

## PHY356 Problem Set 3 — Due October 25, 2022

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### 4. Spreading of a free wave packet

Consider a free particle.

- Show, applying Ehrenfest's theorem, that  $\langle X \rangle$  is a linear function of time, the mean value  $\langle P \rangle$  remaining constant.
- Write the equations of motion for the mean values  $\langle X^2 \rangle$  and  $\langle XP + PX \rangle$ . Integrate these equations.
- Show that, with a suitable choice of the time origin, the root mean square deviation  $\Delta X$  is given by:

$$(\Delta X)^2 = \frac{1}{m^2} (\Delta P)_0^2 t^2 + (\Delta X)_0^2$$

where  $(\Delta X)_0$  and  $(\Delta P)_0$  are the root mean square deviations at the initial time.

How does the width of the wave packet vary as a function of time (see § 3-c of Complement G<sub>I</sub>)? Give a physical interpretation.

(a) I begin by apply Ehrenfest's theorem to determine the time evolution of  $\langle \hat{X} \rangle$ . It is important to mention that the time evolution of  $\langle \hat{X} \rangle$  is not given implicitly by the operator itself (that is,  $\frac{d}{dt} \hat{X} = 0$ ) and instead determined by the wavefunction time evolution  $|\psi(t)\rangle$ . To the question: because we are considering a free particle, there is no potential fluxuation which affects the particle's behaviour. Therefore  $V(\mathbf{r}) = 0$  for every point in space. The Hamiltonian operator of the system is then just  $\hat{H} = \frac{\hat{P}^2}{2m}$ . Hence Ehrenfest's theorem determines time evolution of  $\langle \hat{X} \rangle$ :

$$\begin{aligned} \frac{d}{dt} \langle \hat{X} \rangle &= \frac{1}{i\hbar} \langle [\hat{X}, \hat{H}] \rangle + \left\langle \frac{d\hat{X}}{dt} \right\rangle \\ &= \frac{1}{i\hbar} \left\langle \left[ \hat{X}, \frac{\hat{P}^2}{2m} \right] \right\rangle. \end{aligned}$$

As a brief aside, which will be useful for solving the rest of the problem, will be determining the commutator  $\left[ \hat{X}, \frac{\hat{P}^2}{2m} \right]$ . We have that

$$\begin{aligned} \left[ \hat{X}, \frac{\hat{P}^2}{2m} \right] &= \frac{1}{2m} [\hat{X}, \hat{P}^2] \\ &= \frac{1}{2m} \left( \hat{P}[\hat{X}, \hat{P}] + [\hat{X}, \hat{P}]\hat{P} \right) \end{aligned} \quad (\text{by linearity})$$

$$\begin{aligned}
&= \frac{1}{2m} \left( i\hbar \hat{P} + i\hbar \hat{P} \right) && \text{(by commutator expansion)} \\
&= \frac{i\hbar}{m} \hat{P}. && \text{(by commutation relation)}
\end{aligned}$$

Thus the time evolution of  $\hat{X}$  is

$$\begin{aligned}
\frac{d}{dt} \langle \hat{X} \rangle &= \frac{1}{i\hbar} \left\langle \left[ \hat{X}, \frac{\hat{P}^2}{2m} \right] \right\rangle \\
&= \frac{1}{i\hbar} \cdot \frac{2i\hbar}{2m} \langle \hat{P} \rangle \\
&= \frac{1}{m} \langle \hat{P} \rangle,
\end{aligned}$$

which is just given by linearity in factoring out the constant from the expectation value. The result  $m \frac{d\langle \hat{X} \rangle}{dt} = \langle \hat{P} \rangle$  is what we would also expect classically, given by Newton's laws of motion. Now consider: what if we take the second time derivative of  $\langle \hat{X} \rangle$ ? Here, we can use the above relation and apply Ehrenfest's theorem a second time but this time to  $\langle \hat{P} \rangle$ :

$$\begin{aligned}
\frac{d^2}{dt^2} \langle \hat{X} \rangle &= \frac{1}{m} \frac{d}{dt} \langle \hat{P} \rangle \\
&= \frac{1}{i\hbar m} \left\langle \left[ \hat{P}, \frac{\hat{P}^2}{2m} \right] \right\rangle + \left\langle \frac{d\hat{P}}{dt} \right\rangle \xrightarrow{0} \\
&= \frac{1}{2i\hbar m^2} \langle [\hat{P}, \hat{P}^2] \rangle \\
&= 0,
\end{aligned}$$

which is only because the commutator of  $\hat{P}$  with itself is zero:  $[\hat{P}, \hat{P}^2] = 0$ . This implies that  $\langle \hat{P} \rangle$  is constant, since its time derivative is indeed zero. We may now integrate the equation of motion of  $\langle \hat{X} \rangle$  to determine the explicit trajectory of the expected position of the particle:

$$\begin{aligned}
\frac{d}{dt} \langle \hat{X} \rangle &= \frac{\langle \hat{P} \rangle}{m} \longrightarrow \int \frac{d\langle \hat{X} \rangle}{dt} dt = \frac{\langle \hat{P} \rangle}{m} \int dt \\
&\implies \langle \hat{X} \rangle(t) = \frac{\langle \hat{P} \rangle}{m} t + x_0,
\end{aligned}$$

where  $x_0$  is the initial position of the expected value of position of the particle at time  $t = 0$ . This determines the equation of motion of the expected value of the position of the particle.

