Worksheet 1 FMMC

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Exercise 1.

Demonstrate the next properties of the A and B matrices

a) The trace of a matrix is invariant under and unitary transformation. $\mathbf{tr(B) = tr(U^\dagger BU)}$.

One of the key properties of the trace is its cyclic property. Applying this property to the term $\mathrm{tr}(\mathbf{U^\dagger BU})$, we cyclically shift the matrices:

$$\mathrm{tr}(\mathbf{U^\dagger BU}) = \mathrm{tr}(\mathbf{BUU^\dagger}). \tag{1}$$

Since $\mathbf{U}$ is a unitary matrix, it satisfies the property:

$$\mathbf{U^\dagger U} = \mathbf{I}, \tag{2}$$

Substituting :

$$\mathrm{tr}(\mathbf{BUU^\dagger}) = \mathrm{tr}(\mathbf{BI}) = \mathrm{tr}(\mathbf{B}). \tag{3}$$

Thus:

$$\boxed{\mathrm{tr}(\mathbf{B}) = \mathrm{tr}(\mathbf{U^\dagger BU}),}$$

b) Proof that the inverse of a Hermitian matrix is also Hermitian

By definition:

$$\mathbf{AA^{-1}} = \mathbf{I} \tag{4}$$

Apply the conjugate transpose to both sides:

$$(\mathbf{AA^{-1}})^\dagger = \mathbf{I^\dagger} \tag{5}$$

Simplifying using the conjugate transpose properties:

$$(\mathbf{A^{-1}})^\dagger \mathbf{A^\dagger} = \mathbf{I} \tag{6}$$

Since A is Hermitian:

$$(\mathbf{A^{-1}})^\dagger \mathbf{A} = \mathbf{I} \tag{7}$$

Thus, $\mathbf{A^{-1}}$ is Hermitian:

$$\boxed{(\mathbf{A^{-1}})^\dagger = \mathbf{A^{-1}}}$$

c) If the product $C = AB$ of two Hermitian matrices is also Hermitian, then A and B commute

By definition, the product of two matrices A and B is:

$$C = AB \tag{8}$$

Since C is Hermitian, it satisfies:

$$C^\dagger = C \tag{9}$$

Apply the conjugate transpose to the product $C = AB$:

$$(AB)^\dagger = B^\dagger A^\dagger \tag{10}$$

Since A and B are Hermitian, we know that:

$$B^\dagger = B \quad \text{and} \quad A^\dagger = A \tag{11}$$

Therefore, the conjugate transpose of C becomes:

$$(AB)^\dagger = BA \tag{12}$$

Using the assumption that C is Hermitian, we have:

$$C^\dagger = C \implies BA = AB \tag{13}$$

Thus, A and B commute:

$$\boxed{AB = BA}$$

Exercise 2.

Prove the Schwarz inequality

$$|\langle\varphi_1|\varphi_2\rangle|^2 \leq \langle\varphi_1|\varphi_1\rangle\langle\varphi_2|\varphi_2\rangle$$

Definition of the vector $|\psi\rangle$:

$$|\psi\rangle = |\varphi_1\rangle - \lambda|\varphi_2\rangle,$$

where λ is a complex number.

The inner product of $|\psi\rangle$ with itself is:

$$\langle\psi|\psi\rangle = \langle\varphi_1|\varphi_1\rangle - \lambda^*\langle\varphi_1|\varphi_2\rangle - \lambda\langle\varphi_2|\varphi_1\rangle + |\lambda|^2\langle\varphi_2|\varphi_2\rangle,$$

Since the inner product is always non-negative, we have:

$$\langle\psi|\psi\rangle \geq 0.$$

Choosing $\lambda = \frac{\langle\varphi_1|\varphi_2\rangle}{\langle\varphi_2|\varphi_2\rangle}$ and substituting into the expression for $\langle\psi|\psi\rangle$:

1. The term $-\lambda^*\langle\varphi_1|\varphi_2\rangle$ becomes:

$$-\lambda^*\langle\varphi_1|\varphi_2\rangle = -\frac{\langle\varphi_1|\varphi_2\rangle^*}{\langle\varphi_2|\varphi_2\rangle}\langle\varphi_1|\varphi_2\rangle = -\frac{|\langle\varphi_1|\varphi_2\rangle|^2}{\langle\varphi_2|\varphi_2\rangle}.$$

2. The term $-\lambda\langle\varphi_2|\varphi_1\rangle$ becomes:

$$-\lambda\langle\varphi_2|\varphi_1\rangle = -\frac{\langle\varphi_1|\varphi_2\rangle}{\langle\varphi_2|\varphi_2\rangle}\langle\varphi_2|\varphi_1\rangle = -\frac{|\langle\varphi_1|\varphi_2\rangle|^2}{\langle\varphi_2|\varphi_2\rangle}.$$

3. The term $|\lambda|^2\langle\varphi_2|\varphi_2\rangle$ becomes:

$$|\lambda|^2\langle\varphi_2|\varphi_2\rangle = \left|\frac{\langle\varphi_1|\varphi_2\rangle}{\langle\varphi_2|\varphi_2\rangle}\right|^2\langle\varphi_2|\varphi_2\rangle = \frac{|\langle\varphi_1|\varphi_2\rangle|^2}{\langle\varphi_2|\varphi_2\rangle}.$$

Simplifying the expression for $\langle\psi|\psi\rangle$

$$\langle\psi|\psi\rangle = \langle\varphi_1|\varphi_1\rangle - \frac{|\langle\varphi_1|\varphi_2\rangle|^2}{\langle\varphi_2|\varphi_2\rangle} - \frac{|\langle\varphi_1|\varphi_2\rangle|^2}{\langle\varphi_2|\varphi_2\rangle} + \frac{|\langle\varphi_1|\varphi_2\rangle|^2}{\langle\varphi_2|\varphi_2\rangle}.$$

Therefore:

$$\langle\psi|\psi\rangle = \langle\varphi_1|\varphi_1\rangle - \frac{|\langle\varphi_1|\varphi_2\rangle|^2}{\langle\varphi_2|\varphi_2\rangle}.$$

Since $\langle\psi|\psi\rangle \geq 0$:

$$\langle\varphi_1|\varphi_1\rangle \geq \frac{|\langle\varphi_1|\varphi_2\rangle|^2}{\langle\varphi_2|\varphi_2\rangle}.$$

Multiply through by $\langle\varphi_2|\varphi_2\rangle$ to obtain:

$$|\langle\varphi_1|\varphi_2\rangle|^2 \leq \langle\varphi_1|\varphi_1\rangle\langle\varphi_2|\varphi_2\rangle.$$

Thus, the Schwarz inequality is proved.

Exercise 3.

In a two-dimensional vector space, consider the operator whose matrix, in an orthonormal basis $\{|1\rangle, |2\rangle\}$, is written:

$$M = \begin{pmatrix} 2 & i\sqrt{2} \\ -i\sqrt{2} & 3 \end{pmatrix}.$$

a) Is M Hermitian? Calculate its eigenvalues and eigenvectors (giving their normalized expansion in terms of the basis $\{|1\rangle, |2\rangle\}$.

The conjugate transpose of M is:

$$M^\dagger = \begin{pmatrix} 2 & i\sqrt{2} \\ -i\sqrt{2} & 3 \end{pmatrix}. \tag{14}$$

Since $M^\dagger = M$, the matrix M is Hermitian.

The eigenvalues of M are obtained from the characteristic equation:

$$\det(M - \lambda I) = 0, \tag{15}$$

where λ is the eigenvalue, and I is the identity matrix. Subtracting λ from the diagonal of M, we have:

$$M - \lambda I = \begin{pmatrix} 2-\lambda & i\sqrt{2} \\ -i\sqrt{2} & 3-\lambda \end{pmatrix}. \tag{16}$$

The determinant is:

$$\det(M - \lambda I) = (2-\lambda)(3-\lambda) - (i\sqrt{2})(-i\sqrt{2}). \tag{17}$$

Simplifying:

$$\det(M - \lambda I) = (2-\lambda)(3-\lambda) - 2. \tag{18}$$

Expanding:

$$\det(M - \lambda I) = \lambda^2 - 5\lambda + 4. \tag{19}$$

Factoring the quadratic equation:

$$\lambda^2 - 5\lambda + 4 = (\lambda - 4)(\lambda - 1). \tag{20}$$

The eigenvalues are:

$$\boxed{\lambda_1 = 4, \quad \lambda_2 = 1.} \tag{21}$$

For each eigenvalue λ, to obtain the eigenvectors $\mathbf{v}$, we solve:

$$(M - \lambda I)\mathbf{v} = 0, \tag{22}$$

Eigenvector for $\lambda_1 = 4$:

$$M - 4I = \begin{pmatrix} 2-4 & i\sqrt{2} \\ -i\sqrt{2} & 3-4 \end{pmatrix} = \begin{pmatrix} -2 & i\sqrt{2} \\ -i\sqrt{2} & -1 \end{pmatrix}. \tag{23}$$

Solving the system:

$$\begin{pmatrix} -2 & i\sqrt{2} \\ -i\sqrt{2} & -1 \end{pmatrix} \begin{pmatrix} v_1 \\ v_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}. \tag{24}$$

From the first row:

$$-2v_1 + i\sqrt{2}v_2 = 0 \implies v_2 = -i\sqrt{2}v_1. \tag{25}$$

Thus, the eigenvector is:

$$\mathbf{v}_1 = \begin{pmatrix} v_1 \\ -i\sqrt{2}v_1 \end{pmatrix} = v_1 \begin{pmatrix} 1 \\ -i\sqrt{2} \end{pmatrix} \tag{26}$$

Normalizing the eigenvector:

$$|\mathbf{v}_1| = \sqrt{|1|^2 + |-i\sqrt{2}|^2} = \sqrt{1+2} = \sqrt{3}. \tag{27}$$

Thus, the normalized eigenvector is:

$$\boxed{\mathbf{v}_1 = \frac{1}{\sqrt{3}} \begin{pmatrix} 1 \\ -i\sqrt{2} \end{pmatrix}} \tag{28}$$

