Topic 0

Course Prep

0.1 Chapter 1: Introduction to Inorganic Chemistry

From Miessler et al. (2014).

0.1.1 Notes

- **Inorganic chemistry**: The chemistry of everything that is not organic chemistry (the chemistry of hydrocarbon compounds and their derivatives).

- **Organometallic chemistry**: The chemistry of compounds containing metal-carbon bonds and the catalysis of many organic reactions.

- There is also both **bioinorganic chemistry** and **environmental chemistry** (Miessler et al., 2014, p. 1), as well as **analytical chemistry**, **physical chemistry**, **petroleum chemistry**, **polymer chemistry** (Miessler et al., 2014, p. 4).

  - Note, though, that there are no strict dividing lines between subfields of chemistry nowadays, and most professionals work in multiple fields.

- Single, double, and triple bonds (both metal-metal and metal-carbon bonds) are found in organic and inorganic chemistry.

- Quadruple bonds exist between metal atoms in some compounds.

(a) Sigma (σ) bond. (b) Pi (π) bond. (c) Delta (δ) bond.
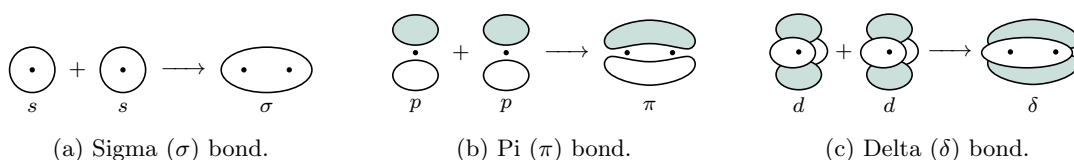
Figure 1: Examples of bonding interactions.

  - No such bonds exist between carbon atoms because two carbon atoms max out at a triple bond.
  - Quadruple bonds possess one sigma bond, two pi bonds, and one delta (δ) bond.
  - The delta bond is only possible with metal atoms because these atoms possess energetically accessible d orbitals.

- Quintuple bonds between transition metals have been reported, but scientists have not yet reached a consensus on to what extent these exist.
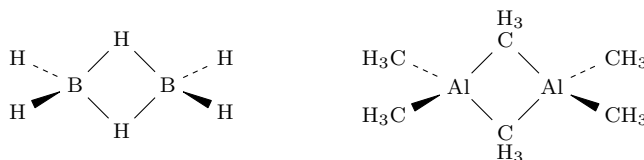
Figure 2: Inorganic compounds containing bridging hydrogens and alkyl groups.

- Hydrogen atoms and alkyl groups can act as bridges in inorganic chemistry, excessively disobeying the octet rule (see Figure 2).

- **Coordination number**: The number of other atoms, molecules, or ions to which an atom is bonded.

- "Numerous inorganic compounds have central atoms with coordination numbers of five, six, seven, and higher" (Miessler et al., 2014, p. 2).

  – The most common coordination geometry for transition metals is octahedral.

- 4-coordinate carbon is almost always tetrahedral. 4-coordinate metals and nonmetals can be either tetrahedral or square planar.

- **Coordination complex**: A compound with a metal as the central atom or ion and some number of **ligands** bonded to it.

- **Ligand**: An anion or neutral molecule bonded to a central atom (frequently through N, O, or S).

- **Organometallic complex**: A coordination complex where carbon (potentially bonded to other things) is one of the ligands.
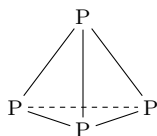
Figure 3: Tetrahedral geometry without a central atom.

- There are multiple kinds of tetrahedral structures. There is the standard arrangement seen in molecules such as methane, but there is also a form that lacks a central atom, as in elemental phosphorous P_4 (see Figure 3).

  – Other atoms such as boron and carbon also form units that surround a central cavity (e.g., icosahedral B_{12} and buckyballs C_{60}).

- Aromatic rings can bond to metals using all of their pi orbitals. This results in a metal suspended above the ring's center.

- **Cluster compound**: A compound where "a carbon atom is at the center of a polyhedron of metal atoms" (Miessler et al., 2014, p. 3).

  – There exist examples of carbon surrounded by five, six, or more metal atoms[1].

- Many new forms of elemental carbon have been discovered since the mid-1980s, notably including fullerenes (such as buckminsterfullerene, or buckyballs), carbon nanotubes, graphene, and polyyne wires.

- Miessler et al. (2014) give a brief history of inorganic chemistry for context.

  – Be aware of **crystal field theory** and **ligand field theory**.

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[1]This provides a challenge to theoretical inorganic chemists.

0.2 Chapter 2: Atomic Structure

From Miessler et al. (2014).

0.2.1 Notes

12/22:
- **Coinage metals**: Copper, silver, and gold, i.e., the transition metals in IUPAC Group 11.

- **Chalcogens**: Oxygen, sulfur, selenium, tellurium, and polonium, i.e., the nonmetals in Group 16.

- The energies of visible light emitted by the hydrogen atom are given by[2]

$$E = R_H \left(\frac{1}{2^2} - \frac{1}{n_h^2} \right)$$

  where n_h is an integer greater than 2 and R_H is the Rydberg constant for hydrogen (H).

  - Note that $R_H = 1.097 \times 10^7 \, \text{m}^{-1} = 2.179 \times 10^{-18} \, \text{J} = 13.61 \, \text{eV}$.
  - This equation was first discovered by Johann Balmer in 1885.
  - Infrared and ultraviolet emissions can be described by replacing 2^2 with integers n_l^2 in the above equation on the condition that $n_l < n_h$[3].

- The energy of the light emitted is related to its wavelength, frequency, and wavenumber by the equations

$$E = h\nu = \frac{hc}{\lambda} = hc\bar{\nu}$$

  where h is Planck's constant ($6.626 \times 10^{-34} \, \text{J s}$), c is the speed of light ($2.998 \times 10^8 \, \text{m s}^{-1}$), and ν, λ, and $\bar{\nu}$ are the frequency, wavelength, and **wavenumber**, respectively, of the light.

- **Wavenumber**: The number of waves that exist between two points along the light's path a given distance apart. *Measured in* waves per centimeter (SI: cm^{-1}).

  - Wavenumber is proportional to energy. This is why m^{-1} or cm^{-1} can be used as an energy unit.

- **Principal quantum number**: One of the quantities n in Balmer's equation.