**(b)** To proceed, I will determine the equations of motion of  $\langle \hat{X}^2 \rangle$  and  $\langle \hat{X}\hat{P} + \hat{P}\hat{X} \rangle$ . These may be determined by applying Ehrenfest's theorem as before. Before I begin determining time derivatives of expectation values, I will evaluate the commutators  $[\hat{X}^2, \hat{H}]$  and  $[\hat{X}\hat{P} + \hat{P}\hat{X}, \hat{H}]$ , for they will be useful in finding the time evolution:

$$\begin{aligned}
[\hat{X}^2, \hat{H}] &= [\hat{X}^2, \hat{H}] && \text{(by linearity)} \\
&= \left( \hat{X}[\hat{X}, \hat{H}] + [\hat{X}, \hat{H}]\hat{X} \right) && \text{(by commutator expansion)}
\end{aligned}$$

$$\begin{aligned}
&= \left( \hat{X} \cdot \frac{i\hbar}{m} \hat{P} + \frac{i\hbar}{m} \hat{P} \cdot \hat{X} \right) && \text{(as determined before)} \\
&= \frac{2i\hbar}{m} (\hat{X} \hat{P} + \hat{P} \hat{X}),
\end{aligned}$$

$$\begin{aligned}
[\hat{X} \hat{P} + \hat{P} \hat{X}, \hat{H}] &= ([\hat{X} \hat{P}, \hat{H}] + [\hat{P} \hat{X}, \hat{H}]) && \text{(by linearity)} \\
&= \left( \hat{X} \left[ \hat{P}, \frac{\hat{P}^2}{2m} \right] + \left[ \hat{X}, \frac{\hat{P}^2}{2m} \right] \hat{P} + \hat{P} \left[ \hat{X}, \frac{\hat{P}^2}{2m} \right] + \left[ \hat{P}, \frac{\hat{P}^2}{2m} \right] \hat{X} \right) \\
&&& \text{(by commutation relation)} \\
&= \left( 0\hat{X} + \frac{i\hbar}{m} \hat{P}^2 + \frac{i\hbar}{m} \hat{P}^2 + 0\hat{X} \right) && \text{(as determined before)} \\
&= \frac{2i\hbar}{m} \hat{P}^2.
\end{aligned}$$

This implies that the above equation of motion for  $\langle \hat{X} \rangle$  is given by:

$$\begin{aligned}
\frac{d}{dt} \langle \hat{X}^2 \rangle &= \frac{1}{i\hbar} \langle [\hat{X}^2, \hat{H}] \rangle \\
&= \frac{1}{i\hbar} \left\langle \frac{i\hbar}{m} (\hat{X} \hat{P} + \hat{P} \hat{X}) \right\rangle \\
&= \frac{1}{m} \langle \hat{X} \hat{P} + \hat{P} \hat{X} \rangle
\end{aligned}$$

which implies that

$$\begin{aligned}
\frac{d^2}{dt^2} \langle \hat{X}^2 \rangle &= \frac{d}{dt} \frac{1}{m} \langle \hat{X} \hat{P} + \hat{P} \hat{X} \rangle \\
&= \frac{1}{m} \frac{1}{i\hbar} \langle [\hat{X} \hat{P} + \hat{P} \hat{X}, \hat{H}] \rangle \\
&= \frac{1}{i\hbar} \frac{1}{m} \left\langle \frac{2i\hbar}{m} \hat{P}^2 \right\rangle \\
&= \frac{2}{m^2} \langle \hat{P}^2 \rangle.
\end{aligned}$$

To find the explicit trajectory of  $\langle \hat{X}^2 \rangle$ , we can integrate the equation of motion twice:

$$\langle \hat{X}^2 \rangle(t) = \frac{\langle \hat{P}^2 \rangle}{m^2} t^2 + Dt + E,$$

where  $E = x'_0$  is the initial value of expectation term  $\langle \hat{X}^2 \rangle$ . Here,  $D = 0$  because the initial time derivative  $\frac{d}{dt} \langle \hat{X}^2 \rangle = \frac{2}{m^2} \langle \hat{P}^2 \rangle t$  has  $D = 0$ . Therefore our equations of motion are given by:

$$\begin{aligned}
\langle \hat{X} \rangle(t) &= \frac{\langle \hat{P} \rangle}{m} t + x_0 \\
\langle \hat{X}^2 \rangle(t) &= \frac{\langle \hat{P}^2 \rangle}{m^2} t^2 + x'_0
\end{aligned}$$

$$\langle \hat{X}\hat{P} + \hat{P}\hat{X} \rangle(t) = \frac{2\langle \hat{P}^2 \rangle}{m}t.$$

(c) We may now apply our findings from parts (a) and (b) to determine the time evolution of the uncertainty in the position of the particle. Generally, the root mean square deviation of an operator is given by

$$\Delta\hat{A} = \sqrt{\langle (\hat{A} - \langle \hat{A} \rangle)^2 \rangle} = \sqrt{\langle \hat{A}^2 \rangle - \langle \hat{A} \rangle^2}.$$

Applying this concept to the uncertainty in position, by applying the equations of motion as found above, we have that

$$(\Delta\hat{X})^2 = \langle \hat{X}^2 \rangle - \langle \hat{X} \rangle^2 = \frac{\langle \hat{P}^2 \rangle}{m^2}t^2 + x_0'^2 - \left( \frac{\langle \hat{P} \rangle}{m}t + x_0 \right)^2.$$

Expanding the above out and simplifying yields:

