat{\mathcal{V}} \Psi_{100} | \hat{\mathcal{V}} \Psi_{100} \rangle - \langle \hat{\mathcal{V}} \Psi_{100} | \hat{H} \Psi_{100} \rangle - \langle \hat{H} \Psi_{100} | \hat{\mathcal{V}} \Psi_{100} \rangle
\]

(10.42)

Recollecting that \( \hat{H} \Psi = E \Psi \) and that from the virial theorem \( E = -\langle \hat{T} \rangle = \frac{1}{2} \langle \hat{\mathcal{V}} \rangle \) as well as utilizing the hermiticity of the \( \hat{H} \) operator we are getting

\[
\langle \hat{H}_r \rangle = \frac{1}{2\mu c^2} (3E^2 - \langle \hat{\mathcal{V}}^2 \rangle) \]

(10.43)

Yet one must find the \( \langle \hat{\mathcal{V}}^2 \rangle \)

\[
\langle \hat{\mathcal{V}}^2 \rangle = \frac{1}{\pi} \left( \frac{Z}{a_0} \right)^3 \int_0^{2\pi} d\varphi \int_0^\pi \sin \theta d\theta \int_0^\infty \Psi_{100}^* \left( \frac{Ze^2}{4\pi \epsilon_0 r} \right)^2 \Psi_{100} r^2 dr = 4 \left( \frac{Z}{a_0} \right)^3 \frac{Z^2 e^4}{(4\pi \epsilon_0)^2} \int_0^\infty e^{-2Zr/a_0} dr = 4Z^5 e^4 \frac{h^4}{a_0^4 \mu^2 e^4} \frac{e_0^2}{2Z} = \frac{2Z^4 h^4}{\mu^2 a_0^4}
\]

(10.44)

And substituting this result as well as the expression for energy of \( \Psi_{nlm} \) state \( i \) \( E = -\frac{Z^2 e^2}{2\mu a_0^2 n^2} \) (where here \( n = 1 \)) into the equation for average value \( \langle \hat{H}_r \rangle \) one is finally getting

\[
\langle \hat{H}_r \rangle = \frac{1}{2\mu c^2} \left( \frac{3Z^4 h^4}{4\mu^2 a_0^3} - 2 \frac{Z^4 h^4}{\mu^2 a_0^3} \right) = -\frac{Z^4 h^4}{8\epsilon_0^2 \mu^2 e^4 a_0^6} = -\frac{5}{2\mu c^2} E^2
\]

(10.46)

10.3 Möller-Plesset’s (MP’s) perturbation method

In this method the \( \hat{H}_0 \) was represented as a sum of Fock operators, while the perturbation \( \hat{\mathcal{V}} \) was defined as a difference between the whole Hamiltonian and the \( \hat{H}_0 \). 

The Fock operator \( \hat{h}(i) \) is a one-electron operator and for \( i \) – th electron

\[
\hat{h}(i) = \hat{h}_0(i) + \hat{f}(i)
\]

(10.47)

where the \( \hat{h}_0(i) \) represents the kinetic energy of \( i \) – th electron and its interaction with all nuclei

\[
\hat{h}_0(i) = -\frac{1}{2} \nabla_i^2 + \sum_a \frac{Z_a}{r_{ia}}
\]

(10.48)
while

$$f(i) = \sum_q \left( J_q(i) - K_q(i) \right)$$

(10.49)

where the operators $\hat{J}$ and $\hat{K}$ correspond to coulombic and exchange operators, respectively. Hartree-Fock equation can be written as

$$\hat{h}(i)\psi_k(i) = \epsilon_k \psi_k(i)$$

(10.50)

Thus the $\hat{H}_0$ takes the form

$$\hat{H}_0 = \sum_i \hat{h}(i)$$

(10.51)

and the perturbation $\hat{V} = \hat{H} - \hat{H}_0$. The whole Hamiltonian

$$\hat{H} = \sum_i \hat{h}_0(i) + \sum_{i>j} \frac{1}{r_{ij}}$$

(10.52)

Thus

$$\hat{V} = \hat{H} - \hat{H}_0 = \sum_i \hat{h}_0(i) + \sum_{i>j} \frac{1}{r_{ij}} - \sum_i \hat{h}_0(i) + \sum_i f(i) = \sum_{i>j} \frac{1}{r_{ij}} - \sum_i f(i) = \hat{V}_1 + \hat{V}_2$$

(10.53)

The zeroth-order wave function is the HF determinant, and the zeroth-order energy is just a sum of MO energies.

$$E^{(0)} = \langle \psi_0 | \hat{H}_0 | \psi_0 \rangle = \langle \psi_0 | \sum_i \hat{h}(i) | \psi_0 \rangle = \sum_i \epsilon_i$$

(10.54)

Orbital energy is the energy of an electron in the field of all the nuclei and includes the repulsion to all other electrons, and therefore counts the electron-electron repulsion twice. The first-order energy correction is the average of the perturbation operator over the zeroth-order wave function and it equals the energy of the Hartree-Fock operator.

$$E^{(1)} = \langle \psi_0 | \hat{V} | \psi_0 \rangle = E_{HF}$$

(10.55)

Thus the first-order energy correction doesn’t correct anything yet.

The second-order energy correction involves matrix elements of the perturbation operator $\hat{V}$ between the HF reference and all possible excited states. Since the perturbation is a two-electron operator, all matrix elements involving triple, quadruple, etc., excitations are zero. When canonical HF orbitals are used, matrix elements with singly excited states are also zero

$$\langle \psi_0 | \hat{V} | \psi_i^a \rangle = \langle \psi_0 | \hat{H} - \sum_j \hat{h}(j) | \psi_i^a \rangle$$

(10.56)

$$= \langle \psi_0 | \hat{H} | \psi_i^a \rangle - \langle \psi_0 | \sum_j \hat{h}(j) | \psi_i^a \rangle$$

(10.57)

$$= \langle \psi_0 | \hat{H} | \psi_i^a \rangle - \sum_j e_j \langle \psi_0 | \psi_i^a \rangle = 0$$

(10.58)

The first bracket is zero owing to Brillouin’s theorem and the second set of brackets is zero owing to the orbitals being eigenfunctions of the Fock operators and orthogonal to each other. The second-order correction to the energy, which is the first contribution to the correlation energy, thus only involves a sum over doubly excited determinants. These can be generated by promoting two electrons from occupied orbitals $i$ and $j$ to virtual orbitals $a$ and $b$. The summation must be restricted such that each excited state is only counted once
10. Rayleigh-Schrödinger perturbation theory

\[ E^{(2)} = \sum_{i<j}^{\text{occ.}} \sum_{a<b}^{\text{virt.}} \left( \phi_i | \hat{V} | \phi_a \right) \left( \phi_j | \hat{V} | \phi_b \right) \frac{E_0 - E_{ab}}{e_i + e_j - e_a - e_b} \]  

(10.59)

The matrix elements between the HF and a doubly excited state are given by two-electron integrals over MOs. The difference in total energy between two Slater determinants becomes a difference in MO energies (essentially Koopmans’ theorem), and the explicit formula for the second-order Møl ler-Plesset correction is given by

\[ E^{(2)} = \sum_{i<j}^{\text{occ.}} \sum_{a<b}^{\text{virt.}} \left( \phi_i | \phi_j | \phi_a | \phi_b \right) - \left( \phi_i | \phi_j | \phi_b | \phi_a \right) \frac{e_i + e_j - e_a - e_b}{e_i + e_j - e_a - e_b} \]  

(10.60)

Once the two-electron integrals over MOs are available, the second-order energy correction can be calculated as a sum over such integrals. There are of the order of \( M^4 \) basis integrals, thus the calculation of the energy (only) increases as \( M^4 \) with the system basis size. However, the transformation of the integrals from the AO to the MO basis grows as \( M^5 \). MP2 is an \( M^5 \) method, but fairly inexpensive as not all two-electron integrals over MOs are required. Only those corresponding to the combination of two occupied and two virtual MOs are needed. In practical calculations, this means that the MP2 energy for systems with a few hundred basis functions can be calculated at a cost similar to or less than what is required for calculating the HF energy. MP2 typically accounts for 80-90% of the correlation energy, and it is the most economical method for including electron correlation.

10.4 Case of degenerate levels

\[ \ldots \]

10.5 Slater determinants

Exercise ??

Solution

Find Slater determinants for electronic configurations of hydrogen molecule assuming the molecular orbitals are denoted as \( \phi \). If it is possible, represent the determinant as a product of only spin and only spatial functions.

\[ \chi_1 = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_1(1)\alpha(1) & \phi_1(2)\alpha(2) \\ \phi_1(1)\beta(1) & \phi_1(2)\beta(2) \end{vmatrix} \]

Figure 36. \( H_2 \) molecular orbitals’ occupations of each of the electronic configurations. The names of the configurations are denoted by \( \chi \). The lower row correspond to molecular orbital \( \phi_1 \), while the upper row correspond to the \( \phi_2 \) molecular orbital.
\[ \chi_2 = \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_1(1)\alpha(1) & \varphi_1(2)\alpha(2) \\ \varphi_2(1)\alpha(1) & \varphi_2(2)\alpha(2) \end{vmatrix} = \frac{1}{\sqrt{2}} \varphi_1(1)\varphi_1(2)[\alpha(1)\beta(2) - \alpha(2)\beta(1)] \] (10.61)

\[ \chi_3 = \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_1(1)\beta(1) & \varphi_1(2)\beta(2) \\ \varphi_2(1)\beta(1) & \varphi_2(2)\beta(2) \end{vmatrix} = \frac{1}{\sqrt{2}} \varphi_1(1)\varphi_2(2)\beta(2) \] (10.62)

\[ \chi_4 = \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_1(1)\alpha(1) & \varphi_1(2)\alpha(2) \\ \varphi_2(1)\beta(1) & \varphi_2(2)\beta(2) \end{vmatrix} = \frac{1}{\sqrt{2}} [\varphi_1(1)\alpha(1)\varphi_2(2)\beta(2) - \varphi_1(2)\alpha(2)\varphi_2(1)\beta(1)] \] (10.63)

\[ \chi_5 = \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_1(1)\beta(1) & \varphi_1(2)\beta(2) \\ \varphi_2(1)\alpha(1) & \varphi_2(2)\alpha(2) \end{vmatrix} = \frac{1}{\sqrt{2}} [\varphi_1(1)\beta(1)\varphi_2(2)\alpha(2) - \varphi_1(2)\beta(2)\varphi_2(1)\alpha(1)] \] (10.64)

\[ \chi_6 = \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_2(1)\alpha(1) & \varphi_2(2)\alpha(2) \\ \varphi_2(1)\beta(1) & \varphi_2(2)\beta(2) \end{vmatrix} = \frac{1}{\sqrt{2}} [\varphi_2(1)\alpha(1)\varphi_2(2)\beta(2) - \varphi_2(2)\alpha(2)\varphi_2(1)\beta(1)] \] (10.65)

As one can see, the Slater determinants \( \chi_4 \) and \( \chi_5 \) cannot be represented as products of only spin and only spatial functions. They’re singlet open-shell states. However, one can construct linear combinations of those functions.

