POTENTIAL BOX

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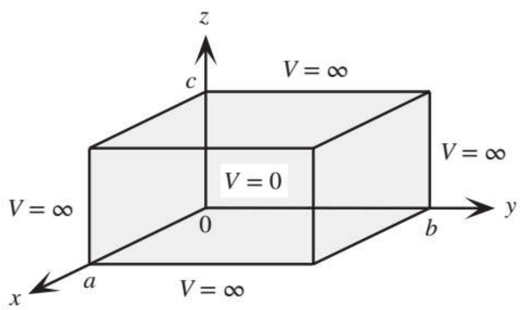
Potential Box



- A particle confined in a three-dimensional potential box: $V = 0$ in $0 < x < a$, $0 < y < b$, and $0 < z < c$, and V infinite outside.
- The electron essentially lives in the "box."
- What will the behavior of the electron be in this box?

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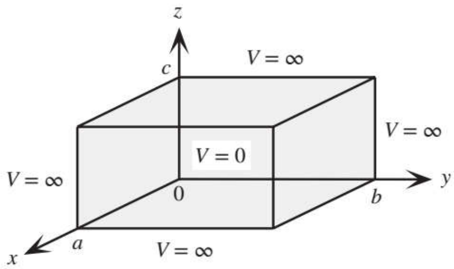
Wavefunctions

- Schrodinger's equation:

$$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}+\frac{2m_e}{\hbar^2}(E-V)\psi=0$$



- Separation of variables:

$$\psi(x,y,z)=\psi_x(x)\,\psi_y(y)\,\psi_z(z)$$

- Wavefunction:

$$\psi(x,y,z)=A\sin(k_x x)\sin(k_y y)\sin(k_z z)$$

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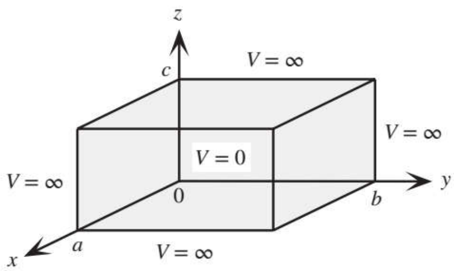
Wavefunctions

- Boundary conditions:

  $\psi(x, y, z) = 0$ at $x = a$, $y = b$ and $z = c$

$$k_x a = n_1\pi \rightarrow k_x = \frac{n_1\pi}{a}$$
$$k_y a = n_2\pi \rightarrow k_y = \frac{n_2\pi}{b}$$
$$k_z a = n_3\pi \rightarrow k_z = \frac{n_3\pi}{c}$$



- Three quantum numbers n_1, n_2, and n_3 associated with $\psi_x(x)$, $\psi_y(y)$, and $\psi_z(z)$.

$$\psi_{n_1n_2n_3}(x,y,z)=A\sin\left(\frac{n_1\pi x}{a}\right)\sin\left(\frac{n_2\pi y}{b}\right)\sin\left(\frac{n_3\pi z}{c}\right)$$

- Normalization: $\int\left|\psi_{n_1n_2n_3}(x,y,z)\right|^2 dxdydz \quad A=\left(\frac{2}{a}\right)^{3/2}$

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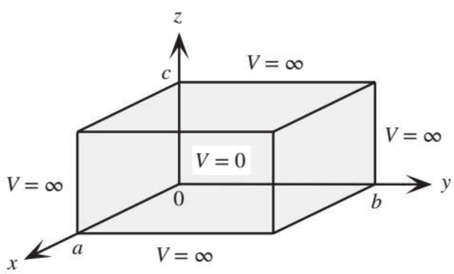
Electronic Energies

- Substituting the wavefunction into the Schrödinger:

$$E = E(k_x, k_y, k_z) = \frac{\hbar^2}{2m_e}(k_x^2 + k_y^2 + k_z^2)$$

$$E_{n_1 n_2 n_3} = \frac{h^2}{8m_e}\left(\frac{n_1^2}{a^2} + \frac{n_2^2}{b^2} + \frac{n_3^2}{c^2}\right)$$

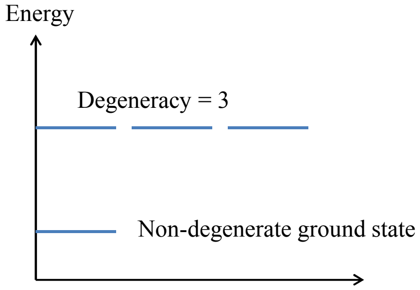


- For a square box for which $a = b = c$:

$$E_{n_1 n_2 n_3} = \frac{h^2(n_1^2 + n_2^2 + n_3^2)}{8m_e a^2} = \frac{h^2 N^2}{8m_e a^2}$$

Degenerate States

- E_{111} is the lowest energy for the electron when $n_1 = 1$, $n_2 = 1$, and $n_3 = 1$.
- The number of states that have the same energy is termed the degeneracy of that energy level. The second energy level E_{211} is thus three-fold degenerate.
- How many states (eigenfunctions) are there at energy level E_{443} for a square potential energy box?