- Bohr's atomic theory first explained the phenomenon of Balmer's equation, positing that "electrons may absorb light of certain specific energies and be excited to orbits of higher energy; they may also emit light of specific energies and fall to orbits of lower energy" (Miessler et al., 2014, pp. 11–12).

  - Bohr rewrote the Rydberg constant in terms of other quantities:

  $$R = \frac{2\pi^2 \mu Z^2 e^4}{(4\pi\varepsilon_0)^2 h^2}$$

  where. . .
    - μ is the reduced mass of the electron/nucleus combination $\frac{1}{\mu} = \frac{1}{m_e} + \frac{1}{m_{\text{nucleus}}}$, where $m_e = 9.11 \times 10^{-31} \, \text{kg}$ is the mass of the electron and m_{nucleus} is the mass of the nucleus.
    - Z is the nuclear charge.
    - $e = 1.602 \times 10^{-19} \, \text{C}$ is the charge of the electron.
    - h is Planck's constant.
    - $4\pi\varepsilon_0$ is the permittivity of a vacuum.
  - Importantly, note that the Rydberg constant for hydrogen R_H is not universal, and changes for the atom at hand based on factors like the mass of the nucleus.

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[2]Refer to Labalme (2020a), specifically Figure 7.6 and the accompanying discussion.
[3]n_l denotes the lower final energy level while n_h denotes the higher initial energy level.
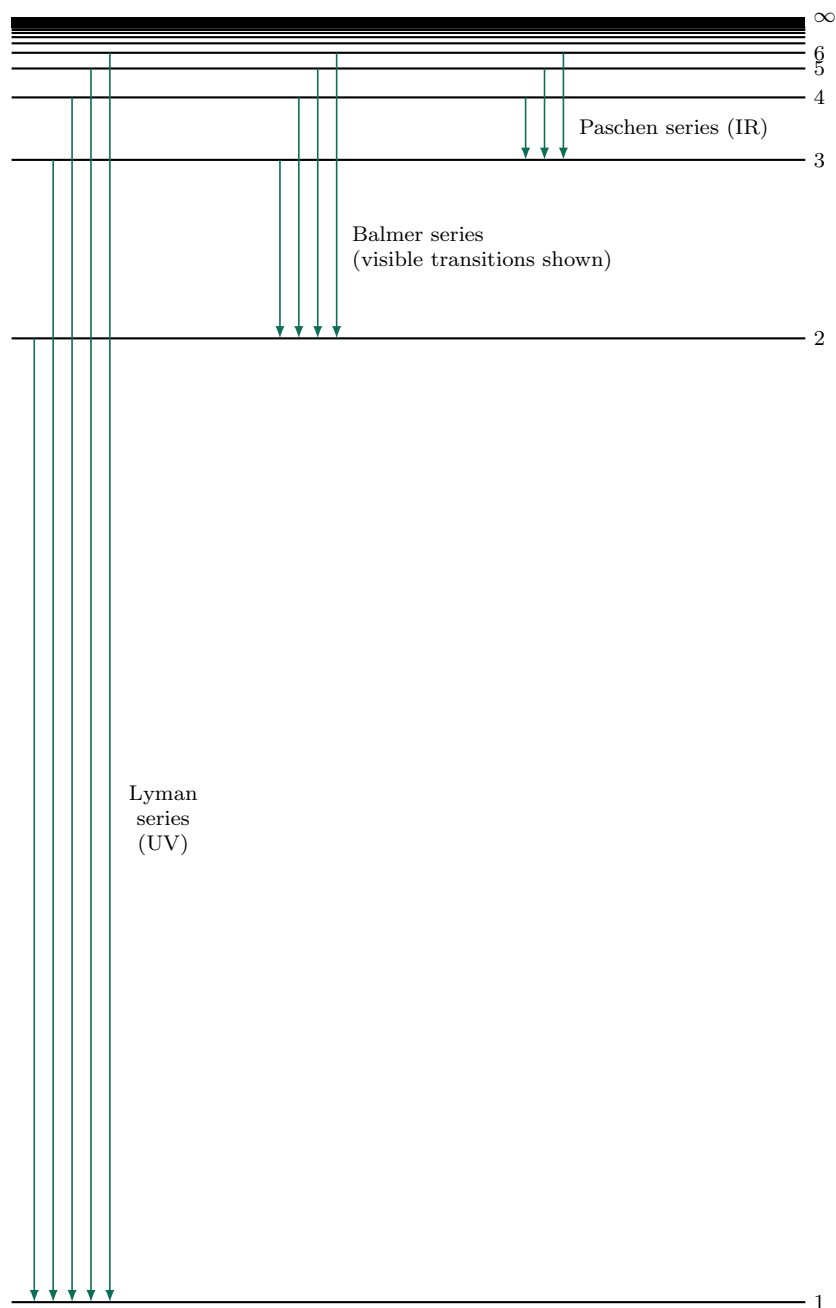
Figure 4: Hydrogen atom energy levels.

- **Balmer series**: The four main electron transitions in hydrogen that release electromagnetic radiation in the visible spectrum.

- **Lyman series**: The five main electron transitions in hydrogen that release electromagnetic radiation in the ultraviolet spectrum.

- **Paschen series**: The three main electron transitions in hydrogen that release electromagnetic radiation in the infrared spectrum.

- "The inverse square dependence of energy on n results in energy levels that are far apart in energy at small n and become much closer in energy at larger n" (Miessler et al., 2014, p. 12)

– Individual electrons can have more energy than they would possess in the infinite energy level, but at and above this point, the nucleus and electron are considered to be separate entities.

- **Heisenberg's uncertainty principle**: "There is a relationship between the inherent uncertainties in the location and momentum of an electron" (Miessler et al., 2014, p. 14).

$$\Delta x \, \Delta p_x \geq \frac{h}{4\pi}$$

– The above equation describes the x-component of the uncertainty, where Δx is the uncertainty in the position of the electron and Δp_x is the uncertainty in the momentum of the electron in the x-direction.

- Because of the uncertainty principle, we cannot treat electrons as particles with precisely described motion; instead, we must describe them in **orbitals**.

- **Orbital**: A region that describes the probable locations of an electron.

- **Electron density**: "The probability of finding the electron at a particular point in space" (Miessler et al., 2014, p. 14).

– This can be calculated in principle.