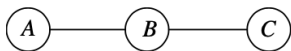
$$\begin{aligned} (\Delta\hat{X})^2 &= \frac{\langle \hat{P}^2 \rangle}{m^2}t^2 + x_0'^2 - \left( \frac{\langle \hat{P} \rangle^2}{m^2}t^2 + x_0^2 + \frac{2\langle \hat{P} \rangle x_0}{m}t \right) \\ &= \frac{1}{m^2} \left( \langle \hat{P}^2 \rangle - \langle \hat{P} \rangle^2 \right) t^2 + (x_0' - x_0)^2 - \frac{2\langle \hat{P} \rangle x_0}{m}t \\ &= \frac{1}{m^2} (\Delta\hat{P})^2 t^2 + (x_0' - x_0)^2 - 2x_0 \left( \frac{\langle \hat{P} \rangle}{m}t \right) \\ &= \frac{1}{m^2} (\Delta\hat{P})^2 t^2 + (\langle \hat{X}^2 \rangle_0 - \langle \hat{X} \rangle_0^2) + 2\langle \hat{X} \rangle_0 (\langle \hat{X} \rangle - \langle \hat{X} \rangle_0). \end{aligned}$$

Now, since the uncertainty of a wavepacket in either  $\Delta\hat{X}$  or  $\Delta\hat{P}$  can never be zero, we require  $\Delta\hat{P}$  to have an initial non-zero value at  $t = 0$ . Let me call this value  $(\Delta\hat{P})_0^2$ . Since at  $t = 0$ ,  $\langle \hat{X} \rangle = \langle \hat{X} \rangle_0$ , then for an arbitrary initial time, the root-mean square value of the uncertainty in the position is

$$(\Delta\hat{X})^2 = \frac{1}{m^2} (\Delta\hat{P})_0^2 t^2 + (\Delta\hat{X})_0^2.$$

This follows because the initial position of the expectation value of the wave coincides with  $\langle \hat{X} \rangle_0$ , meanwhile the initial value in the position uncertainty may not be zero:  $(\Delta\hat{P})_0^2 \neq 0$  by Heisenberg's uncertainty principle.

8. Consider an electron of a linear triatomic molecule formed by three equidistant atoms.



We use  $|\varphi_A\rangle$ ,  $|\varphi_B\rangle$ ,  $|\varphi_C\rangle$  to denote three orthonormal states of this electron, corresponding respectively to three wave functions localized about the nuclei of atoms  $A$ ,  $B$ ,  $C$ . We shall confine ourselves to the subspace of the state space spanned by  $|\varphi_A\rangle$ ,  $|\varphi_B\rangle$  and  $|\varphi_C\rangle$ .

When we neglect the possibility of the electron jumping from one nucleus to another, its energy is described by the Hamiltonian  $H_0$  whose eigenstates are the three states  $|\varphi_A\rangle$ ,  $|\varphi_B\rangle$ ,  $|\varphi_C\rangle$  with the same eigenvalue  $E_0$ . The coupling between the states  $|\varphi_A\rangle$ ,  $|\varphi_B\rangle$ ,  $|\varphi_C\rangle$  is described by an additional Hamiltonian  $W$  defined by:

$$\begin{aligned} W|\varphi_A\rangle &= -a|\varphi_B\rangle \\ W|\varphi_B\rangle &= -a|\varphi_A\rangle - a|\varphi_C\rangle \\ W|\varphi_C\rangle &= -a|\varphi_B\rangle \end{aligned}$$

where  $a$  is a real positive constant.

- a. Calculate the energies and stationary states of the Hamiltonian  $H = H_0 + W$ .
- b. The electron at time  $t = 0$  is in the state  $|\varphi_A\rangle$ . Discuss qualitatively the localization of the electron at subsequent times  $t$ . Are there any values of  $t$  for which it is perfectly localized about atom  $A$ ,  $B$  or  $C$ ?
- c. Let  $D$  be the observable whose eigenstates are  $|\varphi_A\rangle$ ,  $|\varphi_B\rangle$ ,  $|\varphi_C\rangle$  with respective eigenvalues  $-d$ ,  $0$ ,  $d$ .  $D$  is measured at time  $t$ ; what values can be found, and with what probabilities?
- d. When the initial state of the electron is arbitrary, what are the Bohr frequencies that can appear in the evolution of  $\langle D \rangle$ ? Give a physical interpretation of  $D$ . What are the frequencies of the electromagnetic waves that can be absorbed or emitted by the molecule?

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(a) To determine the energies and stationary states of the Hamiltonian  $\hat{H} = \hat{H}_0 + \hat{W}$ , I will proceed by determining the matrix representations of each individual operator  $\hat{H}_0$  and  $\hat{W}$ . Then, the sum of both matrices produces the matrix representation of  $\hat{H}$ . With this, I may follow the process of determining the eigenvalues of eigenvectors of  $\hat{H}$ , which correspond to the energies and eigenstates of  $\hat{H}$ .

Now, since  $|\varphi_A\rangle$ ,  $|\varphi_B\rangle$  and  $|\varphi_C\rangle$  are all stationary states of  $\hat{H}_0$  with energy  $E_0$ , then the matrix

representation is

$$\hat{H}_0 = E_0 \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$

This is not difficult to determine. For  $\hat{W}$ , we have that  $\hat{W} \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} = \hat{W} \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} = -a \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}$ , and  $\hat{W} \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} = -a \begin{pmatrix} 1 \\ 0 \\ 1 \end{pmatrix}$ . By direct matrix multiplication, it is easy to determine the matrix representation of  $\hat{W}$ :

$$\hat{W} = -a \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}.$$

Thus by matrix addition, the matrix representation of  $\hat{H}$  is

$$\hat{H} = \hat{H}_0 + \hat{W} = \begin{pmatrix} E_0 & -a & 0 \\ -a & E_0 & -a \\ 0 & -a & E_0 \end{pmatrix}.$$