Eigenvector for $\lambda_2 = 1$:

$$M - I = \begin{pmatrix} 2-1 & i\sqrt{2} \\ -i\sqrt{2} & 3-1 \end{pmatrix} = \begin{pmatrix} 1 & i\sqrt{2} \\ -i\sqrt{2} & 2 \end{pmatrix} \tag{29}$$

Solving the system:

$$\begin{pmatrix} 1 & i\sqrt{2} \\ -i\sqrt{2} & 2 \end{pmatrix} \begin{pmatrix} v_1 \\ v_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix} \tag{30}$$

From the first row:

$$v_1 + i\sqrt{2}v_2 = 0 \implies v_2 = \frac{i}{\sqrt{2}}v_1 \tag{31}$$

Thus, the eigenvector is:

$$\mathbf{v}_2 = \begin{pmatrix} v_1 \\ \frac{i}{\sqrt{2}}v_1 \end{pmatrix} = v_1 \begin{pmatrix} 1 \\ \frac{i}{\sqrt{2}} \end{pmatrix} \tag{32}$$

Normalize the eigenvector:

$$|\mathbf{v}_2| = \sqrt{|1|^2 + \left|\frac{i}{\sqrt{2}}\right|^2} = \sqrt{1 + \frac{1}{2}} = \sqrt{\frac{3}{2}} \tag{33}$$

Thus, the normalized eigenvector is:

$$\boxed{\mathbf{v}_2 = \sqrt{\frac{2}{3}} \begin{pmatrix} 1 \\ \frac{i}{\sqrt{2}} \end{pmatrix}} \tag{34}$$

Final Answer:
The eigenvalues and normalized eigenvectors are:

$$\boxed{\begin{aligned} \lambda_1 = 4, \quad \mathbf{v}_1 &= \frac{1}{\sqrt{3}}|1\rangle - i\sqrt{\frac{2}{3}}|2\rangle \qquad (35) \\ \lambda_2 = 1, \quad \mathbf{v}_2 &= \sqrt{\frac{2}{3}}|1\rangle + i\frac{1}{\sqrt{3}}|2\rangle \qquad (36) \end{aligned}}$$

b) Calculate the matrices that represent the projectors on these eigenvectors. Then verify that they satisfy the orthogonality and closure relations.

For an eigenvector $|v\rangle$, the projector P_v is defined as:

$$P_v = \frac{|v\rangle\langle v|}{\langle v|v\rangle}. \tag{37}$$

If $|v\rangle$ is normalized the projector is:

$$P_v = |v\rangle\langle v|. \tag{38}$$

The normalized eigenvectors of M are:

$$\text{For } \lambda_1 = 4: \quad |v_1\rangle = \frac{1}{\sqrt{3}} \begin{pmatrix} 1 \\ -i\sqrt{2} \end{pmatrix}, \tag{39}$$

$$\text{For } \lambda_2 = 1: \quad |v_2\rangle = \sqrt{\frac{2}{3}} \begin{pmatrix} 1 \\ \frac{i}{\sqrt{2}} \end{pmatrix}. \tag{40}$$

The projector P_1 on $|v_1\rangle$ is given by:

$$P_1 = |v_1\rangle\langle v_1|. \tag{41}$$

Substituting $|v_1\rangle$:

$$P_1 = \frac{1}{\sqrt{3}} \begin{pmatrix} 1 \\ -i\sqrt{2} \end{pmatrix} \frac{1}{\sqrt{3}} \begin{pmatrix} 1 & i\sqrt{2} \end{pmatrix}. \tag{42}$$

Simplifying the product:

$$\boxed{P_1 = \frac{1}{3} \begin{pmatrix} 1 & i\sqrt{2} \\ -i\sqrt{2} & 2 \end{pmatrix}}$$

The projector P_2 on $|v_2\rangle$ is given by:

$$P_2 = |v_2\rangle\langle v_2|. \tag{43}$$

Substituting $|v_2\rangle$:

$$P_2 = \sqrt{\frac{2}{3}} \begin{pmatrix} 1 \\ \frac{i}{\sqrt{2}} \end{pmatrix} \sqrt{\frac{2}{3}} \begin{pmatrix} 1 & -\frac{i}{\sqrt{2}} \end{pmatrix}. \tag{44}$$

Simplifying the product:

$$\boxed{P_2 = \frac{2}{3} \begin{pmatrix} 1 & -\frac{i}{\sqrt{2}} \\ \frac{i}{\sqrt{2}} & \frac{1}{2} \end{pmatrix}} \tag{45}$$

Two projectors P_1 and P_2 are orthogonal if:

$$P_1 P_2 = 0, \quad \text{and} \quad P_2 P_1 = 0. \tag{46}$$

Calculating $P_1 P_2$

We define the unscaled matrices M_1 and M_2:

$$M_1 = \begin{pmatrix} 1 & i\sqrt{2} \\ -i\sqrt{2} & 2 \end{pmatrix}, \tag{47}$$

$$M_2 = \begin{pmatrix} 1 & -\frac{i}{\sqrt{2}} \\ \frac{i}{\sqrt{2}} & \frac{1}{2} \end{pmatrix}. \tag{48}$$

The product $P_1 P_2$ is:

$$P_1 P_2 = \frac{1}{3} M_1 \cdot \frac{2}{3} M_2 = \frac{2}{9}(M_1 M_2). \tag{49}$$

Now, computing $M_1 M_2$:

$$M_1 M_2 = \begin{pmatrix} 1 & i\sqrt{2} \\ -i\sqrt{2} & 2 \end{pmatrix} \begin{pmatrix} 1 & -\frac{i}{\sqrt{2}} \\ \frac{i}{\sqrt{2}} & \frac{1}{2} \end{pmatrix}. \tag{50}$$

Calculate each component:

$$(M_1 M_2)_{11} = 1 \cdot 1 + (i\sqrt{2}) \left(-\frac{i}{\sqrt{2}} \right) = 1 + 1 = 0, \tag{51}$$

$$(M_1 M_2)_{12} = 1 \left(-\frac{i}{\sqrt{2}} \right) + (i\sqrt{2}) \cdot \frac{1}{2} = -\frac{i}{\sqrt{2}} + \frac{i\sqrt{2}}{2} = 0, \tag{52}$$

$$(M_1 M_2)_{21} = (-i\sqrt{2}) \cdot 1 + 2 \left(\frac{i}{\sqrt{2}} \right) = -i\sqrt{2} + i\sqrt{2} = 0, \tag{53}$$

$$(M_1 M_2)_{22} = (-i\sqrt{2}) \left(-\frac{i}{\sqrt{2}} \right) + 2 \cdot \frac{1}{2} = 1 + 1 = 0. \tag{54}$$

Thus:

$$M_1 M_2 = \begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix}, \quad \text{and} \quad P_1 P_2 = \frac{2}{9} M_1 M_2 = 0. \tag{55}$$

Calculating $P_2 P_1$

Similarly:

$$P_2 P_1 = \frac{2}{3} M_2 \cdot \frac{1}{3} M_1 = \frac{2}{9} (M_2 M_1). \tag{56}$$

Now, computing $M_2 M_1$:

$$M_2 M_1 = \begin{pmatrix} 1 & -\frac{i}{\sqrt{2}} \\ \frac{i}{\sqrt{2}} & \frac{1}{2} \end{pmatrix} \begin{pmatrix} 1 & i\sqrt{2} \\ -i\sqrt{2} & 2 \end{pmatrix}. \tag{57}$$

Calculating each component:

$$(M_2 M_1)_{11} = 1 \cdot 1 + \left(-\frac{i}{\sqrt{2}}\right)(-i\sqrt{2}) = 1 + 1 = 0, \tag{58}$$

$$(M_2 M_1)_{12} = 1 \cdot (i\sqrt{2}) + \left(-\frac{i}{\sqrt{2}}\right)(2) = i\sqrt{2} - i\sqrt{2} = 0, \tag{59}$$

$$(M_2 M_1)_{21} = \left(\frac{i}{\sqrt{2}}\right)(1) + \frac{1}{2}(-i\sqrt{2}) = \frac{i}{\sqrt{2}} - \frac{i\sqrt{2}}{2} = 0, \tag{60}$$

$$(M_2 M_1)_{22} = \left(\frac{i}{\sqrt{2}}\right)(i\sqrt{2}) + \frac{1}{2}(2) = -1 + 1 = 0. \tag{61}$$

Thus:

$$M_2 M_1 = \begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix}, \quad \text{and} \quad P_2 P_1 = \frac{2}{9} M_2 M_1 = 0. \tag{62}$$

We have shown that:

$$P_1 P_2 = 0, \quad \text{and} \quad P_2 P_1 = 0. \tag{63}$$

Thus, P_1 and P_2 are orthogonal

The closure relation states that the sum of projectors P_1 and P_2 is equal to the identity matrix I.

Adding the projectors:

$$P_1 + P_2 = \frac{1}{3} \begin{pmatrix} 1 & i\sqrt{2} \\ -i\sqrt{2} & 2 \end{pmatrix} + \frac{2}{3} \begin{pmatrix} 1 & -\frac{i}{\sqrt{2}} \\ \frac{i}{\sqrt{2}} & \frac{1}{2} \end{pmatrix} \tag{64}$$

$$(P_1 + P_2)_{11} = \frac{1}{3} \cdot 1 + \frac{2}{3} \cdot 1 = 1, \tag{65}$$

$$(P_1 + P_2)_{12} = \frac{1}{3} \cdot i\sqrt{2} + \frac{2}{3} \cdot \left(-\frac{i}{\sqrt{2}}\right) = \frac{i\sqrt{2}}{3} - \frac{i\sqrt{2}}{3} = 0, \tag{66}$$

$$(P_1 + P_2)_{21} = \frac{1}{3} \cdot (-i\sqrt{2}) + \frac{2}{3} \cdot \frac{i}{\sqrt{2}} = -\frac{i\sqrt{2}}{3} + \frac{i\sqrt{2}}{3} = 0, \tag{67}$$

$$(P_1 + P_2)_{22} = \frac{1}{3} \cdot 2 + \frac{2}{3} \cdot \frac{1}{2} = \frac{2}{3} + \frac{1}{3} = 1. \tag{68}$$

Combining all components, we find:

$$P_1 + P_2 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = I. \tag{69}$$

We have verified the closure relation:

$$\boxed{P_1 + P_2 = I.}$$

Exercise 4.