**Exercise ??**

Use the determinant functions \( \chi_4 \) and \( \chi_5 \) and create functions which can be represented as products of only spin and only spatial functions.

**Solution**

The functions \( \chi_4 \) and \( \chi_5 \) are orthogonal and are normalized to unity. Thus, one may propose the new functions for instance as

\[ 3\chi_7 = \frac{1}{\sqrt{2}} (\chi_4 + \chi_5) \] (10.67)

\[ 1\chi_8 = \frac{1}{\sqrt{2}} (\chi_4 - \chi_5) \] (10.68)

\[ 3\chi_7 = \frac{1}{\sqrt{2}} \frac{1}{\sqrt{2}} \left( \varphi_1(1)\alpha(1)\varphi_2(2)\beta(2) - \varphi_1(2)\alpha(2)\varphi_2(1)\beta(1) + \varphi_1(1)\beta(1)\varphi_2(2)\alpha(2) - \varphi_1(2)\beta(2)\varphi_2(1)\alpha(1) \right) \]
The new \( \chi_7 \) and \( \chi_8 \) are since now the eigenfunctions of \( \hat{S}_z \) and \( \hat{S}_z \) operators and correspond to triplet and singlet states, respectively (the upper index standing on the left side of the name of the state).

**Exercise 10.71**

Find the electronic energy of a system consisting of 3 electrons.

**Solution**

We assume the electrons occupy spatial functions \( \varphi_1, \varphi_2, \varphi_3 \), while to each of them \( \sigma_1, \sigma_2, \sigma_3 \) spin functions have been assigned. Functions \( \sigma \) can be \( \alpha \) or \( \beta \).

Electronic energy has the following formula

\[
E^{\text{el}} = \frac{\iint \Psi^* \hat{H}^{\text{el}} \Psi \ dx \ dy \ dz}{\iint \Psi^* \Psi \ dx \ dy \ dz} \tag{10.71}
\]

Further, for simplicity, we assume the functions \( \Psi \) are real, so that \( \Psi^* = \Psi \). The integration formally goes over all spatial and all spin coordinates. In the case of normalized wavefunction the denominator equals 1.

For a system of 3 electrons the Hamiltonian can be expressed as

\[
\hat{H}^{\text{el}} = \hat{H}_i^c + \hat{H}_j^c + \hat{H}_k^c + \frac{e^2}{r_{12}} + \frac{e^2}{r_{13}} + \frac{e^2}{r_{23}} \tag{10.72}
\]

where the \( \hat{H}_i^c \) is the so-called core hamiltonian of \( i \)-th electron

\[
\hat{H}_i^c = -\frac{\hbar^2}{2m} \nabla_i^2 - \sum_k Z_k e^2 \frac{r_{ik}}{r_{ik}} \tag{10.73}
\]

Thus, it is a kinetic energy operator of \( i \)-th electron as well as additionaly involves the potential energy of attraction of \( i \)-th electron to all nucleus. If we will further assume the nucleus are immovable the core hamiltonian depends on only \( i \)-th electron positions.

Slater determinant for the system of electrons

\[
\Psi = \frac{1}{\sqrt{3!}} \begin{vmatrix}
\varphi_1(1)\sigma_1(1) & \varphi_1(2)\sigma_1(2) & \varphi_1(3)\sigma_1(3) \\
\varphi_2(1)\sigma_2(1) & \varphi_2(2)\sigma_2(2) & \varphi_2(3)\sigma_2(3) \\
\varphi_3(1)\sigma_3(1) & \varphi_3(2)\sigma_3(2) & \varphi_3(3)\sigma_3(3)
\end{vmatrix} \tag{10.74}
\]

where in the parenthesis the numbers indicate the number of electron, while the indices number the functions.

\[
\Psi = \frac{1}{\sqrt{6}} \left[ \varphi_1(1)\sigma_1(1)\varphi_2(2)\sigma_2(2)\varphi_3(3)\sigma_3(3) + \varphi_1(2)\sigma_1(2)\varphi_2(3)\sigma_2(3)\varphi_3(1)\sigma_3(1) \\
+ \varphi_1(3)\sigma_1(3)\varphi_2(1)\sigma_2(1)\varphi_3(2)\sigma_3(2) - \varphi_1(3)\sigma_1(3)\varphi_2(1)\sigma_2(1)\varphi_3(2)\sigma_3(2) \\
- \varphi_1(2)\sigma_1(2)\varphi_2(1)\sigma_2(1)\varphi_3(3)\sigma_3(3) - \varphi_1(1)\sigma_1(1)\varphi_2(3)\sigma_2(3)\varphi_3(2)\sigma_3(2) \right] \tag{10.75}
\]
We can denote each term of the sum by $W_1$ to $W_6$ and the electronic energy will be thus equal

$$E^{el} = \int \int \frac{1}{\sqrt{6}} \left( \sum_{i=1}^{6} W_i \right) \left( \hat{H}_1^c + \hat{H}_2^c + \hat{H}_3^c + \frac{e^2}{r_{12}} + \frac{e^2}{r_{13}} + \frac{e^2}{r_{23}} \right) \frac{1}{\sqrt{6}} \left( \sum_{i=1}^{6} W_i \right) d\tau d\sigma$$  \hspace{1cm} (10.76)

We must find all necessary terms. At the beginning we will utilize operator $\hat{H}_1^c$.

$$R_{1,1} = \int \int W_1 \hat{H}_1^c W_1 d\tau d\sigma =$$

$$= \int \int \varphi_1(1)\sigma_1(1)\varphi_2(2)\sigma_2(2)\varphi_3(3)\sigma_3(3)\hat{H}_1^c\varphi_1(1)\sigma_1(1)\varphi_2(2)\sigma_2(2)\varphi_3(3)\sigma_3(3) d\tau d\sigma$$ \hspace{1cm} (10.77)

Because the operator $\hat{H}_1^c$ doesn’t act on spin functions and regarding the spatial functions it acts on only the functions of electron number 1, we may rewrite

$$R_{1,1} = \int \int \sigma_1^2(1)d\sigma_1 \int \sigma_2^2(2)d\sigma_2 \int \sigma_3^2(3)d\sigma_3 \int \varphi_2^2(2)d\tau_2 \int \varphi_3^2(3)d\tau_3 \cdot \int \varphi_1(1)\hat{H}_1^c\varphi_1(1)d\tau_1 = E_1^c$$ \hspace{1cm} (10.78)

We utilized the fact that one-electron spin as well as one-electron spatial functions are normalized. We also utilized the following notation

$$E_{\mu}^c = \int \varphi_\mu(i)\hat{H}_i^c \varphi_\mu(i)d\tau_i$$ \hspace{1cm} (10.79)

Next term with the same $\hat{H}_1^c$ operator.

$$R_{1,2} = \int \int W_1 \hat{H}_1^c W_2 d\tau d\sigma =$$

$$= \int \int \varphi_1(1)\sigma_1(1)\varphi_2(2)\sigma_2(2)\varphi_3(3)\sigma_3(3)\hat{H}_1^c\varphi_1(1)\sigma_1(1)\varphi_2(2)\sigma_2(2)\varphi_3(3)\sigma_3(3) d\tau d\sigma =$$

$$= \int \sigma_2^2(2)\sigma_1(1)d\sigma_1 \cdot \int \sigma_3^2(3)\sigma_2(2)d\sigma_2 \cdot \int \varphi_3(3)d\tau_3 \cdot \int \varphi_2(2)d\tau_2 \cdot \int \varphi_1(1)\hat{H}_1^c\varphi_3(3) d\tau_3$$ \hspace{1cm} (10.80)

To calculate this integral, first let’s consider the following product of two integrals

$$\int \sigma_2^2(2)\sigma_1(1)d\sigma_1 \cdot \int \varphi_2(2)d\tau_2$$ \hspace{1cm} (10.81)

If the functions $\varphi_1$ and $\varphi_2$ are different the the appropriate integral over space coordinates equals zero due to orthogonality of the functions ($R_{1,2} = 0$). If the spatial functions are different then the spin functions for electron number 2 must different, for instance if $\sigma_1$ is function $\alpha$ then the function $\sigma_2$ must be function $\beta$, which means the integral $\int \sigma_2^2(2)\sigma_1(1)d\sigma_2 = 0$. Thus, in both cases $R_{1,2} = 0$.