To proceed, I will determine all the eigenvalues of  $\hat{H}$ , which will yield the eigen-energies of each eigenstate of the operator. By definition:

$$\begin{aligned} |\hat{H} - \lambda \mathbb{I}_{3 \times 3}| &= \begin{vmatrix} E_0 - \lambda & -a & 0 \\ -a & E_0 - \lambda & -a \\ 0 & -a & E_0 - \lambda \end{vmatrix} \\ &= (E_0 - \lambda)^3 + (-a)^2(0) + (0)(-a)^2 - (0)(E_0 - \lambda) - (-a)^2(E_0 - \lambda) - (-a)^2(E_0 - \lambda) \\ &= (E_0 - \lambda) [(E_0 - \lambda)^2 - 2a^2] \\ &= (E_0 - \lambda) [\lambda^2 - 2E_0\lambda + E_0^2 - 2a^2]. \end{aligned}$$

By applying the quadratic formula to the second term, one can determine that

$$\lambda_1 = E_0, \quad \lambda_{2,3} = \frac{1}{2} \left[ -2E_0 \pm \sqrt{4E_0^2 - 4(1)(E_0^2 - 2a^2)} \right] = E_0 \pm \sqrt{2}a.$$

These are the eigenvalues, or the corresponding energies, of the perturbed Hamiltonian operator. What follows is to now determine each eigenstate corresponding to each of the three energies, via the method of determining the kernel:  $\ker(\hat{H} - \lambda_k \mathbb{I}_{3 \times 3})$  for  $k = 1, 2, 3$ . We have:

$$\begin{aligned} \ker(\hat{H} - E_0 \mathbb{I}_{3 \times 3}) &= \ker \begin{pmatrix} 0 & -a & 0 \\ -a & 0 & -a \\ 0 & -a & 0 \end{pmatrix} \\ &\longrightarrow = \ker \begin{pmatrix} 0 & 0 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} && \text{(row reduction)} \\ &\longrightarrow = \begin{pmatrix} 0 & 0 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} v_1 \\ v_2 \\ v_3 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix} \end{aligned}$$

$$\implies v_1 = -v_3, \quad v_2 = 0.$$

Thus the corresponding eigenstate of energy  $E_0$  is the vector  $v = \begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix}$ , or the stationary state

$|\varphi_A\rangle - |\varphi_C\rangle$  of  $\hat{H}$ . Similarly,

$$\begin{aligned} \ker(\hat{H} - (E_0 + \sqrt{2}a)\mathbb{I}_{3 \times 3}) &= \ker \begin{pmatrix} -\sqrt{2}a & -a & 0 \\ -a & -\sqrt{2}a & -a \\ 0 & -a & -\sqrt{2}a \end{pmatrix} \\ &\longrightarrow \ker \begin{pmatrix} \sqrt{2} & 1 & 0 \\ 1 & \sqrt{2} & 1 \\ 0 & 1 & \sqrt{2} \end{pmatrix} \longrightarrow \ker \begin{pmatrix} 2 & \sqrt{2} & 0 \\ 1 & \sqrt{2} & 1 \\ 0 & \sqrt{2} & 2 \end{pmatrix} \\ &\longrightarrow \ker \begin{pmatrix} 2 & \sqrt{2} & 0 \\ -1 & 0 & 1 \\ -2 & 0 & 2 \end{pmatrix} \longrightarrow \ker \begin{pmatrix} \sqrt{2} & 1 & 0 \\ -1 & 0 & 1 \\ 0 & 0 & 0 \end{pmatrix} \\ &\hspace{15em} \text{(row reduction)} \\ &\longrightarrow = \begin{pmatrix} \sqrt{2} & 1 & 0 \\ -1 & 0 & 1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} u_1 \\ u_2 \\ u_3 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix} \\ &\implies \sqrt{2}u_1 = -u_2, \quad u_1 = u_3. \end{aligned}$$

This eigenvector corresponds to the eigenstate  $|\varphi_A\rangle - \sqrt{2}|\varphi_B\rangle + |\varphi_C\rangle$  of the operator  $\hat{H}$  with energy  $E_0 + \sqrt{2}a$ . The similar process of determining the kernel of  $\ker(\hat{H} - (E_0 - \sqrt{2}a)\mathbb{I}_{3 \times 3})$  yields the eigenstate  $|\varphi_A\rangle + \sqrt{2}|\varphi_B\rangle + |\varphi_C\rangle$  of  $\hat{H}$  with energy  $E_0 - \sqrt{2}a$ ; the process is identical. Therefore the eigenstates of  $\hat{H}$  are given by

$$\begin{aligned} \hat{H} [|\varphi_A\rangle - |\varphi_C\rangle] &= E_0 [|\varphi_A\rangle - |\varphi_C\rangle], \\ \hat{H} [|\varphi_A\rangle - \sqrt{2}|\varphi_B\rangle + |\varphi_C\rangle] &= (E_0 + \sqrt{2}a) [|\varphi_A\rangle - \sqrt{2}|\varphi_B\rangle + |\varphi_C\rangle], \\ \hat{H} [|\varphi_A\rangle + \sqrt{2}|\varphi_B\rangle + |\varphi_C\rangle] &= (E_0 - \sqrt{2}a) [|\varphi_A\rangle + \sqrt{2}|\varphi_B\rangle + |\varphi_C\rangle]. \end{aligned}$$

It is important to note that  $E_0 \pm \sqrt{2}a$  has units of energy, since  $E_0$  and  $a$  both independently have units of energy. It is relatively simple to show that each of these three states are orthonormal to each other, hence the eigenstates form a complete basis in the eigenspace.

