

1 Web exercise 1

- a. Calculate the probability that a particle will be found between $0.49L$ and $0.51L$ in a box of length L when it has (a) $n = 1$, (b) $n = 2$. Take the wavefunction to be a constant in this range.
- b. Calculate the probability that a particle will be found between $0.65L$ and $0.67L$ in a box of length L when it has (a) $n = 1$, (b) $n = 2$. Take the wavefunction to be a constant in this range.

2 Web exercise 2

- a. Consider a particle in a cubic box. What is the degeneracy of the level that has an energy three times that of the lowest level?
- b. Consider a particle in a cubic box. What is the degeneracy of the level that has an energy $\frac{14}{3}$ times that of the lowest level?

3 Web exercise 3

- a. Calculate the percentage change in a given energy level of a particle in a cubic box when the length of the edge of the cube is decreased by 10 per cent in each direction.
- b. A nitrogen molecule is confined in a cubic box of volume 1.00 m^3 . Assuming that the molecule has an energy equal to $\frac{3}{2}kT$ at $T = 300 \text{ K}$, what is the value of $n = \sqrt{n_x^2 + n_y^2 + n_z^2}$ for this particle? What is the energy separation between the levels n and $n + 1$? What is its de Broglie wavelength? Would it be appropriate to describe this particle as classical?

4 Web exercise 4

- a. Consider the $2s$ radial wavefunction. Show that it has two extrema in its amplitude, and locate them.
- b. Consider the $3s$ radial wavefunction. Show that it has three extrema in its amplitude, and locate them.

5 Web exercise 5

- a. Locate the radial nodes in the $3s$ orbital of an H atom.
- b. Locate the radial nodes in the $3p$ orbital of an H atom.

6 Web exercise 6

- a. Write down the expression for the radial distribution function of a $2s$ electron in a hydrogenic atom and determine the radius at which the electron is most likely to be found.
- b. Write down the expression for the radial distribution function of a $3s$ electron in a hydrogenic atom and determine the radius at which the electron is most likely to be found.

7 Web exercise 7

- a. What is the orbital angular momentum of an electron in the orbitals (a) $1s$, (b) $3s$, (c) $3d$? Give the numbers of the angular and radial nodes in each case.
- b. What is the orbital angular momentum of an electron in the orbitals (a) $4d$, (b) $2p$, (c) $3p$? Give the numbers of the angular and radial nodes in each case.

8 Web exercise 8

- a. Which of the following transitions are allowed in the normal electronic emission spectrum of an atom: (a) $2s \rightarrow 1s$, (b) $2p \rightarrow 1s$, (c) $3d \rightarrow 2p$?
- b. Which of the following transitions are allowed in the normal electronic emission spectrum of an atom: (a) $5d \rightarrow 2s$, (b) $5p \rightarrow 3s$, (c) $5p \rightarrow 3f$?

9 Web exercise 9

- a. How many electrons can occupy the following subshells: (a) $1s$, (b) $3p$, (c) $3d$, and (d) $6g$?
- b. How many electrons can occupy the following subshells: (a) $2s$, (b) $4d$, (c) $6f$, and (d) $6h$?

10 Web exercise 10

The Humphreys series is another group of lines in the spectrum of atomic hydrogen. It begins at 12368 nm and has been traced to 3281.4 nm. What are the transitions involved? What are the wavelengths of the intermediate transitions?

11 Web exercise 11

A series of lines in the spectrum of hydrogen lie at 656.46 nm, 486.27 nm, 434.17 nm, and 410.29 nm. What is the wavelength of the next line in the series? What is the ionization energy of the atom when it is in the lower state of the transitions?

12 Web exercise 12

Is an electron further from the nucleus on average when it is in a $2s$ orbital or in a $2p$ orbital?

13 Web exercise 13

The 'size' of an atom is sometimes considered to be measured by the radius of a sphere that contains 90 per cent of the charge density of the electrons in the outermost occupied orbital. Calculate the 'size' of a hydrogen atom in its ground state according to this definition.

14 Web exercise 14

- Use the electron configurations of NO and N₂ to predict which is likely to have the shorter bond length.
- Arrange the species O₂⁺, O₂, O₂⁻, O₂²⁻ in order of increasing bond length.

15 Web exercise 15

What is the composition of the hybrid orbitals in H₂S in which the bond angle is 92°?

16 Web exercise 16

Which of the molecules N₂, NO, O₂, C₂, F₂, and CN would you expect to be stabilized by (a) the addition of an electron to form AB⁻, (b) the removal of an electron to form AB⁺?

17 Web exercise 17

Sketch the molecular orbital energy level diagrams for (a) CO and (b) XeF and deduce their ground-state electron configurations. Is XeF likely to have a shorter bond length than XeF⁺?

18 Extra exercise 1: Properties of the solutions of the Schrödinger equation for a particle in a box

The solution of the Schrödinger equation for the particle in a box with walls at $x = 0$ and $x = \pi$ are given by

$$\psi_n(x) = c_n \sin(nx), \text{ with } n = 1, 2, 3, \dots,$$

and c_n a coefficient that takes care of the normalization.