$$R_{1,3} = \int \int W_1 \hat{H}_1^c W_3 d\tau d\sigma =$$

$$= \int \int \varphi_1(1)\sigma_1(1)\varphi_2(2)\sigma_2(2)\varphi_3(3)\sigma_3(3)\hat{H}_1^c\varphi_3(3)\sigma_1(1)\varphi_2(2)\sigma_2(2)\varphi_3(3)\sigma_3(3) d\tau d\sigma =$$
Applying the same analyze as in the case of term $R_{12} = 0$, we also conclude the $R_{13} = 0$. It is now easy to notice that non-zero terms will reveal only for the same $W_i$ before and after the core hamiltonians. In those cases we are getting core energy with index of appropriate function for electron number 1 (with respect for the operator $\hat{H}_i^c$). Therefore we have

$$R_{2,2} = E_3^c, \ R_{3,3} = E_2^c, \ R_{4,4} = E_3^c, \ R_{5,5} = E_2^c, \ R_{6,6} = E_1^c$$

(10.83)

$$\int \int \Psi \hat{H}_i^c \Psi d\tau d\sigma = 2 (E_1^c + E_2^c + E_3^c)$$

(10.84)

Now let’s utilize the core hamiltonian of electron number 2 ($\hat{H}_2^c$). It is easy to find that non-zero terms will again reveal only for the same $W_i$ before and after the core hamiltonian in integrals (non-zero $R_{ij}$). Index of the core energy will correspond to the index of spatial one-electron function corresponding to electron number 2 in the term $W_i$ (as well as in $R_{ij}$). What will be different is only the order of appropriate terms. Analogously we will obtain the $2 (E_1^c + E_2^c + E_3^c)$ utilizing core hamiltonian of electron number 3 ($\hat{H}_3^c$). Therefore, utilizing core hamiltonians for 3-electron system ($\hat{H}_i^c + \hat{H}_2^c + \hat{H}_3^c$) we will obtain core energy of a system of 3-electrons

$$E^{elc} = \int \int \frac{1}{\sqrt{6}} \left( \sum_{i=1}^{6} W_i \right) (\hat{H}_i^c + \hat{H}_2^c + \hat{H}_3^c) \frac{1}{\sqrt{6}} \left( \sum_{i=1}^{6} W_i \right) d\tau d\sigma =$$

$$\frac{1}{6} \cdot 3 \cdot 2 (E_1^c + E_2^c + E_3^c) = E_1^c + E_2^c + E_3^c$$

(10.85)

Now, let’s utilize the operator $e^2/r_{12}$.

$$C_{1,1} = \int \int W_1 \frac{e^2}{r_{12}} W_1 d\tau d\sigma =$$

$$= \int \int \frac{\varphi_1(1)\varphi_2(2)\varphi_3(3)\varphi_4(4)\varphi_5(5)\varphi_6(6)}{r_{12}} d\tau d\sigma =$$

$$= \int \int \frac{1}{r_{12}} \varphi_1(1)\varphi_2(2)\varphi_3(3)\varphi_4(4)\varphi_5(5)\varphi_6(6) d\tau d\sigma =$$

$$= \frac{1}{12} \int \int \varphi_1(1)\varphi_2(2)\varphi_3(3) d\tau_1 d\tau_2 = J_{12}$$

(10.86)

The integral $J_{12}$ by definition defines the repulsion of two electrons, accordingly to the Coulomb’s law. Under this integral there must be the same functions for the same electrons, which in turn causes under the integral there are two squares of two different functions. The indices 12 correspond to the indices of functions, not particle’s numbers. For the same classes of functions, the boundaries of integrations remain the same, while the value of the integral depends on functions. Generally, the Coulomb integral has the following form:

$$J_{\mu\nu} = \int \int \frac{\varphi_\mu^2(1)}{r_{12}^2} \varphi_\nu^2(2) d\tau_1 d\tau_2$$

(10.87)
Another term - $C_{12}$

\[
C_{12} = \int \int W_1 \frac{e^2}{r_{12}} W_2 d\tau d\sigma = \\
= \int \int \varphi_1(1)\sigma_1(1)\varphi_2(2)\sigma_2(2)\varphi_3(3)\sigma_3(3) \frac{e^2}{r_{12}} \varphi_1(2)\sigma_1(2)\varphi_2(1)\sigma_2(1)\varphi_3(3)\sigma_3(3) d\tau d\sigma = \\
= \int \sigma_1(1)\sigma_3(3) d\sigma_1 \cdot \int \sigma_2(2)\sigma_1(2) d\sigma_2 \cdot \int \sigma_3(3)\sigma_2(2) d\sigma_3 \cdot \int \varphi_3(3)\varphi_2(2) d\tau_3.
\]

Let’s consider product of spatial and spin integrals for electron number 3

\[
\int \sigma_3(3)\sigma_2(2) d\sigma_3 \cdot \int \varphi_3(3)\varphi_2(2) d\tau_3
\]

(10.88)

If the function $\varphi_2$ is identical to function $\varphi_3$ (we didn’t assume the two functions must be different, however this type of assumption is present within some class of methods) then the spin functions must be different (Pauli’s principle). For instance $\sigma_3 = \sigma$ and $\sigma_2 = \sigma$ or $\sigma_3 = \sigma$ and $\sigma_2 = \sigma$. In the case the space functions are different the integration gives 0 due to orthogonality of the spatial functions. On the other hand, if the two spatial functions are exactly the same, then the spin functions $\sigma_3$ and $\sigma_2$ must be different and the integral $\int \sigma_3(3)\sigma_2(2) d\sigma_3 = 0$, so that $C_{1,2} = 0$. It’s easy to examine that among the other terms only the $C_{1,5}$ is a non-zero one (both in $W_1$ and in $W_5$ the electron no. 3 is described by the same spatial function $\varphi_3$).

\[
C_{1,5} = -\int \int W_1 \frac{e^2}{r_{12}} W_5 d\tau d\sigma = \\
= -\int \int \varphi_1(1)\sigma_1(1)\varphi_2(2)\sigma_2(2)\varphi_3(3)\sigma_3(3) \frac{e^2}{r_{12}} \varphi_1(2)\sigma_1(2)\varphi_2(1)\sigma_2(1)\varphi_3(3)\sigma_3(3) d\tau d\sigma = \\
= -\int \sigma_1(1)\sigma_2(2) d\sigma_1 \cdot \int \sigma_2(2)\sigma_1(2) d\sigma_2 \cdot \int \sigma_3(3)\sigma_2(2) d\sigma_3 \cdot \int \varphi_3(3)\varphi_2(2) d\tau_3 \\
\cdot \int \varphi_1(1)\varphi_2(1) \frac{e^2}{r_{12}} \varphi_2(2)\varphi_1(2) d\tau_1 d\tau_2
\]

(10.90)

This integral is not equal zero only if the spin functions $\sigma_1$ and $\sigma_2$ are exactly the same, which happens only if the electrons 1 and 2 have the same spin. Thus, if this is the case then

\[
C_{1,5} = -\int \varphi_1(1)\varphi_2(1) \frac{e^2}{r_{12}} \varphi_2(2)\varphi_1(2) d\tau_1 d\tau_2 \equiv -K_{12}
\]

(10.91)

As it can be easily seen exchange of two indices in the $K_{12}$ gives us the Coulomb integral $J_{12}$. This is the reason for calling the $K_{ij}$ integrals the exchange integrals. In general they can be written as

\[
K_{\mu\nu} = \int \int \varphi_{\mu}(i)\varphi_{\nu}(i) \frac{e^2}{r_{12}} \varphi_{\mu}(j)\varphi_{\nu}(j) d\tau_i d\tau_j
\]

(10.92)

It’s worth noticing the indices correspond to the indices of functions, not electrons.

In similar way, one can achieve the other terms

\[
\begin{align*}
C_{2,2} &= J_{13} \\
C_{2,6} &= -K_{13} \\
C_{3,3} &= J_{23} \\
C_{3,4} &= -K_{23} \\
C_{4,4} &= J_{23} \\
C_{4,3} &= -K_{32} = -K_{23} \\
C_{5,5} &= J_{12} \\
C_{5,1} &= -K_{12} \\
C_{6,6} &= J_{13} \\
C_{6,2} &= -K_{13}
\end{align*}
\]
Of course, the $K_{\mu\nu}$ integrals reveals only when the electrons described by spatial functions $\phi_\mu$ and $\phi_\mu^*$ have the same spin. Therefore, for the operator $\frac{e^2}{r_{12}}$, we are getting

$$\int \int \left( \sum_i^6 W_i \right) \frac{e^2}{r_{12}} \left( \sum_i^6 W_i \right) d\tau d\sigma = 2 \left( \sum_{\mu<\nu} \sum_{\mu<\nu} J_{\mu\nu} - \sum_{\mu<\nu} \sum_{\mu<\nu} K_{\mu\nu} \right)$$

(10.93)

The arroww in equation above indicate they reveal only when the spins are parallel for the pair of electrons. It's relatively simple to check that for the operators $\frac{e^2}{r_{13}}$ and $\frac{e^2}{r_{23}}$ we will obtain the same result but with different order of components. Thus, we can conclude that

$$E_{\text{el}} = \int \int \bar{\Psi} \hat{H} \Psi d\tau d\sigma =$$

$$\frac{1}{6} \cdot 3 \cdot 2 \left( E_1^c + E_2^c + E_3^c \right) + \frac{1}{6} \cdot 3 \cdot 2 \left( \sum_{i<j} \sum_{i<j} J_{\mu\nu} - \sum_{i<j} \sum_{i<j} K_{\mu\nu} \right)$$

$$= \sum_{i=1}^3 E_{\mu}^c + \sum_{i<j} J_{\mu\nu} - \sum_{i<j} K_{\mu\nu}$$

(10.94)

In the equation above the summation goeas over electrons' indices ($i$ and $j$) while we intentionaly write the indices of functions corresponding to the electrons.

