Physical Chemistry: Quantum Mechanics and Molecular Interactions

Objectives Review Questions

Chapter 1

1.1 We use Eq. 1.1 to convert wavelength to frequency (taking advantage of the constant speed of light c) and we use Eq. 1.2 to convert frequency to photon energy:

$$\begin{aligned} \nu &= \frac{c}{\lambda} = \frac{2.998 \cdot 10^{8}\,\mathrm{m\,s^{-1}}}{1.0 \cdot 10^{-3}\,\mathrm{m}} = \boxed{3.0 \cdot 10^{11}\,\mathrm{s^{-1}}} && \text{by Eq. 1.1} \\ E_{\text{photon}} &= h\nu = (6.626 \cdot 10^{-34}\,\mathrm{J\,s})(3.0 \cdot 10^{11}\,\mathrm{s^{-1}}) = \boxed{2.0 \cdot 10^{-22}\,\mathrm{J}.} && \text{Eq. 1.2} \end{aligned}$$

1.2 The de Broglie wavelength (Eq. 1.3) is our yardstick (if you will) for the degree of quantum character in our system. We calculate λ_{dB} and compare it to the domain to determine if we need quantum mechanics to describe the physics. In this case, to find the de Broglie wavelength we need to calculate the momentum p from the kinetic energy, but we can do that:

$$\begin{aligned} K &= \frac{mv^2}{2} = \frac{p^2}{2m} \\ p &= \sqrt{2mK} = \sqrt{2(1.008\,\mathrm{amu})(1.661 \cdot 10^{-27}\,\mathrm{kg\,amu^{-1}})(4.0 \cdot 10^{-21}\,\mathrm{J})} = 3.66 \cdot 10^{-24}\,\mathrm{kg\,m\,s^{-1}} \\ \lambda_{\text{dB}} &= \frac{h}{p} = \frac{6.626 \cdot 10^{-34}\,\mathrm{J\,s}}{3.66 \cdot 10^{-24}\,\mathrm{kg\,m\,s^{-1}}} = 1.8 \cdot 10^{-10}\,\mathrm{m} = \boxed{1.8\,\text{Å}.} \end{aligned}$$

Because $1.8 \cdot 10^{-10}\,\mathrm{m} \ll 1.0\mu\mathrm{m} = 1.0 \cdot 10^{-6}\,\mathrm{m}$, it is unlikely that quantum effects arising from this motion will be significant.

1.3 The atom is in an $n = 2$ state, and we can use the Bohr model of the atom to calculate the correct values of the energies. From Eq. 1.15 we can calculate the total energy, and from Eq. 3.7 we can calculate the potential energy. The question does not specify units, and the most convenient units for the total energy are E_{h}:

$$E_n = -\frac{Z^2}{2n^2}\,E_{\text{h}} = -\frac{2^2}{2(2^2)}\,E_{\text{h}} = \boxed{-0.5\,E_{\text{h}}.}$$

The potential energy depends on the radius of the electron orbit in the Bohr model,

$$r_n = \frac{n^2}{Z}a_0 = \frac{2^2}{2}a_0 = 2a_0,$$

which gives us

$$U = -\frac{Ze^2}{4\pi\epsilon_0 r} = -\frac{2e^2}{(4\pi\epsilon_0)(2a_0)} = -\frac{e^2}{(4\pi\epsilon_0)a_0} = \boxed{-1.00\,E_{\text{h}}.}$$

Chapter 2

2.1 We apply the operator to the function, and see if we can find the original function again afterward:

$$\begin{aligned} \hat{\alpha} f(x) &= \frac{1}{x}\frac{d}{dx}\left(3x\,e^{2x}\right) = \frac{1}{x}\left(3e^{2x} + 3x(2e^{2x})\right) \\ &= \frac{1}{x}3e^{2x} + 2 \cdot 3e^{2x} = \left(\frac{1}{x^2} + \frac{2}{x}\right) f(x). \end{aligned}$$

The result is equal to $f(x)$ times another function of x, so this is $\boxed{\text{not}}$ an eigenvalue equation.

$$\begin{aligned}\hat{\alpha}g(x) &= \frac{1}{x}\frac{d}{dx}\left(3\,e^{2x^2}\right) = \frac{1}{x}\left(3(4x)e^{2x^2}\right)\\ &= 4\cdot 3e^{2x^2} = 4f(x).\end{aligned}$$

But $g(x)$ *is* an eigenfunction of $\hat{\alpha}$, because the result is the original function $g(x)$ times the eigenvalue $\boxed{4.}$

2.2 We use the average value theorem, Eq. 2.10, integrating between 0 and a. The integral over $x^4\sin(cx)$ can be found using a symbolic math program. Setting $c = 2\pi/a$ for now to simplify the notation, we have:

$$\int_o^a \psi^*\,(x^4)\,\psi\,dx = \frac{2}{a}\int_0^a \sin^2(cx)\,x^4\,dx = \boxed{0.176a^4.}$$

2.3 To write the Schrödinger equation we need the Hamiltonian, which consists of the kinetic energy operator $-(\hbar^2/2m)\partial^2/\partial x^2$, and the potential energy function described in the problem. In this case, the potential energy is given by the formula for a line, to which we assign a slope U_0. We can also add a constant, but it will have no effect on the relative energies or the wavefunctions, so we may as well set it equal to zero. Our potential energy function therefore is U_0x, and the Schrödinger equation becomes

$$\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + U_0x\right)\psi = E\psi.$$

2.4 We use Eq. 2.41 to calculate the energy, with a mass m_p and the volume given:

$$\begin{aligned}E_{n_x,n_y,n_z} &= \frac{h^2}{8mV^{2/3}}(n_x^2+n_y^2+n_z^2) && \text{Eq. 2.41}\\ E_{100,1,1} &= \frac{(6.626\cdot 10^{-34}\,\mathrm{J\,s})^2}{8(1.673\cdot 10^{-27}\,\mathrm{kg})(1.0\cdot 10^{-18}\,\mathrm{m}^3)^{2/3}}(100^2+1^2+1^2)\\ &= \boxed{3.28\cdot 10^{-25}\,\mathrm{J}.}\end{aligned}$$

Chapter 3

3.1 We combine the radial and angular parts of the wavefunction as dictated by the quantum numbers, and also substitute $Z = 3$ for lithium:

$$\begin{aligned}\psi_{3,1,-1}(r,\theta,\phi) &= R_{3,1}(r)\,Y_1^{-1}(\theta,\phi)\\ &= \frac{4\sqrt{2}}{27\sqrt{3}}\left(\frac{3}{a_0}\right)^{3/2}\left(\frac{3r}{a_0}\right)\left(1-\frac{r}{2a_0}\right)e^{-r/a_0}\sqrt{\frac{3}{8\pi}}\sin\theta\;e^{-i\phi}.\end{aligned}$$

3.2 We are using an integral to find an average value, so we use the average value theorem (Eq. 2.10), where the operator is r (the distance from the nucleus) and the wavefunction is given by $\psi_{3,1,-1}(r,\theta\phi)$ with $Z = 3$ for lithium:

$$\frac{32}{3^7}\left(\frac{3}{a_0}\right)^3\int_0^\infty\left(\frac{3r}{a_0}\right)^2\left(1-\frac{r}{2a_0}\right)^2 e^{-2r/a_0}\,r^3\,dr = 25a_0/3.$$

3.3 The number of angular nodes is given by l, which is 1 for a p orbital, and the number of radial nodes is equal to $n - l - 1 = 3 - 1 - 1 = 1$: $\boxed{\text{1 angular node, 1 radial node.}}$

Chapter 4

4.1 This ion has three electrons and an atomic number $Z = 4$. We need one kinetic energy term for each electron, three terms for the attraction of each electron for the nucleus, and then three terms for electron–electron repulsions, one for each distinct pairing of the electrons: 1 and 2, 2 and 3, and 1 and 3:

$$\boxed{-\frac{\hbar^2}{2m_e}\left(\nabla(1)^2+\nabla(2)^2+\nabla(3)^2\right)-\frac{4e^2}{4\pi\epsilon_0 r_1}-\frac{4e^2}{4\pi\epsilon_0 r_2}-\frac{4e^2}{4\pi\epsilon_0 r_3}+\frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{r_{12}}+\frac{1}{r_{23}}+\frac{1}{r_{13}}\right).}$$

4.2 Neutral beryllium has 4 electrons, so Be^+ has 3 electrons, which we place in the lowest energy subshells $1s$ and $2s$ for an electron configuration $\boxed{1s^2 2s^1.}$ The zero-order energy is then the sum of the energies we would calculate if each electron were alone in that subshell. That one-electron energy is $-Z^2\,E_\text{h}/(2n^2)$. We have two $n = 1$ electrons and one $n = 2$ electron in the configuration, and $Z = 4$ for Be, so we arrive at

$$\begin{aligned} E_0 &= -\frac{4^2}{2}\left(\frac{1}{1^2}+\frac{1}{1^2}+\frac{1}{2^2}\right)E_\text{h} \\ &= \frac{16}{2}\left(\frac{9}{4}\right) = \boxed{-18\,E_\text{h}.} \end{aligned}$$

4.3 We use Eq. 4.30, which calculates the effective atomic number by treating the electron as though it were a single electron in an atom with a variable atomic number:

$$Z_\text{eff} = \left(-\frac{2\epsilon(i)n^2}{E_\text{h}}\right)^{1/2} = \left(\frac{2(0.182)\,E_\text{h}(3^2)}{E_\text{h}}\right)^{1/2} = \boxed{1.81.}$$

4.4 We reverse the labels 1 and 2 in the function and then check to see whether the function has changed sign: Then we find that

$$\hat{P}_{21}\psi(1,2) = \cos(-x_2)\cos(y_1) - \cos(-x_1)\cos(y_2) = -\cos(-x_1)\cos(y_2) + \cos(-x_2)\cos(y_1) = -\psi(1,2).$$

Therefore, the function is $\boxed{\text{antisymmetric.}}$

4.5 According to the arrow diagrams, we have

	$m_l = 0$	m_l	m_s		$m_l = -1$	0	1	m_l	m_s	M_L	M_S	
$1s^1$	$\uparrow$	0	$+1/2$	$2p^1$	$\uparrow$	—	—	-1	$+1/2$	-1	$+1$	^3P
	$\uparrow$	0	$+1/2$		—	$\uparrow$	—	0	$+1/2$	0	$+1$	^3P
	$\uparrow$	0	$+1/2$		—	—	$\uparrow$	$+1$	$+1/2$	$+1$	$+1$	^3P
	$\uparrow$	0	$+1/2$		$\downarrow$	—	—	-1	$-1/2$	-1	0	^3P
	$\uparrow$	0	$+1/2$		—	$\downarrow$	—	0	$-1/2$	0	0	^3P
	$\uparrow$	0	$+1/2$		—	—	$\downarrow$	$+1$	$-1/2$	$+1$	0	^3P
	$\downarrow$	0	$-1/2$		$\uparrow$	—	—	-1	$+1/2$	-1	0	^1P
	$\downarrow$	0	$-1/2$		—	$\uparrow$	—	0	$+1/2$	0	0	^1P
	$\downarrow$	0	$-1/2$		—	—	$\uparrow$	$+1$	$+1/2$	$+1$	0	^1P
	$\downarrow$	0	$-1/2$		$\downarrow$	—	—	-1	$-1/2$	-1	-1	^3P
	$\downarrow$	0	$-1/2$		—	$\downarrow$	—	0	$-1/2$	0	-1	^3P
	$\downarrow$	0	$-1/2$		—	—	$\downarrow$	$+1$	$-1/2$	$+1$	-1	^3P

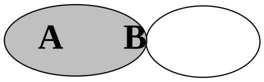
where we found maximum values of $L = 1$ and $S = 1$ initially (based on the largest values of M_L and M_S), and then after assigning the 9 ^3P states, we were left with three $M_S = 0$ states, which gave $L = 1, S = 0$ for the ^1P term. Breaking the ^3P into its component J values from $L - S = 0$ to $L + S = 2$, and ordering according to Hund's rules, the final list of states is $\boxed{^3P_0,\ ^3P_1,\ ^3P_2,\ ^1P_1.}$

Chapter 5

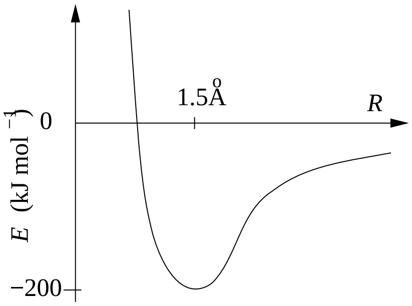
5.1 This molecular ion has 2 nuclei with $Z_{\mathrm{Li}} = 3$ and $Z_{\mathrm{H}} = 1$ and 3 electrons, for a total of 5 particles. That means we should have 5 kinetic energy terms (one for each particle), 6 electron–nucleus attraction terms, 1 nucleus–nucleus repulsion term, and 3 electron–electron repulsion terms. (The total number of potential energy terms for N particles is always $N(N-1)/2$, in this case $5 \cdot 4/2 = 10$, which gives the number of distinct pairs of particles. There is a potential energy term for each pair of interacting particles.) Using the standard form of the kinetic energy operator for each particle and the Coulomb potential for each pair of particles, we end up with the following:

$$\hat{H} = -\frac{\hbar^2}{2m_e}\left(\nabla(1)^2 + \nabla(2)^2 + \nabla(3)^2\right) + \frac{e^2}{4\pi\epsilon_0}\left[-\frac{3}{r_{\mathrm{Li}1}} - \frac{1}{r_{\mathrm{H}1}} - \frac{3}{r_{\mathrm{Li}2}} - \frac{1}{r_{\mathrm{H}2}} - \frac{3}{r_{\mathrm{Li}3}} - \frac{1}{r_{\mathrm{H}3}} + \frac{1}{r_{12}} + \frac{1}{r_{23}} + \frac{1}{r_{13}} + \frac{3}{R_{\mathrm{AB}}}\right] - \frac{\hbar^2}{2m_{\mathrm{Li}}}\nabla(\mathrm{Li})^2 - \frac{\hbar^2}{2m_{\mathrm{H}}}\nabla(\mathrm{H})^2.$$

5.2 The orbital we're constructing combines an s orbital (spherical) with a p orbital lying along the bond axis. If we keep the same orientation of nuclei A and B with respect to the z axis direction that is used elsewhere in the chapter, then the s and p orbitals have the same phase where they overlap, so we will get constructive interference between the two nuclei. However, we expect a node (where the new wavefunction will change sign) somewhere to the $+z$ side of nucleus B, where the negative phase of the p orbital cancels the positive phase of the exponentially decaying s orbital.