- Schrödinger and Heisenberg published (in 1926 and 1927, respectively) papers on atomic wave mechanics. Although they used very different mathematical techniques, their theories can be shown to be equivalent. However, we will introduce Schrödinger's more commonly used differential equations.

- "The Schrödinger equation describes the wave properties of an electron in terms of its position, mass, total energy, and potential energy" (Miessler et al., 2014, p. 14).

$$H\Psi = E\Psi$$

– In its simplest form, it is given by the above, where H is the **Hamiltonian operator**, E is the energy of the electron, and Ψ is the **wave function**.

- **Wave function**: A function that describes an electron wave in space, i.e., an atomic orbital.

- Energy values are another way of describing the quantization introduced with the Bohr model — different orbitals, characterized by different wave functions, each have characteristic energies.

- **Operator**: "An instruction or set of instructions that states what to do with the function that follows it" (Miessler et al., 2014, p. 14).

- **Hamiltonian operator**: An operator including derivatives that transforms the wave function into a constant (the energy) times Ψ. *Also known as $\hat{\boldsymbol{H}}$.*

$$H = \frac{-h^2}{8\pi^2 m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) - \frac{Ze^2}{4\pi\varepsilon_0 \sqrt{x^2 + y^2 + z^2}}$$

– In the form used for calculating the energy levels of one-electron systems, it is given by the above, where. . .

  - h is Planck's constant.
  - m is the mass of the electron.
  - e is the charge of the electron.
  - $\sqrt{x^2 + y^2 + z^2} = r$ is the distance from the nucleus.
  - Z is the charge of the nucleus.
  - $4\pi\varepsilon_0$ is the permittivity of a vacuum.

– The first part describes the kinetic energy of the electron, its energy of motion.

– The second part describes the potential energy of the electron, the result of the electrostatic attraction between it and the nucleus. It is commonly designated as $V(x, y, z)$.

- "Because n varies from 1 to ∞, and every atomic orbital is described by a unique Ψ, there is no limit to the number of solutions of the Schrödinger equation for an atom. Each Ψ describes the wave properties of a given electron in a particular orbital" (Miessler et al., 2014, p. 15).

- Electron density is proportional to Ψ^2.

- Necessary conditions for a physically realistic solution for Ψ:

    1. Ψ must be single-valued: There cannot be two probabilities for an electron at any position in space.

    2. Ψ and its first derivatives must be continuous: The probability must be defined at all positions in space and cannot change abruptly from one point to the next.

    3. Ψ must approach zero as $r \to \infty$: For large distances from the nucleus, the probability must grow smaller and smaller (the atom must be finite).

    4. The integral

    $$\int_{\text{all space}} \Psi_A \Psi_A{}^* \, d\tau = 1$$

    The total probability of an electron being somewhere in space must be 1. Applying this stipulation is called **normalizing** the wave function[4].

    5. The integral

    $$\int_{\text{all space}} \Psi_A \Psi_B{}^* \, d\tau = 0$$

    Ψ_A and Ψ_B are different orbitals within the same atom, and this stipulation reflects the fact that all orbitals in the same atom must be **orthogonal** to each other.

12/23:
- The Particle in a Box.

    – Imagine a one-dimensional "box" between $x = 0$ and $x = a$ with potential energy everywhere zero inside the "box" and everywhere infinite outside the box.

        ■ These energy constraints mean that the particle is completely trapped within the box (it would take an infinite amount of energy to leave), but also that no forces act on it within the box.

    – It follows that the wave equation for locations within the box is

    $$\frac{-h^2}{8\pi^2 m} \left(\frac{\partial^2 \Psi(x)}{\partial x^2} \right) = E\Psi(x)$$

    – Since sine and cosine functions have properties associated with waves, we propose that a general solution describing possible waves in the box is

    $$\Psi(x) = A \sin rx + B \cos sx$$

    where A, B, r, s are constants.

    – As seen in Problem 2.8a, substituting the above general solution into the wave equation allows us to solve for

    $$r = s = \sqrt{2mE}\frac{2\pi}{h}$$

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[4]$\Psi_A{}^*$ denotes the complex conjugate of Ψ_A. This is necessary because wave functions may have imaginary values. However, in many cases, the wave functions are real and the integrand reduces to Ψ_A^2.

- Because Ψ must be continuous and equal 0 for $x < 0$ and $x > a$, Ψ must approach 0 as $x \to 0$ and $x \to a$. Since $\cos(s \cdot 0) = 1$, $\Psi(0)$ can only equal 0 if $B = 0$. Therefore, the wave function reduces to
$$\Psi(x) = A \sin rx$$

- We must also have $\Psi(a) = 0$, which is only possible if rx is an integer multiple of π. This means that
$$ra = \pm n\pi$$
$$r = \frac{\pm n\pi}{a}$$

- Combining the two expressions for r, we can solve for E:
$$E = \frac{n^2 h^2}{8ma^2}$$

  - ■ "These are the energy levels predicted by the particle-in-a-box model for any particle in a one dimensional box of length a. The energy levels are quantized according to quantum numbers $n = 1, 2, 3, \ldots$" (Miessler et al., 2014, p. 17).

- As seen in Problem 2.8d, substituting $r = n\pi/a$ into $\Psi(x)$ and applying the normalizing requirement allows us to solve for the total solution
$$\Psi(x) = \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a}$$

(a) $n = 1$.   (b) $n = 2$.   (c) $n = 3$.
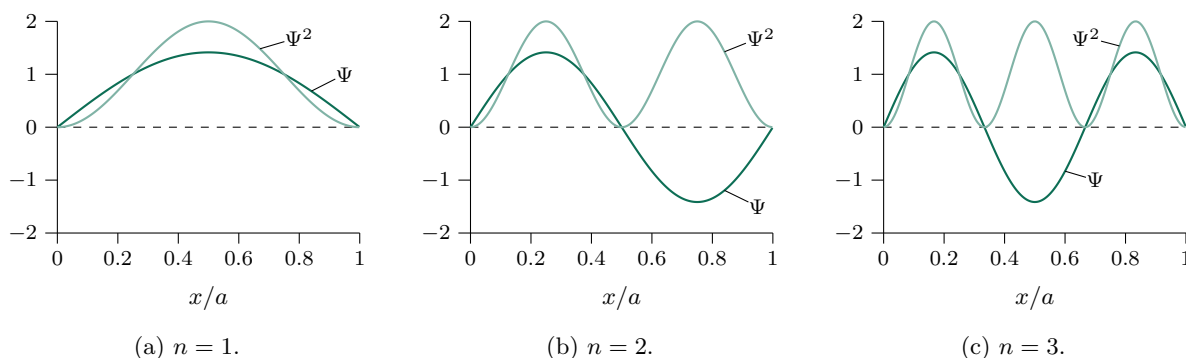
Figure 5: Particle in a box: Wave functions and their squares at different energy levels.