**(b)** We may now proceed by determining a wavefunction which depicts the behaviour of the electron around the triatomic molecule. Since the stationary states of  $\hat{H}$  are all orthonormal and all span the eigenspace, one may construct any wavefunction  $|\psi\rangle$  as a linear combination of said eigenstates:

$$|\psi\rangle = \sum_{k=1}^3 c_k |\xi_k\rangle,$$

where the  $c_k$  are complex amplitudes with the normalization requirement  $\sum_k |c_k|^2 = 1$  which yields a normalized  $|\psi\rangle$ ; normalized probability of measuring each of the  $|\xi_k\rangle$ . Then, the time evolution

of the superposed state is governed by Schrödinger's equation:

$$|\psi(t)\rangle = \sum_{k=1}^3 c_k |\xi_k\rangle e^{-iE_k t/\hbar}.$$

It follows that if  $|\psi(t=0)\rangle$  is normalized, then  $|\psi(t)\rangle$  will be normalized for all time. I will proceed by determining a general form of  $|\psi(t)\rangle$ , and then proceed with normalization (this result will be useful in part (d) of this question). Generally:

$$\begin{aligned} |\psi(t)\rangle = & c_1 [|\varphi_A\rangle - |\varphi_C\rangle] e^{-iE_0 t/\hbar} + c_2 \left[ |\varphi_A\rangle - \sqrt{2} |\varphi_B\rangle + |\varphi_C\rangle \right] e^{-i(E_0 + \sqrt{2}a)t/\hbar} \\ & + c_3 \left[ |\varphi_A\rangle + \sqrt{2} |\varphi_B\rangle + |\varphi_C\rangle \right] e^{-i(E_0 - \sqrt{2}a)t/\hbar}. \end{aligned}$$

To simplify the state representation more, I will follow by grouping together each of the individual states  $|\varphi_A\rangle, |\varphi_B\rangle, |\varphi_C\rangle$ :

$$\begin{aligned} |\psi(t)\rangle = & \left[ c_1 e^{-iE_0 t/\hbar} + c_2 e^{-i(E_0 + \sqrt{2}a)t/\hbar} + c_3 e^{-i(E_0 - \sqrt{2}a)t/\hbar} \right] |\varphi_A\rangle \\ & + \left[ -\sqrt{2}c_2 e^{-i(E_0 + \sqrt{2}a)t/\hbar} + \sqrt{2}c_3 e^{-i(E_0 - \sqrt{2}a)t/\hbar} \right] |\varphi_B\rangle \\ & + \left[ -c_1 e^{-iE_0 t/\hbar} + c_2 e^{-i(E_0 + \sqrt{2}a)t/\hbar} + c_3 e^{-i(E_0 - \sqrt{2}a)t/\hbar} \right] |\varphi_C\rangle. \end{aligned}$$

That is easy to show just by expansion and grouping like terms. Furthermore, one may factor out the common term  $e^{-iE_0 t/\hbar}$  and other common factors, such as the  $\sqrt{2}$ . Furthermore, let me define the frequency  $\omega = \frac{\sqrt{2}a}{\hbar}$ :

$$\begin{aligned} |\psi(t)\rangle = & e^{-iE_0 t/\hbar} \left[ c_1 + c_2 e^{-i\omega t} + c_3 e^{i\omega t} \right] |\varphi_A\rangle \\ & + \sqrt{2} e^{-iE_0 t/\hbar} \left[ -c_2 e^{-i\omega t} + c_3 e^{i\omega t} \right] |\varphi_B\rangle \\ & + e^{-iE_0 t/\hbar} \left[ -c_1 + c_2 e^{-i\omega t} + c_3 e^{i\omega t} \right] |\varphi_C\rangle. \end{aligned}$$

This determines the general form of the electron in the triatomic molecule. Now, allow me to consider the initial condition  $|\psi(0)\rangle = |\varphi_A\rangle$ . At this time, I will ignore any phase contributions from each of the  $c_k$  (since the  $c_k$  are complex, they may be expressed as  $c_k = r_k e^{i\alpha_k}$  for real radius  $r_k$  and phase  $\alpha_k$ ) and just assume the  $c_k$  are real, else I must continue to determine the conditions on the relative phase for the initial conditions to be satisfied, and that is too much work. Hence we arrive at the system of equations:

$$\begin{aligned} c_1 + c_2 + c_3 &= 1, \\ -c_2 + c_3 &= 0, \\ -c_1 + c_2 + c_3 &= 0. \end{aligned}$$

In matrix form, that is  $\begin{pmatrix} 1 & 1 & 1 \\ 0 & -1 & 1 \\ -1 & 1 & 1 \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}$ . Row reduction reveals that  $\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} 1/2 \\ 1/4 \\ 1/4 \end{pmatrix}$ .

Therefore the  $|\psi(t)\rangle$  which satisfies this initial condition is

$$|\psi(t)\rangle = e^{-iE_0 t/\hbar} \left[ \frac{1}{2} + \frac{1}{4} e^{-i\omega t} + \frac{1}{4} e^{i\omega t} \right] |\varphi_A\rangle + \frac{\sqrt{2}}{4} e^{-iE_0 t/\hbar} \left[ -e^{-i\omega t} + e^{i\omega t} \right] |\varphi_B\rangle$$



$$+ e^{-iE_0t/\hbar} \left[ -\frac{1}{2} + \frac{1}{4}e^{-i\omega t} + \frac{1}{4}e^{i\omega t} \right] |\varphi_C\rangle.$$