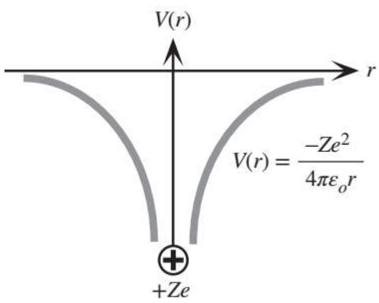


HYDROGEN ATOM

Potential Energy

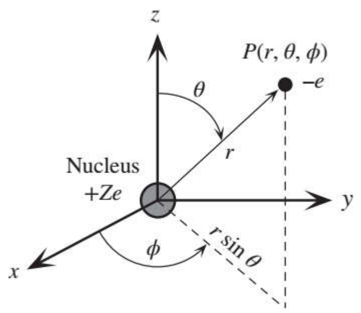
- Consider the behavior of the electron in a hydrogenic (hydrogen-like) atom, which has a nuclear charge of $+Ze$.
- For the hydrogen atom, $Z = 1$, whereas for an ionized helium atom He+, $Z = 2$. For a doubly ionized lithium atom Li++, $Z = 3$
- Potential energy:

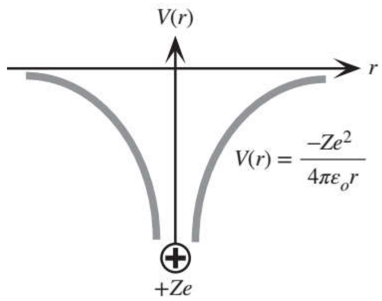
$$V(r) = \frac{-Ze^2}{4\pi\varepsilon_0 r}$$



Wavefunctions

- The problem has a spherical symmetry.
- In an analogy with the three-dimensional potential well, there should be three quantum numbers to characterize the wavefunction, energy, and momentum of the electron.
- The three quantum numbers are called the **principal, orbital angular momentum,** and **magnetic quantum numbers** → n, l, and m_l.





Wavefunctions

$$\psi(r,\theta,\phi) = R(r)\,Y(\theta,\phi)$$

- $R(r)$: radial function → depends only on r.
- $Y(\theta, \phi)$: spherical harmonic → expresses the angular dependence of the wavefunction.
- These functions are characterized by the quantum numbers n, l, m_l. The radial part $R(r)$ depends on n and l, whereas the spherical harmonic depends on l and m_l, so

$$\psi(r,\theta,\phi) = \psi_{n,l,m_l}(r,\theta,\phi) = R_{n,l}(r)\,Y_{l,m_l}(\theta,\phi)$$

Quantum Numbers

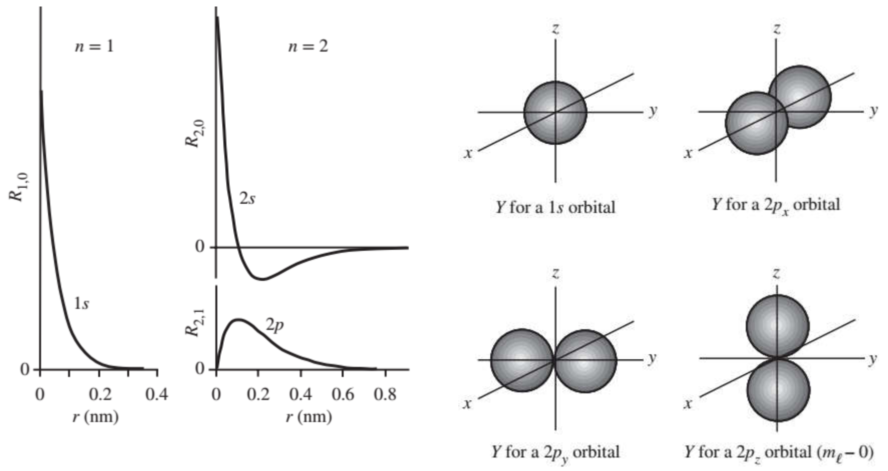
Principal quantum number	$n = 1, 2, 3, \ldots$
Orbital angular momentum quantum number	$l = 0, 1, 2, \ldots, (n-1) < n$
Magnetic quantum number	$m_l = -l, -(-l-1), \ldots, 0, \ldots, (l-1), l$ or $\lvert m_l \rvert \le l$

	ℓ				
n	**0**	**1**	**2**	**3**	**4**
1	1*s*				
2	2*s*	2*p*			
3	3*s*	3*p*	3*d*		
4	4*s*	4*p*	4*d*	4*f*	
5	5*s*	5*p*	5*d*	5*f*	5*g*

R(r) and Y(θ,ϕ)

n	ℓ	$R(r)$	m_ℓ	$Y(\theta, \phi)$		
1	0	$\left(\frac{1}{a_o}\right)^{3/2} 2 \exp\left(-\frac{r}{a_o}\right)$	0	$\frac{1}{2\sqrt{\pi}}$		
2	0	$\left(\frac{1}{2a_o}\right)^{3/2}\left(2-\frac{r}{a_o}\right)\exp\left(-\frac{r}{2a_o}\right)$	0	$\frac{1}{2\sqrt{\pi}}$		
			0	$\frac{1}{2}\sqrt{\frac{3}{\pi}}\cos\theta$		
2	1	$\left(\frac{1}{2a_o}\right)^{3/2}\left(\frac{r}{\sqrt{3}a_o}\right)\exp\left(-\frac{r}{2a_o}\right)$	1	$\frac{1}{2}\sqrt{\frac{3}{2\pi}}\sin\theta e^{j\phi}$	$\propto \sin\theta\cos\phi$	Correspond to $m_\ell = -1$ and $+1$.
			−1	$\frac{1}{2}\sqrt{\frac{3}{2\pi}}\sin\theta e^{-j\phi}$	$\propto \sin\theta\sin\phi$	

R(r) and Y(θ,ϕ)



n = 1
R1,0
1s
0
0
0.2
0.4
r (nm)
n = 2
R2,0
2s
0
R2,1
2p
0
0
0.2
0.4
0.6
0.8
r (nm)
Y for a 1s orbital
Y for a 2px orbital
Y for a 2py orbital
Y for a 2pz orbital (mℓ = 0)

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