Particle in a Spherical Box

For a particle enclosed in a spherical box, the potential is piecewise:

$$V(r) = \begin{cases} 0 & 0 \leq r \leq a = 2\mathring{A} \\ \infty & otherwise \end{cases}$$

To determine the possible energies, W, of the system, we must first solve the 3D Schrodinger equation for a particle in a spherical box:

$$-\frac{\hbar^2}{2m_0}\nabla^2\Psi = W\Psi$$

Where ∇^2 is the Laplacian operator in spherical coordinates and m_0 is the mass of the particle. Relying upon seperation of variables to determine the form of the solution, we substitute $Y_l^m(\theta,\phi)R_{n,l}(r)$. In this case, the angular components of the wavefunction are equivalent to the spherical harmonics from the hydrogen atom:

$$\begin{aligned} Y_l^m(\theta,\phi) &= P_l^m(\cos\theta)e^{\pm im\phi} \\ P_l^m(x) &= (1-x^2)^{|m|/2}\frac{d}{dx}^{|m|}P_l(x) \\ P_l(x) &= \frac{1}{2^l l!}(\frac{d}{dx})^l(x^2-1)^l \end{aligned}$$

Inside the sphere, the separated radial equation is, where $k = \frac{\sqrt{2mW}}{\hbar}$:

$$\frac{d}{dr}(r^2\frac{dR_{n,l}}{dr}) + \frac{2mr^2}{\hbar}W_{n,l}R = l(l+1)R_{n,l}$$

If we let $x = kr$ so $dx = kdr$, the equation becomes:

$$\frac{d}{dx}(x^2\frac{dR_{n,l}}{dx}) + (x^2 - l(l+1))R_{n,l} = 0$$

We know the solution takes the form:

$$R(r) = \frac{J_{l+1/2}(kr)}{\sqrt{kr}}$$

n, l	$zero$	Degeneracy	$Energy(\frac{\hbar^2}{2m_0a^2})$	$Energy(eV)$
n=1, l=0	3.142	1	3.142^2	$3.142^2 * 0.9524 = 9.402$
n=1, l=1	4.493	3	4.493^2	$4.493^2 * 0.9524 = 19.226$
n=1, l=2	5.763	7	5.763^2	$5.763^2 * 0.9524 = 31.631$
n=2, l=0	6.283	1	6.283^2	$6.283^2 * 0.9524 = 37.597$

Table 1: Table 2: Four lowest energies for spherical box

Where $J_{n+1/2}$ is the Bessel function of half integral order. At the boundary, $R(a) = 0$, so:

$$\frac{J_{l+1/2}(ka)}{\sqrt{ka}} = 0$$
$$ka = z_{n,l}$$

Where $z_{n,l}$ is the nth zero of the Bessel function. Rearranging for W gives:

$$W_{n,l} = z_{n,l}^2 \frac{\hbar^2}{2m_0a^2}$$

Clearly, the energy does not depend on the magnetic quantum number m, so for every value of the azimuthal quantum number l we can have $m = -l..0..l$ that will yield the same energy. Therefore each energy level is $2l + 1$-fold degenerate.

Particle in a Cubic Box

For a particle enclosed in a spherical box, the potential is piecewise ($a = 2\mathring{A}$):

$$V(r) = \begin{cases} 0 & 0 < x < a\sqrt[3]{\frac{4\pi}{3}}, 0 < y < a\sqrt[3]{\frac{4\pi}{3}}, 0 < z < a\sqrt[3]{\frac{4\pi}{3}}, \\ \infty & otherwise \end{cases}$$

The 3D Schrodinger equation for a particle in a cubic box (for simplification, let $b = a\sqrt[3]{\frac{4\pi}{3}}$):

$$-\frac{\hbar^2}{2m}\nabla^2\Psi = W\Psi$$

Where ∇^2 is the Laplacian operator in Cartesian coordinates. Using separation of variables $[\Psi(x,y,z) = X(x)Y(y)Z(z)]$ to solve the 3D Schrodinger Equation for a particle in a (cubic) box, we find:

$$-\frac{\hbar^2}{2m}\frac{X''}{X} = W_1$$
$$-\frac{\hbar^2}{2m}\frac{Y''}{Y} = W_2$$
$$-\frac{\hbar^2}{2m}\frac{Z''}{Z} = W_3$$

Where each equation is equivalent to that describing a 1D particle in the box with the same boundary conditions ($[X(0), Y(0), Z(0)] = 0$ and $[X(b), Y(b), Z(b)] = 0$) Therefore, we can write:

$$X(x)_n = \sqrt{\frac{1}{2b}}\sin(\frac{n_x\pi}{b}x)$$
$$Y(y)_n = \sqrt{\frac{1}{2b}}\sin(\frac{n_y\pi}{b}y)$$
$$Z(z)_n = \sqrt{\frac{1}{2b}}\sin(\frac{n_z\pi}{b}z)$$

The overall wavefunction is then:

$$\Psi(x,y,z)_n = \sqrt{\frac{8}{b^3}}\sin(\frac{n_x\pi}{b}x)\sin(\frac{n_y\pi}{b}y)\sin(\frac{n_z\pi}{b}z)$$

The energies are:

$$W_{1n} = \frac{n_x^2\pi^2\hbar^2}{2mb^2}$$
$$W_{2n} = \frac{n_y^2\pi^2\hbar^2}{2mb^2}$$
$$W_{3n} = \frac{n_z^2\pi^2\hbar^2}{2mb^2}$$

We observe what is formally known as degeneracy, where different combinations of of n_x, n_y, n_z, bring about the same total energy of the system.

$$W_n = W_{1n} + W_{2n} + W_{3n}$$

(n_x, n_y, n_z)	Degeneracy	Energy ($\frac{\hbar^2}{2mb^2}$)	Energy (Ev)
(1,1,1)	1	$3\pi^2$	10.8532
(2,1,1),(1,2,1),(1,1,2)	3	$6\pi^2$	21.706
(2,2,1),(2,1,2),(1,2,2)	3	$9\pi^2$	32.5596
(3,1,1),(1,3,1),(1,1,3)	3	$11\pi^2$	39.795

Table 2: Table 2: Four lowest energies for cubic box

Examining Table 1 and 2, we see that the cubic box case has slightly higher energies for each of the four lowest energy states; cubic energies are approximately 1 to 2 eV greater than the spherical energies. Also, the degeneracies are practically incomparable; the ground state and the first excited state share the same number of degeneracies in both the spherical and cubic case but the higher order excited states are incongruent.