21.2: Eigenfunctions and Eigenvalues

As we have already seen, an eigenfunction of an operator $\hat{A}$ is a function f such that the application of $\hat{A}$ on f gives f again, times a constant:

$$\hat{A} f=k f, \tag{21.2.1}$$

where k is a constant called the eigenvalue.

When a system is in an eigenstate of observable A (i.e., when the wave function is an eigenfunction of the operator $\hat{A}$) then the expectation value of A is the eigenvalue of the wave function. Therefore:

$$\hat{A} \psi(\mathbf{r})=a \psi(\mathbf{r}), \tag{21.2.2}$$

then:

$$\begin{aligned}
\langle A\rangle & =\int \psi^*(\mathbf{r}) \hat{A} \psi(\mathbf{r}) d \mathbf{r} \\
& =\int \psi^*(\mathbf{r}) a \psi(\mathbf{r}) d \mathbf{r} \\
& =a \int \psi^*(\mathbf{r}) \psi(\mathbf{r}) d \mathbf{r}=a,
\end{aligned} \tag{21.2.3}$$

which implies that:

$$\int \psi^*(\mathbf{r}) \psi(\mathbf{r}) d \mathbf{r}=1. \tag{21.2.4}$$

This property of wave functions is called normalization, and in the one-electron TISEq guarantees that the maximum probability of finding an electron over the entire space is one.[1]

A unique property of quantum mechanics is that a wave function can be expressed not just as a simple eigenfunction, but also as a combination of several of them. We have in part already encountered such property in the previous chapter, where complex hydrogen orbitals have been combined to form corresponding linear ones. As a general example, let us consider a wave function written as a linear combination of two eigenstates of $\hat{A}$, with eigenvalues a and b:

$$\psi=c_a \psi_a+c_b \psi_b, \tag{21.2.5}$$

where $\hat{A} \psi_a=a \psi_a$ and $\hat{A} \psi_b=b \psi_b$. Then, since ψ_a and ψ_b are orthogonal and normalized (usually abbreviated as orthonormal), the expectation value of A is:

$$\begin{aligned}
\langle A\rangle & =\int \psi^* \hat{A} \psi d \mathbf{r} \\
& =\int\left[c_a \psi_a+c_b \psi_b\right]^* \hat{A}\left[c_a \psi_a+c_b \psi_b\right] d \mathbf{r} \\
& =\int\left[c_a \psi_a+c_b \psi_b\right]^*\left[a c_a \psi_a+b c_b \psi_b\right] d \mathbf{r} \\
& =a\left|c_a\right|^2 \int \psi_a^* \psi_a d \mathbf{r}+b c_a^* c_b \int \psi_a^* \psi_b d \mathbf{r}+a c_b^* c_a \int \psi_b^* \psi_a d \mathbf{r}+b\left|c_b\right|^2 \int \psi_b^* \psi_b d \mathbf{r} \\
& =a\left|c_a\right|^2+b\left|c_b\right|^2 .
\end{aligned} \tag{21.2.6}$$

This result shows that the average value of A is a weighted average of eigenvalues, with the weights being the squares of the coefficients of the eigenvectors in the overall wavefunction.[2]

1. Imposing the normalization condition is the best way to find the constant A in the solution of the TISEq for the particle in a box, a topic that we delayed in chapter 20.
2. This section was adapted in part from Prof. C. David Sherrill's A Brief Review of Elementary Quantum Chemistry Notes available here.