In more general form (where the number of electrons is not necessarily equal 3).

$$E_{\text{el}} = \sum_{i} E_{\mu}^c + \sum_{i<j} J_{\mu\nu} - \sum_{i<j} K_{\mu\nu}$$

(10.95)

The Slater-Condon rules express the integrals for more individual cases.

**Exercice ??**
Find the total energy of ground-state hydrogen molecule and compare it with the energies of other configurations of this molecule.

**Solution**

$$\chi_1 = \frac{1}{\sqrt{2}} \phi_1(1)\phi_1(2) [\alpha(1)\beta(2) - \alpha(2)\beta(1)]$$

(10.96)

$$\hat{H} = \hat{H}_1^c + \hat{H}_2^c + \frac{e^2}{r_{12}} + \frac{e^2}{r_{AB}}$$

(10.97)

$$\hat{H}^{\text{el}} = \hat{H}_1^c + \hat{H}_2^c + \frac{e^2}{r_{12}}$$

(10.98)

$$E_{\text{el}} = \int \int \chi_1 \hat{H}^{\text{el}} \chi_1 d\tau d\sigma = \int \int \frac{1}{\sqrt{2}} \phi_1(1)\phi_1(2) [\alpha(1)\beta(2) - \alpha(2)\beta(1)] \cdot$$

$$\cdot \left( \hat{H}_1^c + \hat{H}_2^c + \frac{e^2}{r_{12}} \right) \cdot \frac{1}{\sqrt{2}} \phi_1(1)\phi_1(2) [\alpha(1)\beta(2) - \alpha(2)\beta(1)] d\tau d\sigma =$$
\[ \psi = \sum_i c_i \Phi_i \] (10.103)

The CI method is a variational one. The parameters \( c_i \) are linear and typically one uses the Ritz method for solving the problem. The solution leads to the set of linear parameters for each of the eigenvalues (the energies).

\[ \Psi_n = c_0(n) \Phi_0 + \sum_{ia} c_i^a(n) \Phi_i^a + \sum_{ijab} c_{ijab}^a(n) \Phi_{ij}^{ab} + \sum_{ijklab} c_{ijklab}^a(n) \Phi_{ijkl}^{ab} + \ldots \] (10.104)

where the \( n \) numerates appropriate state. If the equation above takes into account all possible configurations then the method is named as Full Configuration Interaction (FCI).

If the number of atomic orbitals equals \( M \) (occupied and unoccupied) then the number of corresponding spinorbitals equals \( 2M \). Creation of \( N \)-electron Slater determinant for this case boils down to typical combinatorial problem of picking out \( N \) elements from a set of \( 2M \) functions. The number of possible combinations is equal to binomial coefficient.
\[ K = \binom{2M}{N} = \frac{(2M)!}{N!(2M-N)!} \quad (10.105) \]

Example 1. CH\(^+\) ion. DZ basis.

6 electrons. The atomic orbitals are as follows:
- Carbon: 1s, 2s, 2p\(_x\), 2p\(_y\), 2p\(_z\), 1s', 2s', 2p\(_x'\), 2p\(_y'\), 2p\(_z'\), i.e. 10 functions.
- Hydrogen: 1s, 1s', i.e. 2 functions.

In total 12 atomic orbitals, i.e. 24 spinorbitals.

\[ K = \binom{24}{6} = \frac{24!}{6!18!} = 134596 \quad (10.106) \]

Example 2. benzene (C\(_6\)H\(_6\)). DZP basis (Double zeta plus polarization)

42 electrons
- Carbon: 1s, 2s, 2p\(_x\), 2p\(_y\), 2p\(_z\), 1s', 2s', 2p\(_x'\), 2p\(_y'\), 2p\(_z'\), 3d\(_{xy}\), 3d\(_{xz}\), 3d\(_{yz}\), 3d\(_{x^2-y^2}\), 3d\(_{z^2}\), i.e. 15 functions.
- Hydrogen: 1s, 1s', 2p\(_x\), 2p\(_y\), 2p\(_z\), i.e. 5 functions

In total: \(6 \cdot 15 + 6 \cdot 5 = 120\) atomic orbitals, i.e. 240 spinorbitals.

\[ K = \binom{240}{42} = \frac{240!}{42!198!} \approx 1.4 \cdot 10^{51} \quad (10.107) \]

As one can see the number of all determinants even for small basis functions is huge. After the spin analysis the number decreases, but not so much. Thus the application of FCI methodology remains strongly limited to only very small systems. In practice therefore we limit the number of possible configurations to only those which correspond to given excitation level. For instance we define the Configuration Interaction Singles (CIS) which involves only singly-excited configurations (and the ground state configuration), the CI Singles and Doubles (CISD) which involves only ground-state configuration, singly- and doubly-excited configurations, and similarly: CISDT, CISDTQ, etc. Fortunately, in many cases involvement of given excitation level leads to zero energy matrix elements, as shown in the table below.

<table>
<thead>
<tr>
<th>H</th>
<th>(\Phi_0)</th>
<th>(\Phi_1)</th>
<th>(\Phi_{12})</th>
<th>(\Phi_{123})</th>
<th>(\Phi_{1234})</th>
<th>(\Phi_{12345})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\Phi_0)</td>
<td>(E_0)</td>
<td>0</td>
<td>X</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(\Phi_1)</td>
<td>0</td>
<td>X</td>
<td>X</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(\Phi_{12})</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(\Phi_{123})</td>
<td>0</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>0</td>
</tr>
<tr>
<td>(\Phi_{1234})</td>
<td>0</td>
<td>0</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>(\Phi_{12345})</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
</tbody>
</table>

Table 16. Zero and non-zero (denoted as X) energy matrix elements for CI calculations.

**Exercise ??**

Find the wave function of hydrogen molecule utilizing the Configuration Interaction (CI) method. Take into account two electronic configurations: the ground-state and the doubly-excited one.

**Solution**

\[ \chi_1 = \frac{1}{\sqrt{2}}\varphi_1(1)\varphi_1(2)\left[\alpha(1)\beta(2) - \alpha(2)\beta(1)\right] \quad (10.108) \]
\[ \chi_2 = \frac{1}{\sqrt{2}} \varphi_2(1) \varphi_2(2) [\alpha(1) \beta(2) - \alpha(2) \beta(1)] \] (10.109)

The functions \( \varphi_1 \) and \( \varphi_2 \) are orthonormal.

The CI wavefunction has the following form

\[ \Psi = A_1 \chi_1 + A_2 \chi_2 \] (10.110)

The problem comes down to the problem of finding the \( A_1 \) and \( A_2 \) coefficients because the \( \chi_1 \) and \( \chi_2 \) remain unchanged within the CI methodology. The coefficients one finds by means of the Ritz method, where one needs the energy-operator matrix and has to solve appropriate secular equation. The energy matrix elements

\[
\begin{align*}
H_{11} &= \int \int \chi_1 \hat{H}^{el} \chi_1 d\tau d\sigma = 2E_1^c + J_{11} \\
H_{22} &= \int \int \chi_2 \hat{H}^{el} \chi_2 d\tau d\sigma = 2E_2^c + J_{22} \\
H_{12} &= H_{21} = \int \int \chi_1 \hat{H}^{el} \chi_2 d\tau d\sigma =
\end{align*}
\]

\[
\begin{align*}
&= \int \int \frac{1}{\sqrt{2}} [\alpha(1) \beta(2) - \alpha(2) \beta(1)] \varphi_1(1) \varphi_1(2) \hat{H}^{el} \frac{1}{\sqrt{2}} [\alpha(1) \beta(2) - \alpha(2) \beta(1)] \varphi_2(1) \varphi_2(2) d\tau d\sigma = \\
&= \frac{1}{2} \int \int [\alpha(1) \beta(2) - \alpha(2) \beta(1)]^2 d\sigma_1 d\sigma_2 \int \int \varphi_1(1) \varphi_1(2) \left( \hat{H}_1^c + \hat{H}_2^c + \frac{e^2}{r_{12}} \right) \varphi_2(1) \varphi_2(2) d\tau_1 d\tau_2 = \\
&= 1 \cdot \int \int \varphi_1(1) \varphi_1(2) \hat{H}_1^c \varphi_2(1) \varphi_2(2) d\tau_1 d\tau_2 + \int \int \varphi_1(1) \varphi_1(2) \hat{H}_2^c \varphi_2(1) \varphi_2(2) d\tau_1 d\tau_2 + \\
&+ \int \int \varphi_1(1) \varphi_1(2) \frac{e^2}{r_{12}} \varphi_2(1) \varphi_2(2) d\tau_1 d\tau_2 \\
&= \int \varphi_1(1) \hat{H}_1^c \varphi_2(1) d\tau_1 + \varphi_1(1) \varphi_2(1) d\tau_1 \int \varphi_2(2) \hat{H}_2^c d\tau_2 + \\
&+ \int \varphi_1(1) \varphi_2(1) \frac{e^2}{r_{12}} \varphi_2(2) d\tau_1 d\tau_2 = 0 + 0 + K_{12} = K_{12} \\
\end{align*}
\] (10.111)

Secular determinant

\[
\begin{vmatrix}
2E_1^c + J_{11} - E & K_{12} \\
K_{12} & 2E_2^c + J_{22} - E
\end{vmatrix} = 0
\] (10.112)

\[
\begin{align*}
(2E_1^c + J_{11} - E) (2E_2^c + J_{22} - E) - K_{12}^2 &= 0 \\
E^2 - E (2E_1^c + J_{11} + 2E_2^c + J_{22}) + (2E_1^c + J_{11}) (2E_2^c + J_{22}) - K_{12}^2 &= 0
\end{align*}
\] (10.113)

Solving the equation above one is getting two energy values - lower will correspond to the ground state, higher - to excited state of hydrogen molecule. Substituting the two energy values into the secular equation one can find the \( A_1 \) and \( A_2 \) coefficients and determine the wavefunction

\[
\begin{bmatrix}
2E_1^c + J_{11} - E \\
K_{12}
\end{bmatrix} \begin{bmatrix}
A_1 \\
A_2
\end{bmatrix} = 0
\] (10.114)

\[
A_1 (2E_1^c + J_{11} - E) + A_2 K_{12} = 0 \\
A_1 K_{12} + A_2 (2E_2^c + J_{22} - E) = 0
\] (10.115)

which means we are getting two sets of the coefficients. One will correspond to the ground state and the second will correspond to the wave function for doubly-excited state (higher value of energy).
11 Mathematical background

11.1 Informations on linear algebra methods

11.1.0.1 Matrix representation of a state  Let $Q$ be an Hermitian operator, its eigenfunctions $u_n(x)$ is a complete orthonormal set. Quantum theory can be expressed through $u_n(x)$ set and this formulation is called Q-representation.