Consider a physical system whose three-dimensional state space is spanned by the orthonormal basis formed by three kets $|u_1\rangle, |u_2\rangle, |u_3\rangle$. In the basis of these three vectors, taken in this order, the following operators are defined by:

$$H = \hbar\omega_0 \begin{pmatrix} 1 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & 2 \end{pmatrix}, \quad A = a \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}, \quad B = b \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$

a) Are A, H and B hermitian?

To determine whether the matrices H, A, and B are Hermitian, it is necessary to verify if each matrix equals its conjugate transpose. Since all the elements of these matrices are real, their conjugate is identical to the original matrix. Furthermore, because the matrices are symmetric with respect to the diagonal, their transpose is also equal to the original matrix. Therefore, the matrices H, A, and B are all Hermitian.

b) Calculate the possible commutators [H,A], [H,B] and [A,B]

The commutator $[H, A]$ is:

$$[H, A] = HA - AH \tag{70}$$

Calculating HA:

$$HA = \hbar\omega_0 \begin{pmatrix} 1 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & 2 \end{pmatrix} \cdot a \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} = a\hbar\omega_0 \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 2 \\ 0 & 2 & 0 \end{pmatrix} \tag{71}$$

Calculating AH:

$$AH = a \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \cdot \hbar\omega_0 \begin{pmatrix} 1 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & 2 \end{pmatrix} = a\hbar\omega_0 \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 2 \\ 0 & 2 & 0 \end{pmatrix} \tag{72}$$

Since $HA = AH$, it follows that:

$$[H, A] = HA - AH = 0 \tag{73}$$

Therefore H and A commute.

The commutator $[H, B]$ is:

$$[H, B] = HB - BH \tag{74}$$

Calculating HB:

$$HB = \hbar\omega_0 \begin{pmatrix} 1 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & 2 \end{pmatrix} \cdot b \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} = b\hbar\omega_0 \begin{pmatrix} 0 & 1 & 0 \\ 2 & 0 & 0 \\ 0 & 0 & 2 \end{pmatrix} \tag{75}$$

Calculating BH:

$$BH = b \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \cdot \hbar\omega_0 \begin{pmatrix} 1 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & 2 \end{pmatrix} = b\hbar\omega_0 \begin{pmatrix} 0 & 2 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 2 \end{pmatrix} \tag{76}$$

Computing $[H, B]$:

$$[H, B] = b\hbar\omega_0 \begin{pmatrix} 0 & 1 & 0 \\ 2 & 0 & 0 \\ 0 & 0 & 2 \end{pmatrix} - b\hbar\omega_0 \begin{pmatrix} 0 & 2 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 2 \end{pmatrix} = b\hbar\omega_0 \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \tag{77}$$

Therefore, H and B do not commute.

The commutator $[A, B]$ is:

$$[A, B] = AB - BA \tag{78}$$

Calculating AB:

$$AB = a \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \cdot b \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} = ab \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix} \tag{79}$$

Calculating BA:

$$BA = b \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \cdot a \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} = ab \begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix} \tag{80}$$

Computing $[A, B]$:

$$[A, B] = ab \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix} - ab \begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix} = ab \begin{pmatrix} 0 & 1 & -1 \\ -1 & 0 & 1 \\ 1 & -1 & 0 \end{pmatrix} \tag{81}$$

Therefore, A and B do not commute.

c) Give a basis of eigenvectors common to H and A

Eigenvectors of H:

$$H = \hbar\omega_0 \begin{pmatrix} 1 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & 2 \end{pmatrix}$$

The eigenvectors are:

$$H\mathbf{v} = \lambda\mathbf{v} \tag{82}$$

where $\mathbf{v} = \begin{pmatrix} x \\ y \\ z \end{pmatrix}$ and λ is the eigenvalue.

Eigenvector Calculation

$$H\mathbf{v} = \hbar\omega_0 \begin{pmatrix} 1 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & 2 \end{pmatrix} \cdot \begin{pmatrix} x \\ y \\ z \end{pmatrix} \tag{83}$$

$$= \begin{pmatrix} \hbar\omega_0 \cdot x \\ 2\hbar\omega_0 \cdot y \\ 2\hbar\omega_0 \cdot z \end{pmatrix} \tag{84}$$

Eigenvalues and Eigenvectors

1. For $\mathbf{v}_1 = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}$:

$$H\mathbf{v}_1 = \hbar\omega_0 \begin{pmatrix} 1 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & 2 \end{pmatrix} \cdot \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \tag{85}$$

$$= \begin{pmatrix} \hbar\omega_0 \\ 0 \\ 0 \end{pmatrix} \tag{86}$$

$$= \hbar\omega_0 \cdot \mathbf{v}_1 \tag{87}$$

2. For $\mathbf{v}_2 = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}$:

$$H\mathbf{v}_2 = \hbar\omega_0 \begin{pmatrix} 1 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & 2 \end{pmatrix} \cdot \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} \tag{88}$$

$$= \begin{pmatrix} 0 \\ 2\hbar\omega_0 \\ 0 \end{pmatrix} \tag{89}$$

$$= 2\hbar\omega_0 \cdot \mathbf{v}_2 \tag{90}$$

3. For $\mathbf{v}_3 = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$:

$$H\mathbf{v}_3 = \hbar\omega_0 \begin{pmatrix} 1 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & 2 \end{pmatrix} \cdot \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \tag{91}$$

$$= \begin{pmatrix} 0 \\ 0 \\ 2\hbar\omega_0 \end{pmatrix} \tag{92}$$

$$= 2\hbar\omega_0 \cdot \mathbf{v}_3 \tag{93}$$

Eigenvectors of A

$$A = a \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}$$

The eigenvectors are:

$$A\mathbf{e} = \lambda\mathbf{e} \tag{94}$$

where $\mathbf{v} = \begin{pmatrix} x \\ y \\ z \end{pmatrix}$ and λ is the eigenvalue.

Characteristic Polynomial

$$\det(A - \lambda I) = \det\left(\begin{pmatrix} 1-\lambda & 0 & 0 \\ 0 & -\lambda & 1 \\ 0 & 1 & -\lambda \end{pmatrix}\right) \tag{95}$$

$$= (1-\lambda)\det\begin{pmatrix} -\lambda & 1 \\ 1 & -\lambda \end{pmatrix} \tag{96}$$

$$= (1-\lambda)(\lambda^2 - 1) \tag{97}$$

$$= (1-\lambda)(\lambda - 1)(\lambda + 1) \tag{98}$$

The eigenvalues are $\lambda_1 = 1$ and $\lambda_2 = -1$.

Eigenvectors

1. For $\lambda_1 = 1$:

$$(A - I)\mathbf{e} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & -1 & 1 \\ 0 & 1 & -1 \end{pmatrix} \mathbf{e} = 0 \tag{99}$$

The eigenvector for $\lambda_1 = 1$ is:

$$\mathbf{e}_1 = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}$$

2. For $\lambda_2 = -1$:

$$(A+I)\mathbf{e} = \begin{pmatrix} 2 & 0 & 0 \\ 0 & 1 & 1 \\ 0 & 1 & 1 \end{pmatrix} \mathbf{e} = 0 \tag{100}$$

To solve this system, we find that the eigenvectors corresponding to $\lambda_2 = -1$ are:

$$\mathbf{e}_2 = \begin{pmatrix} 0 \\ 1 \\ -1 \end{pmatrix}, \quad \mathbf{e}_3 = \begin{pmatrix} 0 \\ 1 \\ 1 \end{pmatrix}$$

Summary

1. Eigenvectors and Eigenvalues of H:

$$\mathbf{v}_1 = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}, \quad \lambda_1 = \hbar\omega_0 \tag{101}$$

$$\mathbf{v}_2 = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}, \quad \lambda_2 = 2\hbar\omega_0 \tag{102}$$

$$\mathbf{v}_3 = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}, \quad \lambda_3 = 2\hbar\omega_0 \tag{103}$$

2. Eigenvectors and Eigenvalues of A:

$$\mathbf{e}_1 = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}, \quad \lambda_1 = 1 \tag{104}$$

$$\mathbf{e}_2 = \begin{pmatrix} 0 \\ 1 \\ -1 \end{pmatrix}, \quad \lambda_2 = -1 \tag{105}$$

$$\mathbf{e}_3 = \begin{pmatrix} 0 \\ 1 \\ 1 \end{pmatrix}, \quad \lambda_2 = -1 \tag{106}$$

Since $\mathbf{e}_1$ is an eigenvector of both H and A, it is a common eigenvector. For the other two eigenvectors:

$$H\mathbf{e}_3 = \frac{1}{\sqrt{2}} H \begin{pmatrix} 0 \\ 1 \\ 1 \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 \\ 2\hbar\omega_0 \\ 2\hbar\omega_0 \end{pmatrix} = \frac{2\hbar\omega_0}{\sqrt{2}} \begin{pmatrix} 0 \\ 1 \\ 1 \end{pmatrix} = 2\hbar\omega_0 \, \mathbf{e}_3.$$

Similarly,

$$H\mathbf{e}_2 = \frac{1}{\sqrt{2}} H \begin{pmatrix} 0 \\ 1 \\ -1 \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 \\ 2\hbar\omega_0 \\ -2\hbar\omega_0 \end{pmatrix} = \frac{2\hbar\omega_0}{\sqrt{2}} \begin{pmatrix} 0 \\ 1 \\ -1 \end{pmatrix} = 2\hbar\omega_0 \, \mathbf{e}_2.$$

Thus, the common eigenvectors of H and A are:

$$\mathbf{e}_1 = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}, \quad \mathbf{e}_3 = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 \\ 1 \\ 1 \end{pmatrix}, \quad \mathbf{e}_2 = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 \\ 1 \\ -1 \end{pmatrix}.$$

(d) Choose a Complete Set of Commuting Observables (CSCO)

To form a CSCO, we need a set of observables that commute with each other and whose simultaneous eigenbasis spans the entire Hilbert space.