- The predicted probability densities for an electron at different energy levels (see Figure 5) showcase a difference between classical mechanics' and quantum mechanics' predictions about the behavior of this particle: Classical predicts an equal probability at any point in the box, but the wave nature of the particle (as described by quantum) predicts varied probabilities in different locations.

  - ■ "The greater the square of the electron amplitude, the greater the probability of the electron being located at the specified coordinate when at the quantized energy defined by Ψ" (Miessler et al., 2014, p. 17).

- Atomic orbitals, mathematically, are discrete solutions of the three-dimensional Schrödinger equations.

  - These orbital equations include four quantum numbers (see Table 1).

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[5] *Also known as* **azimuthal** (quantum number).

Symbol	Name	Values	Role
n	Principal	$1, 2, 3, \ldots$	Determines the major part of the energy.
l	Angular momentum[5]	$0, 1, 2, \ldots, n-1$	Describes angular dependence and contributes to the energy.
m_l	Magnetic	$0, \pm 1, \pm 2, \ldots, \pm l$	Describes orientation in space (angular momentum in the z-direction).
m_s	Spin	$\pm \frac{1}{2}$	Describes orientation of the electron spin (magnetic moment) in space.

Table 1: Quantum numbers and their properties.

- Orbitals with l values $0, 1, 2, 3, 4, \ldots$ are known by the labels $s, p, d, f, g, \ldots$ (continuing alphabetically), respectively, derived from early terms for different families of spectroscopic lines.
- n is the primary quantum number affecting the overall energy.
- l determines the type of shape. See Table 2.
- m_l determines the "orientation of the angular momentum vector in a magnetic field, or the position of the orbital in space" (Miessler et al., 2014, p. 18). See Table 2.
- m_s determines the electron spin[6] in the orbital, or "the orientation of the electron's magnetic moment in a magnetic field, either in the direction of the field $(+\frac{1}{2})$ or opposed to it $(-\frac{1}{2})$" (Miessler et al., 2014, p. 18).
- n, l, and m_l specify an orbital; m_s specifies one of the two electrons in the orbital.

- A note on $i = \sqrt{-1}$ in Table 2:

  - Any linear combination of solutions to the wave equation is another solution.
  - Because it is more convenient to work with real functions as opposed to complex functions, we make use of the above fact to decomplexify the solutions, as in the following examples.

$$\Psi_{2p_x} = \frac{1}{\sqrt{2}}(\Psi_{+1} + \Psi_{-1})$$

$$= \frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2\pi}}e^{i\phi} \cdot \frac{\sqrt{3}}{2}\sin\theta \cdot [R(r)] + \frac{1}{\sqrt{2\pi}}e^{-i\phi} \cdot \frac{\sqrt{3}}{2}\sin\theta \cdot [R(r)]\right)$$

$$= \left(\frac{1}{\sqrt{\pi}}\frac{\sqrt{3}}{2}[R(r)]\sin\theta\right)\frac{e^{i\phi} + e^{-i\phi}}{2}$$

$$= \frac{1}{2}\sqrt{\frac{3}{\pi}}[R(r)]\sin\theta\cos\phi$$

$$\Psi_{2p_y} = \frac{-i}{\sqrt{2}}(\Psi_{+1} - \Psi_{-1})^{[7]}$$

$$= \left(\frac{1}{\sqrt{\pi}}\frac{\sqrt{3}}{2}[R(r)]\sin\theta\right)\frac{e^{i\phi} - e^{-i\phi}}{2i}$$

$$= \frac{1}{2}\sqrt{\frac{3}{\pi}}[R(r)]\sin\theta\sin\phi$$

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[6]Note that the spin of an electron is purely quantum mechanical, and should not be related back to classical mechanics.
[7]Errata: Miessler et al. (2014) incorrectly normalizes this expression with $i/\sqrt{2}$.
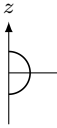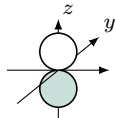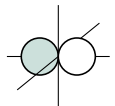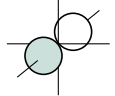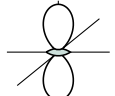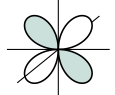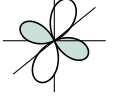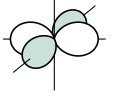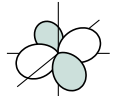
Angular factors				Functions of θ	Real Wave Functions		Shapes	Label
Related to Angular Momentum					In Polar Coordinates	In Cartesian Coordinates		
l	m_l	Φ	Θ		$\Theta\Phi(\theta,\phi)$	$\Theta\Phi(x,y,z)$		
$0(s)$	0	$\dfrac{1}{\sqrt{2\pi}}$	$\dfrac{1}{\sqrt{2}}$		$\dfrac{1}{2\sqrt{\pi}}$	$\dfrac{1}{2\sqrt{\pi}}$		s
$1(p)$	0	$\dfrac{1}{\sqrt{2\pi}}$	$\dfrac{\sqrt{6}}{2}\cos\theta$		$\dfrac{1}{2}\sqrt{\dfrac{3}{\pi}}\cos\theta$	$\dfrac{1}{2}\sqrt{\dfrac{3}{\pi}}\dfrac{z}{r}$		p_z
	$+1$	$\dfrac{1}{\sqrt{2\pi}}e^{i\phi}$	$\dfrac{\sqrt{3}}{2}\sin\theta$		$\dfrac{1}{2}\sqrt{\dfrac{3}{\pi}}\sin\theta\cos\phi$	$\dfrac{1}{2}\sqrt{\dfrac{3}{\pi}}\dfrac{x}{r}$		p_x
	-1	$\dfrac{1}{\sqrt{2\pi}}e^{-i\phi}$	$\dfrac{\sqrt{3}}{2}\sin\theta$		$\dfrac{1}{2}\sqrt{\dfrac{3}{\pi}}\sin\theta\sin\phi$	$\dfrac{1}{2}\sqrt{\dfrac{3}{\pi}}\dfrac{y}{r}$		p_y
$2(d)$	0	$\dfrac{1}{\sqrt{2\pi}}$	$\dfrac{1}{2}\sqrt{\dfrac{5}{2}}(3\cos^2\theta-1)$		$\dfrac{1}{4}\sqrt{\dfrac{5}{\pi}}(3\cos^2\theta-1)$	$\dfrac{1}{4}\sqrt{\dfrac{5}{\pi}}\dfrac{2z^2-x^2-y^2}{r^2}$		d_{z^2}
	$+1$	$\dfrac{1}{\sqrt{2\pi}}e^{i\phi}$	$\dfrac{\sqrt{15}}{2}\cos\theta\sin\theta$		$\dfrac{1}{2}\sqrt{\dfrac{15}{\pi}}\cos\theta\sin\theta\cos\phi$	$\dfrac{1}{2}\sqrt{\dfrac{15}{\pi}}\dfrac{xz}{r^2}$		d_{xz}
	-1	$\dfrac{1}{\sqrt{2\pi}}e^{-i\phi}$	$\dfrac{\sqrt{15}}{2}\cos\theta\sin\theta$		$\dfrac{1}{2}\sqrt{\dfrac{15}{\pi}}\cos\theta\sin\theta\sin\phi$	$\dfrac{1}{2}\sqrt{\dfrac{15}{\pi}}\dfrac{yz}{r^2}$		d_{yz}
	$+2$	$\dfrac{1}{\sqrt{2\pi}}e^{2i\phi}$	$\dfrac{\sqrt{15}}{4}\sin^2\theta$		$\dfrac{1}{4}\sqrt{\dfrac{15}{\pi}}\sin^2\theta\cos2\phi$	$\dfrac{1}{4}\sqrt{\dfrac{15}{\pi}}\dfrac{x^2-y^2}{r^2}$		$d_{x^2-y^2}$
	-2	$\dfrac{1}{\sqrt{2\pi}}e^{-2i\phi}$	$\dfrac{\sqrt{15}}{4}\sin^2\theta$		$\dfrac{1}{4}\sqrt{\dfrac{15}{\pi}}\sin^2\theta\sin2\phi$	$\dfrac{1}{4}\sqrt{\dfrac{15}{\pi}}\dfrac{xy}{r^2}$		d_{xy}