Premise: $u_n(x)$ set is known and forms a complete orthonormal set. Any wavefunction $\psi(x)$ can be expanded upon $u_n(x)$ set

$$\psi(x) = \sum_n c_n u_n(x)$$  \hspace{1cm} (11.1)

with

$$c_n = \int u_n^*(x') \psi(x') dx$$ \hspace{1cm} (11.2)

State function $\psi(x)$ and the set of coefficients $c_n$ are uniquely connected. This means, for the given wave function $\psi(x)$, the coefficients $c_n$ are completely known. On the other hand, knowing the coefficients $c_n$, the state function is uniquely determined.

The coefficients $c_n$ uniquely determine the state of the system just as the wavefunction $\psi(x)$ does. The coefficients $c_n$ is called $Q$-representation of the state.

Formally the $Q$-representation is expressed as a „column matrix”, i.e. the $N$-tuple of the component of a vector $c_n$, with respect to a specified orthonormal basis

$$\psi(x) = \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ \vdots \end{pmatrix}$$ \hspace{1cm} (11.3)

The Hermitian conjugate of $\psi$ is denoted by $\psi^*$

$$\psi^*(x) = \psi^*(x) = (c_1^* c_2^* c_3^* \ldots)$$ \hspace{1cm} (11.4)

Normalization:

$$\int \psi^*(x) \psi(x) dx = \int \sum_n c_n^* u_n^* \sum_n c_n u_n dx = \sum_n c_n^* c_n = 1$$ \hspace{1cm} (11.5)

is expressed in $Q$ representation as

$$\psi^* \psi = (c_1^* c_2^* c_3^* \ldots) \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ \vdots \end{pmatrix} = 1$$ \hspace{1cm} (11.6)

Similarly inner product of $\psi$ and another vector $\phi$

$$\phi = \sum_n a_n u_n(x) = \begin{pmatrix} a_1 \\ a_2 \\ a_3 \\ \vdots \end{pmatrix}$$ \hspace{1cm} (11.7)

More general, the inner product is a complex number

$$\int \psi^*(x) \phi(x) dx = \psi^* \phi = (c_1^* c_2^* c_3^* \ldots) \begin{pmatrix} a_1 \\ a_2 \\ a_3 \\ \vdots \end{pmatrix} = \sum_n c_n^* a_n$$ \hspace{1cm} (11.8)
The set of all square integrable functions constitutes a vector space, which physicists call the Hilbert space after David Hilbert, who studied linear spaces in infinite dimensions.

11.1.0.2 Matrix representation of operators

In $Q$-representation, the states are expressed by column (row) matrix, how would an operator $\hat{F}$ be expressed in $Q$-representation?

The action of an operator $\hat{F}$ upon a certain wave function changes it into another function $\phi(x)$

$$\phi = \hat{F}\psi(x)$$  \hspace{1cm} (11.9)

Both of the functions can be expressed upon the complete set $u_n(x)$ in $Q$-representation

$$\phi(x) = \sum_n b_n u_n(x), \quad \psi(x) = \sum_n a_n u_n(x)$$  \hspace{1cm} (11.10)

thus

$$\sum_n b_n u_n(x) = \hat{F} \sum_n a_n u_n(x)$$  \hspace{1cm} (11.11)

multiplaying by $u_m^*(x)$ from left and integrating

$$\int u_m^*(x) \left( \sum_n b_n u_n(x) = \hat{F} \sum_n a_n u_n(x) \right) dx$$  \hspace{1cm} (11.12)

and because of the orthogonality of the basis we are getting

$$b_m = \sum_n \int u_m^*(x) \hat{F} u_n(x) a_n dx = \sum_n F_{mn} a_n$$  \hspace{1cm} (11.13)

In matrix form it looks like

$$\begin{pmatrix} b_1 \\ b_2 \\ b_3 \\ \vdots \end{pmatrix} = \begin{pmatrix} F_{11} & F_{12} & F_{13} & \cdots \\ F_{21} & F_{22} & F_{23} & \cdots \\ F_{31} & F_{32} & F_{33} & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \\ a_3 \\ \vdots \end{pmatrix}$$  \hspace{1cm} (11.14)

or

$$\phi = F\psi$$  \hspace{1cm} (11.15)

with elements of the operator $F$

$$F_{mn} = \int u_m^*(x) \hat{F} u_n(x) dx$$  \hspace{1cm} (11.16)

11.1.0.3 Property of matrix of Hermitian operator

The matrix element $F_{mn}$ and its conjugate

$$F_{mn}^* = \int u_m(x) (\hat{F} u_n(x))^* dx = \int (\hat{F} u_n(x))^* u_m(x) dx$$  \hspace{1cm} (11.17)

satisfy

$$F_{mn}^* = F_{nm}$$  \hspace{1cm} (11.18)

Thus the matrix $F$ representing a Hermitian operator $\hat{F}$ is a Hermitian matrix

$$F^\dagger = F$$  \hspace{1cm} (11.19)
Indeed

\[
F^\dagger = \begin{pmatrix}
F_{11} & F_{12} & F_{13} & \cdots \\
F_{21} & F_{22} & F_{23} & \cdots \\
F_{31} & F_{32} & F_{33} & \cdots \\
\vdots & \vdots & \vdots & \ddots
\end{pmatrix}^\dagger = \begin{pmatrix}
F^*_{11} & F^*_{12} & F^*_{13} & \cdots \\
F^*_{21} & F^*_{22} & F^*_{23} & \cdots \\
F^*_{31} & F^*_{32} & F^*_{33} & \cdots \\
\vdots & \vdots & \vdots & \ddots
\end{pmatrix} = F
\]  
(11.20)

11.1.0.4 Vector space and its basis  Example. Let’s find the matrix form of \( \hat{L}_y \) (the y-component of angular momentum).

\[
\hat{L}_y = -i\hbar \cos \varphi \frac{\partial}{\partial \theta} + i\hbar \cot \theta \sin \varphi \frac{\partial}{\partial \varphi}
\]  
(11.21)

We need yet a basis of functions for our operator and we choose the spherical harmonics for \( l = 1 \) thus with \( m = 1, 0, -1 \) and we denote them as

\[
u_1 = Y_{1,1} = -\sqrt{\frac{3}{8\pi}} \sin \theta e^{i\varphi}
\]

\[
u_2 = Y_{1,0} = \sqrt{\frac{3}{4\pi}} \cos \theta
\]

\[
u_3 = Y_{1,-1} = \sqrt{\frac{3}{8\pi}} \sin \theta e^{-i\varphi}
\]

Let’s find products of

\[
\hat{L}_y \nu_1 = \hat{L}_y Y_{1,1} = i\hbar \sqrt{\frac{3}{8\pi}} \cos \varphi \cos \theta \sin \varphi - i\hbar \sqrt{\frac{3}{8\pi}} \cot \theta \sin \varphi \sin \theta e^{i\varphi} =
\]

\[
= i\hbar \sqrt{\frac{3}{8\pi}} \cos (\cos \phi - i \sin \phi) e^{i\varphi} =
\]

\[
= \frac{i\hbar}{\sqrt{2}} \sqrt{\frac{3}{4\pi}} \cos \theta = \frac{i\hbar}{\sqrt{2}} Y_{1,0}
\]  
(11.23)

Thus we have

\[
\int \int \nu_1^* \hat{L}_y \nu_1 d\Omega = \int \int Y_{1,1}^* \hat{L}_y Y_{1,1} (\sin \theta d\theta d\varphi) = 0
\]

\[
\int \int \nu_2^* \hat{L}_y \nu_1 d\Omega = \int \int Y_{1,0}^* \hat{L}_y Y_{1,1} (\sin \theta d\theta d\varphi) = \frac{i\hbar}{\sqrt{2}}  
\]  
(11.24)

\[
\int \int \nu_3^* \hat{L}_y \nu_1 d\Omega = \int \int Y_{1,-1}^* \hat{L}_y Y_{1,1} (\sin \theta d\theta d\varphi) = 0
\]