5.3 The problem describes a curve such as Fig. 5.14, but a with minimum at $R = 1.5\,\text{Å}$ where the potential energy reaches a value $U = -200\,\mathrm{kJ\,mol^{-1}}$.



5.4 We can deduce from the orientation of the orbitals that (i) only the s, p_x, and p_y atomic orbitals are involved (because the orbitals lie in the xy plane) and (ii) orbital 1 consists of only s and p_x character (because it points along the x axis). All of the original p_x orbital density must be distributed somewhere among all three hybrid orbitals, so if we increase the amount of p_x in orbital 1, then the p_x character of orbitals 2 and 3 must decrease. The p_x orbital character tends to elongate the hybrid orbital along the x axis. By removing that character from orbitals 2 and 3, we elongate them more along the y axis instead, which will $\boxed{\text{increase}}$ the angle between orbitals 2 and 3. (That angle approaches 180° in the limit that only s and p_y character remains, because then you have an sp hybrid, rather than an sp^2 hybrid.) As the angle between orbitals 2 and 3 diverges, the angles between 1 and 2 and between 1 and 3 $\boxed{\text{decrease.}}$

5.5 For the proton NMR, we have two chemical shifts, one at about $\delta = 3.0$ for the protons adjacent to the Br and another at about $\delta = 3.5$ for the protons adjacent to the Cl. Each of these is then split into

a triplet by the interaction with the two protons at the neighboring carbon atom. The actual chemical shifts turn out to be shifted downfield (to higher δ) because we have two electronegative atoms relatively close together: $\boxed{^1\text{H: 2 triplets, equal intensity, } \delta \approx 3.55, 3.75.}$ For the ^{13}C, we get two chemical shifts (one for each carbon atom). The J-coupling to the protons is usually very large and potentially a source of confusion, so ^{13}C spectra are usually purposely gathered under conditions that eliminate the J-coupling, resulting in singlets:
$\boxed{^{13}\text{C: 2 singlets, equal intensity, } \delta \approx 25, 35.}$

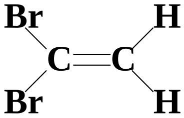
Chapter 6

6.1 For this one, we can use the mathematical approach:

$$\hat{I}\hat{\sigma}_{xy}\psi(x,y,z) = \hat{I}\psi(x,y,-z) = \psi(-x,-y,z) = \hat{C}_2(z)\psi(x,y,z).$$

Therefore, $\hat{I}\hat{\sigma}_{xy} = \boxed{\hat{C}_2(z).}$

6.2



This molecule has a $\hat{C}_2$ symmetry axis along the C=C bond and two vertical mirror planes that contain that bond. Those and the identity are the only symmetry elements, so the point group is $\boxed{C_{2v}}$ and the symmetry elements are $\boxed{\hat{E},\ \hat{C}_2,\ \hat{\sigma}_{xz},\ \hat{\sigma}_{yz}.}$

6.3 1,1-Dibromoethene is in the point group C_{2v}. We evaluate the results of the direct product $\Gamma_i \otimes \Gamma_\mu$, where Γ_μ may be any of A_1, B_1, and B_2 for electric dipole transitions (because these correspond to the functions x, y, and z), or A_1, A_2, B_1, and B_2 for Raman transitions (because each of these corresponds to some quadratic function such as x^2 or xy). Therefore, the possible upper states for an electric dipole transition would be $\boxed{^1A_1,\ ^1B_1,\ ^1B_2}$, and for a Raman transition would be $\boxed{^1A_1,\ ^1B_1,\ ^1B_2,\ ^1A_2.}$

6.4 The molecule is in the point group C_{2h}. The π bond lies perpendicular to the plane of the nuclei—the xy plane. That π orbital must be symmetric under the $\hat{C}_2$ rotation of the molecule (which doesn't change what lies above or below the xy plane) but changes sign under inversion and under reflection through the xy plane. The representation is therefore $\boxed{a_u.}$

Chapter 7

7.1 The molecule has 7 electrons, but 4 of them are in the 1s core orbitals and are not expected to contribute to the bonding. In the ground state, we would put 2 of the remaining 3 electrons into the $2\sigma_g$ bonding orbital and the last electron in the $2\sigma_u$ antibonding orbital, predicting a bond order of $(2-1)/2 = \boxed{1/2.}$

7.2 The molecule has 7 electrons, and we would predict the MO configuration $\boxed{1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^1.}$

7.3 Because the superscripts are not the same, the spins of the two states are not the same and the transition is $\boxed{\text{forbidden}}$ by the spin selection rule $\Delta S = 0$.

7.4 The transition would be an emission transition, forbidden by the spin selection rule (because $\Delta S \neq 0$). Therefore, the transition would occur by the process of $\boxed{\text{phosphorescence.}}$

Chapter 8

8.1 According to Eq. 8.17,

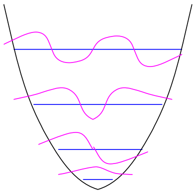
$$E_v = \left(v + \frac{1}{2}\right)\omega_e = (1450\,\mathrm{cm}^{-1})(2.5) = \boxed{3625\,\mathrm{cm}^{-1}.}$$

The wavefunction for the $v = 2$ state we can assemble from the normalization constant A_2, the Hermite polynomial $H_2(y)$, and the exponential function $e^{-y^2/2}$ (Eq. 8.16):

$$\left(\frac{k\mu}{\hbar^2}\right)^{1/8}\left(\frac{1}{8\sqrt{\pi}}\right)^{1/2}(4y^2 - 2)e^{-y^2/2}$$

where $y = (R - R_e)(k\mu/\hbar^2)^{1/4}$.

8.2 The spacing increases with E (because the walls are steeper than in the harmonic oscillator potential), but more slowly than particle in box (because the walls are not infinitely steep). The wavefunctions are similar to those in the harmonic oscillator, but with less variation in amplitude from the center to the walls (because the bottom of the well is flatter). And because the walls are steeper than in the harmonic oscillator, the tunneling does not extend as far.



8.3 The reduced mass μ of a diatomic is given by $m_\mathrm{A}m_\mathrm{B}/(m_\mathrm{A} + m_\mathrm{B})$, and if $m_\mathrm{A} = m_\mathrm{B}$ (i.e., any homonuclear diatomic), then $\mu = m_\mathrm{A}/2$. For $^{39}\mathrm{K}_2$, where each atom has a mass of 39.098 amu, the reduced mass is $\boxed{\mu{=}19.55\,\mathrm{amu.}}$ To estimate the vibrational constant, we need a guess of the force constant. Choosing $k \approx 12\,\mathrm{N\,m}^{-1}$, halfway between the values of $17\,\mathrm{N\,m}^{-1}$ for Na_2 and $7\,\mathrm{N\,m}^{-1}$ for Cs_2 in Table 8.2, we predict

$$\omega_e\,(\mathrm{cm}^{-1}) = 130.28\sqrt{\frac{k\,(\mathrm{N\,m}^{-1})}{\mu\,(\mathrm{amu})}} \approx (130.28)\sqrt{\frac{12}{19.55}} = \boxed{102\,\mathrm{cm}^{-1}.}$$

8.4 The point group is $D_{\infty h}$. There are two equivalent C—H bonds. In group theory, we consider all the equivalent bonds at the same time, so we can either have the two bonds move in phase to get the symmetric stretch, which has σ_g symmetry, or they can move exactly out of phase to get the antisymmetric stretch, which has symmetry σ_u. Checking the functions for whether these correspond to functions for an IR active mode (x, y, or z) or a Raman active mode (any quadratic function of x, y, and z), we obtain the following results, in summary: $\boxed{\sigma_g\text{ (Raman active), }\sigma_u\text{ (IR active).}}$

Chapter 9

9.1 We use Eq. 9.5, combining the reduced mass of 7.55 amu and the equilibrium bond length to get

$$B_e\,(\mathrm{cm}^{-1}) = \frac{16.858}{\mu\,(\mathrm{amu})\,R_e\,(\text{Å})^2} = \frac{16.858}{(7.55)(1.128)^2} = \boxed{1.755\,\mathrm{cm}^{-1}.}$$

9.2 From Table 9.2 we obtain the values $A = B = 9.94\,\mathrm{cm}^{-1}$ and $C = 6.30\,\mathrm{cm}^{-1}$, which corresponds to an oblate top with energy levels given by Eq. 9.22:

$$E_\mathrm{rot} = K_c^2(C - B) + BJ(J+1) = \left[(1^2)(6.30 - 9.94) + (9.94)(2)(3)\right]\,\mathrm{cm}^{-1} = \boxed{56.0\,\mathrm{cm}^{-1}.}$$

9.3 The rotational constant will increase, according to Eq. 9.16, as the moment of inertia decreases. Of the three molecules, ${}^{12}C^{16}O$ has the lowest moment of inertia, because it has only two atoms (of the same masses as the atoms that make up the CO_2 molecules). Between the two CO_2 isotopologues, the ${}^{18}O$-substituted molecule has the greater isotopic mass, so the greater moment of inertia. The ordering is therefore $\boxed{{}^{12}C^{18}O_2,\ {}^{12}C^{16}O_2,\ {}^{12}C^{16}O.}$

9.4 We fold the values of the rotational constants from Table 9.1 into Eqs. 9.8 and 9.9, setting $v = 1$, to find the rotational energies for $J = 2$ and $J = 3$. The difference between those energies is the transition energy ΔE that we're looking for:

$$\begin{aligned}
B_{v=1} &= B_e - \left(v + \frac{1}{2}\right)\alpha_e = [20.9557 - (1.5)(0.798)]\ \mathrm{cm}^{-1} = 19.759\,\mathrm{cm}^{-1} \\
E_{\mathrm{rot}} &= B_v J(J+1) - D_v\left[J(J+1)\right]^2 \\
E_{\mathrm{rot}}(J=2) &= (19.759\,\mathrm{cm}^{-1})(2)(3) - (2.15\cdot 10^{-3}\,\mathrm{cm}^{-1})\left[(2)(3)\right]^2 \\
E_{\mathrm{rot}}(J=3) &= (19.759\,\mathrm{cm}^{-1})(3)(4) - (2.15\cdot 10^{-3}\,\mathrm{cm}^{-1})\left[(3)(4)\right]^2 \\
\Delta E &= E_{\mathrm{rot}}(J=3) - E_{\mathrm{rot}}(J=2) = \boxed{118.32\,\mathrm{cm}^{-1}.}
\end{aligned}$$

Chapter 10

10.1 $\boxed{\text{Repulsion}}$ applies to all examples, and is expected to be roughly proportional to e^{-aR}, although other forms are used to model this (such as the R^{-12} repulsive term in the Lennard–Jones potential). (a) dispersion: $U(R) \propto \alpha_A\alpha_B/R^6$ (by Eq. 10.38). (b) H-bonding: $U(R) \propto \mu_A^2\mu_B^2/R^6$ (by Eq. 10.19), although a case can be made that hydrogen bonding is strong enough that the structures cannot be treated as freely rotating at typical temperatures, in which case the $\mu_A\mu_B/R^3$ of Eq. 10.16 would be more appropriate. In at least one popular model potential used to predict biochemical structure, the distance-dependence of hydrogen bonding is given using either a Lennard–Jones 6-12 potential (as in our Eq. 10.44) or a 10-12 potential (in which the distance dependence is a much more quickly decaying R^{-10} [1]). (c) dipole–dipole, dipole–induced dipole: $U(R) \propto \mu_A^2\mu_B^2/R^6, \mu_A\alpha_B/R^6$ (Eqs. 10.19, 10.23). The dipole–induced dipole is important here because CO is only very weakly *polar*, but has a relatively high *polarizability.* Note the important distinction between these two terms: *polar* means the positive and negative charges in the molecule are already well separated to create a permanent dipole moment, while *polarizable* means that an external electric field can easily separate the charges, whether or not they are already well separated. (d) dipole–dipole (non-rotating): $U(R) \propto \mu_A^2\alpha_B/R^3$ (by Eq. 10.16). You could make a good case that dipole–induced dipole is important here as well. I have only left it off because the interaction between non-rotating dipoles, varying as R^3, will tend to be more important if only because it decays so much more slowly than the dipole–induced dipole interaction.