Table 2: Hydrogen atom wave functions: Angular functions.

- Note that d_{z^2} actually uses the function $2z^2-x^2-y^2$, so we should write $d_{2z^2-x^2-y^2}$ but we shorthand for convenience.

- Since the functions in the polar and Cartesian coordinates columns of Table 2 are real, $\Psi=\Psi^*$ and $\Psi\Psi^*=\Psi^2$.

12/25:

- Ψ may be expressed in terms of Cartesian coordinates (x,y,z) or in terms of spherical coordinates (r,θ,ϕ).

    - Using spherical coordinates comes with the advantage that r is the distance from the nucleus (see Figure 6).

12/23:

Radial Functions $R(r)$, with $\sigma = Zr/a_0$			
Orbital	n	l	$R(r)$
$1s$	1	0	$R_{1s} = 2 \left[\dfrac{Z}{a_0} \right]^{3/2} e^{-\sigma}$
$2s$	2	0	$R_{2s} = \left[\dfrac{Z}{2a_0} \right]^{3/2} (2 - \sigma) e^{-\sigma/2}$[8]
$2p$		1	$R_{2p} = \dfrac{1}{\sqrt{3}} \left[\dfrac{Z}{2a_0} \right]^{3/2} \sigma e^{-\sigma/2}$
$3s$	3	0	$R_{3s} = \dfrac{2}{27} \left[\dfrac{Z}{3a_0} \right]^{3/2} (27 - 18\sigma + 2\sigma^2) e^{-\sigma/3}$
$3p$		1	$R_{3p} = \dfrac{1}{81\sqrt{3}} \left[\dfrac{2Z}{a_0} \right]^{3/2} (6 - \sigma) \sigma e^{-\sigma/3}$
$3d$		2	$R_{3d} = \dfrac{1}{81\sqrt{15}} \left[\dfrac{2Z}{a_0} \right]^{3/2} \sigma^2 e^{-\sigma/3}$

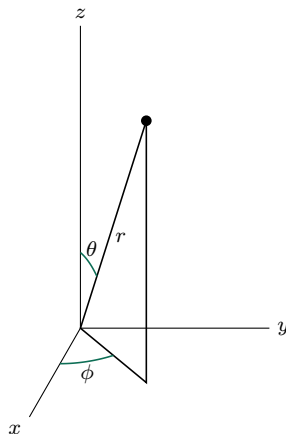Table 3: Hydrogen atom wave functions: Radial functions.

12/25:

Figure 6: Spherical coordinates.

– Know the following volume element conversions[9].

$$\mathrm{d}V = \mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z = r^2 \sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi\,\mathrm{d}r$$

– The volume of the thin shell between r and $r + \mathrm{d}r$ is as follows[10], and is useful for describing the electron density as a function of distance from the nucleus.

$$\int_0^{2\pi} \int_0^{\pi} 1\, r^2 \sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi\,\mathrm{d}r = \int_0^{2\pi} 2 r^2 \,\mathrm{d}\phi\,\mathrm{d}r$$
$$= 4\pi r^2 \,\mathrm{d}r$$

[8]Errata: This differs from the corresponding equation in Miessler et al. (2014) because the textbook is wrong.
[9]Refer to Labalme (2020b), specifically Figure 16.9 and the accompanying discussion.
[10]Errata: Miessler et al. (2014) flips the bounds over which θ and ϕ should be evaluated, but I use the right ones.

- Ψ can be factored into a **radial component** R and two **angular components** Θ and Φ, which are sometimes combined into a single component Y:

$$\Psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi) = R(r)Y(\theta, \phi)$$

- ■ Refer to Table 2 for examples of Θ and Φ, and Table 3 for examples of R.
- ■ Note that in Table 2, the shaded orbital lobes correspond to where the wave function is negative. Distinguishing regions of opposite signs is useful for bonding purposes.

- The radial component can also be manipulated to give the **radial probability function** $4\pi r^2 R^2$.