The expansion of the exponentials  $e^{i\omega t} + e^{-i\omega t}$  by Euler's identity yields a appropriate form in which we can analyze the behaviour of the electron localization around the atoms. Here,  $e^{i\omega t} + e^{-i\omega t} = 2 \cos(\omega t)$  and  $e^{i\omega t} - e^{-i\omega t} = 2i \sin(\omega t)$ . Once I factor out common scalars (like the  $1/4$ ) and multiply through some constants, the state is now expressed as

$$|\psi(t)\rangle = \frac{1}{2}e^{-iE_0t/\hbar} [1 + \cos(\omega t)] |\varphi_A\rangle + \frac{\sqrt{2}}{2}ie^{-iE_0t/\hbar} [\sin(\omega t)] |\varphi_B\rangle + \frac{1}{2}e^{-iE_0t/\hbar} [-1 + \cos(\omega t)] |\varphi_C\rangle.$$

Now we may begin analyzing the localization behaviour of the electron. First, notice that the localization of the electron is constantly shifting at the frequency  $\omega$ , since this is the origin of the time-dependence. Whenever  $\cos(\omega t) = \pm 1$ , the electron is perfectly localized around state  $|\varphi_A\rangle$  or  $|\varphi_C\rangle$ , respectively. This corresponds to  $\omega t = \pi n$  being an integer multiple of  $\pi$ . In this case,  $\sin(\pi n) = 0$  for any  $n$ , so the electron is perfectly localized around atom  $A$  or  $C$ , but not  $B$  at all.

Furthermore, whenever  $\sin(\omega t) = \pm 1$ , then  $\omega t = \pi \left( m + \frac{1}{2} \right)$  is an odd integer multiple of  $\pi$ . Thus

$\cos \left( \pi \left( m + \frac{1}{2} \right) \right) = 0$  for any  $m$ . However, in this sense, the state  $|\psi(t)\rangle$  is in a linear combination of atom states  $|\varphi_A\rangle, |\varphi_B\rangle, |\varphi_C\rangle$ , but never purely  $|\varphi_B\rangle$ . Therefore  $|\psi(t)\rangle$  is never purely localized around  $|\varphi_B\rangle$ , but it is localized around  $|\varphi_A\rangle$  whenever  $t = \frac{\pi(2n)}{\omega} = \frac{\sqrt{2}\pi n \hbar}{a}$  and is purely localized

around  $|\varphi_C\rangle$  whenever  $t = \frac{\pi(2n+1)}{\omega} = \frac{\sqrt{2}\pi(2n+1)\hbar}{2a}$ , for any  $n \in \mathbb{Z}^+ \cup \{0\}$  (positive integers union zero, since  $t \in [0, \infty)$ ).

I will briefly bring attention to the dimensions of these quantities:  $\hbar$  has units of [energy  $\times$  time], and  $a$  has units of [energy], thus  $\frac{\hbar}{a}$  has units of [time], while the rest ( $\pi, \sqrt{2}, n, \dots$ ) are dimensionless scalars.

(c) Now, sticking with our previous normalized  $|\psi(t)\rangle$  in initial state  $|\psi(0)\rangle = |\varphi_A\rangle$ ,

$$|\psi(t)\rangle = \frac{1}{2}e^{-iE_0t/\hbar} [1 + \cos(\omega t)] |\varphi_A\rangle + \frac{\sqrt{2}}{2}ie^{-iE_0t/\hbar} [\sin(\omega t)] |\varphi_B\rangle + \frac{1}{2}e^{-iE_0t/\hbar} [-1 + \cos(\omega t)] |\varphi_C\rangle,$$

the observable  $\hat{D}$  has the same eigenstates as that as  $\hat{H}_0$  (this implies  $[\hat{D}, \hat{H}_0] = 0$ ) which are  $|\varphi_A\rangle, |\varphi_B\rangle, |\varphi_C\rangle$  with respective eigenvalues  $d, 0$ , and  $-d$ . It's matrix representation, like that of  $\hat{H}$  in the basis  $\{|\varphi_A\rangle, |\varphi_B\rangle, |\varphi_C\rangle\}$ , is given by the diagonal  $3 \times 3$  matrix

$$\hat{D} = \begin{pmatrix} d & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -d \end{pmatrix}.$$

As stated before when I mentioned the expansion of the ket  $|\psi(t)\rangle$  with eigenstates  $|\xi_k\rangle$ , I will reiterate that the probability of measuring any one of the  $|\xi_k\rangle$  for *any operator* is just given by the complex modulus of the coefficient  $c_k$ , which is  $|c_k|^2$ . Not only is this true for states expanded in an basis of eigenvectors, but also true for states expanded in any other orthonormal basis. In our case, we have arrived at the result

$$|\psi(t)\rangle = c_1 |\xi_1\rangle + c_2 |\xi_2\rangle + c_3 |\xi_3\rangle = c'_1 |\varphi_A\rangle + c'_2 |\varphi_B\rangle + c'_3 |\varphi_C\rangle$$

with the initial condition  $|\psi(0)\rangle = |\varphi_A\rangle$  (we have just implicitly exploited a change in basis from the  $\{|\xi_1\rangle, |\xi_2\rangle, |\xi_3\rangle\}$  basis to the  $\{|\varphi_A\rangle, |\varphi_B\rangle, |\varphi_C\rangle\}$ ). By the normalization condition, we then require that  $\sum_k |c_k|^2 = \sum_k |c'_k|^2 = 1$ .

