10.3: A Refresher on Electronic Quantum Numbers

Each electron in an atom is described by four different quantum numbers.

- Principal quantum number: $n = 1, 2, 3 ... \infty$. It determines the overall size and energy of an orbital.
- Angular momentum quantum number: $l = 0, 1, 2...(n-1)$. It is related with the shape of the orbital. In chemistry, we usually use the letters $s, p, d, f...$ to denote an orbital with $l = 0, 1, 2, 3...$ For example, for the 1s orbital, $n = 1$ and $l = 0$.
- Magnetic quantum number: $m_l = -l, -l+1, ..., 0, ... l-1, l$. It specifies the orientation of the orbital. For a p orbital, for example, $l = 1$ and therefore m_l can take the values $-1, 0, 1$. In general, there are $2l+1$ values of m_l for a given value of l. That is why p orbitals come in groups of 3, d orbitals come in groups of 5, etc.
- Spin quantum number: $m_s = -1/2$ or $1/2$. The Pauli exclusion principle states that no two electrons in the same atom can have identical values for all four of their quantum numbers. This means that no more than two electrons can occupy the same orbital, and that two electrons in the same orbital must have opposite spins.

The first three quantum numbers specify the particular orbital the electron occupies. For example, the orbital $2p_{-1}$ is the orbital with $n = 2$, $l = 1$ and $m_l = -1$. Two electrons of opposite spin can occupy this orbital.

So far we've been limited to the 1s orbital, but now that we are more comfortable with the nomenclature of orbitals, we can start doing some math with orbitals that have more complex expressions.

Example 10.3.1:

After solving the Schrödinger equation for the hydrogen atom, we obtain the following expression for the $2p_{+1}$ orbital:

$$\psi_{2p_{+1}} = Are^{-r/(2a_0)} \sin\theta e^{i\phi}$$

as usual, we obtain the constant A from the normalization condition. Calculate A.

Solution

In three dimensions, the normalization condition is:

$$\int\limits_{all\ space} |\psi|^2 \, dV = 1$$

Because the orbital is expressed in spherical coordinates:

$$\int\limits_{all\ space} |\psi|^2 \, dV = \int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} \psi^*(r,\theta,\phi)\psi(r,\theta,\phi)\, r^2 \sin\theta \, dr d\theta d\phi = 1$$

For this particular orbital:

$$\psi_{2p_{+1}} = Are^{-r/(2a_0)} \sin\theta e^{i\phi}$$

$$\psi^*_{2p_{+1}} = Are^{-r/(2a_0)} \sin\theta e^{-i\phi}$$

$$\psi^*_{2p_{+1}}\psi_{2p_{+1}} = A^2r^2e^{-r/(a_0)} \sin^2\theta \left(e^{i\phi}e^{-i\phi}\right) = A^2r^2e^{-r/(a_0)} \sin^2\theta$$

so,

$$\int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} \psi^*(r,\theta,\phi)\psi(r,\theta,\phi)\, r^2 \sin\theta \, dr d\theta d\phi = \int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} {\color{red}A^2r^2e^{-r/(a_0)}\sin^2\theta}\, {\color{blue}r^2 \sin\theta \, dr d\theta d\phi} = 1$$

where the part of the integrand highlighted in blue comes from the differential of volume (dV) and the part in red comes from $|\psi|^2$. We need to integrate the whole expression, so:

$$\int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} A^2 r^2 e^{-r/(a_0)} \sin^2\theta\, r^2 \sin\theta\, dr d\theta d\phi = A^2 \int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} r^4 e^{-r/(a_0)} \sin^3\theta\, dr d\theta d\phi = A^2 \int_0^{2\pi} d\phi \int_0^{\pi} \sin^3\theta\, d\theta \int_0^{\infty} r^4 e^{-r/(a_0)}\, dr$$

$$\int_0^{2\pi} d\phi = 2\pi$$

$$\int_0^{\pi} \sin^3\theta\, d\theta = ?$$

From the formula sheet: $\int sin^3(ax)\, dx = \frac{1}{12a}\cos(3ax) - \frac{3}{4a}\cos(ax) + C$ so,

$$\int_0^{\pi} sin^3\theta\, d\theta = \frac{1}{12}\cos(3\pi) - \frac{3}{4}\cos(\pi) - \frac{1}{12}\cos(0) + \frac{3}{4}\cos(0) = \frac{1}{12}(-1) - \frac{3}{4}(-1) - \frac{1}{12}(1) + \frac{3}{4}(1) = \frac{4}{3}$$

$$\int_0^{\infty} r^4 e^{-r/(a_0)}\, dr = ?$$

From the formula sheet:

$\int_0^{\infty} x^n e^{-ax} dx = \frac{n!}{a^{n+1}}$, $a > 0, n$ is a positive integer.

Here, $a = 1/a_o$ and $n = 4$, so:

$$\int_0^{\infty} r^4 e^{-r/(a_0)}\, dr = \frac{4!}{(1/a_0)^5} = 24a_0^5$$

Putting the three pieces together:

$$A^2 \int_0^{2\pi} d\phi \int_0^{\pi} \sin^3\theta\, d\theta \int_0^{\infty} r^4 e^{-r/(a_0)}\, dr = A^2 \times 2\pi \times \frac{4}{3} \times 24a_0^5 = 64a_0^5\pi A^2 = 1$$

Solving for A:

$$A = \frac{1}{8\left(a_0^5\pi\right)^{1/2}}$$

The normalized orbital is, therefore,

$$\psi_{2p_{+1}} = \frac{1}{8\left(a_0^5\pi\right)^{1/2}} r e^{-r/(2a_0)} \sin\theta e^{i\phi}$$