It is not necessary that an electron be described by an eigenfunction of the Hamiltonian operator. Many problems encountered by quantum chemists and computational chemists lead to wavefunctions that are not eigenfunctions of the Hamiltonian operator. Science is like that; interesting problems are not simple to solve. They require adaptation of current techniques, creative energy, and a good set of skills developed by studying solutions to previously solved interesting problems.

Consider a free electron in one dimension that is described by the wavefunction

\[ \psi(x) = C_1 \psi_1(x) + C_2 \psi_2(x) \]

with

\[ \begin{align} \psi_1(x) &= \left( \frac{1}{2L} \right)^{1/2} e^{ik_1x} \\ \psi_2(x) &= \left( \frac{1}{2L} \right)^{1/2} e^{ik_2x} \end{align} \]

where \( (k_{1}) \) and \( (k_{2}) \) have different magnitudes. Although such a function is not an eigenfunction of the momentum operator or the Hamiltonian operator, we can calculate the average momentum and average energy of an electron in this state from the expectation value integral. (Note: "in-this-state" means "described-by-this-wavefunction".)

Exercise \( \PageIndex{1} \)

Show that the function \( \psi(x) \) defined by Equation \( \ref{5-21} \) is not an eigenfunction of the momentum operator or the Hamiltonian operator for a free electron in one dimension.

The function shown in Equation \( \ref{5-21} \) belongs to a class of functions known as superposition functions, which are linear combinations of eigenfunctions. A linear combination of functions is a sum of functions, each multiplied by a weighting coefficient, which is a constant. The adjective linear is used because the coefficients are constants. The constants, e.g. \( (C_{1}) \) and \( (C_{2}) \) in Equation \( \ref{5-21} \), give the weight of each component \( (\psi_{1}) \) and \( (\psi_{2}) \) in the total wavefunction. Notice from the discussion previously that each component in Equation \( \ref{5-21} \) is an eigenfunction of the momentum operator and the Hamiltonian operator although the linear combination function (i.e., \( \psi(x) \)) is not.

The expectation value, i.e. average value, of the momentum operator is found as follows. First, write the integral for the expectation value and then substitute into this integral the superposition function and its complex conjugate as shown below. Since we are considering a free particle in one dimension, the limits on the integration are \( (-L) \) and \( (+L) \) with \( (L) \) going to infinity.

\[ \begin{align} \langle p \rangle &= \int \psi^*(x) \left( -i\hbar \frac{d}{dx} \right) \psi(x) \, dx \\ &= \frac{-i\hbar}{2L} \int_{-L}^{+L} \left( C_1^* e^{-ik_1x} + C_2^* e^{-ik_2x} \right) \left( (ik_1)C_1 e^{ik_1x} + (ik_2)C_2 e^{ik_2x} \right) \, dx \end{align} \]

Cross-multiplying the two factors in parentheses yields four terms.

\[ \langle p \rangle = I_1 + I_2 + I_3 + I_4 \]
An integral of two different functions, e.g. $\int \psi_1^* \psi_2 \, dx$, is called an **overlap integral** or **orthogonality integral**. When such an integral equals zero, the functions are said to be orthogonal. The integrals in ($I_3$) and ($I_4$) are zero because the functions ($\psi_1$) and ($\psi_2$) are orthogonal. We know ($\psi_1$) and ($\psi_2$) are orthogonal because of the **Orthogonality Theorem**, described previously, that states that eigenfunctions of any Hermitian operator, such as the momentum operator or the Hamiltonian operator, with different eigenvalues, which is the case here, are orthogonal. Also, by using **Euler's formula** and following Example ($\PageIndex{1}$) below, you can see why these integrals are zero.

**Example ($\PageIndex{1}$)**

For the integral part of ($I_3$) obtain

\[
\int \cos[(k_2 - k_1)x] \, dx + i \int \sin[(k_2 - k_1)x] \, dx \nonumber
\]

from Euler's formula.

**Solution**

Here we have the integrals of a cosine and a sine function along the x-axis from minus infinity to plus infinity. Since these integrals are the area under the cosine and sine curves, they must be zero because the positive lobes are canceled by the negatives lobes when the integration is carried out from $(-\infty)$ to $(+\infty)$.

As a result of this orthogonality, ($\langle p \rangle$) is just ($I_1 + I_2$), which is

\[
\begin{align}
\langle p \rangle &= C_1^* C_1 \hbar k_1 + C_2^* C_2 \hbar k_2 \\
&= C_1^* C_1 p_1 + C_2^* C_2 p_2
\end{align}
\]

where ($\hbar k_1$) is the momentum ($p_1$) of state ($\psi_1$), and ($\hbar k_2$) is the momentum ($p_2$) of state ($\psi_2$). As explained in Chapter 3, an average value can be calculated by summing, over all possibilities, the possible values times the probability of each value. Equation ($\langle E \rangle$) has this form if we interpret ($C_1^* C_1$) and ($C_2^* C_2$) as the probability that the electron has momentum ($p_1$) and ($p_2$), respectively. These coefficients therefore are called probability amplitude coefficients, and their absolute value squared gives the probability that the electron is described by ($\psi_1$) and ($\psi_2$), respectively. This interpretation of these coefficients as probability amplitudes is very important.

**Exercise ($\PageIndex{2}$)**

- Find the expectation value for the energy ($\langle E \rangle$) for the superposition wavefunction given by Equation ($\langle E \rangle$).

- Explain why ($C_1^* C_1$) is the probability that the electron has energy ($\hbar^2 k^2_1/2m$) and ($C_2^* C_2$) is the probability that the electron has energy ($\hbar^2 k^2_2/2m$).
What is the expectation value for the energy when both components have equal weights in the superposition function, i.e. when \( C_1 = C_2 = 2^{-1/2} \)?

Contributors

- David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski ("Quantum States of Atoms and Molecules")