For function \( \nu_2 \)

\[
\hat{L}_y \nu_2 = \hat{L}_y Y_{1,0} = -i\hbar \cos \varphi \sqrt{\frac{3}{4\pi}} (-\sin \theta) = i\hbar \sqrt{\frac{3}{4\pi}} \sin \theta \cos \varphi =
\]

\[
= -i\hbar \sqrt{\frac{3}{4\pi}} \sin \theta \left( e^{i\varphi} + e^{-i\varphi} \right) = \frac{i\hbar}{\sqrt{2}} \sqrt{\frac{3}{8\pi}} \sin \theta e^{i\varphi} + \frac{i\hbar}{\sqrt{2}} \sqrt{\frac{3}{8\pi}} \sin \theta e^{-i\varphi} =
\]  
(11.25)

\[
= \frac{i\hbar}{\sqrt{2}} Y_{1,1} + \frac{i\hbar}{\sqrt{2}} Y_{1,-1}
\]
And the integrals
\[
\int \int u_1^* \hat{L}_y u_2 d\Omega = \int \int Y_{1,1}^* \hat{L}_y Y_{1,0} \sin \theta d\theta d\varphi = -\frac{i\hbar}{\sqrt{2}} \\
\int \int u_2^* \hat{L}_y u_2 d\Omega = \int \int Y_{1,1}^* \hat{L}_y Y_{1,0} \sin \theta d\theta d\varphi = 0 \\
\int \int u_3^* \hat{L}_y u_2 d\Omega = \int \int Y_{1,-1}^* \hat{L}_y Y_{1,0} \sin \theta d\theta d\varphi = \frac{i\hbar}{\sqrt{2}}
\]

(11.26)

In summary, the matrix form of \( L_y \) is
\[
L_y = \begin{bmatrix}
0 & -\frac{i\hbar}{\sqrt{2}} & 0 \\
\frac{i\hbar}{\sqrt{2}} & 0 & -\frac{i\hbar}{\sqrt{2}} \\
0 & \frac{i\hbar}{\sqrt{2}} & 0
\end{bmatrix}
\]

(11.27)

11.1.0.5 Matrix formulation of eigenproblem in \( Q \) representation

\[\psi(x) = \sum_n c_n u_n(x)\]  

(11.28)

The expectation value of observable \( F \)
\[\langle F \rangle = \int \psi^* F \psi dx = \sum_m c_m^* u_m^*(x) \hat{F} \sum_n c_n u_n(x) = \sum_{mn} c_m^* F_{mn} c_n\]  

(11.29)

In matrix form this is expressed as
\[
\begin{pmatrix} c_1^* \ c_2^* \ c_3^* \ \cdots \end{pmatrix} = \begin{pmatrix} F_{11} & F_{12} & F_{13} & \cdots \\
F_{21} & F_{22} & F_{23} & \cdots \\
F_{31} & F_{32} & F_{33} & \cdots \\
\vdots & \vdots & \vdots & \ddots
\end{pmatrix} \begin{pmatrix} c_1 \\
c_2 \\
c_3 \\
\vdots
\end{pmatrix} = \psi^* F \psi
\]

(11.30)

In short the expectation value of an observable \( F \) is
\[\langle F \rangle = \int \psi^* F \psi dx = \psi^* F \psi\]  

(11.31)

Secondly, one can formulate the eigenvalue equation of operator \( \hat{F} \) in matrix language. Starting from the
\[\hat{F} \psi = \lambda \psi\]  

(11.32)

we multiply this equation by \( u_m^* \) and integrate it
\[\int u_m^*(x) \left( \hat{F} \sum_n c_n u_n(x) = \lambda \sum_n c_n u_n(x) \right) dx\]  

(11.33)

which leads to
\[\sum_n c_n \int u_m^* \hat{F} u_n dx = \lambda c_m\]  

(11.34)

or
\[\sum_n F_{mn} c_n = \lambda c_m\]  

(11.35)
In matrix form it reads

\[
\begin{pmatrix}
F_{11} & F_{12} & F_{13} & \cdots \\
F_{21} & F_{22} & F_{23} & \cdots \\
F_{31} & F_{32} & F_{33} & \cdots \\
\vdots & \vdots & \vdots & \ddots
\end{pmatrix}
\begin{pmatrix}
c_1 \\
c_2 \\
c_3 \\
\vdots
\end{pmatrix}
= \lambda
\begin{pmatrix}
c_1 \\
c_2 \\
c_3 \\
\vdots
\end{pmatrix}
\]

(11.36)

Thus, the eigenproblem of operator $\hat{F}$ is called down to find the eigenvalues and corresponding eigenvectors of an hermitian matrix $F$. A special instance is a square $F$ matrix of finite number of rows and finite number of columns

\[
\begin{pmatrix}
F_{11} & F_{12} & \cdots & F_{1k} \\
F_{21} & F_{22} & \cdots & F_{2k} \\
\vdots & \vdots & \ddots & \vdots \\
F_{k1} & F_{k2} & \cdots & F_{kk}
\end{pmatrix}
\begin{pmatrix}
c_1 \\
c_2 \\
\vdots \\
c_k
\end{pmatrix}
= \lambda
\begin{pmatrix}
c_1 \\
c_2 \\
\vdots \\
c_k
\end{pmatrix}
\]

(11.37)

Rewriting the equation above into more compact form

\[
Fc = \lambda c \\
IFc = I\lambda c \\
(F - \lambda I)c = 0
\]

(11.38)

which is

\[
\begin{pmatrix}
F_{11} - \lambda & F_{12} & \cdots & F_{1k} \\
F_{21} & F_{22} - \lambda & \cdots & F_{2k} \\
\vdots & \vdots & \ddots & \vdots \\
F_{k1} & F_{k2} & \cdots & F_{kk} - \lambda
\end{pmatrix}
= 0
\]

(11.39)

The equation above is an algebraic equation of k-th power of $\lambda$. Solving this equation one gets the eigenvalues of matrix $F$ which are the roots of the algebraic equation. Substituting appropriate $\lambda$ into the equation 11.38 one obtains corresponding eigenvectors, which means the wavefunction was found.

11.1.0.6 Gram-Schmidt orthogonalization

11.1.0.7 Löwdin orthogonalization We have $\phi = [\phi_1, \phi_2, \ldots, \phi_N]^T$ normalized (i.e. $\langle \phi_i | \phi_j \rangle = 1$) but not orthogonal, $\langle \phi_i | \phi_j \rangle = S_{ij}$. In Löwdin’s method the vectors are treated equally, i.e. there is not any arbitrary choice of one of them which will not be changed at all. We assume:

\[
\phi' = S^{-\frac{1}{2}}\phi
\]

(11.40)

where the $S^{-\frac{1}{2}}$ and its cousin, the $S^{\frac{1}{2}}$, are defined in this way that their properties are analogous to properties of typical real values, i.e. $S^{-\frac{1}{2}}S^{-\frac{1}{2}} = S^{-1}$, $S^{\frac{1}{2}}S^{\frac{1}{2}} = S$, and $S^{-\frac{1}{2}}S^{\frac{1}{2}} = I$.

First, we diagonalize the $S$ by means of orthogonal matrix $U$ (for real $S$, while for complex $S$ it is the unitary matrix, $U^\dagger U = UU^\dagger = I$).

\[
S_{\text{diag}} = U^\dagger SU
\]

(11.41)

Eigenvalues of $S$ are always positive so that we can put their square roots in some matrix getting the $S^{\frac{1}{2}}_{\text{diag}}$. We then define the $S^{\frac{1}{2}}_{\text{diag}} = US^{\frac{1}{2}}_{\text{diag}}U^\dagger$ and the $S^{-\frac{1}{2}}_{\text{diag}} = US^{-\frac{1}{2}}_{\text{diag}}U^\dagger$. Their symbols are related to their properties (like in the case of ordinary real numbers, i.e.

\[
S^{\frac{1}{2}}_{\text{diag}}S^{\frac{1}{2}}_{\text{diag}} = US^{\frac{1}{2}}_{\text{diag}}U^\dagger US^{\frac{1}{2}}_{\text{diag}}U^\dagger = US^{\frac{1}{2}}_{\text{diag}}S^{-\frac{1}{2}}_{\text{diag}}U^\dagger = US^{\frac{1}{2}}_{\text{diag}}U^\dagger = S
\]

(11.42)
Analogously, one gets that $S^{-\frac{1}{2}} S^{-\frac{1}{2}} = S^{-1}$ $S^{-\frac{1}{2}} S^{\frac{1}{2}} = I$.

What is very important in case of Löwdin’s orthogonalization is the fact that the new basis is as subtly changed as possible, i.e.

$$\sum_{i}^{N} |\phi_i - \phi'| = \text{min.} \quad (11.43)$$

**Example**

We have two nonorthogonal vectors $u_i$ and $v$ with their length equal to 1 and with inner product $\langle u|v \rangle = a$. Orthogonalize the vectors by means of Löwdin algorithm.

**Solution**

$S$ matrix

$$S = \begin{pmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{pmatrix} = \begin{pmatrix} 1 & a \\ a & 1 \end{pmatrix} \quad (11.44)$$

First, we diagonalize $S$ by utilizing (here) unitary transformation $S_{\text{diag}} = U^\dagger S U$, and to ensure the $U$ remains orthogonal we define its elements accordingly to Jacobi’s methodology

$$U = \begin{pmatrix} \cos \theta & \sin \theta \\ -\sin \theta & \cos \theta \end{pmatrix} \quad (11.45)$$

Thus

$$U^\dagger = \begin{pmatrix} \cos \theta & -\sin \theta \\ \sin \theta & \cos \theta \end{pmatrix} \quad (11.46)$$

whereas the $\theta$ angle we will adjust appropriately. After the unitary transformation we have

$$U^\dagger = \begin{pmatrix} 1 - a \sin 2\theta & a \cos 2\theta \\ a \cos 2\theta & 1 + a \sin 2\theta \end{pmatrix} \quad (11.47)$$

If $\theta = 45^\circ$, then we have diagonal $S_{\text{diag}}$ and

$$U = \begin{pmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ -1 & 1 \end{pmatrix} \quad (11.48)$$