- Show that the wave functions ψ_n are normalized if $c_n = \sqrt{2/\pi}$.

- b. Show that the wave functions ψ_n are orthogonal. (Two wave functions are called orthogonal if the integral of their product equals zero. So here you have to show that

$$\int_0^\pi dx \psi_n(x) \psi_m(x) = 0$$

if n and m differ. Orthogonality is not something specific for a particle in a box. Different solutions of a Schrödinger equation are always orthogonal.)

To simplify the calculation of integrals of trigonometric functions it often helps to write these functions in terms of complex exponential. For example,

$$\begin{aligned} & \int_a^b dx \cos^2(x) \\ &= \int_a^b dx \left[\frac{1}{2}(e^{ix} + e^{-ix}) \right]^2 \\ &= \frac{1}{4} \int_a^b dx [e^{i2x} + e^{-i2x} + 2] \\ &= \frac{1}{4} \left[\frac{1}{2i}(e^{i2b} - e^{i2a}) - \frac{1}{2i}(e^{-i2b} - e^{-i2a}) + 2(b-a) \right] \\ &= \frac{1}{4} \left[\frac{1}{2i}(e^{i2b} - e^{-i2b}) - \frac{1}{2i}(e^{i2a} - e^{-i2a}) + 2(b-a) \right] \\ &= \frac{1}{4} [\sin 2b - \sin 2a] + \frac{1}{2}(b-a) \end{aligned}$$

19 Extra exercise 2: The momentum representation

When one writes a wave function with coordinates as arguments, one works in the coordinates representation. It is also possible to work in the momentum representation: the momenta are then the arguments. If $\psi(x)$ is a wave function in the coordinate representation and $\varphi(p)$ the same wave function in momentum representation then

$$\begin{aligned} \varphi(p) &= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dx e^{ipx/\hbar} \psi(x), \\ \psi(x) &= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dp e^{-ipx/\hbar} \varphi(p). \end{aligned}$$

a. Write the following wave functions in momentum representation.

$$\psi_n(x) = \begin{cases} \sqrt{2/\pi} \sin(nx), & \text{if } 0 \leq x \leq \pi, \\ 0, & \text{otherwise} \end{cases}$$

with $n = 1, 2, 3, \dots$. These are solutions of the Schrödinger equation for a particle in a box with walls at $x = 0$ and $x = a$

b. Calculate

$$\int_{-\infty}^{\infty} dp p^m |\varphi_1(p)|^2$$

for $m = 1$ and $m = 2$. Compare the results with the expectation values for p and p^2 .

20 Extra exercise 3: Expansion in solutions of the Schrödinger equation

The solutions of the Schrödinger equation form a complete basis. This means that any wavefunction can be written as a linear combination of the solutions. Take, for example, the function

$$\varphi(x) = \begin{cases} 1/\sqrt{\pi}, & \text{if } 0 \leq x < \pi/2, \\ -1/\sqrt{\pi}, & \text{if } \pi/2 \leq x \leq \pi, \\ 0, & \text{otherwise.} \end{cases}$$

(Strictly speaking this is not an acceptable wavefunction as explained on page 299 of Atkins. However, the function does illustrate how to write an arbitrary wavefunction as a linear combination of a set of functions that are normalized and orthogonal: i.e., an orthonormal set.) This function can be written as

$$\varphi(x) = \sum_{n=1}^{\infty} c_n \left[\sqrt{\frac{2}{\pi}} \sin(nx) \right].$$

You will recognize on the right-hand-side the solutions of the Schrödinger equation for a particle in a box with walls at $x = 0$ and $x = \pi$. The task is to determine the coefficients c_n .

a. Show that the coefficients can be determined by

$$c_n = \int_0^{\pi} dx \sqrt{\frac{2}{\pi}} \sin(nx) \varphi(x).$$

(Hint: use the fact that the solutions of the Schrödinger equation form an orthonormal set.)

b. Show that $c_{2m-1} = 0$ with $m = 1, 2, 3, \dots$ (Hint: compare the integral over $[0, \pi/2]$ with the one over $[\pi/2, \pi]$.)

c. Show that $c_{4m} = 0$ with $m = 1, 2, 3, \dots$ (Hint: compare the integral over $[0, \pi/4]$ with the one over $[\pi/4, \pi/2]$, and the one over $[\pi/2, 3\pi/4]$ with the one over $[3\pi/4, \pi]$.)

d. Show that

$$c_{4m-2} = \frac{2\sqrt{2}}{(2m-1)\pi},$$

with $m = 1, 2, 3, \dots$

e. Plot

$$\sum_{m=1}^M \frac{4}{(2m-1)\sqrt{\pi^3}} \sin[(4m-2)x],$$

for several values of M and compare the result with $\varphi(x)$.