Therefore a suitable CSCO is:

$$\{H, A\}.$$

With a common eigenbasis

$$\{\mathbf{v}_1, \frac{\mathbf{v}_2 + \mathbf{v}_3}{\sqrt{2}}, \frac{\mathbf{v}_2 - \mathbf{v}_3}{\sqrt{2}}\}$$

Exercise 5:

Calculate the Fourier transform of the following functions:

a) A "wave packet":

$$\Psi(x) = \begin{cases} he^{-ik_0 x} & \text{if } -d/2 \leq x \leq d/2, \\ 0 & \text{otherwise (rest).} \end{cases}$$

The Fourier transform of $\tilde{\Psi}(k)$ is defined as:

$$\tilde{\Psi}(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \Psi(x) e^{-ikx} \, dx. \tag{107}$$

Since $\Psi(x) = he^{-ik_0x}$ only within the interval $-\frac{d}{2} \leq x \leq \frac{d}{2}$, the integral is:

$$\tilde{\Psi}(k) = \frac{1}{\sqrt{2\pi}} \int_{-\frac{d}{2}}^{\frac{d}{2}} he^{-ik_0x} e^{-ikx}\, dx. \tag{108}$$

Combining the exponents:

$$\tilde{\Psi}(k) = \frac{1}{\sqrt{2\pi}} h \int_{-\frac{d}{2}}^{\frac{d}{2}} e^{-i(k+k_0)x}\, dx. \tag{109}$$

Solving the integral
The integral of the exponential function is:

$$\int e^{-iax}\, dx = -\frac{e^{-iax}}{ia}, \quad \text{for } a \neq 0.$$

Therefore:

$$\tilde{\Psi}(k) = -\frac{h}{\sqrt{2\pi}} \left[\frac{e^{-i(k+k_0)x}}{i(k+k_0)} \right]_{-\frac{d}{2}}^{\frac{d}{2}}. \tag{110}$$

Substituting the limits:

$$\tilde{\Psi}(k) = -\frac{h}{\sqrt{2\pi}} \left(\frac{e^{-i(k+k_0)\frac{d}{2}} - e^{-i(k+k_0)\left(-\frac{d}{2}\right)}}{i(k+k_0)} \right). \tag{111}$$

Simplifying the exponents:

$$\tilde{\Psi}(k) = -\frac{h}{\sqrt{2\pi}} \left(\frac{e^{-i(k+k_0)\frac{d}{2}} - e^{i(k+k_0)\frac{d}{2}}}{i(k+k_0)} \right). \tag{112}$$

The identity for the sine function is:

$$e^{-ia} - e^{ia} = -2i \sin(a).$$

Substituting this in equation 112:

$$\tilde{\Psi}(k) = -\frac{h}{\sqrt{2\pi}} \left(\frac{-2i \sin\left((k+k_0)\frac{d}{2}\right)}{i(k+k_0)} \right). \tag{113}$$

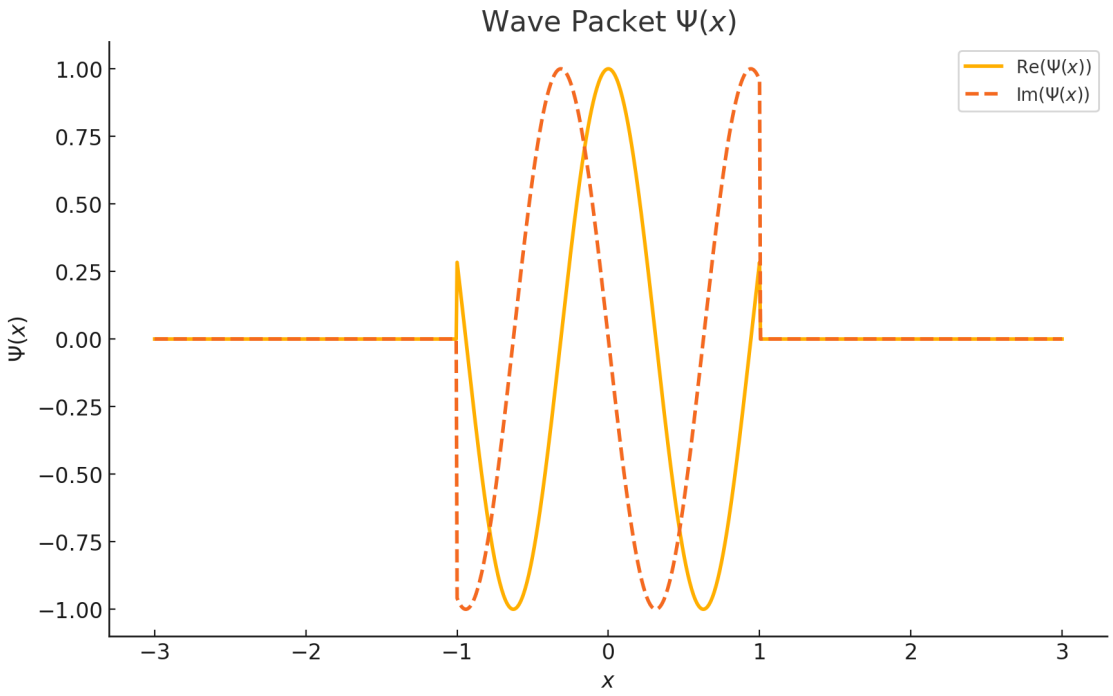
The Fourier transform of the wave packet $\Psi(x)$ is:

$$\boxed{\tilde{\Psi}(k) = \frac{2h}{\sqrt{2\pi}} \frac{\sin\left((k+k_0)\frac{d}{2}\right)}{k+k_0}.} \tag{114}$$

To represent $\Psi(x)$ the Euler's identity can be used:

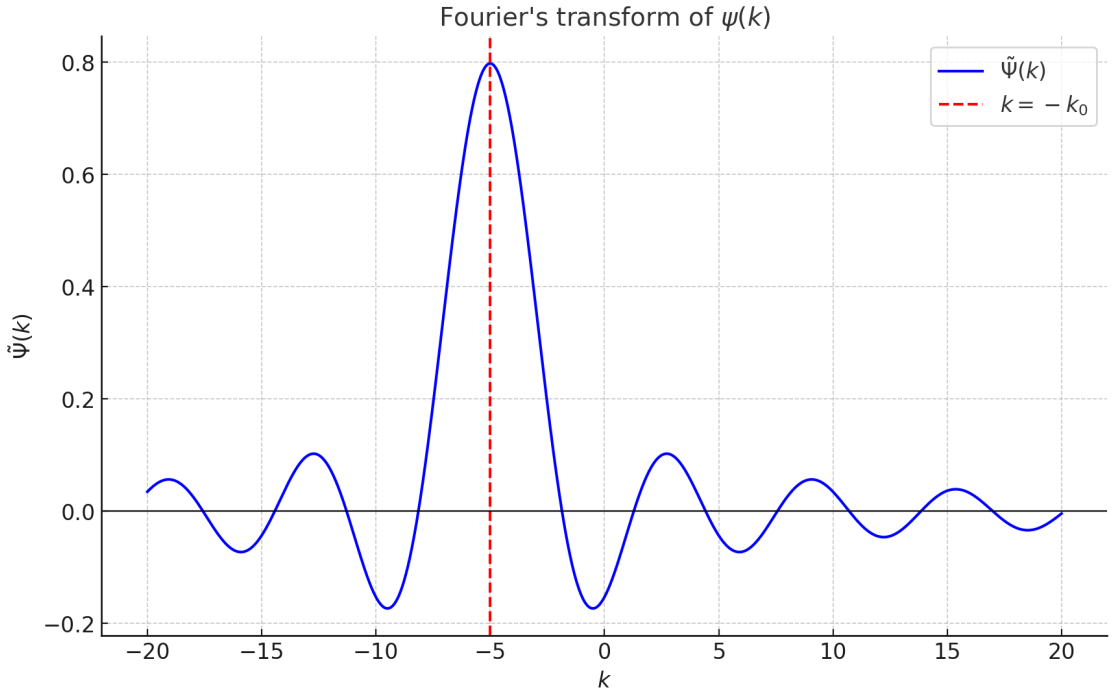
$$e^{-ik_0x} = cos(k_0x) - isen(k_0x) \tag{115}$$

Giving an arbitrary value of $k_0 = 5$ and $d = 2$:



The real part is represented in orange and the imaginary part in red. Within the interval, the function oscillates periodically (cosine and sine). Outside the interval, the function abruptly disappears, remaining at zero

The representation $\tilde{\Psi}(k)$ with $k_0 = 5$ and $d = 2$ is:



As it is shown in equation 114, when k is equal to k_0 the function has no value since it is a $\frac{0}{0}$ indetermination. But the value of the function tends to $\frac{2h}{\sqrt{2\pi}}$, which in this case is 0.8 as shown in the graph

b) A gaussian function:

$$\Psi(k) = ce^{-\frac{a^2}{4}(k-k_0)^2}, \quad c = \frac{\sqrt{a}}{(2\pi)^{1/4}}$$

By definition, the *inverse Fourier transform* is:

$$\Psi(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \Psi(k) e^{ikx}\, dk. \tag{116}$$

Substituting $\Psi(k)$:

$$\Psi(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \left(ce^{-\frac{a^2}{4}(k-k_0)^2} \right) e^{ikx}\, dk. \tag{117}$$

Using a change of variable:

$$q = k - k_0 \implies k = q + k_0, \quad dk = dq. \tag{118}$$

Therefore:

$$\Psi(x) = \frac{c}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{-\frac{a^2}{4}q^2} \cdot e^{ix(q+k_0)}\, dq. \tag{119}$$

Taking e^{ixk_0} out of the integral:

$$\Psi(x) = \frac{c}{\sqrt{2\pi}} e^{ixk_0} \int_{-\infty}^{\infty} e^{-\frac{a^2}{4}q^2} \cdot e^{ixq}\, dq. \tag{120}$$