Therefore, by definition,

$$\begin{aligned}\mathcal{P}_{|\varphi_A\rangle}(t) &= |\langle\varphi_A|\psi(t)\rangle|^2 = |c'_1|^2 \\ &= \left| \frac{1}{2} e^{-iE_0 t/\hbar} [1 + \cos(\omega t)] \right|^2 \\ &= \frac{[1 + \cos(\omega t)]^2}{4}\end{aligned}$$

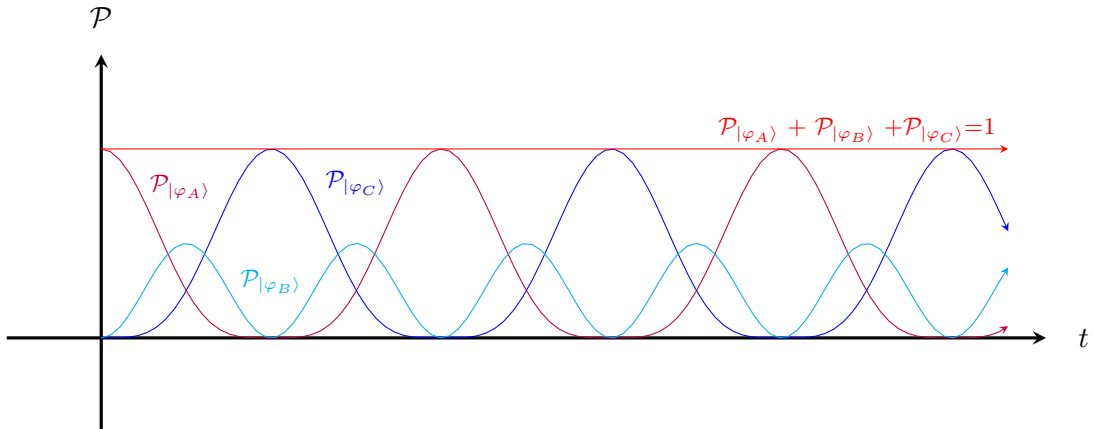
$$\begin{aligned}\mathcal{P}_{|\varphi_B\rangle}(t) &= |\langle\varphi_B|\psi(t)\rangle|^2 = |c'_2|^2 \\ &= \left| \frac{\sqrt{2}}{2} i e^{-iE_0 t/\hbar} [\sin(\omega t)] \right|^2 \\ &= \frac{\sin^2(\omega t)}{2}\end{aligned}$$

$$\begin{aligned}\mathcal{P}_{|\varphi_C\rangle}(t) &= |\langle\varphi_C|\psi(t)\rangle|^2 = |c'_3|^2 \\ &= \left| \frac{1}{2} e^{-iE_0 t/\hbar} [-1 + \cos(\omega t)] \right|^2 \\ &= \frac{[-1 + \cos(\omega t)]^2}{4}.\end{aligned}$$

It is quite easy to see that the sum of each of these probabilities is equal to one:

$$\begin{aligned}\mathcal{P}_{|\varphi_A\rangle}(t) + \mathcal{P}_{|\varphi_B\rangle}(t) + \mathcal{P}_{|\varphi_C\rangle}(t) &= \frac{[1 + \cos(\omega t)]^2}{4} + \frac{2 \sin^2(\omega t)}{4} + \frac{[-1 + \cos(\omega t)]^2}{4} \\ &= \frac{1}{4} [1 + \cos^2(\omega t) + 2 \cos(\omega t) + 2 \sin^2(\omega t) + 1 + \cos^2(\omega t) - 2 \cos(\omega t)] \\ &= \frac{1}{4} [1 + 1 + 1 + 1] \\ &= 1.\end{aligned}$$

The probabilities, as functions of time, for this state can be plotted as well:



Now, suppose we measured  $\hat{D}|\psi(t)\rangle$ . As just stated, we would find each state  $|\varphi_k\rangle$  with probability  $|c_k|^2$ , for  $k = A, B, C$ . The measurement  $\hat{D}|\psi(t)\rangle$  then yields

$$\begin{aligned}\hat{D}|\psi(t)\rangle &= \frac{1}{2}e^{-iE_0t/\hbar}[1 + \cos(\omega t)]\hat{D}|\varphi_A\rangle + \frac{\sqrt{2}}{2}ie^{-iE_0t/\hbar}[\sin(\omega t)]\hat{D}|\varphi_B\rangle \\ &\quad + \frac{1}{2}e^{-iE_0t/\hbar}[-1 + \cos(\omega t)]\hat{D}|\varphi_C\rangle \\ &= \frac{d}{2}e^{-iE_0t/\hbar}[1 + \cos(\omega t)]|\varphi_A\rangle + 0 - \frac{d}{2}e^{-iE_0t/\hbar}[-1 + \cos(\omega t)]|\varphi_C\rangle.\end{aligned}$$

For an arbitrary time  $t$ , due to the time evolution of the new wavefunction  $\hat{D}|\psi(t)\rangle$ , the particle will either be entirely found localized around atom  $A$  (that is, if  $t = \frac{\sqrt{2}\pi n\hbar}{a}$ ), entirely around atom  $C$  (if measured at time  $t = \frac{\sqrt{2}\pi(2n+1)\hbar}{2a}$ ), or a linear time-dependent combination of  $|\varphi_A\rangle$  and  $|\varphi_C\rangle$ , as seen above. These are the values which can be found upon measurement.