10.2 From Eq. 10.17, the interaction between a multipole of 2^k charges and another of $2^{k'}$ charges has a potential energy proportional to $R^{-k-k'-1}$. A quadrupole is formed by an arrangement of 4 charges, for which $k = 2$, so the interaction between two quadrupoles will vary in proportion to $R^{-2-2-1} = \boxed{R^{-5}.}$

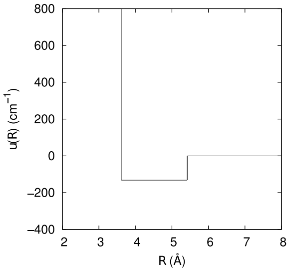
10.3 The dipole moment of HI is 0.45 D and the polarizability of N_2 is $0.20\,\text{Å}^3$. Plugging these values and the distance of 3.90 Å into Eq. 10.23 yields the following:

$$\begin{aligned}
u_{2-2^*}(R) &= -\frac{4\mu_A^2\alpha}{(4\pi\epsilon_0)R^6} \\
&= -\frac{4(0.45\,\mathrm{D})^2(3.3356\cdot 10^{-30}\,\mathrm{C\,m/D})^2(0.20\cdot 10^{-30}\,\mathrm{m}^3)}{(1.113\cdot 10^{-10}\,\mathrm{C^2\,J^{-1}\,m^{-1}})(3.90\cdot 10^{-10}\,\mathrm{m})^6} \\
&= \boxed{-4.60\cdot 10^{-24}\,\mathrm{J} = -0.00277\,\mathrm{kJ\,mol^{-1}}.}
\end{aligned}$$

This interaction energy is quite weak, partly because the N_2 polarizability is so small.

10.4 We can expect dispersion to be most important, because the bromine atoms are so large (and consequently have high polarizabilities). The molecule should also be quite polar, given the electronegativity of the Br atom, and so dipole–dipole interactions will also run high. The dipole–induced dipole attraction will also be present, but is usually weaker than the direct dipole–dipole interaction: $\boxed{\text{b<a<c.}}$

10.5 The well should extend from 3.61 Å to 5.42 Å and be 190 K ($132\,\text{cm}^{-1}$) deep, as in the following graph.



10.6 The degrees of freedom that couple most strongly are usually those that have the most similar energy spacing. In this case, there is a transfer of energy away from vibrations in molecule A. Rotational energy spacings tend to be at least two orders of magnitude smaller than the vibrational spacings, and electronic transitions are typically an order of magnitude greater. Therefore, the likeliest place for vibrational energy to go is into other vibrations. In this case, if A has lost vibrational energy, it is most likely to have gone into $\boxed{\text{vibrational excitation of B.}}$

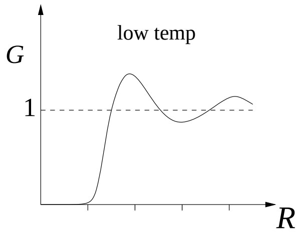
Chapter 11

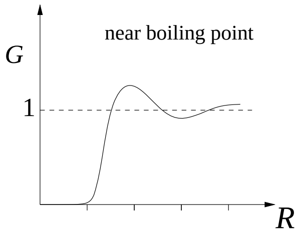
11.1 The $\boxed{\text{dispersion}}$ force binds CO_2 molecules together in a cluster, because there is no monopole (ionic charge) or dipole moment to bind them. As the cluster adds more units, the average binding energy per molecule will generally $\boxed{\text{decrease}}$ when the cluster is very small. For small clusters, removing one unit reduces the overall binding significantly. But the effect depends on the cluster and the cluster size. For larger clusters, the loss of one unit has little effect on the remaining cluster. We expect the molecules at the surface of the cluster to be the most weakly bound, because they are not completely surrounded by the stabilizing neighbors. As the cluster size increases, the ratio of the volume (proportional to the cluster size N) to the surface area (proportional to $N^{2/3}$) steadily increases, assuming the cluster shape remains roughly spherical, so on average for large clusters the binding energy may increase slightly with N.

11.2 The weak bonding interactions will be modeled by the van der Waals term (which includes dispersion forces) and the electrostatic potential energy term (which accounts for charge-charge interactions across distances longer than the typical chemical bond): $\boxed{U_{\text{vdW}} \text{ and } U_{\text{electrostatic}}.}$

Chapter 12

12.1 The pair correlation function for this system should resemble the curves shown for water in Figs. 12.3g–i. The oscillations should become smoother as we approach the boiling point.





12.2 $\boxed{\text{Yes.}}$ Molecules of the two substances will attract one another, principally through dispersion.

Chapter 13

13.1 The unit cell has two square faces opposite one another, and the rest of the faces are equivalent rectangles. There is one $\hat{C}_4$ principal rotation axis, a horizontal mirror plane, and four vertical mirror planes. The crystallographic point group is therefore $\boxed{D_{4h}.}$

13.2 $\boxed{\text{No.}}$ The reason is that no charge separation can exist in a regular monatomic crystal, and polarity is one of the requirements for piezoelectricity.

End of Chapter Problems

Chapter A

A.1 This problem uses a common manipulation, one of the features of logarithms that makes them so useful:

$$\begin{aligned} \mathrm{pK_a} = -\log_{10} K_\mathrm{a} &= -\log_{10}\, e^{-\Delta G/(RT)} \\ &= -\left[-\frac{\Delta G}{RT}\right] \log_{10}\, e && \log x^a = a \log x \\ &= \frac{\Delta G}{RT}(0.434). \end{aligned}$$

This shows, if you don't mind us getting ahead of ourselves a little, that the $\mathrm{pK_a}$ is directly proportional to the free energy of dissociation, ΔG, and inversely proportional to the temperature, T.

A.2 The idea here is that, even if we think at first we have no idea what the number ought to be, a closer look at the available choices makes it clear that we can spot some potentially ridiculous answers:

a. $2 \cdot 10^{10}\,\mathrm{m\,s^{-1}}$ is faster than the speed of light.

b. $2 \cdot 10^{5}\,\mathrm{m\,s^{-1}}$ has no obvious objections.

c. $2\,\mathrm{m\,s^{-1}}$ is the speed of a slow walk, and would imply, for example, that you could send an e-mail message over a cable connection to a friend half a mile away, and then run the half-mile to arrive and deliver the message in person before the e-mail finishes traveling through the wires.

When we have calculations that toss around factors of 10^{-34}, for one example, this is a significant skill. The correct answer is $\boxed{2 \cdot 10^{5}\,\mathrm{m\,s^{-1}}.}$

A.3 The volume is roughly $125\,\text{Å}^3$, which we can show is not big enough to hold more than about 15 atoms. Chemical bonds, formed between *overlapping* atoms, are roughly 1 Å long, and so typical atomic diameters are roughly 2 Å or more, and occupy a volume on the order of $(2\,\text{Å})^3 = 8\,\text{Å}^3$. A volume of $125\,\text{Å}^3$, therefore, cannot hold more than about $125/8 = 15.6$ atoms. Among the choices, the only reasonable value is $\boxed{8.}$

A.4 a. Chemical bond lengths in molecules are always in the range 0.6–4.0 Å, or $0.6 \cdot 10^{-10}$ to $4.0 \cdot 10^{-10}$ m. $25 \cdot 10^{-8}$ m is much too large for a bond length. $\boxed{\text{no}}$

b. Six carbon atoms have a mass of $6 \cdot 12 = 72$ amu. With the added mass of a few hydrogen atoms at 1 amu each, 78 amu is a reasonable value. $\boxed{\text{yes}}$

A.5 a. The derivatives $d[\mathrm{A}]$ and dt have the same units as the parameters [A] and t, respectively. Both sides of the equation should therefore have units of $\mathrm{mol\,L^{-1}\,s^{-1}}$. That means that k needs to provide the units of $\mathrm{s^{-1}}$ and cancel one factor of concentration units on the righthand side. k has units of $\boxed{\mathrm{L\,s^{-1}\,mol^{-1}}.}$

b. The argument of the exponential function must be unitless, so k_B must cancel units of energy (J) in the numerator and temperature (K) in the denominator. The correct units are $\boxed{\mathrm{J\,K^{-1}}.}$

c. The units all cancel, and K_eq is $\boxed{\text{unitless.}}$

d. Squaring both sides of the equation, we can solve for k: $\mu\omega^2 = k$. k must therefore have units of $\boxed{\mathrm{kg\,s^{-2}}.}$

A.6 There are two factors on the lefthand side, $(2x+1)^2$ and e^{-ax^2}. For the product to be zero, at least one of these factors must be zero. If $(2x+1) = 0$, then $\boxed{x = -\frac{1}{2}\ .}$ If $e^{-ax^2} = 0$, then $\boxed{x \to\ \pm\ \infty\ .}$ All three are valid solutions.

A.7 In general, for any complex number $(a + ib)$, the complex conjugate is $(a + b)^* = a - ib$. We look for the imaginary component and and invert its sign:

a. $x - iy : a = x \quad b = -y,\ \boxed{x\ +\ iy.}$

b. $ix^2y^2 : a = 0 \quad b = x^2y^2,\ \boxed{-ix^2y^2\ .}$

c. $xy(x + iy + z) :\ a = x^2y + xyz \quad b = xy^2,\ \ x^2y + xyz - ixy^2,\ \boxed{xy(x - iy + z).}$

d. $a = x/z \quad b = y/z,\ \boxed{(x - iy)/z\ .}$

e.

$$\begin{aligned} e^{ix} &= 1 + ix - x^2 - ix^3 + x^4 + ix^5 - \ldots \\ a &= 1 - x^2 + x^4 - \ldots \\ b &= x - x^3 + x^5 - \ldots \\ a - ib &= 1 - ix - x^2 + ix^3 + x^4 - ix^5 - \ldots = \boxed{e^{-ix}.} \end{aligned}$$

f. 54.3: $a = 54.3 \quad b = 0,\ \boxed{54.3.}$

A.8 This problem tests a few algebraic operations involving vectors, particularly useful to know when we look at angular momentum and (often related) magnetic field effects.

a. The length of a vector is calculated using the Pythagorean theorem: $|\vec{C}| = \sqrt{0^2 + 2^2 + 1^2} = \boxed{\sqrt{5}\ .}$

b. We add vectors one coordinate at a time: $\vec{A} + \vec{B} = (1 + 1, 0 + 0, 0 + 1) = \boxed{(2,\ 0,\ 1).}$

c. The dot product of two vectors multiplies the values for each coordinate of the two vectors and sums the results: $\vec{A}\ \cdot\ \vec{B} = (1 \cdot 1) + (0 \cdot 0) + (0 \cdot 1) = \boxed{1.}$

d. In the case of perpendicular vectors, this gives us zero: $\vec{A} \cdot \vec{C} = (1 \cdot 0) + (0 \cdot 2) + (0 \cdot 1) = \boxed{0.}$

e. The cross product involves a little more work, and yields a new vector, perpendicular to the two original vectors: $\vec{A} \times \vec{B} = (0 \cdot 1 - 0 \cdot 0, 0 \cdot 1 - 1 \cdot 1, 1 \cdot 0 - 0 \cdot 1) = \boxed{(0, -1, 0).}$

A.9 If we accept that the Taylor series expansion is exact if we take it to infinite order, then the Euler formula can be proven by the expansions of e^x (Eq. A.25), $\sin x$ (Eq. A.26), and $\cos x$ (Eq. A.27):

$$\begin{aligned}
e^{ix} &= \sum_{n=0}^{\infty} \frac{1}{n!}(ix)^n \\
&= 1 + ix - \tfrac{1}{2}x^2 - \frac{i}{6}x^3 + \frac{1}{24}x^4 + \frac{i}{120}x^5 - \ldots \\
&= (1 - \tfrac{1}{2}x^2 + \frac{1}{24}x^4 - \ldots) + i(x - \frac{1}{6}x^3 + \frac{1}{120}x^5 - \ldots) \\
&= \boxed{\cos x + i \sin x\ .}
\end{aligned}$$

This equation is of practical importance to us, and is famous among mathematicians for tying together three fundamental mathematical values—π, i, and e—in one equation:

$$e^{i\pi} = 1.$$

A.10
- **Maple**: After checking that all of the units are indeed consistent, enter the Maple command

  ```
  solve((1.000-(3.716/V^2))(V-0.0408)/(0.083145298.15),V);
  ```

  The resulting solution, 24.8, is in the same units as b, namely $\boxed{24.8 \text{ L mol}^{-1}.}$

- **Successive approximation**: There are several ways to solve this, corresponding to different forms of the equation that leaves V_m on one side. One way to set up the equation quickly is to recognize that $(V_\text{m} - b)$ will vary rapidly compared to $P - (a/V_\text{m}^2)$, so we can isolate V_m as follows:

$$\begin{aligned}
\frac{\left(P - \frac{a}{V_\text{m}^2}\right)(V_\text{m} - b)}{RT} &= 1 \\
\left(P - \frac{a}{V_\text{m}^2}\right)(V_\text{m} - b) &= RT \\
V_\text{m} - b &= \frac{RT}{\left(P - \frac{a}{V_\text{m}^2}\right)} \\
V_\text{m} &= \frac{RT}{\left(P - \frac{a}{V_\text{m}^2}\right)} + b.
\end{aligned}$$