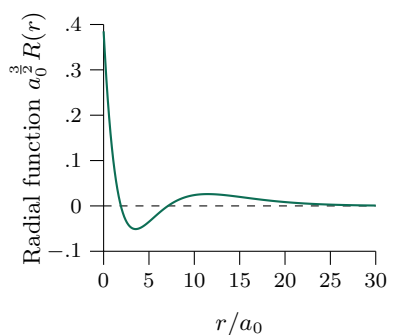- ■ R is the radial function, so R^2 is the probability function (think $\Psi = RY$, so $\Psi^2 = R^2 Y^2$).
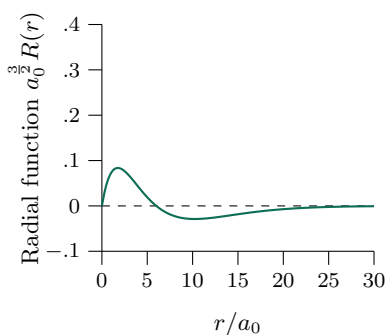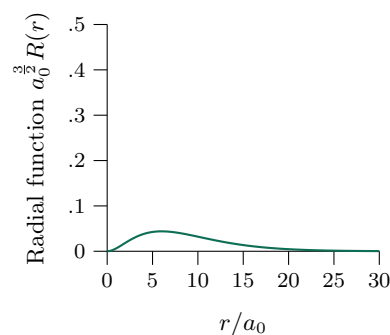

(a) $1s$.

(b) $2s$.

(c) $2p$.
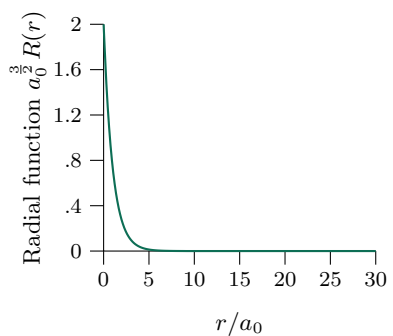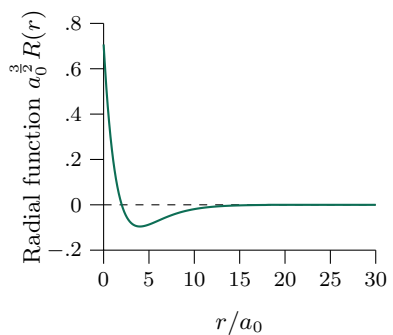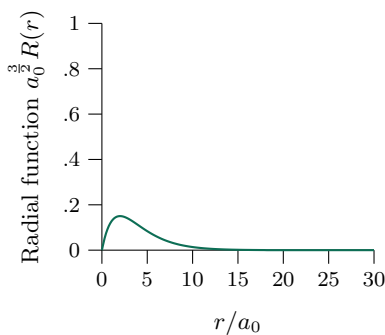
(d) $3s$.

(e) $3p$.

(f) $3d$.

Figure 7: Radial wave functions.

(a) $1s$.

(b) $2s$.

(c) $2p$.

(d) $3s$.

(e) $3p$.

(f) $3d$.
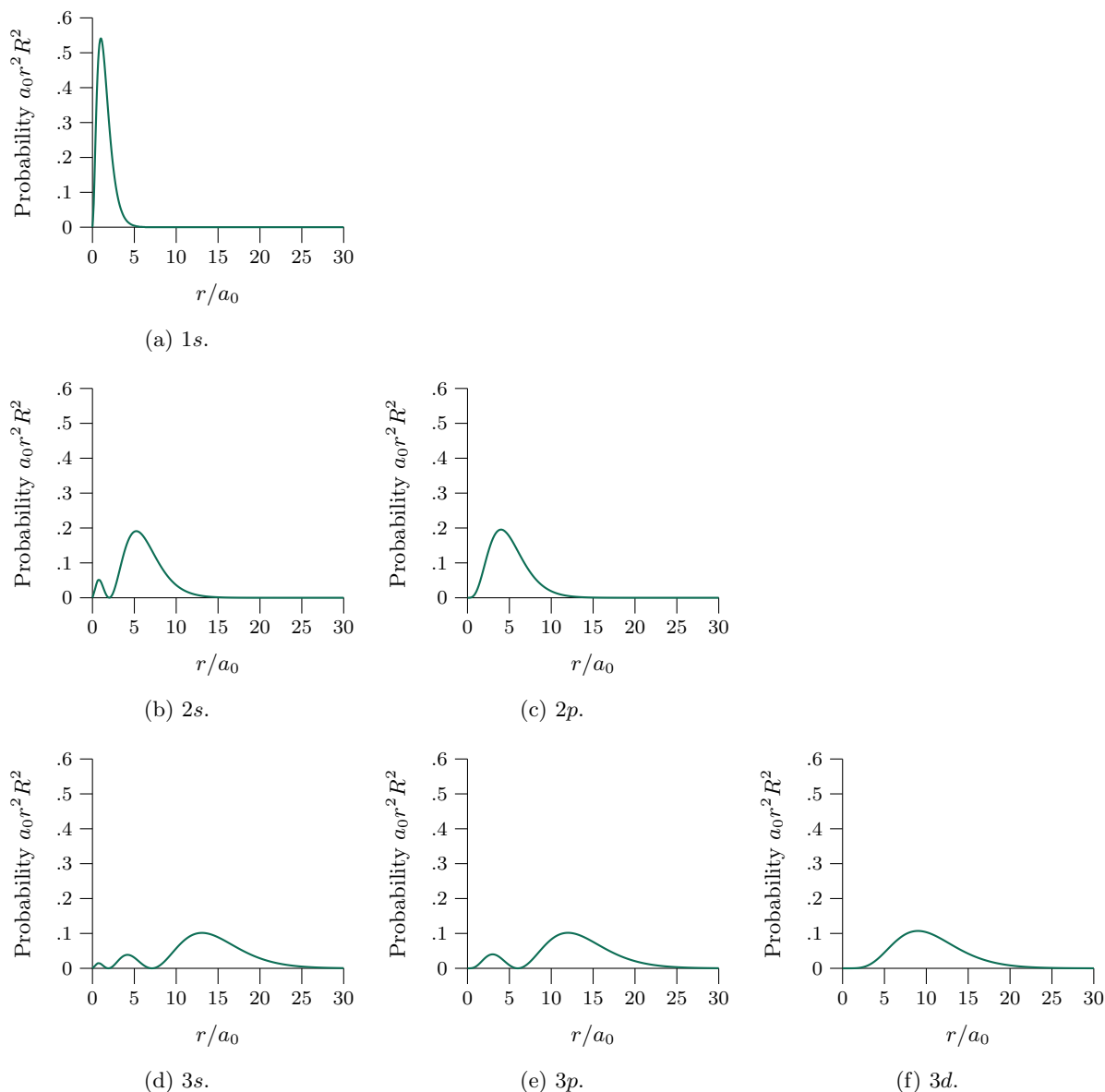
Figure 8: Radial probability functions.