The general Gaussian integral of this form is:

$$\int_{-\infty}^{\infty} e^{-\alpha q^2} e^{i\beta q}\, dq = e^{\frac{\beta^2}{4\alpha}} \sqrt{\frac{\pi}{\alpha}} \tag{121}$$

Proof. Evaluating the integral:

$$\int_{-\infty}^{\infty} e^{-\alpha x^2 + i\beta x}\, dx$$

Rewriting the exponent:

$$-\alpha x^2 + i\beta x = -\alpha \left(x^2 - \frac{i\beta}{\alpha} x \right)$$

Completing the square:

$$-\alpha\left(x^2-\frac{i\beta}{\alpha}x\right)=-\alpha\left(\left(x-\frac{i\beta}{2\alpha}\right)^2-\frac{\beta^2}{4\alpha^2}\right)$$

Simplifying:

$$-\alpha\left(\left(x-\frac{i\beta}{2\alpha}\right)^2-\frac{\beta^2}{4\alpha^2}\right)=-\alpha\left(x-\frac{i\beta}{2\alpha}\right)^2+\frac{\beta^2}{4\alpha}$$

Change of variable:

$$u=x-\frac{i\beta}{2\alpha},\quad dx=d\nu$$

The integral becomes:

$$\int_{-\infty}^{\infty}e^{-\alpha\nu^2+\frac{\beta^2}{4\alpha}}d\nu=e^{\frac{\beta^2}{4\alpha}}\int_{-\infty}^{\infty}e^{-\alpha\nu^2}d\nu$$

Using the Gaussian integral formula:

$$\int_{-\infty}^{\infty}e^{-\alpha\nu^2}d\nu=\sqrt{\frac{\pi}{\alpha}}$$

The final result is:

$$\int_{-\infty}^{\infty}e^{-\alpha x^2+i\beta x}\,dx=e^{\frac{\beta^2}{4\alpha}}\sqrt{\frac{\pi}{\alpha}}.$$

□

Applying this to equation 120 with $\alpha=\frac{a^2}{4}$ and $\beta=x$:

$$\Psi(x)=\frac{c}{\sqrt{2\pi}}e^{ixk_0}\cdot\sqrt{\frac{\pi\cdot 4}{a^2}}\cdot e^{-\frac{x^2}{a^2}}. \tag{122}$$

Simplifying the constants:

$$\Psi(x)=\frac{\sqrt{2}}{a}c\cdot e^{\left(ixk_0-\left(\frac{x}{a}\right)^2\right)}. \tag{123}$$

Substituting $c=\frac{\sqrt{a}}{(2\pi)^{1/4}}$:

$$\boxed{\psi(x)=\frac{\sqrt{2}}{\sqrt{a}(2\pi)^{1/4}}e^{\left(ixk_0-\left(\frac{x}{a}\right)^2\right)}} \tag{124}$$

To check if the function $\Psi(k)$ is normalized, we must ensure that the integral of $|\Psi(k)|^2$ over the entire domain is equal to 1:

$$\int_{-\infty}^{\infty}|\Psi(k)|^2\,dk=1. \tag{125}$$

The definition of $\Psi(k)$ is:

$$\Psi(k) = c\, e^{-\frac{a^2}{4}(k-k_0)^2}, \quad c = \frac{\sqrt{a}}{(2\pi)^{1/4}}. \tag{126}$$

Calculating $|\Psi(k)|^2$

$$|\Psi(k)|^2 = \left(c\, e^{-\frac{a^2}{4}(k-k_0)^2}\right)^2 \tag{127}$$

$$= c^2\, e^{-\frac{a^2}{2}(k-k_0)^2}. \tag{128}$$

Normalization condition:

$$\int_{-\infty}^{\infty} c^2\, e^{-\frac{a^2}{2}(k-k_0)^2} dk = 1 \tag{129}$$

$$c^2 \int_{-\infty}^{\infty} e^{-\frac{a^2}{2}(k-k_0)^2} dk = 1 \tag{130}$$

Using a change of variable

$$u = k - k_0 \implies dk = du \tag{131}$$

$$\int_{-\infty}^{\infty} e^{-\frac{a^2}{2}(k-k_0)^2}\, dk = \int_{-\infty}^{\infty} e^{-\frac{a^2}{2}u^2}\, du. \tag{132}$$

Using the Gaussian integral

$$\int_{-\infty}^{\infty} e^{-\alpha u^2}\, du = \sqrt{\frac{\pi}{\alpha}}, \quad \text{for} \quad \alpha > 0. \tag{133}$$

In this case, $\alpha = \frac{a^2}{2}$, so we have:

$$c^2 \int_{-\infty}^{\infty} e^{-\frac{a^2}{2}u^2}\, du = c^2 \sqrt{\frac{\pi}{\frac{a^2}{2}}} \tag{134}$$

$$= c^2 \sqrt{\frac{2\pi}{a^2}} \tag{135}$$

$$= c^2 \frac{\sqrt{2\pi}}{a}. \tag{136}$$

Substituting into the normalization condition:

$$c^2\, \frac{\sqrt{2\pi}}{a} = 1 \tag{137}$$

$$c^2 = \frac{a}{(2\pi)^{1/2}} \tag{138}$$

$$c = \frac{\sqrt{a}}{(2\pi)^{1/4}} \tag{139}$$

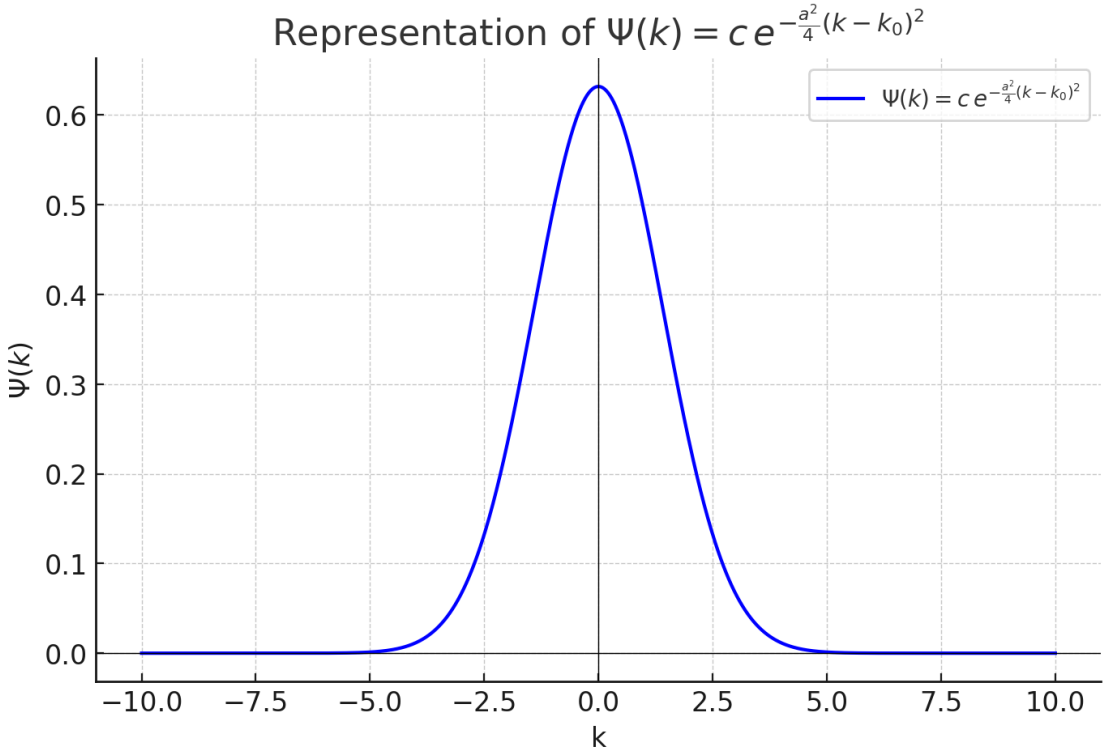
We have verified that the constant c is correctly defined as:

$$\boxed{c = \frac{\sqrt{a}}{(2\pi)^{1/4}}.}$$

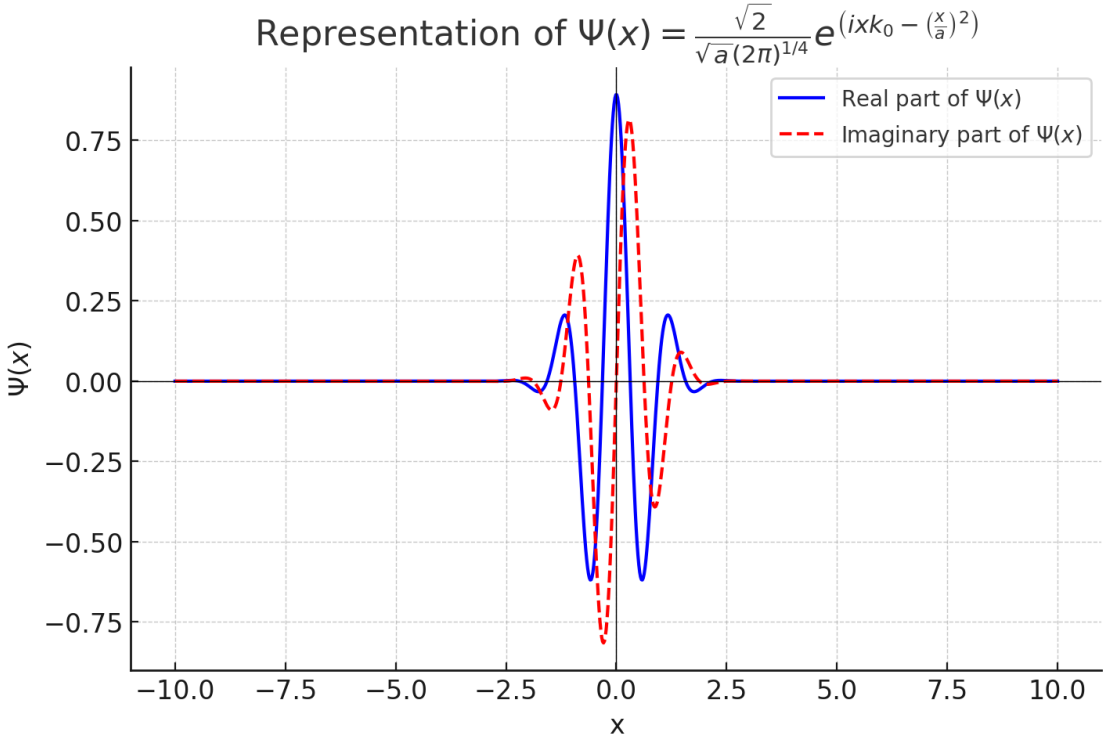
This ensures that the normalization condition is satisfied:

$$\int_{-\infty}^{\infty} |\Psi(k)|^2 \, dk = 1. \tag{140}$$

The representation of $\Psi(k)$ with $k_0 = 0$ and $a = 1$ is:



The representation of $\Psi(x)$ with $k_0 = 0$ and $a = 1$ is:



Worksheet 2 FMMC

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Exercise 1: Consider a system described by the following Hamiltonian (H_0) and where a perturbation (described by H_p) is applied.

$$H_0 = \begin{pmatrix} 1 & -1 & 0 \\ -1 & 1 & 0 \\ 0 & 0 & 2 \end{pmatrix}, \qquad H_p = \lambda \begin{pmatrix} 1 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 1 \end{pmatrix}.$$

a) Calculate the energy of all levels up to second order perturbation theory

Eigenvalues of H_0

$$\det(H_0 - \mu I) = 0$$

$$\begin{vmatrix} 1-\mu & -1 & 0 \\ -1 & 1-\mu & 0 \\ 0 & 0 & 2-\mu \end{vmatrix} = (1-\mu)(1-\mu)(2-\mu) - (-1)(-1)(2-\mu) = 0$$

$$(1-\mu)(1-\mu)(2-\mu) - (2-\mu) = 0$$

$$((1-\mu)^2 - 1)(2-\mu) = 0 \implies \mu = 2$$

$$(1-\mu)^2 - 1 = 0$$

$$\mu^2 - 2\mu + 1 - 1 = 0$$

$$\mu(\mu - 2) = 0 \implies \mu = 0 \text{ and } \mu = 2$$

Therefore, $\mu_1 = 0$ and $\mu_2 = 2, \mu_3 = 2$.
There is one non-degenerate state and one degenerate state.

The eigenvalues correspond to the energies:

$$E_1^{(0)} = 0, \quad E_2^{(0)} = 2, \quad E_3^{(0)} = 2$$

Eigenvectors of H_0

With $\mu_1 = 0$:

$$(H_0 - 0I)|\psi_1\rangle = 0 \implies \begin{pmatrix} 1 & -1 & 0 \\ -1 & 1 & 0 \\ 0 & 0 & 2 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}$$

From this, $x - y = 0$ and $2z = 0$. Therefore, $x = y$ and $z = 0$. The eigenvector is:

$$|\psi_1\rangle = \begin{pmatrix} 1 \\ 1 \\ 0 \end{pmatrix}.$$

With $\mu_2 = 2$ and $\mu_3 = 2$:

$$(H_0 - 2I)|\psi\rangle = 0 \implies \begin{pmatrix} -1 & -1 & 0 \\ -1 & -1 & 0 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}.$$

From this, $-x - y = 0$. Therefore, $x = -y$ and z is arbitrary. The eigenvectors are:

$$|\psi_2\rangle = \begin{pmatrix} 1 \\ -1 \\ 0 \end{pmatrix}, \quad |\psi_3\rangle = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}.$$

So the normalized eigenvectors are:

$$|\psi_1^{(0)}\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \\ 0 \end{pmatrix}, \quad |\psi_2^{(0)}\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \\ 0 \end{pmatrix}, \quad |\psi_3^{(0)}\rangle = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$$

Perturbation theory first order

For the non-degenerate state with $E_1^{(0)} = 0$:

$$E_1^{(1)} = \langle\psi_1^{(0)}|H_p|\psi_1^{(0)}\rangle.$$

Calculating $H_p|\psi_1^{(0)}\rangle$:

$$|\psi_1^{(0)}\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \\ 0 \end{pmatrix}.$$

$$H_p|\psi_1^{(0)}\rangle = \lambda \begin{pmatrix} 1 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 1 \end{pmatrix} \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \\ 0 \end{pmatrix} = \frac{\lambda}{\sqrt{2}} \begin{pmatrix} 1+0 \\ 1 \\ 1+0 \end{pmatrix} = \frac{\lambda}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix}.$$

Therefore:

$$E_1^{(1)} = \langle\psi_1^{(0)}|H_p|\psi_1^{(0)}\rangle = \frac{1}{\sqrt{2}}(1,1,0) \cdot \frac{\lambda}{\sqrt{2}}(1,1,1) = \frac{\lambda}{2}(1+1) = \lambda.$$

For the degenerate levels $E_2^{(0)} = E_3^{(0)} = 2$, we must build the perturbation matrix with basis $\{|\psi_2^{(0)}\rangle, |\psi_3^{(0)}\rangle\}$:

$$M = \begin{pmatrix} \langle\psi_2^{(0)}|H_p|\psi_2^{(0)}\rangle & \langle\psi_2^{(0)}|H_p|\psi_3^{(0)}\rangle \\ \langle\psi_3^{(0)}|H_p|\psi_2^{(0)}\rangle & \langle\psi_3^{(0)}|H_p|\psi_3^{(0)}\rangle \end{pmatrix}.$$

Calculating the elements:

$$|\psi_2^{(0)}\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\-1\\0\end{pmatrix}, \quad |\psi_3^{(0)}\rangle = \begin{pmatrix}0\\0\\1\end{pmatrix}.$$

1. $\langle\psi_2^{(0)}|H_p|\psi_2^{(0)}\rangle$:

$$H_p|\psi_2^{(0)}\rangle = \lambda\begin{pmatrix}1&0&1\\0&1&0\\1&0&1\end{pmatrix}\frac{1}{\sqrt{2}}\begin{pmatrix}1\\-1\\0\end{pmatrix} = \frac{\lambda}{\sqrt{2}}\begin{pmatrix}1\\-1\\1\end{pmatrix}.$$

$$\langle\psi_2^{(0)}|H_p|\psi_2^{(0)}\rangle = \frac{1}{\sqrt{2}}(1,-1,0)\cdot\frac{\lambda}{\sqrt{2}}(1,-1,1) = \frac{\lambda}{2}(1+1+0) = \lambda.$$

2. $\langle\psi_3^{(0)}|H_p|\psi_3^{(0)}\rangle$:

$$H_p|\psi_3^{(0)}\rangle = \lambda\begin{pmatrix}1&0&1\\0&1&0\\1&0&1\end{pmatrix}\begin{pmatrix}0\\0\\1\end{pmatrix} = \lambda\begin{pmatrix}1\\0\\1\end{pmatrix}.$$

$$\langle\psi_3^{(0)}|H_p|\psi_3^{(0)}\rangle = (0,0,1)\cdot\lambda(1,0,1) = \lambda.$$

3. $\langle\psi_2^{(0)}|H_p|\psi_3^{(0)}\rangle$:

$$\langle\psi_2^{(0)}|H_p|\psi_3^{(0)}\rangle = \frac{1}{\sqrt{2}}(1,-1,0)\cdot\lambda(1,0,1) = \frac{\lambda}{\sqrt{2}}.$$

4. $\langle\psi_3^{(0)}|H_p|\psi_2^{(0)}\rangle = \frac{\lambda}{\sqrt{2}}$.

The matrix in the degenerate subspace is:

$$M = \begin{pmatrix}\lambda & \frac{\lambda}{\sqrt{2}}\\ \frac{\lambda}{\sqrt{2}} & \lambda\end{pmatrix}.$$

Diagonalizing the matrix:

$$\det(M-\mu I) = (\lambda-\mu)^2 - \frac{\lambda^2}{2} = 0.$$

Then:

$$(\lambda-\mu)^2 = \frac{\lambda^2}{2} \implies \lambda-\mu = \pm\frac{\lambda}{\sqrt{2}}.$$

Therefore:

$$\mu_1 = \lambda(1+\tfrac{1}{\sqrt{2}}), \quad \mu_2 = \lambda(1-\tfrac{1}{\sqrt{2}}).$$

They are the first order corrections for the degenerate levels with $E^{(0)} = 2$. Then the energies up to first orderfor these states are:

$$E_2 = 2+\lambda\left(1+\frac{1}{\sqrt{2}}\right), \quad E_3 = 2+\lambda\left(1-\frac{1}{\sqrt{2}}\right).$$

Perturbation theory second order

For the non-degenerate state $|\psi_1^{(0)}\rangle$ with energy $E_1^{(0)} = 0$:

The second order correction is:

$$E_1^{(2)} = \sum_{m \neq 1} \frac{|\langle \psi_m^{(0)} | H_p | \psi_1^{(0)} \rangle|^2}{E_1^{(0)} - E_m^{(0)}}.$$

Substituting the energy of the other states:

$$E_1^{(2)} = \frac{|\langle \psi_2^{(0)} | H_p | \psi_1^{(0)} \rangle|^2}{0-2} + \frac{|\langle \psi_3^{(0)} | H_p | \psi_1^{(0)} \rangle|^2}{0-2}.$$

Calculating $\langle \psi_2^{(0)} | H_p | \psi_1^{(0)} \rangle$ and $\langle \psi_3^{(0)} | H_p | \psi_1^{(0)} \rangle$:

From previous steps:

$$H_p |\psi_1^{(0)}\rangle = \frac{\lambda}{\sqrt{2}}(1,1,1)^T.$$

Then:

$$\langle \psi_2^{(0)} | H_p | \psi_1^{(0)} \rangle = \frac{1}{\sqrt{2}}(1,-1,0) \cdot \frac{\lambda}{\sqrt{2}}(1,1,1) = \frac{\lambda}{2}(1-1+0) = 0.$$

$$\langle \psi_3^{(0)} | H_p | \psi_1^{(0)} \rangle = (0,0,1) \cdot \frac{\lambda}{\sqrt{2}}(1,1,1) = \frac{\lambda}{\sqrt{2}}.$$