  Substituting in the values for P, a, b, R, and T (making sure that the units are all compatible), we can reduce the equation to the following:

$$V_\text{m}(\text{L mol}^{-1}) = \frac{24.943}{1 + \frac{3.716}{V_\text{m}^2}} + 0.0408.$$

Guessing an initial value of 1 L mol^{-1} yields the following series of approximations:

$$\begin{aligned}
V_\mathrm{m} &= \frac{24.943}{1 \ + \ \frac{3.716}{1^2}} \ + \ 0.0408 \ = \ 5.330 \\
V_\mathrm{m} &= \frac{24.943}{1 \ + \ \frac{3.716}{5.330^2}} \ + \ 0.0408 \ = \ 22.099 \\
V_\mathrm{m} &= \frac{24.943}{1 \ + \ \frac{3.716}{22.099^2}} \ + \ 0.0408 \ = \ 24.796 \\
V_\mathrm{m} &= \frac{24.943}{1 \ + \ \frac{3.716}{24.796^2}} \ + \ 0.0408 \ = \ 24.834 \\
V_\mathrm{m} &= \frac{24.943}{1 \ + \ \frac{3.716}{24.834^2}} \ + \ 0.0408 \ = \ 24.835.
\end{aligned}$$

The series has converged to the three significant digits requested. The final value for V_m is $\boxed{24.8 \text{ L mol}^{-1}.}$

A.11 Here we apply the rules of differentiation summarized in Table A.3.

a.

$$\begin{aligned}
f(x) &= (x+1)^{1/2} \\
\frac{df}{dx} &= \tfrac{1}{2}(x+1)^{-1/2}.
\end{aligned}$$

b.

$$\begin{aligned}
f(x) &= [x/(x+1)]^{1/2} \\
\frac{df}{dx} &= \tfrac{1}{2}\left(\frac{x}{x+1}\right)^{-1/2}\left[\frac{1}{x+1}\,\frac{dx}{dx} + x\frac{d}{dx}\left(\frac{1}{x+1}\right)\right] \\
&= \tfrac{1}{2}\left(\frac{x}{x+1}\right)^{-1/2}\left[\frac{1}{x+1} - \frac{x}{(x+1)^2}\right].
\end{aligned}$$

c.

$$\begin{aligned}
\frac{df}{dx} &= \exp\left[x^{1/2}\right]\ \frac{d}{dx}\left(x^{1/2}\right) \\
&= \tfrac{1}{2}x^{-1/2}\exp\left[x^{1/2}\right].
\end{aligned}$$

d.

$$\begin{aligned}
\frac{df}{dx} &= \exp\left[\cos\ x^2\right]\frac{d}{dx}(\cos\ x^2) \\
&= \exp\left[\cos\ x^2\right](-\sin\ x^2)\frac{d}{dx}(x^2) \\
&= -2x\ \sin\ x^2\ \exp\left[\cos\ x^2\right].
\end{aligned}$$

A.12 This problem tests our ability to use a few of the analytic integration results given in Table A.5.

a. $\int_0^\infty\ e^{-ax}dx = -\frac{1}{a}e^{-ax}|_0^\infty = -\frac{1}{a}(0-1) = \boxed{\dfrac{1}{a}.}$

b. $\int_1^5 x^2 dx = \frac{1}{3}x^3|_1^5 = \frac{1}{3}(125-1) = \boxed{\frac{124}{3}.}$

c. $\int_1^5 x^{-3/2} dx = -2x^{-1/2}|_1^5 = \boxed{-2(\frac{1}{\sqrt{5}} - 1).}$

d. $r^2 \int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta d\theta = r^2\ (\phi)|_0^{2\pi}\ (-\cos\theta)|_0^{\pi} = r^2(2\pi - 0)[-(-1)-(-1)] = \boxed{4\pi r^2.}$

A.13 We use the Coulomb force law, Eq. A.41, using the charge of the electron $-e$ for both charges and r_{12} set to 1.00 Å:

$$\begin{aligned} F_{\text{Coulomb}} &= \frac{e^2}{4\pi\epsilon_0 r^2} \\ &= \frac{(1.602 \cdot 10^{-19}\,\text{C})^2}{(1.113 \cdot 10^{-10}\,\text{C}^2\,\text{J}^{-1}\,\text{m}^{-1})(1.00\,\text{Å})^2(10^{-10}\,\text{m}\,\text{Å}^{-1})^2} = \boxed{2.31 \cdot 10^{-8}\,\text{N}\ .} \end{aligned}$$

A.14 This problem relies on the definitions of the linear momentum p and the kinetic energy K (Eq. A.36):

$$p = mv$$

$$K = \tfrac{1}{2}mv^2 = \boxed{\frac{p^2}{2m}.}$$

A.15 We're calling the altitude r. Because the acceleration is downward but r increases in the upward direction, the acceleration is negative: $-9.80\,\text{m}\,\text{s}^{-2}$. We invoke the relationship between force and the potential energy, and find that we have to solve an integral:

$$U(r) = -\int_0^r F(r')\,dr' = -\int_0^r (-mg)\,dr' = \boxed{mgr.}$$

A.16

$$\begin{aligned} |F_{\text{Coulomb}}| &= \frac{e^2}{4\pi\epsilon_0 r^2} = \frac{(1.602 \cdot 10^{-19}\,\text{C})^2}{(1.113 \cdot 10^{-10}\,\text{C}^2\,\text{J}^{-1}\,\text{m}^{-1})(0.529\,\text{Å})^2(10^{-10}\,\text{m}\,\text{Å}^{-1})^2} \\ &= \boxed{8.23 \cdot 10^{-8}\,\text{N}} \\ |F_{\text{gravity}}| &= m_H g \\ &= (1.008\,\text{amu})(1.661 \cdot 10^{-27}\,\text{kg}\,\text{amu}^{-1})\left(9.80\,\text{m}\,\text{s}^2\right) \\ &= \boxed{1.64 \cdot 10^{-26}\,\text{N}.} \end{aligned}$$

Sure enough, the gravitational force is smaller than the Coulomb force by orders of magnitude, and the motions of these particles will be dictated—as well as we can measure them—exclusively by the Coulomb force.

A.17 We are proving an equation that depends on L and x and t and v_x, which may look like too many variables. If we use the definition of L to put this equation in terms of K and U, then we can at least put K in terms of speed. Then, because speed itself is a function of position and time, the number of variables is quite manageable. Nonetheless, keeping things in terms of K and U is useful, because of their straightforward dependence on only v and x, respectively.

To prove the equation, we could try working from both sides and seeing if the results meet in the middle. First the lefthand side:

$$\begin{aligned}\frac{\partial L}{\partial x} &= \underbrace{\frac{\partial K}{\partial x}}_{=0} - \frac{\partial U}{\partial x} && K \text{ not a function of } x \\ &= F_x = ma && F_x = -dU/dx \\ &= m\frac{d^2x}{dt^2} && \text{acceleration} = d^2x/dt^2\end{aligned}$$

Next the righthand side:

$$\begin{aligned}\frac{d}{dt}\frac{\partial L}{\partial v_x} &= \frac{d}{dt}\left[\frac{1}{2}m\frac{\partial v_x^2}{\partial v_x} - \frac{\partial U}{\partial v_x}\right] \\ &= \frac{d}{dt}\left[mv_x - \underbrace{\frac{\partial U}{\partial v_x}}_{=0}\right] && U \text{ not a function of } v_x \\ &= m\frac{dv_x}{dt} = m\frac{d^2x}{dt^2}.\end{aligned}$$

And there we are. One of the useful features of the Lagrangian is that the equation proved here can be made to hold for different choices of coordinates. This enables the mechanics problems to be written in coordinates that take advantage of symmetry (for example, if the only force is a radial one, attracting or repelling particles from a single point), and the Lagrangian then provides a starting point to develop relationships between the positions and velocities of the particles.

A.18 The overall energy before the collision is the sum of the two kinetic energies:

$$K = \tfrac{1}{2}m_1v_1^2 + \tfrac{1}{2}m_2v_2^2,$$

and this must equal the energy after the collision:

$$K = \tfrac{1}{2}m_1{v_1'}^2 + \tfrac{1}{2}m_2{v_2'}^2.$$

Similarly, we may set the expressions for the linear momentum before and after the collision equal to each other:

$$p = m_1v_1 + m_2v_2 = m_1v_1' + m_2v_2'.$$

So there are two equations and two unknowns. At this point, the problem is ready to solve with a symbolic math program.

Maple. The problem can be solved in a single step by asking Maple to solve the conservation of energy and conservation of momentum equations simultaneously to get the final speeds (here $vf[1]$ and $vf[2]$ in terms of the masses and initial speeds:

```
solve({m[1]*v[1]+m[2]*v[2] = m[1]*vf[1]+m[2]*vf[2], (1/2) * m[1] * v[1]^2+(1/2) * m[2] *
v[2]^2 = (1/2) * m[1] * vf[1]^2+(1/2) * m[2]*vf[2]^2}, [vf[1], vf[2]]);
```

On paper. This last equation lets us eliminate one variable by writing, for example, the final speed v_2' in terms of v_1':

$$v_2' = \frac{m_1 v_1 + m_2 v_2 - m_1 v_1'}{m_2}.$$

Now we can put this value into the equation for K, and solve for v_1':

$$\begin{aligned}
K &= \tfrac{1}{2} m_1 v_1^2 + \tfrac{1}{2} m_2 v_2^2 && (a)\\
&= \tfrac{1}{2} m_1 {v_1'}^2 + \tfrac{1}{2} m_2 {v_2'}^2\\
&= \tfrac{1}{2} m_1 {v_1'}^2 + \tfrac{1}{2} m_2 \left(\frac{m_1 v_1 + m_2 v_2 - m_1 v_1'}{m_2}\right)^2.
\end{aligned}$$

This is going to be an equation that depends on ${v_1'}^2$ and v_1', so we can solve it using the quadratic formula. In that case, it's easiest to put all the quantities on one side of the equation:

$$\begin{aligned}
0 &= \tfrac{1}{2} m_1 {v_1'}^2 + \tfrac{1}{2} m_2 \left(\frac{m_1 v_1 + m_2 v_2 - m_1 v_1'}{m_2}\right)^2 - \left(\tfrac{1}{2} m_1 v_1^2 + \tfrac{1}{2} m_2 v_2^2\right) && \text{subtract } (a) \text{ above}\\
&= \tfrac{1}{2} m_1 {v_1'}^2 + \tfrac{1}{2} m_2 \left(\frac{\begin{matrix} m_1^2 v_1^2 + m_2^2 v_2^2 + m_1^2 {v_1'}^2 \\ +2 m_1 m_2 v_1 v_2 - 2 m_1^2 v_1 v_1' - 2 m_1 m_2 v_1' v_2 \end{matrix}}{m_2^2}\right) && \text{expand the square}\\
&- \tfrac{1}{2} m_1 v_1^2 - \tfrac{1}{2} m_2 v_2^2\\
&= m_1 {v_1'}^2 + \frac{m_1^2}{m_2} v_1^2 + m_2 v_2^2 + \frac{m_1^2}{m_2} {v_1'}^2 + 2 m_1 v_1 v_2 && \text{divide by } 1/2\\
&- 2\frac{m_1^2}{m_2} v_1 v_1' - 2 m_1 v_1' v_2 - m_1 v_1^2 - m_2 v_2^2\\
&= {v_1'}^2 \left(m_1 + \frac{m_1^2}{m_2}\right) + v_1' \left(-2\frac{m_1^2}{m_2} v_1 - 2 m_1 v_2\right) && \text{group by power of } v_1'\\
&+ \left(\frac{m_1^2}{m_2} v_1^2 + m_2 v_2^2 + 2 m_1 v_1 v_2 - m_1 v_1^2 - m_2 v_2^2\right)\\
&= {v_1'}^2 \left(m_1 + \frac{m_1^2}{m_2}\right) + v_1' \left(-2\frac{m_1^2}{m_2} v_1 - 2 m_1 v_2\right)\\
&+ \left[\left(\frac{m_1^2}{m_2} - m_1\right) v_1^2 + 2 m_1 v_1 v_2\right]\\
v_1' &= \left(2 m_1 + 2\frac{m_1^2}{m_2}\right)^{-1} \left\{\left(2\frac{m_1^2}{m_2} v_1 + 2 m_1 v_2\right)\right. && \text{quadratic formula}\\
&\left.\pm \left[\left(2\frac{m_1^2}{m_2} v_1 + 2 m_1 v_2\right)^2 - 4\left(m_1 + \frac{m_1^2}{m_2}\right)\left[\left(\frac{m_1^2}{m_2} - m_1\right) v_1^2 + 2 m_1 v_1 v_2\right]\right]^{1/2}\right\}.
\end{aligned}$$