- **Radial component**: The part of Ψ that describes "electron density at different distances from the nucleus" (Miessler et al., 2014, p. 20).

  - Determined by quantum numbers n and l.
  - Plotted for the $n = 1, 2, 3$ orbitals in Figure 7.

- **Angular components**: The parts of Ψ that describe "the shape of the orbital and its orientation in space" (Miessler et al., 2014, p. 20).

  - Determined by quantum number l and m_l.

- **Radial probability function**: The function describing "the probability of finding the electron at a given distance from the nucleus, summed over all angles, with the $4\pi r^2$ factor the result of integrating over all angles" (Miessler et al., 2014, p. 21).

       – Plotted for the $n = 1, 2, 3$ orbitals in Figure 8.

- **Bohr radius**: "The value of r at the maximum of Ψ^2 for a hydrogen $1s$ orbital (the most probable distance from the hydrogen nucleus for the $1s$ electron), and it is also the radius of the $n = 1$ orbit according to the Bohr model" (Miessler et al., 2014, p. 23).

       – See Figure 8a.

       – Its value is $a_0 = 52.9 \, \text{pm}$.

       – It is a common unit in quantum mechanics.

       – It is used to scale the functions in Figures 7 and 8 to give reasonable axis units[11].

- Figure 8 shows that the electron density falls off rapidly after the absolute maximum in every case.

       – However, it falls off more quickly for lower energy levels.

- The electron density at the nucleus is always zero.

       – Mathematically, this is because $4\pi r^2 R^2$ naturally equals zero when $r = 0$.

- "Because chemical reactions depend on the shape and extent of orbitals at large distances from the nucleus, the radial probability functions help show which orbitals are most likely to be involved in reactions" (Miessler et al., 2014, p. 23).

12/26:
- **Nodal surface**: A surface within an orbital having zero electron density.

       – The wave function is zero at these because it is changing sign.

           ■ Knowing where the wave function is positive and negative can be useful when working with molecular orbitals.

- To find nodal surfaces, we must find places where

$$0 = \Psi^2 = \Psi = R(r)Y(\theta, \phi)$$

or where

$$0 = R(r) \qquad\qquad\qquad 0 = Y(\theta, \phi)$$

- "The total number of nodes in any orbital is $n - 1$ if the conical nodes of some d and f orbitals count as two nodes" (Miessler et al., 2014, p. 23).

       – The conical node of the d_{z^2} orbital (see Table 2) is mathematically one surface, but we must count it as two (perhaps think of it as a top and bottom section) to fit the pattern.

- **Angular node**: A node that results when $Y = 0$.

       – There are l angular nodes in any orbital.

- **Radial node**: A node that results when $R = 0$. *Also known as* **spherical nodes**.

       – There are $n - l - 1$ radial nodes in any orbital.

- Note that on the basis of relativity, electron density at nodes may not be zero but may in fact be a very small finite value.

       – Alternatively, if we think of an electron wave like a wave in a violin string, which also has places of zero vibration where the string still exists, nodes may just be places where electron waves have zero amplitude, not places where they don't exist.

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[11]Errata?: Should the y-axis in Figure 8 be $a_0^3 r^2 R^2$?

- – A further possible explanation is that electrons can 'teleport' between two places without ever passing in between.

- We now look at a few examples of finding nodes in orbitals.

- Nodal structure of p_z:

  - – From Table 2, the angular factor of this orbital in Cartesian coordinates is

$$Y = \frac{1}{2}\sqrt{\frac{3}{\pi}}\frac{z}{r}$$

  - – When we set this equal to zero, we find that the above is only equal to zero when $z = 0$.
  - – Indeed, $z = 0$, i.e., the xy-plane, is an angular node in the p_z orbital, as we can see in Table 2.
  - – Additionally, we can tell from the above equation that the wave function is positive when $z > 0$ and negative when $z < 0$; this is also reflected in Table 2.

- Nodal structure of $d_{x^2-y^2}$:

  - – The angular factor:

$$Y = \frac{1}{4}\sqrt{\frac{15}{\pi}}\frac{x^2 - y^2}{r^2}$$

  - – This is only equal to zero when

$$0 = x^2 - y^2$$
$$y^2 = x^2$$
$$y = \pm x$$

  - – This translates to Table 2, where we can see that the planes $x = y$ and $x = -y$, i.e., those that contain the z-axis and make 45° angles with the x- and y-axes, are nodes.
  - – Additionally, the function is positive where $x > y$ and negative where $x < y$, and we can see this in Table 2.

- Be aware of lines/surfaces of constant electron density.

- When filling orbitals in polyelectronic atoms, "we start with the lowest n, l, and m_l values (1, 0, and 0, respectively) and either of the m_s values (we will arbitrarily use $+\frac{1}{2}$ first)" (Miessler et al., 2014, p. 26). We then utilize the three following rules.

  - – See them used to fill a p orbital in Table 4.

- **Aufbau principle**: The buildup of electrons in atoms results from continually increasing the quantum numbers. *Etymology* **aufbau** from German "building up."

  - – "Electrons are placed in orbitals to give the lowest total electronic energy to the atom. This means that the lowest values of n and l are filled first. Because the orbitals within each subshell (p, d, etc.) have the same energy, the orders for values of m_l and m_s are indeterminate" (Miessler et al., 2014, p. 26).

- **Pauli exclusion principle**: Each electron in an atom must have a unique set of quantum numbers.

  - – Note that this is experimentally derived, and does not follow from the Schrödinger equation.

- **Hund's rule** (of maximum multiplicity): Electrons must be placed in orbitals to give the maximum total spin (the maximum number of parallel spins).

  - – This is a consequence of the Aufbau principle, as two electrons in the same orbital have higher energy than two in different orbitals due to electrostatic repulsions.