(d) Allow me to return to the initial state of our particle, which I had determined in part (b):

$$\begin{aligned}|\psi(t)\rangle &= e^{-iE_0t/\hbar}[c_1 + c_2e^{-i\omega t} + c_3e^{i\omega t}]|\varphi_A\rangle \\ &\quad + \sqrt{2}e^{-iE_0t/\hbar}[-c_2e^{-i\omega t} + c_3e^{i\omega t}]|\varphi_B\rangle \\ &\quad + e^{-iE_0t/\hbar}[-c_1 + c_2e^{-i\omega t} + c_3e^{i\omega t}]|\varphi_C\rangle.\end{aligned}$$

Now consider the arbitrary initial conditions, so we may express each complex coefficient  $c'_k$  in complex polar form:  $c'_k = r_k e^{i\alpha_k}$  for the real positive radius  $r_k$  and phase  $\alpha_k$ ;  $k = 1, 2, 3$ . The normalization condition on  $|\psi(t)\rangle$  in the  $\{|\varphi_A\rangle, |\varphi_B\rangle, |\varphi_C\rangle\}$  basis is then just  $\sum_{k=1}^3 r_k^2 = 1$ , so each phase  $\alpha_k$  just determines an initial position around each atom. For simplicity, I define  $\Delta\alpha_{jk} = \alpha_j - \alpha_k$ . The time evolution of the expectation value of  $\hat{D}$  is determined by the time evolution of each state vector  $|\psi(t)\rangle, \langle\psi(t)|$  in the inner product. Thus we obtain

$$\begin{aligned}\langle\psi(t)|\hat{D}|\psi(t)\rangle &= \langle\psi(t)|\left(de^{-iE_0t/\hbar}(c_1 + c_2e^{-i\omega t} + c_3e^{i\omega t})|\varphi_A\rangle - de^{-iE_0t/\hbar}(-c_1 + c_2e^{-i\omega t} + c_3e^{i\omega t})|\varphi_C\rangle\right) \\ &= d(|c_1 + c_2e^{-i\omega t} + c_3e^{i\omega t}|^2) - d(|-c_1 + c_2e^{-i\omega t} + c_3e^{i\omega t}|^2) \\ &= d(|c_1|^2 + |c_2|^2 + |c_3|^2 + c_1c_2^*e^{i\omega t} + c_1c_3^*e^{-i\omega t} + c_1^*c_2e^{-i\omega t} + c_1^*c_3e^{i\omega t} + c_2c_3^* + c_2^*c_3) \\ &\quad - d(|c_1|^2 + |c_2|^2 + |c_3|^2 - c_1c_2^*e^{i\omega t} - c_1c_3^*e^{-i\omega t} - c_1^*c_2e^{-i\omega t} - c_1^*c_3e^{i\omega t} + c_2c_3^* + c_2^*c_3) \\ &= 2d(c_1c_2^*e^{i\omega t} + c_1c_3^*e^{-i\omega t} + c_1^*c_2e^{-i\omega t} + c_1^*c_3e^{i\omega t}) \\ &= 2dr_1r_2(e^{i\Delta\alpha_{12}}e^{i\omega t} + e^{-i\Delta\alpha_{12}}e^{-i\omega t}) + 2dr_1r_3(e^{i\Delta\alpha_{13}}e^{-i\omega t} + e^{-i\Delta\alpha_{13}}e^{i\omega t}) \\ &= 2dr_1r_2\left(e^{i(\Delta\alpha_{12}+\omega t)} + e^{-i(\Delta\alpha_{12}+\omega t)}\right) + 2dr_1r_3\left(e^{i(\Delta\alpha_{13}-\omega t)} + e^{-i(\Delta\alpha_{13}-\omega t)}\right) \\ &= 4dr_1r_2\cos(\alpha_1 - \alpha_2 + \omega t) + 4dr_1r_3\cos(\alpha_1 - \alpha_3 - \omega t) \\ &= 4dr_1[r_2\cos(\alpha_1 - \alpha_2 + \omega t) + r_3\cos(\alpha_1 - \alpha_3 - \omega t)].\end{aligned}$$

Since the initial conditions are arbitrary, and  $r_1, r_2, r_3, \alpha_1, \alpha_2, \alpha_3$  are all constant initial scalars, we can observe that the expectation value  $\langle\hat{D}\rangle$  oscillates with frequency  $\omega = \frac{\sqrt{2}a}{\hbar}$ . Thus the Bohr

frequencies appearing in the evolution of  $\hat{D}$  are just  $\pm \frac{\sqrt{2}a}{\hbar}$ . If we examine the energies for various eigenstates of  $\hat{H}$ , we notice that these Bohr frequencies appearing in the  $\hat{D}$  evolution are equivalent to the difference of said energies:

$$\frac{\sqrt{2}a}{\hbar} = \frac{E_0 - (E_0 - \sqrt{2}a)}{\hbar} \quad \text{and} \quad -\frac{\sqrt{2}a}{\hbar} = \frac{E_0 - (E_0 + \sqrt{2}a)}{\hbar},$$

which is valid since again,  $a$  has dimensions of energy. The physical interpretation of the operator  $\hat{D}$  is the distance from the center atom,  $B$ . When the electron is around  $A$ , the measured value is  $+d$ , 0 when around  $B$ , and  $-d$  when around  $C$ , which is as expected. The Bohr frequencies  $\pm \frac{\sqrt{2}a}{\hbar}$  are only appearing due to the coupling of the electron between atoms  $A, B$  or  $B, C$ . The reason there are no Bohr frequencies like  $\frac{1}{\hbar} (E_0 + \sqrt{2}a - E_0 - \sqrt{2}a) = \frac{2\sqrt{2}a}{\hbar}$  is because there exists no coupling between atoms  $A$  and  $C$ , hence no interaction.

The frequencies of the electromagnetic waves which can be absorbed or emitted by the molecule are equivalent to the Bohr frequencies determined above, since the energy difference relates to the required energy for the electron to ‘step up’ into the potential of the surrounding atoms.

Due to the triatomic molecular bond, the potential surrounding atom  $B$  is much greater than that surrounding atom  $A$  or  $C$  because it also takes into account its potential, in addition to the potential of *both*  $A$  and  $C$ ; this implies that while the electron is located around  $A$  or  $C$ , it is perturbed into an unstable state, hence the emission or absorption of these same Bohr frequencies.