To deal with this equation, we can expand the multiplication inside the square brackets:

$$\begin{aligned}
\left(2\frac{m_1^2}{m_2} v_1 + 2 m_1 v_2\right)^2 &= 4\frac{m_1^4}{m_2^2} v_1^2 + 8\frac{m_1^3}{m_2} v_1 v_2 + 4 m_1^2 v_2^2\\
-4\left(m_1 + \frac{m_1^2}{m_2}\right)\left[\left(\frac{m_1^2}{m_2} - m_1\right) v_1^2 + 2 m_1 v_1 v_2\right] &= -4\frac{m_1^3}{m_2} v_1^2 - 4\frac{m_1^4}{m_2^2} v_1^2 + 4 m_1^2 v_1^2 + 4\frac{m_1^3}{m_2} v_1^2
\end{aligned}$$

$$- 8m_1^2 v_1 v_2 - 8\frac{m_1^3}{m_2} v_1 v_2.$$

Nearly all of these terms cancel when we add these two expressions together, leaving:

$$4m_1^2 v_2^2 + 4m_1^2 v_1^2 - 8m_1^2 v_1 v_2.$$

In the quadratic equation, we have to take the square root of this, but that turns out to be easy:

$$\begin{aligned} \left[4m_1^2 v_2^2 + 4m_1^2 v_1^2 - 8m_1^2 v_1 v_2\right]^{1/2} &= 2m_1 \left[v_2^2 + v_1^2 - 2v_1 v_2\right]^{1/2} \\ &= 2m_1 \left(v_2 - v_1\right). \end{aligned}$$

Finally, putting this back into our equation for v_1', we get

$$\begin{aligned} v_1' &= \left(2m_1 + 2\frac{m_1^2}{m_2}\right)^{-1} \left\{\left(2\frac{m_1^2}{m_2} v_1 + 2m_1 v_2\right) \pm 2m_1 \left(v_2 - v_1\right)\right\} \\ &= \left(1 + \frac{m_1}{m_2}\right)^{-1} \left\{\left(\frac{m_1}{m_2} v_1 + v_2\right) \pm \left(v_2 - v_1\right)\right\}. && \text{divide out } 2m_1 \end{aligned}$$

This is correct as far as it goes, but we have two solutions, corresponding to either the + or − sign. If we use the − sign, then we get

$$v_1' = \left(1 + \frac{m_1}{m_2}\right)^{-1} \left\{\frac{m_1}{m_2} v_1 + v_2 - v_2 + v_1\right\} = v_1.$$

This is the solution if the collision *doesn't* occur; particle 1 just keeps moving at the same speed as before. The + sign gives us the correct solution:

$$\begin{aligned} v_1' &= \left(1 + \frac{m_1}{m_2}\right)^{-1} \left\{\frac{m_1}{m_2} v_1 + v_2 + v_2 - v_1\right\} \\ &= \left(1 + \frac{m_1}{m_2}\right)^{-1} \left[\left(\frac{m_1}{m_2} - 1\right) v_1 + 2v_2\right] \\ &= \frac{1}{m_1 + m_2} \left[\left(m_1 - m_2\right) v_1 + 2m_2 v_2\right]. \end{aligned}$$

We can now use the conservation of momentum to solve for v_2'. I'm going to factor out a $1/(m_1 + m_2)$ to get an equation similar to the one for v_1':

$$\begin{aligned} v_2' &= \frac{m_1 v_1 + m_2 v_2 - m_1 v_1'}{m_2} \\ &= \frac{1}{m_2} \left\{m_1 v_1 + m_2 v_2 - \frac{m_1}{m_1 + m_2} \left[\left(m_1 - m_2\right) v_1 + 2m_2 v_2\right]\right\} \\ &= \left(\frac{m_1}{m_2}\right) v_1 + v_2 - \left(\frac{m_1 - m_2}{m_1 + m_2}\right) \left(\frac{m_1}{m_2}\right) v_1 - 2\left(\frac{m_1}{m_1 + m_2}\right) v_2 \\ &= \left(\frac{1}{m_1 + m_2}\right) \left[\frac{m_1(m_1 + m_2)}{m_2} v_1 + (m_1 + m_2) v_2 - \left(\frac{m_1(m_1 - m_2)}{m_2}\right) v_1 - 2m_1 v_2\right] \\ &= \frac{1}{m_1 + m_2} \left[\left(m_2 - m_1\right) v_2 + 2m_1 v_1\right]. \end{aligned}$$

Because there is nothing in the problem that determines which particle is labeled 1 and which is labeled 2, the equations for v_1' and v_2' must be exactly the same, with all the labels 1 and 2 switched.

If you haven't seen this result or simply don't remember it, it's worthwhile to check a few values. For example, if the two particles have equal mass ($m_1 = m_2$), then the final speeds are $v_1' = v_2$ and $v_2' = v_1$; *i.e.*, the particles simply exchange speeds. Another example: if particle 1 is initially at rest ($v_1 = 0$), then it picks up a speed $2m_2v_2/(m_1+m_2)$ from the collision. In that case, if particle 2 dominates the mass ($m_2 \gg m_1$), then particle 1 will find itself with a final speed equal to $2v_2$. In contrast, if particle 1 is much more massive than 2, then the collision will hardly affect it ($v_1' \approx 0$) and particle 2 will simply reverse direction ($v_1' \approx -v_2$).

Note that the two particles don't have to be moving in opposite directions. If particle 1 is behind 2 but moving faster and in the same direction, then they will strike each other, and particle 2 will acquire particle 1's higher speed.

A.19

$$K = U = -\frac{e^2}{4\pi\epsilon_0 r} = \frac{(1.602\cdot 10^{-19}\,\mathrm{C})^2}{(1.113\cdot 10^{-10}\,\mathrm{C}^2\,\mathrm{J}^{-1}\,\mathrm{m}^{-1})(1.0\,\text{Å})(10^{-10}\,\mathrm{m}\,\text{Å}^{-1})} = 2.31\cdot 10^{-18}\,\mathrm{J}$$

$$L = |\vec{r}\times\vec{p}| = rp, \text{ since } \vec{r}\perp\vec{p}.$$

$$p = \sqrt{2m_eK} = \left[2(9.109\cdot 10^{-31}\,\mathrm{kg})\cdot(2.31\cdot 10^{-18}\,\mathrm{J})\right]^{1/2} = 2.05\cdot 10^{-24}\,\mathrm{kg\,m\,s^{-1}}$$

$$L = (1.0\,\text{Å})(10^{-10}\,\mathrm{m}\,\text{Å}^{-1})(2.05\cdot 10^{-24}\,\mathrm{kg\,m\,s^{-1}}) = \boxed{2.05\cdot 10^{-34}\,\mathrm{kg\,m^2\,s^{-1}}\ .}$$

A.20 a. *Find the center of mass positions $\vec{r}_i^{(0)}$ at collision.* Let's call the center of mass of the entire system the origin. The particles have equal mass, so the origin will always lie exactly in between the two particles. At the time of the collision, we may draw a right triangle for each particle, connecting the particle's center of mass, the origin, and with the right angle resting on the z axis. The hypotenuse of the triangle connects the center of mass to the point of contact between the two particles, and must be of length $d/2$ (the radius of the particle). The other two sides are of length $(d/2)\cos\theta$ (along the z axis) and $(d/2)\sin\theta$ (along the x axis), based on the definitions of the sine and cosine functions in Eqs. A.5. These correspond to the magnitudes of the z and x coordinates, respectively, of the particle centers of mass at the collision. The signs of the values may be determined by inspection of the figure: at the time of the collision, x_1 and z_2 are positive while x_2 and z_1 are negative, so the position vectors are:

$$\vec{r}_1^{(0)} = ((d/2)\sin\theta, 0, -(d/2)\cos\theta)$$
$$\vec{r}_2^{(0)} = (-(d/2)\sin\theta, 0, (d/2)\cos\theta)\,.$$

b. *Find the velocities $\vec{v}_i'$ after collision.* Simple collisions obey a simple reflection law: the angle of incidence is equal to the angle of reflection. These are the angles between the velocity vectors and the normal vector—the line at angle θ from the z axis. (This is the normal vector because it lies perpendicular to the plane that lies between the two spheres at the point of collision; this plane is effectively the surface of reflection for the collision.) Therefore, the velocity vector after the collision is at an angle 2θ from the z axis, and the velocity vectors after the collision are

$$\vec{v}_1' = v_0(\sin 2\theta, 0, -\cos 2\theta)$$
$$\vec{v}_2' = v_0(-\sin 2\theta, 0, \cos 2\theta).$$

Notice that the speed after the collision is still v_0 for each particle. Because they each began with the same magnitude of linear momentum, the momentum transfer that takes place only affects the trajectories.

c. *Show that $\vec{L}$ is conserved before and after the collision.* We now have position and velocity vectors before and after the collision:

$$
\begin{aligned}
\vec{r}_1 &= ((d/2)\sin\theta, 0, -(d/2)\cos\theta) \ + \ \vec{v}_1 t & \vec{r}_2 &= (-(d/2)\sin\theta, 0, (d/2)\cos\theta) \ + \ \vec{v}_1 t \\
\vec{v}_1'' &= v_0(0,0,1) & \vec{v}_2'' &= v_0(0,0,-1) \\
\vec{v}_1' &= v_0(\sin 2\theta, 0, -\cos 2\theta) & \vec{v}_2' &= v_0(-\sin 2\theta, 0, \cos 2\theta).
\end{aligned}
$$

We take the cross products of these for each particle to get $\vec{L}$ for each particle, and we add these together to get the total angular momentum for the system. Before the collision,

$$
\begin{aligned}
\vec{r}_1'' &= ((d/2)\sin\theta, 0, -(d/2)\cos\theta) + v_0 t(0,0,1) \\
\vec{L}_1'' &= m\vec{r}_1'' \times \vec{v}_1'' \\
&= m\left(y_1'' v_{z1}'' - z_1'' v_{y1}, z_1'' v_{x1}'' - x_1'' v_{z1}, x_1'' v_{y1}'' - y_1'' v_{x1}\right) \\
&= m\,(0, -(dv_0/2)\sin\theta, 0)
\end{aligned}
$$

and similarly for $\vec{L}_2''$:

$$\vec{L}_2'' = m\,(0, -(dv_0/2)\sin\theta, 0)$$

and combining these yields:

$$\vec{L}'' = \vec{L}_1'' + \vec{L}_2'' = -mdv_0\ (0, \sin\theta, 0).$$

All of the position or velocity vectors have only zero y components, and therefore only the y component of the cross product survives. After the collision,

$$
\begin{aligned}
\vec{r}_1' &= ((d/2)\sin\theta, 0, -(d/2)\cos\theta) + v_0 t(\sin 2\theta, 0, -\cos 2\theta) \\
\vec{L}_1' &= m\vec{r}_1' \times \vec{v}_1'
\end{aligned}
$$

which has a y component

$$\vec{L}_{y1}' = m\left\{-(d/2)\cos\theta\sin 2\theta - v_0 t\cos 2\theta\sin 2\theta - [(d/2)\sin\theta(-\cos 2\theta) + v_0 t\sin 2\theta(-\cos 2\theta)]\right\}$$

and similarly for $\vec{L}_{y2}'$:

$$\vec{L}_{y1}' = m\left\{(d/2)\cos\theta(-\sin 2\theta) + v_0 t\cos 2\theta(-\sin 2\theta) - [-(d/2)\sin\theta\cos 2\theta - (-v_0 t\sin 2\theta)\cos 2\theta]\right\}.$$

Adding the two components together we find that all the t-dependent terms cancel, and trigonometric identities from Table A.2 simplify the rest:

$$
\begin{aligned}
\vec{L}_y' &= \vec{L}_{1y}' + \vec{L}_{2y}' \\
&= \frac{mdv_0}{2}\left[-2\cos\theta\sin 2\theta + 2\sin\theta\cos 2\theta\right] \\
\sin 2\theta &= 2\sin\theta\cos\theta \\
\cos 2\theta &= 2\cos^2\theta - 1 \\
\vec{L}_y' &= \frac{2mdv_0}{2}\left[-\cos\theta\,(2\sin\theta\cos\theta) + \sin\theta\left(2\cos^2\theta - 1\right)\right] \\
&= mdv_0\left[-2\cos^2\theta\sin\theta + 2\cos^2\theta\sin\theta - \sin\theta\right] \\
&= -mdv_0\sin\theta.
\end{aligned}
$$

This is the y component of $\vec{L}'$, and the x and z components are again zero in the cross products, so we have shown that both $\vec{L}'$ and $\vec{L}''$ are equal to

$$\vec{L} = mdv_0\,(0, \sin\theta, 0).$$

If the particles hit head-on, then $\theta = 0$ and the angular momentum is zero. As θ increases, L increases to a maximum value of mdv_0 when the two particles just barely touch each other in passing.

If we had used the conservation of L at the outset, we could have found this solution quickly. Because the angular momentum does not depend on the size of the particles, we can replace our two objects here with point masses. It won't matter that they now won't collide, because if L is conserved we have to get the same answer before the collision takes place anyway. In fact, because L is conserved, we can pick any point in time that's convenient for us to calculate L, so I would pick the time when the two particles reach $z = 0$. At this time, both particles are traveling on trajectories that are exactly perpendicular to their position vectors ($\vec{v}_i$ is perpendicular to $\vec{r}_i$). This makes the cross product for each particle easy to evaluate:

$$\vec{L}_i = m\vec{r}_i \times \vec{v}_i = m(\pm(d/2)\sin\theta, 0, 0) \times (0, 0, \pm v_0) = mdv_0/2(0, \sin\theta, 0),$$

where the minus sign applies to particle 2. There are two particles, so we multiply this vector by 2, arriving at the same $\vec{L}$ as above.