Number of electrons	Arrangement	Unpaired e⁻	Multiplicity
1	↑ __ __ __	1	2
2	↑ __ ↑ __ __	2	3
3	↑ __ ↑ __ ↑ __	3	4
4	↑↓ __ ↑ __ ↑ __	2	3
5	↑↓ __ ↑↓ __ ↑ __	1	2
6	↑↓ __ ↑↓ __ ↑↓ __	0	1

Table 4: Hund's rule and multiplicity.

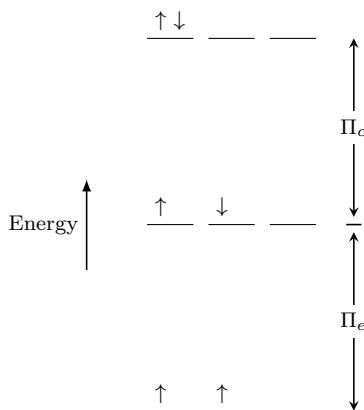- **Spin multiplicity**: The number of unpaired electrons plus 1.

Figure 9: Coulombic energy of repulsion and exchange energy.

- **Coulombic energy of repulsion**: The potential energy of two negatively charged electrons that occupy the same orbital (as opposed to separate orbitals). *Denoted by* $\mathbf{\Pi_c}$.

  - Note that all polyelectronic species are subject to *some* Coulombic repulsions, but the contribution is significantly higher for paired electrons.

- **Exchange energy**: The potential energy of two electrons that have opposite spins (as opposed to the same spin). *Denoted by* $\mathbf{\Pi_e}$.

  - This arises from purely quantum mechanical considerations.

  - Basically, there are three possible ways to arrange two electrons in degenerate orbitals (see Figure 9). The exchange energy between two of the states reflects the fact that electrons with opposite spins are distinguishable, but electrons with identical spins can be exchanged (can switch places) and no observer would be the wiser. This event, when it happens, is called **one exchange of parallel electrons**; the fact that it can happen lowers the energy of the system with electrons of identical spin simply by virtue of creating more possible states that each electron can occupy.

0.2.2   Problems

9/13:   **2.8** The details of several steps in the particle-in-a-box model in this chapter have been omitted. Work out the details of the following steps:

a. Show that if $\Psi = A \sin rx + B \cos sx$ (A, B, r, and s are constants) is a solution to the wave equation for the one-dimensional box, then

$$r = s = \sqrt{2mE} \left(\frac{2\pi}{h} \right)$$

Solution.

$$\frac{-h^2}{8\pi^2 m} \cdot \frac{\partial^2 \Psi(x)}{\partial x^2} = E\Psi(x)$$

$$\frac{-h^2}{8\pi^2 m} \cdot \frac{\partial^2}{\partial x^2} \left(A \sin rx + B \cos sx \right) = E(A \sin rx + B \cos sx)$$

$$\frac{-h^2}{8\pi^2 m} \cdot \frac{\partial}{\partial x} \left(Ar \cos rx - Bs \sin sx \right) = E(A \sin rx + B \cos sx)$$

$$\frac{-h^2}{8\pi^2 m} \cdot \left(-Ar^2 \sin rx - Bs^2 \cos sx \right) = E(A \sin rx + B \cos sx)$$

$$\frac{Ar^2 h^2}{8\pi^2 m} \sin rx + \frac{Bs^2 h^2}{8\pi^2 m} \cos sx = AE \sin rx + BE \cos sx$$

$$0 = \left(\frac{Ar^2 h^2}{8\pi^2 m} - AE \right) \sin rx + \left(\frac{Bs^2 h^2}{8\pi^2 m} - BE \right) \cos sx$$

Choose $x = 0$.

$$= \frac{Bs^2 h^2}{8\pi^2 m} - BE$$

$$E = \frac{s^2 h^2}{8\pi^2 m}$$

$$\frac{8\pi^2 m E}{h^2} = s^2$$

$$s = \sqrt{\frac{8\pi^2 m E}{h^2}}$$

$$\boxed{s = \sqrt{2mE}\frac{2\pi}{h}}$$

With this result ...

$$0 = \left(\frac{Ar^2 h^2}{8\pi^2 m} - AE \right) \sin rx + \left(\frac{Bs^2 h^2}{8\pi^2 m} - BE \right) \cos sx$$

$$= \left(\frac{Ar^2 h^2}{8\pi^2 m} - AE \right) \sin rx + \left(B \left(\frac{s^2 h^2}{8\pi^2 m} \right) - BE \right) \cos sx$$

$$= \left(\frac{Ar^2 h^2}{8\pi^2 m} - AE \right) \sin rx + (BE - BE) \cos sx$$

$$= \left(\frac{Ar^2 h^2}{8\pi^2 m} - AE \right) \sin rx$$

Choose $x = \frac{\pi}{2r}$.

$$= \frac{Ar^2 h^2}{8\pi^2 m} - AE$$

$$\boxed{r = \sqrt{2mE}\frac{2\pi}{h}}$$

□

d. Show that substituting the value of r given in part c into $\Psi = A \sin rx$ and applying the normalizing requirement gives $A = \sqrt{2/a}$.

Solution.

$$1 = \int_{\text{all space}} \Psi \Psi^* \, d\tau$$

$$= \int_0^a \left(A \sin \frac{n\pi x}{a} \right) \left(A \sin \frac{n\pi x}{a} \right) dx$$

$$= \int_0^a A^2 \sin^2 \frac{n\pi x}{a} \, dx$$

Use $\sin^2 u = \frac{1 - \cos 2u}{2}$.

$$= A^2 \int_0^a \frac{1 - \cos \frac{2n\pi x}{a}}{2} \, dx$$

$$= \frac{A^2}{2} \left(\int_0^a dx - \int_0^a \cos \frac{2n\pi x}{a} \, dx \right)$$

$$= \frac{A^2}{2} \left([x]_0^a - \left[\frac{a}{2n\pi} \sin \frac{2n\pi x}{a} \right]_0^a \right)$$

$$= \frac{A^2}{2} \left((a - 0) - \left(\frac{a}{2n\pi} \sin 2n\pi - \frac{a}{2n\pi} \sin 0 \right) \right)$$

$$= \frac{A^2}{2} \left(a - \left(\frac{a}{2n\pi} \sin 2n\pi \right) \right)$$

Since n is an integer, $\sin 2n\pi = 0$.

$$= \frac{aA^2}{2}$$

$$\frac{2}{a} = A^2$$

$$\boxed{A = \sqrt{\frac{2}{a}}}$$

$\square$