21 Extra exercise 4: The Heisenberg uncertainty relation

The Heisenberg uncertainty relation for the position and momentum of a particle that moves only in one dimension is

$$\Delta x \Delta p \geq \frac{1}{2} \hbar.$$

In this expression Δx and Δp are the uncertainties in position and momentum. They are the root-mean-square deviations from the expectation values: i.e.,

$$(\Delta A)^2 = \langle (A - \langle A \rangle)^2 \rangle = \langle A^2 \rangle - \langle A \rangle^2,$$

for an arbitrary operator A . The expectation value $\langle A \rangle$ is defined as

$$\langle A \rangle = \int dx \psi(x)^* A \psi(x)$$

(and a similar expression for A^2) with the system being described by the normalized wavefunction ψ .

- a. Calculate $\langle x \rangle$, $\langle x^2 \rangle$, and Δx for the wavefunctions.

$$\psi_n(x) = \begin{cases} \sqrt{2/\pi} \sin(nx), & \text{if } 0 \leq x \leq \pi, \\ 0, & \text{otherwise,} \end{cases}$$

with $n = 1, 2, 3, \dots$

- b. Calculate $\langle p \rangle$, $\langle p^2 \rangle$, and Δp for the same wavefunctions.
- c. Show that the Heisenberg uncertainty relation indeed holds for these wavefunctions.

22 Extra exercise 5: Electronic configurations of molecules

The electronic configuration of N_2 can be written as $1\sigma_g^2 2\sigma_u^2 3\sigma_g^2 4\sigma_u^2 1\pi_u^4 5\sigma_g^2$. Give similar notations for the electronic configurations of a) H_2 , b) O_2^- , and c) CO .

23 Extra exercise 6: Symmetry adapted basis functions

The basis set that is normally used for H_2 consists of the two $1s$ orbitals: $1s_A$ and $1s_B$. A basis transformation replaces these orbitals by two others that are linear combinations of $1s_A$ and $1s_B$ and are linear independent. Sometimes such a basis transformation can make the solution of the secular equation easier.

The H_2 molecule has a high symmetry. In particular it has a mirror plane perpendicular to and through the middle of the molecular axis. The basis set $1s_A + 1s_B$ and $1s_A - 1s_B$ is adapted to this symmetry: i.e., these basis functions either do not change or only change sign when they are reflected in the mirror plane.

- a. Write down the secular equation with $1s_A + 1s_B$ and $1s_A - 1s_B$ as basis: i.e., write the solutions as $c_+(1s_A + 1s_B) + c_-(1s_A - 1s_B)$ and write the

secular equation to determine the orbital energies and the coefficients c_+ and c_- . For example, the overlap matrix is

$$\begin{pmatrix} \langle 1s_A + 1s_B | 1s_A + 1s_B \rangle & \langle 1s_A + 1s_B | 1s_A - 1s_B \rangle \\ \langle 1s_A - 1s_B | 1s_A + 1s_B \rangle & \langle 1s_A - 1s_B | 1s_A - 1s_B \rangle \end{pmatrix}.$$

Use

$$\alpha = \langle 1s_A | F | 1s_A \rangle = \langle 1s_B | F | 1s_B \rangle,$$

$$\beta = \langle 1s_A | F | 1s_B \rangle = \langle 1s_B | F | 1s_A \rangle,$$

and

$$S = \langle 1s_A | 1s_B \rangle = \langle 1s_B | 1s_A \rangle.$$

- b. Solve the secular equation of a).

24 Extra exercise 7: Covalent and ionic contributions in molecular hydrogen

- a. Show that the electronic ground state of H_2 can be written as

$$\varphi(\mathbf{r}_1)\varphi(\mathbf{r}_2)[\alpha(\sigma_1)\beta(\sigma_2) - \beta(\sigma_1)\alpha(\sigma_2)]$$

$$\text{with } \varphi = (1s_A + 1s_B)/\sqrt{(2 + 2S)}.$$

- b. Write the ground state for H_2 in terms of $1s_A$ and $1s_B$ instead of φ . What are the ionic terms and what are the covalent terms? Which are more important? Any conclusions?

25 Extra exercise 8: Atomic charges in HF

The figure shows the MO diagram of HF. The degenerate orbitals are $2p_{xF}$ and $2p_{yF}$ of F. (The molecular axis is parallel to the z axis.) The other orbitals are linear combinations of $1s_H$, $1s_F$, $2s_F$, and $2p_{zF}$. You can assume that the overlaps of these orbitals are all zero. A calculation yields

$$\varphi_1 = 0.010 * 1s_H + 0.990 * 1s_F + 0.140 * 2s_F - 0.002 * 2p_{zF}$$

$$\varphi_2 = 0.365 * 1s_H - 0.133 * 1s_F + 0.918 * 2s_F - 0.084 * 2p_{zF}$$

$$\varphi_3 = -0.544 * 1s_H - 0.034 * 1s_F + 0.284 * 2s_F + 0.789 * 2p_{zF}$$

$$\varphi_4 = 0.755 * 1s_H + 0.028 * 1s_F - 0.240 * 2s_F + 0.609 * 2p_{zF}$$

What are the partial charges of H and F in HF?