A.21 a. *Write $\vec{\mathcal{E}}_1$ in vector form.* The magnitude of the electric field generated by particle 1 is given by $F = q_2\mathcal{E}_1$, and this force must be equal to the Coulomb force $F = -q_1q_2/(4\pi\epsilon_0 r^2)$. The force vector points along the axis separating the two particles, and we can include this direction-dependence by multiplying the magnitude of the vector by $\vec{r}/r$. The Cartesian form of the vector $\vec{r}$ from particle 1 to 2, just working off part (b) of the figure, may be written $(rv_1/c, y_2, 0)$ and has length

$$r = \left[\left(\frac{rv_1}{c}\right)^2 + y_2^2\right]^{1/2}.$$

Therefore, the force vector is

$$\vec{F} = \left(\frac{q_1q_2}{4\pi\epsilon_0 r^2}\right)\frac{\vec{r}}{r} = \frac{q_1q_2}{4\pi\epsilon_0 r^3}(rv_1/c, y_2, 0)$$

and the electric field vector is

$$\vec{\mathcal{E}}_1 = \frac{\vec{F}}{q_2} = \frac{q_1}{4\pi\epsilon_0 r^3}(rv_1/c, y_2, 0).$$

b. *Write $\vec{B}$ in vector form.* Here we just have to be careful to correctly evaluate the cross product. We are using the equation $\vec{B} = \frac{1}{c^2}\vec{\mathcal{E}}_1 \times \vec{v}_1$, and we have an equation for $\vec{\mathcal{E}}_2$ already. The velocity vector consists only of an x-velocity component: $\vec{v}_1 = (v_1, 0, 0)$. Notice that because these two vectors lie in the xy plane, their cross product—which is perpendicular to both vectors—will lie along the z axis. The z component of the cross product $\vec{a} \times \vec{b}$ is equal to $a_xb_y - a_yb_x$, so we have

$$\vec{B} = \frac{1}{c^2}\vec{\mathcal{E}}_1 \times \vec{v}_1 = \frac{q_1}{4\pi\epsilon_0 c^2 r^3}\,(0, 0, v_1y_2)\;.$$

c. *Find the magnetic force vector.* Again, we take a cross product with the velocity. This time, the $\vec{B}$ vector lies along z, and $\vec{v}_1$ lies along x, so the cross product lies along y:

$$\vec{F}_{\text{mag}} = q_2\vec{v}_1 \times \vec{B} = \frac{q_1q_2}{4\pi\epsilon_0 c^2 r^3}\,(0, v_1^2y_2, 0)\;.$$

d. *Calculate the difference between the actual and classical values of the Coulomb force.* To compute the actual Coulomb force, we use the distance r, so $\vec{F}$ has a magnitude

$$F = \frac{q_1 q_2}{4\pi\epsilon_0 r^2}.$$

The classical Coulomb force would be

$$F' = \frac{q_1 q_2}{4\pi\epsilon_0 y_2^2}\ ,$$

and the difference between the two forces is

$$F - F' = \frac{q_1 q_2}{4\pi\epsilon_0}\left[\frac{1}{r^2} - \frac{1}{y_2^2}\right].$$

We can simplify this by relating r^2 and y^2:

$$\begin{aligned} r^2 &= \left(\frac{r v_1}{c}\right)^2 + y_2^2 \\ r^2 &= y_2^2\left[1 - \left(\frac{v_1}{c}\right)^2\right]^{-1} \quad . \end{aligned}$$

So, finally, we have

$$\begin{aligned} F - F' &= \frac{q_1 q_2}{4\pi\epsilon_0}\left[\frac{1}{y^2}\left[1 - \left(\frac{v_1}{c}\right)^2\right] - \frac{1}{y_2^2}\right] \\ &= \frac{q_1 q_2}{4\pi\epsilon_0 y_2^2}\left[-\left(\frac{v_1}{c}\right)^2\right] = -\frac{q_1 q_2 v_1^2}{4\pi\epsilon_0 c^2 y_2^2}. \end{aligned}$$

In comparison, the magnitude of the magnetic force we calculated from the standard equations is

$$F_{\text{mag}} = q_1 q_2 v_1^2 y_2/(4\pi\epsilon_0 c^2 r^3),$$

and for $v \ll c$, we can allow $r \approx y_2$, so that

$$F_{\text{mag}} = q_1 q_2 v_1^2/(4\pi\epsilon_0 c^2 y_2^2).$$

Magnetic forces are a natural result of the motion of electrical charge when special relativity is taken into account. It was this relationship between electric and magnetic forces that was the basis of Einstein's original paper on special relativity.

Chapter 1

1.1 Radiation behaves more classically at large wavelengths, because the smaller frequency allows smaller energy increments to be absorbed or emitted by matter. Therefore, the energy of long-wavelength radiation appears more like a continuous, rather than quantized, variable. Radiation can be expected to behave like a classical wave provided that its wavelength is *long* compared to the system of interest. For example, radiofrequency radiation can be directed by reflection and refraction more easily than the relatively particle-like x-ray and γ radiation. Therefore, a correspondence principle would suggest that radiation must be treated by quantum mechanics as the wavelength becomes *small* compared to the system of interest. (Furthermore, it turns out that photons do carry a momentum, described exactly by de Broglie's equation $p = h/\lambda$, and this decidedly non-classical property is most apparent at short wavelengths.)

1.2 The quantized picture, while accurate in some aspects, is the misleading one. Radiofrequency photons, in particular, carry so little energy that single-photon detection at those wavelengths is quite challenging. Related to this is the fact that, in order to maintain a detectable signal, our transmitter must emit photons at an *enormous* rate. A tiny 100 W transmitter emits more than 10^{27} photons per second at a frequency of 100 MHz. And these are *big* photons, with wavelengths of a few meters. Even 10 km away from the source, nearly 10^{18} photons fly through each square meter of space every second. The numbers are so big that as we move away from the transmitter, the signal appears to drop continuously. Furthermore, as we get to very great distances, photons will continue to strike the source, but at a reduced rate. Although the photon energy itself is a discrete quantity, the rate at which the photons impinge on our antenna remains a continuous variable, and the signal deteriorates smoothly until we can no longer detect it. That said, experiments that detect single photons are not rare, but they are normally carried out with higher energy photons, such as in the visible or UV.

1.3 Although the electron beam leaving the source was incoherent (with random phases), the reflection off the surface sets a boundary condition where the phase goes to zero, in the same way that the wavefunction of our particle in a box goes to zero at the walls of the box. From that point on, the electrons reflected towards the detector are coherent, and the interference pattern becomes observable.

1.4 Mass and energy and charge must each be conserved, at least in chemistry, so the electrons cannot just disappear. Because they have wave-like character, the electrons are not constrained to a single trajectory: they can be detected at angles other than the normal reflection angle for particles. If some particular reflection angle corresponds to destructive interference—where no electron signal is detected – then there will be other angles at which an *excess* signal be detected.

1.5 An exact value of λ_{dB} requires an exact value of the momentum, which the uncertainty principle tells me is only possible for a particle with infinite uncertainty in position. So the answer is yes: if particle 1 has a momentum that is known precisely, then it effectively has an infinite size (it is possible for the particle to be detected anywhere). But this is true of both my measurement λ_{dB} in the laboratory *and* the student's measurement in the reference frame of particle 2. In practice, if I have any idea where the particle is (so the position uncertainty is finite), then I can't know exactly what the momentum is; in other words, I will not always get the same value for p when I measure it. The student on particle 2 will find the same thing—the measured momentum will cover a range of different values. The mean p values (and therefore the apparent de Broglie wavelengths) will be different in the two sets of measurements, but the student will always find that the mean value of λ_{dB} is finite.

1.6

a. The spectrum of the neutral helium atom.

b. The wavefunction of the electron in the neutral hydrogen atom.

c. $\boxed{\text{The second ionization energy of the helium atom.}}$

The Bohr model works only for one-electron atoms, and does *not* correctly predict the distribution of the electron.

1.7 This should be more energy than for the same transition in the H atom, because the greater nuclear charge on He^+ makes the electron more tightly bound and harder to pull out to an excited state orbital. The He atom has two electrons, and the He^+ ion has one electron. He^+ therefore obeys the equations for a one-electron atom, with the atomic number $Z = 2$.

$$\begin{aligned}
E_n &= -\frac{Z^2}{2n^2}(1\,E_\mathrm{h}) \\
E_2 - E_1 &= -\frac{Z^2}{2}\left(\frac{1}{2^2} - \frac{1}{1^2}\right) E_\mathrm{h} = \frac{3}{8}Z^2\,E_\mathrm{h} && \mathrm{He}^+ :\ Z = 2 \\
E_2 - E_1 &= -\frac{3}{8}2^2\,E_\mathrm{h} = \boxed{1.5\,E_\mathrm{h}} = 6.54 \cdot 10^{-18}\,\mathrm{J}.
\end{aligned}$$

1.8 This will be a small transition energy, because the energy levels get very close together at high n. What does that imply for the wavelength λ? That it will be long, because $\lambda \propto 1/E_\mathrm{photon}$. The wavelength, frequency, and energy of radiation are all related through Planck's law $E = h\nu$ and the constancy of the speed of light $\nu = c/\lambda$. For helium, $Z = 2$.

$$\begin{aligned}
\Delta E &= \frac{Z^2}{2}\left(\frac{1}{n''^2} - \frac{1}{n'^2}\right) E_\mathrm{h} \\
&= (2)\left(\frac{1}{100^2} - \frac{1}{101^2}\right) E_\mathrm{h} \\
&= 3.94 \cdot 10^{-6}\,E_\mathrm{h} = 0.865\,\mathrm{cm}^{-1} \\
\lambda &= \frac{1}{\Delta E(\,\mathrm{cm}^{-1})} \ = \ 1.16\,\mathrm{cm} \ = \ \boxed{0.0116\ \mathrm{m},}
\end{aligned}$$

which is in the $\boxed{\text{microwave.}}$

1.9 Energy has been added to the atom by the first photon (to reach state n_1) and removed with the second photon (landing us in the final state n_2), so the final energy change in the atom $\Delta E_{n_2,n_1}$ is equal to the difference in energy of the two photons:

$$\begin{aligned}
\Delta E_{n_2,n_1} &= \frac{Z^2}{2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) E_\mathrm{h} \\
&= \frac{9}{2}\left(1 - \frac{1}{n_2^2}\right) E_\mathrm{h} && Z = 3,\ n_1 = 1 \\
\Delta E_\mathrm{photon} &= \frac{hc}{\lambda_1} - \frac{hc}{\lambda_2} \\
&= (6.626 \cdot 10^{-34}\,\mathrm{J\,s})(2.998 \cdot 10^{8}\,\mathrm{m\,s}^{-1})\left(\frac{1}{10.4 \cdot 10^{-9}\,\mathrm{m}} - \frac{1}{828 \cdot 10^{-9}\,\mathrm{m}}\right) \\
&= 1.89 \cdot 10^{-17}\,\mathrm{J} = 4.33\,E_\mathrm{h} = \frac{9}{2}\left(1 - \frac{1}{n_2^2}\right) E_\mathrm{h} \\
n_2 &= \left[\left(\frac{9}{2} - 4.32\right)\frac{2}{9}\right]^{-1/2} = \boxed{5.}
\end{aligned}$$

Maple. By the time you've entered the constants and worked out the relationships, a symbolic math program may not save you much effort on a problem like this, but the same setup can be applied to numerous problems:

- First, declare the constants in the problem:
  ```
  h := 0.66260755e-33: c := 299792468.: Eh:=4.35980e-18: Z:=3; n1:=1; lambda1 :=
  10.4e-9; lambda2 := 828e-9;
  ```
- Define any equations that relate the variables and parameter values:
  ```
  DeltaE :=(n1,n2)->((Z^2)/2)*((1/n1^2)-(1/n2^2))*Eh;
  ```

- And use the **solve** function to extract the value you're looking for:
  solve(DeltaE(n1,n2)=h*c*(1/lambda1-1/lambda2),n2);

In this case, as with many others, there is more than one solution and you have to choose the one that is valid. Here, the solutions are ±5, and you have to recognize that n_2 must be positive.