Next, we calculate $S_{\text{diag}}^{\frac{1}{2}}$

$$S_{\text{diag}}^{\frac{1}{2}} = \begin{pmatrix} \sqrt{1 - a} & 0 \\ 0 & \sqrt{1 + a} \end{pmatrix} \quad (11.49)$$

and

$$S^{\frac{1}{2}} = U S_{\text{diag}}^{\frac{1}{2}} U^\dagger = \frac{1}{2} \begin{pmatrix} \sqrt{1 - a} + \sqrt{1 + a} & \sqrt{1 + a} - \sqrt{1 - a} \\ \sqrt{1 + a} - \sqrt{1 - a} & \sqrt{1 - a} + \sqrt{1 + a} \end{pmatrix} \quad (11.50)$$

as well as

$$S^{-\frac{1}{2}} = U S^{-\frac{1}{2}} U^\dagger = U \begin{pmatrix} \frac{1}{\sqrt{1 - a}} & 0 \\ 0 & \frac{1}{\sqrt{1 + a}} \end{pmatrix} U^\dagger = \frac{1}{2} \begin{pmatrix} \frac{1}{\sqrt{1 - a}} & \frac{1}{\sqrt{1 + a}} \\ \frac{1}{\sqrt{1 + a}} & \frac{1}{\sqrt{1 - a}} \end{pmatrix} \quad (11.51)$$

Finally we can find the orthogonal vector (orthogonal basis)
\[
\begin{pmatrix}
u' \\
u''
\end{pmatrix}
= \frac{1}{2}
\begin{pmatrix}
\frac{1}{\sqrt{1-a}} + \frac{1}{\sqrt{1+a}} & \frac{1}{\sqrt{1+a}} - \frac{1}{\sqrt{1-a}} \\
\frac{1}{\sqrt{1+a}} + \frac{1}{\sqrt{1-a}} & \frac{1}{\sqrt{1-a}} - \frac{1}{\sqrt{1+a}}
\end{pmatrix}
\begin{pmatrix}
u \\
u'
\end{pmatrix}
\] (11.52)

In other words
\[
\begin{align*}
u' &= ru + sv \\
v' &= su + rv
\end{align*}
\] (11.53) (11.54)

where
\[
\begin{align*}
r &= \frac{1}{2}
\left(
\frac{1}{\sqrt{1-a}} + \frac{1}{\sqrt{1+a}}
\right) \\
s &= \frac{1}{2}
\left(
\frac{1}{\sqrt{1+a}} - \frac{1}{\sqrt{1-a}}
\right)
\end{align*}
\] (11.56) (11.57)

The new orthogonal vectors \(u'\) and \(v'\) develop from the old \(u\) and \(v\) through the same addition of old vectors, i.e. the contribution of \(u\) and \(v\) in the \(u'\) as well as the contribution of \(u\) and \(v\) in the \(v'\) remains the same. The Löwdin method is thus called symmetrical.

11.1.0.8 Complex vectors

11.1.0.9 Matrix diagonalization  Find the eigenvalues and eigenvectors of matrix A

\[
A = \begin{bmatrix}
1 & 0 & 0 \\
3 & 1 & 2 \\
0 & 5 & 4
\end{bmatrix}
\] (11.58)

Solution

Characteristic equation

\[
\begin{vmatrix}
1 - \lambda & 0 & 0 \\
3 & 1 - \lambda & 2 \\
0 & 5 & 4 - \lambda
\end{vmatrix} = 0
\]

\[
= (1 - \lambda)^2 + (4 - \lambda) + 0 + 0 - 0 - 0 - 10(1 - \lambda) = 0
\]

\[
= -\lambda^3 + 6\lambda^2 + \lambda - 6 = 0
\]

We guess the \(\lambda = 1\) is one eigenvalue and we can divide the polynomial by \(\lambda - 1\)

\[
(-\lambda^3 + 6\lambda^2 + \lambda - 6) : (\lambda - 1) = -\lambda^2 + 5\lambda + 6
\]

and the next two eigenvalues \(\lambda_2 = -1, \lambda_3 = 6\). So the spectrum of matrix A: \(\text{sp}(A) = \{-1, 1, 6\}\). For each of the eigenvalues we solve the appropriate system of linear equations

\[
\begin{bmatrix}
1 & 0 & 0 \\
3 & 1 & 2 \\
0 & 5 & 4
\end{bmatrix}
\begin{bmatrix}
\alpha_i \\
\beta_i \\
\gamma_i
\end{bmatrix} = \lambda_i
\begin{bmatrix}
\alpha_i \\
\beta_i \\
\gamma_i
\end{bmatrix}
\]
11. Mathematical background

For $\lambda_1 = -1$

\[
\begin{bmatrix}
    1 & 0 & 0 \\
    3 & 1 & 2 \\
    0 & 5 & 4
\end{bmatrix}
\begin{bmatrix}
    \alpha_1 \\
    \beta_1 \\
    \gamma_1
\end{bmatrix} = -1
\begin{bmatrix}
    \alpha_1 \\
    \beta_1 \\
    \gamma_1
\end{bmatrix}
\Rightarrow
\begin{cases}
    \alpha_1 = -\alpha_1 \\
    3\alpha_1 + \beta_1 + 2\gamma_1 = -\beta_1 \\
    5\beta_1 + 4\gamma_1 = -\gamma_1
\end{cases}
\Rightarrow
\begin{cases}
    \alpha_1 = 0 \\
    \beta_1 = -\gamma_1
\end{cases}
\]

For $\lambda_2 = 1$

\[
\begin{bmatrix}
    1 & 0 & 0 \\
    3 & 1 & 2 \\
    0 & 5 & 4
\end{bmatrix}
\begin{bmatrix}
    \alpha_2 \\
    \beta_2 \\
    \gamma_2
\end{bmatrix} = 1
\begin{bmatrix}
    \alpha_2 \\
    \beta_2 \\
    \gamma_2
\end{bmatrix}
\Rightarrow
\begin{cases}
    \alpha_2 = \alpha_2 \\
    3\alpha_2 + \beta_2 + 2\gamma_2 = \beta_2 \\
    5\beta_2 + 4\gamma_2 = \gamma_2
\end{cases}
\Rightarrow
\begin{cases}
    3\alpha_2 = -2\gamma_2 \\
    5\beta_2 = -3\gamma_2
\end{cases}
\]

and for $\lambda_3 = 6$

\[
\begin{bmatrix}
    1 & 0 & 0 \\
    3 & 1 & 2 \\
    0 & 5 & 4
\end{bmatrix}
\begin{bmatrix}
    \alpha_3 \\
    \beta_3 \\
    \gamma_3
\end{bmatrix} = 6
\begin{bmatrix}
    \alpha_3 \\
    \beta_3 \\
    \gamma_3
\end{bmatrix}
\Rightarrow
\begin{cases}
    \alpha_3 = 6\alpha_3 \\
    3\alpha_3 + \beta_3 + 2\gamma_3 = 6\beta_3 \\
    5\beta_3 + 4\gamma_3 = 6\gamma_3
\end{cases}
\Rightarrow
\begin{cases}
    \alpha_3 = 0 \\
    5\beta_3 = 2\gamma_3
\end{cases}
\]

The equations above allow to delimit the eigenvectors only to within a constant, i.e. to delimit rather the eigendirections. For instance taking $\beta_1 = 1, \gamma_2 = -15, \gamma_3 = 5$, we are getting

\[
\begin{bmatrix}
    0 \\
    1 \\
    -1
\end{bmatrix},
\begin{bmatrix}
    10 \\
    9 \\
    -15
\end{bmatrix},
\begin{bmatrix}
    0 \\
    2 \\
    5
\end{bmatrix}.
\]

Example. Find eigenvalues and eigenvectors of the following matrices

\[
A = \begin{bmatrix}
    -2 & 1 & 1 \\
    -11 & 4 & 5 \\
    -1 & 1 & 0
\end{bmatrix},
B = \begin{bmatrix}
    1 & 2 & 0 \\
    2 & 1 & 0 \\
    0 & 2 & 1
\end{bmatrix},
C = \begin{bmatrix}
    0 & 2 & 0 \\
    2 & 0 & 2 \\
    0 & 2 & 0
\end{bmatrix}
\]

Answer is: $\text{sp}(A) = \{-1,1,2\}$, $\text{sp}(B) = \{-1,1,3\}$, $\text{sp}(C) = \{0,2\sqrt{2},-2\sqrt{2}\}$. Eigenvectors:

\[
\begin{bmatrix}
    v_{1A} \\
    v_{2A} \\
    v_{3A}
\end{bmatrix} = \begin{bmatrix}
    1 \\
    0 \\
    1
\end{bmatrix},
\begin{bmatrix}
    v_{1B} \\
    v_{2B} \\
    v_{3B}
\end{bmatrix} = \begin{bmatrix}
    \frac{1}{\sqrt{3}} \\
    0 \\
    \frac{1}{\sqrt{3}}
\end{bmatrix},
\begin{bmatrix}
    v_{1C} \\
    v_{2C} \\
    v_{3C}
\end{bmatrix} = \begin{bmatrix}
    \frac{1}{\sqrt{2}} \\
    1 \\
    -1
\end{bmatrix}
\]

Check orthogonality of the vectors.

Example. Having square real matrix $A_{n\times n}$ for which $\text{sp}(A) = \{\lambda_1, \lambda_2, \ldots, \lambda_n\}$ while each eigenvalue is different, and for which each eigenvector $v_i = [x_{i1}, x_{i2}, \ldots, x_{in}]^T$, derive the similarity transformation equation.

