

Physical Chemistry
Quantum Mechanics, Spectroscopy, and Molecular Interactions

Solutions Manual

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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:

$$\nu = \frac{c}{\lambda} = \frac{2.998 \cdot 10^8 \text{ m s}^{-1}}{1.0 \cdot 10^{-3} \text{ m}} = \boxed{3.0 \cdot 10^{11} \text{ s}^{-1}} \quad \text{by Eq. 1.1}$$

$$E_{\text{photon}} = h\nu = (6.626 \cdot 10^{-34} \text{ J s})(3.0 \cdot 10^{11} \text{ s}^{-1}) = \boxed{2.0 \cdot 10^{-22} \text{ J.}} \quad \text{Eq. 1.2}$$

1.2 The de Broglie wavelength (Eq. 1.3) is our measure of 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:

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

Because $1.8 \cdot 10^{-10} \text{ m} \ll 1.0 \mu\text{m} = 1.0 \cdot 10^{-6} \text{ m}$, 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:

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

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

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

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

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

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:

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

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 $n - l - 1 = 3 - 1 - 1 = 1$: 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

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

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 $1s^2 2s^1$. 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 $-Z^2 E_h / (2n^2)$. We have two $n = 1$ electrons and one $n = 2$ electron in the configuration, and $Z = 4$ for Be, so we arrive at

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

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:

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

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 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

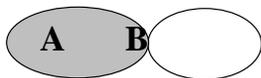
where we found maximum values of $L = 1$ and $S = 1$ initially (based on the largest values of M_L and M_S), and then after assigning the 9 3P states, we were left with three $M_S = 0$ states, which gave $L = 1, S = 0$ for the 1P term. Breaking the 3P into its component J values from $L - S = 0$ to $L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

Chapter 5

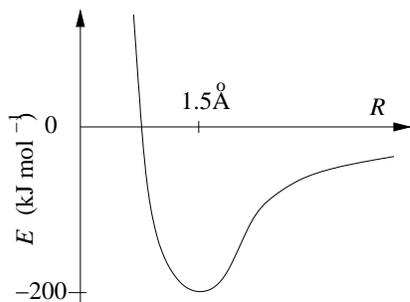
5.1 This molecular ion has 2 nuclei with $Z_{\text{Li}} = 3$ and $Z_{\text{H}} = 1$ and 3 electrons, for a total of 5 particles. That means we should have 5 kinetic energy terms (one for each particle), 6 electron–nucleus attraction terms, 1 nucleus–nucleus repulsion term, and 3 electron–electron repulsion 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:

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

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 $R = 1.5 \text{ \AA}$ where the potential energy reaches a value $U = -200 \text{ kJ mol}^{-1}$.



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 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