1.10 The longest wavelength corresponds to the lowest transition energy:

$$\lambda = \frac{hc}{\Delta E},$$

and $n = 2 \rightarrow 3$ is the lowest-energy absorption from $n = 2$.

$$\begin{aligned}\Delta E &= -\frac{Z^2}{2}\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right) E_\mathrm{h} \\ &= -2\left(\frac{1}{9} - \frac{1}{4}\right) E_\mathrm{h} \\ &= \frac{5}{18} E_\mathrm{h} = \boxed{0.278\, E_\mathrm{h}.}\end{aligned}$$

1.11 [**Thinking Ahead:** Why are these energy values so close together? Based on the pattern of energy levels for the one electron atom, this means that the upper state energies are approaching the ionization energy. This means the upper state n values almost don't matter – it's enough to know that they are large.]

$$\Delta E = E_n - E_1 = -\frac{Z^2}{2n^2}\ (1\ \text{har}) - \left(\frac{-Z^2}{2}\right)\ (1\ \text{har}) \quad 1\, E_\mathrm{h} = 27.2\,\text{eV}$$

The absorption energies differ by small fractions; therefore, n is a large number.

$$\begin{aligned} n\ \text{large},\ \Delta E \approx -E_1 &= \frac{Z^2}{2}\ (1\ \text{har}) \approx 1626\ \text{eV} \\ Z &\approx \sqrt{\frac{2 \cdot 1626\ \text{eV}}{(27.2\ \text{eV}\ (1\ \text{har})^{-1}}} = 10.93 \qquad\qquad Z = 11\end{aligned}$$

The atom is $\boxed{\text{Na}^{10}\ .}$

1.12 Coulomb forces control almost all molecular interactions and structure. In total, these forces wield sufficient strength, for example, to prevent the atoms of a car from sliding between the atoms of the Brooklyn Bridge to fall into the East River. But these forces work individually over tiny, molecule-sized areas. In order to add up to a macroscopic force over a large area, they need to be fairly strong individually. Quantitatively, with charges on the order of 10^{-19} C and distances of 10^{-10} m, the forces should be of magnitude (don't forget the $4\pi\epsilon_0$, which is about 10^{-10} in SI units) $(10^{-19})^2/(10^{-10})(10^{-10})^2 = 10^{-8}$ N, larger than you might have expected.

$$Z = 1 \qquad\qquad r_1 = a_0 = 5.292 \cdot 10^{-11}\,\text{m}$$

$$\begin{aligned} F_\text{Coulomb} &= -\frac{Ze^2}{4\pi\epsilon_0 r^2} \\ &= -\frac{(1)(1.602 \cdot 10^{-19}\,\text{C})^2}{(1.113 \cdot 10^{-10}\,\text{C}^2\,\text{J}^{-1}\,\text{m}^{-1})(5.292 \cdot 10^{-11}\,\text{m})^2} \\ &= \boxed{-8.24 \cdot 10^{-8}\ \text{N}\ .}\end{aligned}$$

1.13 [**Thinking Ahead:** Is this a positive or negative number, and how does it compare to the $2\,E_\mathrm{h}$ ionization energy of He^+? We've defined $U = 0$ for the ionized electron, and the $n = 1$ electron must be at a lower potential energy in order to be bound to the nucleus, so U is a negative number. To ionize the atom, we have to overcome the stabilization represented by this negative potential energy. The kinetic energy of the $n = 1$ state is a positive number, so some of the negative potential energy is already canceled before we ionize the He^+. Therefore, U must be lower than $-2\,E_\mathrm{h}$ to begin with. We expect to find that the potential energy is less than $-2\,E_\mathrm{h}$.] This question takes advantage of the fact that the distance r between the nucleus and the electron is a constant for each state n in the Bohr model. Since the potential energy only depends on r, the potential energy of the electron is also constant:

$$U_n = -\frac{Ze^2}{4\pi\epsilon_0 r_n} = -\frac{Z^2 m_e e^4}{(4\pi\epsilon_0)^2 n^2 \hbar^2}$$

because

$$\begin{aligned}
r_n &= \frac{4\pi\epsilon_0 n^2\hbar^2}{Z m_e e^2} \\
n &= 1. && Z{=}2 \text{ for } \mathrm{He}^+ \\
U_{n=1} &= -\frac{(2)^2(9.109\cdot 10^{-31}\,\mathrm{kg})(1.602\cdot 10^{-19}\,\mathrm{C})^4}{(1.113\cdot 10^{-10}\,\mathrm{C^2\,J^{-1}\,m^{-1}})^2(1)^2(1.055\cdot 10^{-34}\,\mathrm{J\,s})^2} \\
&= \boxed{-1.745\cdot 10^{-17}\ \mathrm{J}}
\end{aligned}$$

or, more quickly by using atomic units,

$$U_{n=1} = -\frac{Z^2}{n^2}\left(\frac{m_e e^4}{(4\pi\epsilon_0)^2\hbar^2}\right) = -4\,E_\mathrm{h}.$$

1.14 [**Thinking Ahead:** Does kinetic energy decrease or increase with Z and with n? It increases with Z (the electron has to move faster when the nucleus pulls on it more strongly) and decreases with n (the electron requires less centripetal force to balance the weaker nuclear attraction at large distances).] The kinetic energy is always $mv^2/2$, which is a handy form in this case because we know the mass (m_e) and the speed is obtainable from the Bohr model:

$$\begin{aligned}
v_n &= \frac{Ze^2}{4\pi\epsilon_0 n\hbar} \\
K_n &= \frac{m_e v_n^2}{2} = \frac{m_e}{2}\left(\frac{Ze^2}{4\pi\epsilon_0 n\hbar}\right)^2 \\
&= \frac{Z^2 m_e e^4}{2(4\pi\epsilon_0)^2 n^2\hbar^2} = -E_n.
\end{aligned}$$

The kinetic energy is equal to the total energy times -1. This result is predicted by the **virial theorem**: for any stable, dynamic system involving a central force law (*i.e.*, the force depends only on r), the average kinetic and potential energies are related as follows:

$$U = -2K.$$

Since the total energy is the sum of these two contributions,

$$E = K + U = -K.$$

1.15 [**Thinking Ahead:** Do the changes in Z and n push these numbers in the same direction? No. Increasing Z from 2 to 3 increases the attraction between electron and nucleus, decreasing r and U

(making it more negative) while increasing v. Increasing n from 2 to 3 pulls the electron further away, having all the opposite effects.] Given the values for He$^+$ $n = 2$, we only need to know how Z and n affect the equations for these parameters, and then substitute Z and $n = 3$ for Z and $n = 2$. The radius r_n varies as n^2/Z (Eq. 1.13), v_n varies as Z/n (Eq. 1.14), and the potential energy U_n as Z/r_n or Z^2/n^2.

	He$^+$ $n = 2$	Li^{2+} $n = 3$
r_n	1.06 Å	1.59 Å
v_n	$2.19 \cdot 10^6$ m s^{-1}	$2.19 \cdot 10^6$ m s^{-1}
U_n	$-4.36 \cdot 10^{-18}$ J	$-4.36 \cdot 10^{-18}$ J

1.16

$$\begin{aligned} -\frac{A\mu_\mathrm{A}\mu_\mathrm{B}}{r^4} &= -\frac{mv^2}{r} && F_\mathrm{d-d} = F_\mathrm{centripetal} \\ A\mu_\mathrm{A}\mu_\mathrm{B} &= mv^2r^3 && \text{multiply through by } r^4 \\ &= \left(\frac{r}{m}\right) m^2v^2r^2 = \left(\frac{r}{m}\right) L^2 && L = mvr \text{ for circular orbit} \end{aligned}$$

$$\begin{aligned} A\mu_\mathrm{A}\mu_\mathrm{B} &= \left(\frac{r}{m}\right)(n\hbar)^2 && L = n\hbar \\ r_n &= \boxed{\frac{A\mu_\mathrm{A}\mu_\mathrm{B}m}{n^2\hbar^2}}. \end{aligned}$$

This is a weird result if you look at it, because the orbit actually gets *smaller* as you increase n. Going further and evaluating the total energy shows that the system is not stable under these assumptions.

1.17

$$\begin{aligned} r_n &= \frac{4\pi\epsilon_0\ n^2\hbar^2}{Zm_ee^2} \\ v_n &= \frac{Ze^2}{4\pi\epsilon_0\ n\hbar} \\ F_n &= \frac{m_ev_n^2}{r_n} \\ &= m_e\left(\frac{Ze^2}{4\pi\epsilon_0\ n\hbar}\right)^2\left(\frac{Zm_ee^2}{4\pi\epsilon_0\ n^2\hbar^2}\right) \\ &= \boxed{\frac{Z^3m_e^2e^6}{(4\pi\epsilon_0)^3n^4\hbar^4}.} \end{aligned}$$

The centripetal force should decrease with n, because it takes less force to keep a particle in a circular orbit when the circle is bigger. (You could also point out that the the Coulomb force, which is equal to the centripetal force, is weaker at higher n because the orbital radius r_n is bigger. Or simply that r increases and v decreases with n, and therefore $F_n = m_erv_n^2/r_n$ must decrease.)

1.18

parameter	$n = 1$	$n = 2$
momentum ($\mathrm{kg\,m\,s^{-1}}$)	$1.99 \cdot 10^{-24}$	$9.95 \cdot 10^{-25}$ ($p = mv$, $v \propto 1/n$)
de Broglie wavelength (nm)	0.333	0.666 ($\lambda_{\mathrm{dB}} \propto 1/p \propto n$)
kinetic energy (E_h)	0.500	0.125 ($K \propto v^2 \propto 1/n^2$)
transition energy to $n = 3$ (E_h)	0.444	0.0694

For the transition energy in the last row,

$$\Delta E = E_3 - E_2 = -\frac{Z^2}{2} E_\mathrm{h} \left(\frac{1}{3^2} - \frac{1}{2^2} \right) = 0.0694 \, E_\mathrm{h}.$$

1.19 We set the speed greater than 0.1 c and solve for Z:

$$v_n = \frac{Ze^2}{4\pi\epsilon_0 n\hbar} > 0.1\ c \qquad n = 1$$

$$Z > \frac{0.1\ (4\pi\epsilon_0)\hbar c}{e^2} = \frac{0.1(1.113 \cdot 10^{-10}\,\mathrm{C^2\,J^{-1}\,m^{-1}})(1.055 \cdot 10^{-34}\,\mathrm{J\,s})(2.998 \cdot 10^{8}\,\mathrm{m\,s^{-1}})}{(1.602 \cdot 10^{-19}\,\mathrm{C})^2}$$

$$= 13.7.$$

The smallest value of Z (rounding up to the nearest integer) is $\boxed{14.}$ So relativistic corrections are likely to start becoming important for atoms beyond aluminum in the periodic table.

1.20 [**Thinking Ahead:** How does this transition energy compare to the ionization energy? Given the ionization energy of $Z^2/2 = 2\,E_\mathrm{h}$ for He^+, this transition energy is a small fraction of the energy range of the He^+ quantum states. The transition must therefore be among the closely grouped, higher energy n values.]

$$n = n'' \to n'' + 1 \qquad Z = 2$$

$$\Delta E = -\frac{Z^2}{2} \left(\frac{1}{(n''+1)^2} - \frac{1}{n''^2} \right) E_\mathrm{h}$$

$$= 2 \left(\frac{1}{n''^2} - \frac{1}{(n''+1)^2} \right) E_\mathrm{h}$$

$$= \boxed{0.045\, E_\mathrm{h}.}$$

This can be solved numerically.

- **Maple**: A command to solve this equation for n'' is
  solve(2*((1/n^2)-(1/((n+1)^2)))=0.045,n);

- **Iteration**:

  $$n'' = \left\{ \frac{0.045}{2} + \frac{1}{(n''+1)^2} \right\}^{-1/2}$$

  Start with $n'' = 1$ on the lefthand side; this predicts $n'' = 1.92$. Plug this into the lefthand side, and this predicts $n'' = 2.67$, then 3.22, 3.56, 3.77, 3.88, converging to $n'' = 4$.

The transition is $\boxed{n = 4 \to 5.}$

1.21 The linear momentum p is mass times speed, and we have an equation for the speed (Eq. 1.14):

$$p = m_e v_n \qquad m_e = 9.109 \cdot 10^{-28}\,\mathrm{g}$$

$$v_n = \frac{Ze^2}{4\pi\epsilon_0 n\hbar} = \frac{2(1.602 \cdot 10^{-19}\,\mathrm{C})^2}{(1.113 \cdot 10^{-10}\,\mathrm{C^2\,J^{-1}\,m^{-1}})2(1.055 \cdot 10^{-34}\,\mathrm{J\,s})} = 2.187 \cdot 10^{6}\,\mathrm{m\,s^{-1}}$$

$$p = (9.109 \cdot 10^{-31}\,\mathrm{kg})(2.187 \cdot 10^{6}\,\mathrm{m\,s^{-1}}) = \boxed{1.99 \cdot 10^{-24}\,\mathrm{kg\,m\,s^{-1}}}$$

1.22 [**Thinking Ahead:** Is this a high or low frequency, compared for example to radiofrequency? High. The speed of the electron in a typical Bohr atom is a significant fraction of the speed of light, and the distance to cover is microscopic. Therefore, the oscillation of the dipole moment would be quite fast.] Radiation is emitted by an oscillating dipole because the electric field generated by the dipole must also be oscillating, and that oscillation propagates through the surroundings at the speed of light. Therefore, the frequency of the radiation – the frequency at which the electric field of the radiation oscillates back and forth—is the same as the frequency at which the dipole oscillates back and forth. For the Bohr atom, with a dipole arising from the separation between the positively charged nucleus and the negatively charged electron, this frequency is the frequency at which the electron orbits the nucleus. This we can obtain from the speed v_n of the Bohr atom electron and the circumference $2\pi r_n$, which gives the distance the electron travels in one orbit.

$$v_n = \frac{Ze^2}{4\pi\epsilon_0 n\hbar} \qquad\qquad r_n = \frac{4\pi\epsilon_0 n^2\hbar^2}{Zm_e e^2}.$$

The time for one revolution of the electron around the nucleus is

$$\tau_n = \frac{2\pi r_n}{v_n} = \frac{2\pi(4\pi\epsilon_0)^2 n^3\hbar^3}{Z^2 m_e e^4},$$

so the frequency of oscillation, and the frequency of any emitted radiation, is

$$\nu_n = \frac{1}{\tau_n} = \frac{Z^2 m_e e^4}{2\pi(4\pi\epsilon_0)^2 n^3\hbar^3}.$$

For Li^{+2}, $Z = 3$. With $n = 4$,

$$\begin{aligned}\nu_{n=4} &= \frac{(3)^2(9.109\cdot 10^{-31}\,\text{kg})(1.602\cdot 10^{-19}\,\text{C})^4}{2\pi(1.113\cdot 10^{-10}\,\text{C}^2\,\text{J}^{-1}\,\text{m}^{-1})^2(4)^3(1.055\cdot 10^{-34}\,\text{J s})^3}\\ &= \boxed{9.247\cdot 10^{14}\,\text{s}^{-1},}\end{aligned}$$

which corresponds to near-ultraviolet radiation.