Solution

Let the $P$ matrix contain the eigenvectors of $A$ matrix and the square $D$ matrix contain the eigenvalues of $A$ matrix

\[
P = \begin{bmatrix}
    v_1 & v_2 & \ldots & v_n
\end{bmatrix},
D = \begin{bmatrix}
    \lambda_1 & 0 & \ldots & 0 \\
    0 & \lambda_2 & \ldots & 0 \\
    \vdots & \vdots & \ddots & \vdots \\
    0 & 0 & \ldots & \lambda_n
\end{bmatrix}
\]

Thus

\[
AP = A \begin{bmatrix}
    v_1 & v_2 & \ldots & v_n
\end{bmatrix} = \begin{bmatrix}
    Av_1 & Av_2 & \ldots & Av_n
\end{bmatrix} = \begin{bmatrix}
    \lambda_1 v_1 & \lambda_2 v_2 & \ldots & \lambda_n v_n
\end{bmatrix} = PD \neq DP.
\]
Therefore, multiplying both sides by $P^{-1}$ from left side

$$P^{-1} A P = D$$

**Example.** ...

### 11.1.1 Solving linear second order equation with constant coefficients

The equation

$$y'' + by' + cy = f(x) \quad (11.59)$$

where $b$ and $c$ are constants while the function $f(x)$ is a given function in a given interval, is called linear second order equation with constant coefficients. When $f(x) \equiv 0$ the equation is called homogeneous, otherwise - inhomogeneous.

Solutions of homogeneous equations

$$y'' + by' + cy = 0 \quad (11.60)$$

one looks for in the form of exponential function

$$y = e^{rx} \quad (11.61)$$

where $r$ is unknown number which can be selected so that the function $11.61$ will satisfy the equation $11.60$. Because $y' = re^{rx}$ and $y'' = r^2e^{rx}$ so the function $11.61$ satisfy the equation only if $r$ is root of quadratic equation

$$r^2 + br + c = 0 \quad (11.62)$$

The equation $11.62$ is called *characteristic* for equation $11.60$ and depending on three possible cases of the value of discriminant one gets different solutions of the differential equation.

1. $\Delta > 0$

The equation $11.62$ has two different real roots $r_1$ and $r_2$ and the functions

$$y_1(x) = e^{r_1x} \quad y_2(x) = e^{r_2x} \quad (11.63)$$

are solutions of the $11.60$. Moreover, the functions constitute complete set of integrals of the equation, because the Wronski’s determinant

$$\begin{vmatrix} y_1 & y_2 \\ y'_1 & y'_2 \end{vmatrix} = \begin{vmatrix} e^{r_1x} & e^{r_2x} \\ r_1 e^{r_1x} & r_2 e^{r_2x} \end{vmatrix} = (r_2 - r_1)e^{(r_1+r_2)x} \neq 0 \quad (11.64)$$

General solution for this case is following

$$y = C_1 e^{r_1x} + C_2 e^{r_2x} \quad (11.65)$$

**Example.** $y'' + 5y' + 4y = 0$. Characteristic equation is following $r^2 + 5r + 4 = 0$, the discriminant $\Delta = 9$ and $r_1 = -1, r_2 = -4$. Accordingly to $11.65$ $y = C_1 e^{-x} + C_2 e^{-4x}$, which is a general integral of the equation.
2. $\Delta = 0$

Characteristic equation has in this case only one real, double root, namely $r_0 = \frac{b}{2}$. Which means we have yet only one particular integral $y_1 = e^{r_0x}$. While general integral $y = Ce^{r_0x}$, which means we can treat the constant as a variable

$$y = C(x)e^{r_0x}$$ (11.66)

Next

$$\begin{align*}
y' &= C'(x)e^{r_0x} + r_0C(x)e^{r_0x} \\
y'' &= C''(x)e^{r_0x} + 2r_0C'(x)e^{r_0x} + r_0^2C(x)e^{r_0x}
\end{align*}$$ (11.67)

Now, substituting the 11.67 and 11.66 into equation 11.59 leads to

$$C''(x) + (2r_0 + b)C'(x) + (r_0^2 + br_0 + c)C(x) = 0$$ (11.68)

Because $r_0$ is the double root of characteristic equation, therefore $2r_0 + b = 0$ and $r_0^2 + br_0 + c = 0$. Hence $C''(x) = 0$ for each $x$, and $C(x) = C_1x + C_2$, where the $C_1$ and $C_2$ are constants.

Thus, function

$$y = (C_1x + C_2)e^{r_0x}$$ (11.69)

satisfy equation 11.60 for each $C_1$ and $C_2$. One combination can be $C_1 = 1$ and $C_2 = 0$, and the $y = xe^{r_0x}$ is an integral of equation 11.60.

Integrals $y_1 = e^{r_0x}$ and $y_2 = xe^{r_0x}$ constitute complete set of integrals of the equation 11.60, because the Wronski’s determinant

$$W(x) = \begin{vmatrix} e^{r_0x} & xe^{r_0x} \\ r_0e^{r_0x} & (1 + r_0x)e^{r_0x} \end{vmatrix} = e^{2r_0x} \neq 0$$ (11.70)

for each $x$. Wherefrom the function 11.69 is for $\Delta = 0$ general solution of equation 11.60.

Example. $y'' + 4y' + 4y = 0$. Characteristic equation is following $r^2 + 4r + 4 = 0$, the discriminant $\Delta = 0$ and $r_0 = -2$. Accordingly to 11.69 $y = (C_1x + C_2)e^{-2x}$, which is a general integral of the equation.

3. $\Delta < 0$

Characteristic equation has two different and conjugated roots $r_1 = a + i\omega$ and $r_2 = a - i\omega$.

Hence the complex functions $y_1^* = e^{(a+i\omega)x}$ and $y_2^* = e^{(a-i\omega)x}$ are integrals of equation 11.60.

Accordingly to Euler’s formula

$$y_1^* = e^{ax} (\cos \omega x + i \sin \omega x)$$ (11.71)

and accordingly to the fact that if a $u(x) = u(x) + iv(x)$ is an integral of equation 11.60 then its real ($u(x)$) and imaginary ($v(x)$) components are separately integrals of the same equation in the same interval, functions

$$y_1 = e^{ax} \sin \omega x, \quad y_2 = e^{ax} \cos \omega x$$ (11.72)

are also integrals of equation 11.60. Moreover, the integrals constitute complete set of integrals, because the Wronski’s determinant

$$W(x) = \begin{vmatrix} y_1 & y_2 \\ y'_1 & y'_2 \end{vmatrix} = \omega e^{2ax} \neq 0$$ (11.73)
Consequently, the functions

$$y = e^{ax}(C_1 \sin \omega x + C_2 \cos \omega x)$$

(11.74)

are general integrals of equation 11.60 for the case where from characteristic equation \( \Delta < 0 \).

**Example.** \( y'' + 4y = 0 \). Characteristic equation is following \( r^2 + 4 = 0 \), the discriminant \( \Delta < 0 \), \( r_1 = 2i \) and \( r_2 = -2i \). \( \alpha = 0 \) and \( \omega = 2 \). Accordingly to 11.74 \( y = C_1 \sin 2x + C_2 \cos 2x \), which is a general integral of the equation.

Solutions of inhomogeneous equation 11.59.

**Example.** \( y'' + y = e^{2x} + 4x \cos x \).

The characteristic equation of so called associated homogeneous equation \( r^2 + 1 = 0 \) has two roots: \( r_1 = i \) and \( r_2 = -i \), and accordingly to equation 11.74

$$y_0 = C_1 \sin x + C_2 \cos x$$

(11.75)

which will be called General Integral (GI) of Associated Homogeneous Equation (GIAHE).

From now on we will use the theorem which says that the sum of Particular Integral (PI) of equation

$$y'' + y = e^{2x}$$

(11.76)

and of equation

$$y'' + y = 4x \cos x$$

(11.77)

equals PI of our given equation.

The GI of equation 11.76 we predict in following form

$$y_1 = ae^{2x}$$

(11.78)

from where \( y' = 2ae^{2x} \) and \( y' = 4ae^{2x} \). So we have \( y'' + y_1 = e^{2x}, \) and \( 4ae^{2x} + ae^{2x} = e^{2x} \). \( a = \frac{1}{2} \). Thus \( y_1 = \frac{1}{2}e^{2x} \) is the PI of InHomogeneous Equation (PIIHE) 11.76.

PIIHE 11.77 we predict in following form

$$y_2 = (a_1 x^2 + b_1 x + c_1) \sin x + (a_2 x^2 + b_2 x + c_2) \cos x$$

(11.79)

Wherefrom

$$y_2' = (2a_1 x + b_1) \sin x + (a_1 x^2 + b_1 x + c_1) \cos x + (2a_2 x + b_2) \cos x - (a_2 x^2 + b_2 x + c_2) \sin x$$

$$y_2'' = 2a_1 \sin x + 2(2a_1 x + b_1) \cos x - (a_1 x^2 + b_1 x + c_1) \sin x + 2a_2 \cos x - 2(2a_2 x + b_2) \sin x - (a_2 x^2 + b_2 x + c_2) \cos x$$

(11.80)

Thus \( y'' + y_2 = 4x \cos x \) and \( 2a_1 \sin x + 2(2a_1 x + b_1) \cos x + 2a_2 \cos x - 2(2a_2 x + b_2) \sin x = 4x \cos x \). It means that the following equations must be satisfied

\[
\begin{align*}
2a_1 - 2b_2 &= 0 \\
2b_1 + 2a_2 &= 0 \\
-4a_2 &= 0 \\
4a_1 &= 4
\end{align*}
\]

which leads to the conclusion that \( a_1 = 1, \ a_2 = 0, \ b_1 = 0, \ b_2 = 1 \). Assuming yet that \( c_1 = c_2 = 0 \) we are getting the
\[ y_2 = x^2 \sin x + x \cos x \]

which is the PIIHE 11.77

Finally, accordingly to the fact that \( y = y_0 + y_1 + y_2 \) the GIIHE given in the example is as follows

\[ y = C_1 \sin x + C_2 \cos x + \frac{1}{5}e^{2x} + x^2 \sin x + x \cos x \]  \hfill (11.81)