Therefore:

$$E_1^{(2)} = \frac{|0|^2}{-2} + \frac{(\lambda/\sqrt{2})^2}{-2} = \frac{\lambda^2/2}{-2} = -\frac{\lambda^2}{4}.$$

So the energy up to second order of the first state is:

$$E_1 \approx 0 + \lambda - \frac{\lambda^2}{4}.$$

After first-order diagonalization, the new eigenstates in the degenerate subspace are:

$$|\psi_2'^{(0)}\rangle = \frac{1}{\sqrt{2}}\left(|\psi_2^{(0)}\rangle + |\psi_3^{(0)}\rangle\right),$$
$$|\psi_3'^{(0)}\rangle = \frac{1}{\sqrt{2}}\left(|\psi_2^{(0)}\rangle - |\psi_3^{(0)}\rangle\right).$$

The second-order correction for $|\psi_2'^{(0)}\rangle$ is given by:

$$E_2^{(2)} = \frac{|\langle \psi_1^{(0)} | H_p | \psi_2'^{(0)} \rangle|^2}{E_2^{(0)} - E_1^{(0)}} = \frac{|\langle \psi_1^{(0)} | H_p | \psi_2'^{(0)} \rangle|^2}{2-0}. \tag{141}$$

Computing the matrix element $\langle \psi_1^{(0)} | H_p | \psi_2'^{(0)} \rangle$:

$$\langle \psi_1^{(0)} | H_p | \psi_2'^{(0)} \rangle = \langle \psi_1^{(0)} | H_p \frac{1}{\sqrt{2}}\left(|\psi_2^{(0)}\rangle + |\psi_3^{(0)}\rangle\right).$$

$$= \frac{1}{\sqrt{2}} \left(\langle \psi_1^{(0)} | H_p | \psi_2^{(0)} \rangle + \langle \psi_1^{(0)} | H_p | \psi_3^{(0)} \rangle \right)$$

$$= \frac{1}{\sqrt{2}} \left[\frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \\ 0 \end{pmatrix}^\top \lambda \begin{pmatrix} 1 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 1 \end{pmatrix} \begin{pmatrix} 1 \\ -1 \\ 0 \end{pmatrix} + \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \\ 0 \end{pmatrix}^\top \lambda \begin{pmatrix} 1 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 1 \end{pmatrix} \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \right].$$

$$= \frac{1}{\sqrt{2}} \left(\frac{1}{\sqrt{2}} \lambda \cdot 0 + \frac{1}{\sqrt{2}} \lambda \cdot 1 \right)$$

$$= \frac{\lambda}{2}$$

Then:

$$\left| \langle \psi_1^{(0)} | H_p | \psi_2'^{(0)} \rangle \right|^2 = \frac{\lambda^2}{4}.$$

Thus, the correction of second order is:

$$E_2^{(2)} = \frac{\lambda^2}{8}.$$

For $E_3^{(2)}$
The correction of second order is:

$$E_3^{(2)} = \frac{\left| \langle \psi_1^{(0)} | H_p | \psi_3'^{(0)} \rangle \right|^2}{E_2^{(0)} - E_1^{(0)}} = \frac{\left| \langle \psi_1^{(0)} | H_p | \psi_3'^{(0)} \rangle \right|^2}{2 - 0}.$$

With the same process as for $E_2^{(2)}$, we obtain:

$$E_3^{(2)} = \frac{\lambda^2}{8}.$$

Final Results Up to Second Order
For the originally non-degenerate level with $E^{(0)} = 0$:

$$E_1 \approx 0 + \lambda - \frac{\lambda^2}{4}. \tag{142}$$

For the two levels originally at $E^{(0)} = 2$:

$$E_2 \approx 2 + \lambda \left(1 + \frac{1}{\sqrt{2}} \right) + \frac{\lambda^2}{8}, \tag{143}$$

$$E_3 \approx 2 + \lambda \left(1 - \frac{1}{\sqrt{2}} \right) + \frac{\lambda^2}{8}. \tag{144}$$

b) Calculate the corresponding wavefunctions up to first order perturbation theory.

The wavefunction of the non degenerate state up to first order of perturbation is:

$$|\psi_1\rangle = |\psi_1^{(0)}\rangle + |\psi_1^{(1)}\rangle$$

The first-order correction to the wavefunction for a non-degenerate state is:

$$|\psi_n^{(1)}\rangle = \sum_{m\neq n} \frac{\langle\psi_m^{(0)}|H_p|\psi_n^{(0)}\rangle}{E_n^{(0)} - E_m^{(0)}}|\psi_m^{(0)}\rangle$$

In the case of $|\psi_1^{(0)}\rangle$, the numerator is:

$$\langle\psi_2^{(0)}|H_p|\psi_1^{(0)}\rangle = 0, \quad \langle\psi_3^{(0)}|H_p|\psi_1^{(0)}\rangle = \frac{\lambda}{\sqrt{2}}$$

Since $E_1^{(0)} = 0$, $E_2^{(0)} = 2$ and $E_3^{(0)} = 2$:

$$|\psi_1^{(1)}\rangle = \frac{0}{0-2}|\psi_2^{(0)}\rangle + \frac{\lambda/\sqrt{2}}{0-2}|\psi_3^{(0)}\rangle = -\frac{\lambda}{2\sqrt{2}}|\psi_3^{(0)}\rangle$$

So up to first order the wavefunction for the state with $E^{(0)} = 0$:

$$|\psi_1\rangle = |\psi_1^{(0)}\rangle + |\psi_1^{(1)}\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\1\\0\end{pmatrix} - \frac{\lambda}{2\sqrt{2}}\begin{pmatrix}0\\0\\1\end{pmatrix}$$

The degenerate states with energies $E_2^{(0)} = 2$ and $E_3^{(0)} = 2$ can be can be described using the linear combinations at first order

$$|\psi_2'^{(0)}\rangle = \frac{1}{\sqrt{2}}\left(|\psi_2^{(0)}\rangle + |\psi_3^{(0)}\rangle\right), \quad |\psi_3'^{(0)}\rangle = \frac{1}{\sqrt{2}}\left(|\psi_2^{(0)}\rangle - |\psi_3^{(0)}\rangle\right).$$

The wave function for the first one of them up to first order perturbation is:

$$|\psi_2\rangle = |\psi_2'^{(0)}\rangle + |\psi_2'^{(1)}\rangle$$

Where:

$$|\psi_2'^{(1)}\rangle = \frac{\langle\psi_1^{(0)}|H_p|\psi_2'^{(0)}\rangle}{E_2^{(0)} - E_1^{(0)}}|\psi_1^{(0)}\rangle = \frac{\frac{1}{\sqrt{2}}\left(\langle\psi_1^{(0)}|H_p|\psi_2^{(0)}\rangle + \langle\psi_1^{(0)}|H_p|\psi_3^{(0)}\rangle\right)}{E_2^{(0)} - E_1^{(0)}}|\psi_1^{(0)}\rangle$$

$$= \frac{\frac{1}{\sqrt{2}}\left(0 + \frac{\lambda}{\sqrt{2}}\right)}{2-0}|\psi_1^{(0)}\rangle = \frac{\lambda}{4}|\psi_1^{(0)}\rangle = \frac{\lambda}{4}\frac{1}{\sqrt{2}}\begin{pmatrix}1\\1\\0\end{pmatrix}$$

Therefore:

$$|\psi_2\rangle = |\psi_2'^{(0)}\rangle + |\psi_2'^{(1)}\rangle = \begin{pmatrix} \frac{1}{2} \\ \frac{-1}{2} \\ \frac{1}{\sqrt{2}} \end{pmatrix} + \frac{\lambda}{4\sqrt{2}} \begin{pmatrix} 1 \\ 1 \\ 0 \end{pmatrix}$$

The wave function for the other degenerate state up to first order perturbation is:

$$|\psi_3\rangle = |\psi_3'^{(0)}\rangle + |\psi_3'^{(1)}\rangle$$

Where:

$$|\psi_3'^{(1)}\rangle = \frac{\langle\psi_1^{(0)}|H_p|\psi_3'^{(0)}\rangle}{E_3^{(0)} - E_1^{(0)}}|\psi_1^{(0)}\rangle = \frac{\frac{1}{\sqrt{2}}\left(\langle\psi_1^{(0)}|H_p|\psi_2^{(0)}\rangle - \langle\psi_1^{(0)}|H_p|\psi_3^{(0)}\rangle\right)}{E_3^{(0)} - E_1^{(0)}}|\psi_1^{(0)}\rangle$$

$$= \frac{\frac{1}{\sqrt{2}}\left(0 - \frac{\lambda}{\sqrt{2}}\right)}{2-0}|\psi_1^{(0)}\rangle = -\frac{\lambda}{4}|\psi_1^{(0)}\rangle = -\frac{\lambda}{4}\frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \\ 0 \end{pmatrix}$$

Therefore:

$$|\psi_3\rangle = |\psi_2'^{(0)}\rangle + |\psi_3'^{(1)}\rangle = \begin{pmatrix} \frac{1}{2} \\ \frac{-1}{2} \\ \frac{1}{\sqrt{2}} \end{pmatrix} - \frac{\lambda}{4\sqrt{2}} \begin{pmatrix} 1 \\ 1 \\ 0 \end{pmatrix}$$

Exercise 2. Perturbative treatment of He-atom first excited states

The electronic states of He can be approached by considering that the electronic repulsion term is a perturbation. Under this approach, the zero-order Hamiltonian corresponds to the sum of two hydrogen-like Hamiltonians.

$$\hat{H}^0 = \hat{H}_1^0 + \hat{H}_2^0, \quad \hat{H}_1^0 = -\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{Ze^2}{r_1}, \quad \hat{H}_2^0 = -\frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{Ze^2}{r_2}.$$

$$\hat{H} = \hat{H}^0 + \hat{H}' \quad \text{with} \quad \hat{H}' = \frac{e^2}{r_{12}}.$$