1.23 This is an application of Bohr's expression for energy levels of one-electron atoms. The lower quantum state is known (ground state, so $n_1 = 1$) and the energy is known, so the upper quantum states can be found: $E_n = -\frac{Z^2}{2n^2}\,E_\text{h}$, where $Z = 4$ for Be.

$$\begin{aligned}\Delta E(n\to n') = E_{n'} - E_n &= -\frac{Z^2}{2}\left(\frac{1}{n'^2} - \frac{1}{n^2}\right)\\ &= -\frac{Z^2}{2}\left(\frac{1}{n'^2} - 1\right)\\ n' &= \left[1 - \frac{2\Delta E}{Z^2}\right]^{-\frac{1}{2}}\\ &= \left[1 - \frac{2\Delta E}{16}\right]^{-\frac{1}{2}} \qquad\qquad Z = 4\end{aligned}$$

$$\begin{aligned}\Delta E &= 7.50\,E_\text{h} \quad n' = \boxed{4}\\ \Delta E &= 7.68\,E_\text{h} \quad n' = \boxed{5}\end{aligned}$$

1.24 The $n\to\infty$ transition energy gets smaller as n climbs, and the photon wavelength *increases.* Therefore, we are looking for the lowest value of n'' such that the photon wavelength is more than

1.0 mm, where $Z = 2$ for He$^+$:

$$\begin{aligned}
\Delta E &= -\frac{Z^2}{2}\left(\frac{1}{\infty^2} - \frac{1}{n^2}\right) E_\mathrm{h} = -\frac{Z^2}{2}\left(-\frac{1}{n^2}\right) E_\mathrm{h} = \frac{Z^2}{2n^2} E_\mathrm{h} \\
\lambda &= \frac{hc}{\Delta E} = \frac{hc}{Z^2 E_\mathrm{h}/(2n^2)} = \frac{hcn^2}{2\,E_\mathrm{h}} \geq 1.0 \cdot 10^{-3}\,\mathrm{m} \\
n^2 &\geq \frac{2(1.0 \cdot 10^{-3}\,\mathrm{m})\,E_\mathrm{h}}{hc} \\
n &\geq \left(\frac{2(1.0 \cdot 10^{-3}\,\mathrm{m})\,E_\mathrm{h}}{hc}\right)^{1/2} = \left(\frac{2(1.0 \cdot 10^{-3}\,\mathrm{m})(4.360 \cdot 10^{-18}\,\mathrm{J})}{(6.626 \cdot 10^{-34}\,\mathrm{J\,s})(2.998 \cdot 10^{8}\,\mathrm{m\,s^{-1}})}\right)^{1/2} = 209.5.
\end{aligned}$$

So n is the smallest integer greater than 209.5, so $\boxed{n = 210.}$

1.25 [**Thinking Ahead:** What about the energy level distribution allows us to solve for two unknown n values with a single equation? It's the converging value of the energy as n increases. It is straightforward to prove that no two values of n have the same energy spacing as any other two values.] This problem approaches atomic spectroscopy from a more realistic perspective: when the transition energy is measured, how does the spectroscopist determine the quantum states involved? The Li atom has atomic number $Z = 3$, so Li^{+2} is a one-electron atom. This time we have the energy and need to obtain n.

$$\begin{aligned}
E_n &= -\frac{Z^2}{n^2}\frac{m_e e^4}{2(4\pi\epsilon_0)^2\hbar^2} \\
&= -\frac{(3)^2}{n^2}\,\frac{(9.109 \cdot 10^{-31}\,\mathrm{kg})(1.602 \cdot 10^{-19}\,\mathrm{C})^4}{2(1.113 \cdot 10^{-10}\,\mathrm{C^2\,J^{-1}\,m^{-1}})^2(1.055 \cdot 10^{-34}\,\mathrm{J\,s})^2} \\
&= -\frac{1.96 \cdot 10^{-17}\,\mathrm{J}}{n^2}
\end{aligned}$$

$$\begin{aligned}
1.74 \cdot 10^{-17}\,\mathrm{J} &= 1.96 \cdot 10^{-17}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \\
\frac{1}{n_1^2} - \frac{1}{n_2^2} &= \frac{1.74}{1.96} = 0.888
\end{aligned}$$

We have one equation and two unknowns. However, the pattern of energy levels is such that all the energy levels except $n = 1$ are crowded together within $E_{n=1}/4$ of zero. Therefore, transitions between any two states $n \neq 1$ must have transition energy less than $E_{n=1}/4$. Since

$$1.74 \cdot 10^{-17}\,\mathrm{J} > -\frac{E_{n=1}}{4} = \frac{1.96 \cdot 10^{-17}}{4}\,\mathrm{J},$$

then $\boxed{n_1 = 1}$, so

$$n_2 = [-(0.888 - 1)]^{-1/2} = \boxed{3.}$$

1.26 These parameters are all related to the speed at which the electron travels the circumference of its orbit, which can be calculated from Eqs. 1.13 and 1.14.

a. Time to complete one orbit τ = distance/speed:

$$\tau_n = \frac{2\pi r_n}{v_n} = \frac{(2\pi(4\pi\epsilon_0)n^2\hbar^2/Zm_e e^2)}{Ze^2/(4\pi\epsilon_0)n\hbar)} = \frac{2\pi(4\pi\epsilon_0)^2 n^3\hbar^3}{Z^2 m_e e^4}$$

Number of orbits per second $= \frac{1}{\tau_n} \equiv f_n$: $\boxed{f_n = \frac{Z^2 m_e e^4}{2\pi(4\pi\epsilon_0)^2 n^3\hbar^3}}$

b.

$$\begin{aligned}\Delta f_n = f_5 - f_4 &= \frac{Z^2 m_e e^4}{2\pi(4\pi\epsilon_0)^2\hbar^3}\left(\frac{1}{5^3} - \frac{1}{4^3}\right)\\ &= \frac{(1)^2(9.109\cdot 10^{-31}\,\mathrm{kg})(1.602\cdot 10^{-19}\,\mathrm{C})^4}{2\pi(1.113\cdot 10^{-10}\,\mathrm{C^2\,J^{-1}\,m^{-1}})^2(1.055\cdot 10^{-34}\,\mathrm{J\,s})^3}(-7.625\cdot 10^{-3})\\ &= \boxed{-5.01\cdot 10^{13}\,\mathrm{s^{-1}}}\end{aligned}$$

c.

$$\begin{aligned}\nu = \frac{\Delta E}{h} = \frac{E_5 - E_4}{h} &= -\frac{Z^2(4.360\cdot 10^{-18}\,\mathrm{J}\,E_\mathrm{h}^{-1})}{2h}\left(\frac{1}{5^2} - \frac{1}{4^2}\right)\\ &= -\frac{(1)^2(4.360\cdot 10^{-18}\,\mathrm{J}\,E_\mathrm{h}^{-1})}{2(6.626\cdot 10^{-34}\,\mathrm{J\,s})}(-0.0225)\\ &= \boxed{7.40\cdot 10^{13}\ \mathrm{s^{-1}}}\end{aligned}$$

This value and the magnitude of the answer in part (b) become more similar as n'' and n' increase.

1.27 [**Thinking Ahead:** Is this going to be high Z, given that the wavelength for the H atom ionization is 91.1 nm? No. Increasing Z increases the energy as Z^2 and shortens the wavelength for the transition as $1/Z^2$. Here the wavelength is only about a factor of 4 lower.]

In units of E_h:

$$\begin{aligned}\Delta E = E_{n'} - E_{n''} &= -\frac{Z^2}{2n'^2} + \frac{Z^2}{2n''^2}\\ &= \frac{Z^2}{2}\left(-\frac{1}{9} + \frac{1}{1}\right)\\ &= \frac{4Z^2}{9}\\ \lambda = 25.6\cdot 10^{-9}\,\mathrm{m} = \frac{hc}{\Delta E} &= \frac{hc}{\left(\frac{4Z^2}{9}\right)(4.36\cdot 10^{-18}\,\mathrm{J}\,E_\mathrm{h}^{-1})}\\ Z &= \left[\frac{9(6.626\cdot 10^{-34}\,\mathrm{J\,s})(2.998\cdot 10^{8}\,\mathrm{m\,s^{-1}})}{4(4.36\cdot 10^{-18})(25.6\cdot 10^{-9})}\right]^{1/2} = \boxed{2.}\end{aligned}$$

The atom is $\boxed{\mathrm{He}^+.}$

1.28 This expression for F_grav has the same dependence on distance as F_Coulomb. The difference is that the constants $Ze^2/(4\pi\epsilon_0)$ have been replaced by $m_1 m_2 G$, where (since the masses are unchanged) $m_1 m_2 = m_e m_p$. We could follow the same steps used to obtain the Bohr energy expression, but since all we have done is change one set of constants for another, we can just take the result for the Bohr energy and change out those constants:

$$\begin{aligned}E_n &= -\frac{Z^2 m_e e^4}{2(4\pi\epsilon_0)n^2\hbar^2} && \text{real atom, Eq. 1.20}\\ E_n &= -\frac{(m_e m_p G)^2 m_e}{2n^2\hbar^2} && \text{gravity atom}\\ &= -\frac{m_e^3 m_p^2 G^2}{2n^2\hbar^2}.\end{aligned}$$

For the ground state, we set $n = 1$:

$$E_1 = -\frac{(9.109 \cdot 10^{-31}\,\mathrm{kg})^3 (1.673 \cdot 10^{-27}\,\mathrm{kg})^2 (6.67 \cdot 10^{-11}\,\mathrm{m^3\,kg^{-1}\,s^{-2}})^2}{2(1.055 \cdot 10^{-34}\,\mathrm{J\,s})^2} = \boxed{-4.23 \cdot 10^{-97}\,\mathrm{J}.}$$

Comparing this to the ground state energy using the charged particles ($E_1 = 2.18 \cdot 10^{-18}$ J), you can see why we never worry about gravity when solving the quantum mechanics of atoms and molecules. Note: one topic of ongoing speculation among physicists is whether the gravitational force law stays the same at all distance scales. Although gravitational forces have been measured for individual neutrons, that was over distances of several micrometers—much larger than the distances separating subatomic particles in an atom. For a further exercise, try calculating the radius of the orbit of the particles in this gravity-atom.

1.29 If there's only one electron, we need to know only the atomic number Z to identify the ion. From Eqs. 1.13 and 1.14:

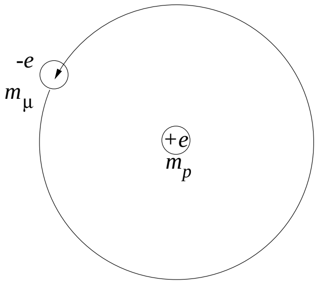
$$r_n = \frac{n^2 a_0}{Z} = 1.286 a_0 \qquad v_n = \frac{Ze^2}{4\pi\epsilon_0 n\hbar} = 2.333\frac{e^2}{4\pi\epsilon_0\hbar}$$

$$\frac{n^2}{Z} = 1.286 \qquad \frac{Z}{n} = 2.333$$

$$Z = (2.333^2)(1.286) = 7.$$

The ion is $\boxed{\mathrm{N}^{+6}.}$

1.30 [**Thinking Ahead:** Is this longer or shorter than λ_{dB} for the electron in hydrogen? Shorter. The heavier mass of the muon compared to the electron makes the system more classical, with wave properties harder to measure. That implies a smaller λ_{dB}.] The solution will be identical to the Bohr atom, except with the muon mass m_μ substituted for m_e.



$$v = \frac{Ze^2}{4\pi\epsilon_0 n\hbar} \qquad Z = 1 \qquad n = 1$$

$$\lambda_{\mathrm{dB}} = \frac{h}{m_\mu v} = \frac{4\pi\epsilon_0 h\hbar}{m_\mu e^2} = \frac{(1.113 \cdot 10^{-10}\,\mathrm{C^2\,J^{-1}\,m^{-1}})(6.626 \cdot 10^{-34}\,\mathrm{J\,s})(1.055 \cdot 10^{-34}\,\mathrm{J\,s})}{(1.884 \cdot 10^{-28}\,\mathrm{kg})(1.602 \cdot 10^{-19}\,\mathrm{C})^2}$$
$$= \boxed{1.61 \cdot 10^{-12}\ \mathrm{m}.}$$

1.31 The total power is the sum of the contribution from each photon emitted, the product of the number of photons per second and the energy per photon. Setting the average photon wavelength equal to $\bar{\lambda}$, the energy per photon is approximately given by

$$E_{\mathrm{photon}} \approx \frac{hc}{\bar{\lambda}} = \frac{(6.626 \cdot 10^{-34}\,\mathrm{J\,s})(2.998 \cdot 10^{8}\,\mathrm{m\,s^{-1}})}{590 \cdot 10^{-9}\,\mathrm{m}}$$
$$= 3.37 \cdot 10^{-19}\,\mathrm{J/photon}.$$