At zero order, the wavefunction can be expressed as the product of two hydrogen-like functions corresponding to electrons 1 and 2, and the zero-order energy is given by:

$$E^{(0)} = E_n(1) + E_n(2), \quad E_n = -\frac{Z^2}{n^2}\frac{e^2}{2a_0} = \frac{e^2}{2a_0} = 13.604\, eV.$$

If we consider only the spatial part of the wavefunction, the ground state is expressed as:

$$\phi_0^{(0)} = \chi_{1s}(1)\chi_{1s}(2),$$

and the first excited state has a degeneracy of 8. The corresponding unperturbed wavefunctions can be expressed as follows:

$$\phi_1^{(0)} = \chi_{1s}(1)\chi_{2s}(2), \quad \phi_2^{(0)} = \chi_{2s}(1)\chi_{1s}(2),$$

$$\phi_3^{(0)} = \chi_{1s}(1)\chi_{2px}(2), \quad \phi_4^{(0)} = \chi_{2px}(1)\chi_{1s}(2),$$

$$\phi_5^{(0)} = \chi_{1s}(1)\chi_{2py}(2), \quad \phi_6^{(0)} = \chi_{2py}(1)\chi_{1s}(2),$$

$$\phi_7^{(0)} = \chi_{1s}(1)\chi_{2pz}(2), \quad \phi_8^{(0)} = \chi_{2pz}(1)\chi_{1s}(2).$$

Consider this basis of functions (do not consider spin) to evaluate:

Data:

Coulomb Integrals

$$J_{ij} = \left\langle \phi_i(1)\phi_j(2) \left| \frac{1}{r_{12}} \right| \phi_i(1)\phi_j(2) \right\rangle$$

$$J_{1s1s} = \left\langle \phi_{1s}(1)\phi_{1s}(2) \left| \frac{1}{r_{12}} \right| \phi_{1s}(1)\phi_{1s}(2) \right\rangle = \frac{5z}{8}\left(\frac{e^2}{a_0}\right)$$

$$J_{1s2s} = \frac{17z}{81}\left(\frac{e^2}{a_0}\right), \quad J_{1s2p} = \frac{59z}{243}\left(\frac{e^2}{a_0}\right)$$

Exchange Integrals

$$K_{ij} = \left\langle \phi_i(1)\phi_j(2) \left| \frac{1}{r_{12}} \right| \phi_j(1)\phi_i(2) \right\rangle$$

$$K_{1s2s} = \left\langle \phi_{1s}(1)\phi_{2s}(2) \left| \frac{1}{r_{12}} \right| \phi_{2s}(1)\phi_{1s}(2) \right\rangle = \frac{16z}{729}\left(\frac{e^2}{a_0}\right), \quad K_{1s2p} = \frac{112z}{6561}\left(\frac{e^2}{a_0}\right)$$

a) The energy of the ground state of He at first order perturbation theory.

The energy at first perturbation order is:

$$E = E^{(0)} + E^{(1)}$$

The unperturbed energy $E^{(0)}$ is:

$$E^{(0)} = E_{1s}(1) + E_{1s}(2) = 2\left(-\frac{Z^2e^2}{2a_0}\right) = -\frac{Z^2e^2}{a_0}.$$

For helium ($Z = 2$):

$$E^{(0)} = -\frac{(2)^2e^2}{a_0} = -\frac{4e^2}{a_0}.$$

Using the known value $\frac{e^2}{2a_0} = 13.604\,\text{eV}$:

$$E_{1s} = -Z^2 \cdot 13.604\,\text{eV} = -4 \times 13.604\,\text{eV} = -54.416\,\text{eV}.$$

Thus:

$$E^{(0)} = 2 \times (-54.416\,\text{eV}) = -108.832\,\text{eV}.$$

The first-order energy correction is given by:

$$E^{(1)} = \langle \phi_0^{(0)} | \hat{H}' | \phi_0^{(0)} \rangle.$$

Since $\phi_0^{(0)} = \chi_{1s}(1)\chi_{1s}(2)$, we need the Coulomb integral:

$$J_{1s1s} = \left\langle \chi_{1s}(1)\chi_{1s}(2) \left| \frac{1}{r_{12}} \right| \chi_{1s}(1)\chi_{1s}(2) \right\rangle.$$

From the provided data:

$$J_{1s1s} = \frac{5Z}{8} \left(\frac{e^2}{a_0} \right).$$

Evaluating J_{1s1s} for Helium:
Substituting $Z = 2$:

$$J_{1s1s} = \frac{5 \times 2}{8} \left(\frac{e^2}{a_0} \right) = \frac{10}{8} \left(\frac{e^2}{a_0} \right) = \frac{5}{4} \left(\frac{e^2}{a_0} \right).$$

Since $\frac{e^2}{2a_0} = 13.604\,\text{eV}$, thus:

$$\frac{e^2}{a_0} = 2 \times 13.604\,\text{eV} = 27.208\,\text{eV}.$$

Therefore:

$$J_{1s1s} = \frac{5}{4} \times 27.208\,\text{eV} = 1.25 \times 27.208\,\text{eV} \approx 34.01\,\text{eV}.$$

So finally the energy up to first order in perturbation theory is:

$$E \approx E^{(0)} + E^{(1)} = -108.832\,\text{eV} + 34.01\,\text{eV} = -74.822\,\text{eV}.$$

b) The energy of the first-excited state of He (1s2s or 1s2p) at first-order degenerate perturbation theory and the correct combination of the eight degenerate functions indicated above at zero-order correction. Interpret your results.

In helium, if we consider one electron fixed in the $1s$ orbital and the other promoted to the $n = 2$ level, the first excited state includes both $2s$ and $2p$ orbitals. Without the electron-electron interaction, all configurations like $(1s, 2s)$ and $(1s, 2p)$ are degenerate at the same energy. Counting both possibilities of which electron is in which orbital, we get eight degenerate states:

Two states from the combination of $1s$ and $2s$ orbitals:

$$\phi_1^{(0)} = \chi_{1s}(1)\chi_{2s}(2), \quad \phi_2^{(0)} = \chi_{2s}(1)\chi_{1s}(2).$$

Six states from the combination of $1s$ and $2p$ orbitals: The $2p$ orbital has three orientations: $2p_x$, $2p_y$, and $2p_z$:

$$\phi_3^{(0)} = \chi_{1s}(1)\chi_{2p_x}(2), \quad \phi_4^{(0)} = \chi_{2p_x}(1)\chi_{1s}(2),$$

$$\phi_5^{(0)} = \chi_{1s}(1)\chi_{2p_y}(2), \quad \phi_6^{(0)} = \chi_{2p_y}(1)\chi_{1s}(2),$$

$$\phi_7^{(0)} = \chi_{1s}(1)\chi_{2p_z}(2), \quad \phi_8^{(0)} = \chi_{2p_z}(1)\chi_{1s}(2).$$

All these eight states start at the same energy (degenerate) before considering the electron-electron repulsion.

The perturbation is the electron-electron repulsion:

$$\hat{H}' = \frac{e^2}{r_{12}}.$$

To apply degenerate perturbation theory, we calculate the matrix elements:

$$H'_{ij} = \langle \phi_i^{(0)} | \hat{H}' | \phi_j^{(0)} \rangle.$$

Arranging the states in the order $\phi_1^{(0)}, \phi_2^{(0)}, \ldots, \phi_8^{(0)}$. The matrix H' looks like this:

$$H' = \begin{pmatrix} J_{1s2s} & K_{1s2s} & 0 & 0 & 0 & 0 & 0 & 0 \\ K_{1s2s} & J_{1s2s} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & J_{1s2p} & K_{1s2p} & 0 & 0 & 0 & 0 \\ 0 & 0 & K_{1s2p} & J_{1s2p} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & J_{1s2p} & K_{1s2p} & 0 & 0 \\ 0 & 0 & 0 & 0 & K_{1s2p} & J_{1s2p} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & J_{1s2p} & K_{1s2p} \\ 0 & 0 & 0 & 0 & 0 & 0 & K_{1s2p} & J_{1s2p} \end{pmatrix}.$$

Here: J_{1s2s} and K_{1s2s} are Coulomb and exchange integrals for the $(1s, 2s)$ combination. J_{1s2p} and K_{1s2p} are Coulomb and exchange integrals for the $(1s, 2p)$ combination.

Many off-diagonal elements vanish due to symmetry and orthogonality of different orbital types. This gives a block-diagonal structure: one 2×2 block for the $1s2s$ pair and three identical 2×2 blocks for each $1s2p$ pair (x, y, z).

For the $(1s, 2s)$ block:

$$\begin{pmatrix} J_{1s2s} & K_{1s2s} \\ K_{1s2s} & J_{1s2s} \end{pmatrix}.$$

Diagonalizing this gives two eigenvalues:

$$\lambda_1 = J_{1s2s} + K_{1s2s}, \quad \lambda_2 = J_{1s2s} - K_{1s2s}.$$

These correspond to linear combinations:

$$\psi_+ \propto \phi_1^{(0)} + \phi_2^{(0)}, \quad \psi_- \propto \phi_1^{(0)} - \phi_2^{(0)}.$$

Thus, the degeneracy is lifted, and we obtain two different first-order energy corrections for the $1s2s$ sector.

For the $(1s, 2p)$ blocks:

$$\begin{pmatrix} J_{1s2p} & K_{1s2p} \\ K_{1s2p} & J_{1s2p} \end{pmatrix}.$$

Diagonalizing this gives two eigenvalues:

$$\lambda_3 = J_{1s2p} + K_{1s2p}, \quad \lambda_4 = J_{1s2p} - K_{1s2p}.$$

However, due to symmetry and parity properties:

K_{1s2p} is often zero or very small. J_{1s2p} is the same for all three p-orbitals.

Thus, the $1s2p$ states may remain nearly degenerate or completely so at first order.

Interpretation of Results

- Before the perturbation, all eight states had the same energy.
- After including the electron-electron interaction:
  - The two $1s2s$ states mix and split into two energy levels, removing part of the degeneracy.
  - The six $1s2p$ states remain mostly degenerate because symmetry causes their integrals to vanish or be equal.

The new zero-order wavefunctions are linear combinations of the original degenerate states that diagonalize the perturbation matrix.