Problem sheet 1

Revision the Quantum Mechanics course

To follow the current course it is essential to understand the concepts introduced by Professor Dauncey last term and be able to solve the associated problems. The most relevant topics are:

Lecture 05: The finite square well

To test your understanding, login to Blackboard and run applet qm1d (or go to website www.falstad.com/qm1d/). Select “Finite Well” from the menu and vary the well and particle properties. Satisfy yourself that the energy levels and the wavefunctions correspond to the formulae given in the lecture notes and in Handout 02. Redo Problem 3.1.

Lecture 07: The simple harmonic oscillator

In a similar way revise this lecture and Handout 03, and test your understanding of the energies and wavefunctions against the “Harmonic Oscillator” setup in applet qm1d. Redo Problems 4.2 and 4.3.

Lecture 26: Central potentials

Make sure that you understand this lecture and Handout 07. Refer to the earlier lectures if necessary. Redo Problems 10.2 and 10.3. This is the starting point of the current “Applications” course.

A new problem for the current course

1. Simulation of 1D harmonic oscillator

Login to Blackboard or go to website www.falstad.com, run applet qm1d and start with the demonstration you have seen during the first lecture:

- Choose from the menu Setup: Harmonic Oscillator.
- Tick Stopped and click on Ground State.
- Untick View, Momentum and View, Expectation Values.
- Tick View, Values/Dimensions and View, Wave Function, Magnitude + Phase.
- Drag the horizontal lines to make the phasors (the circles) bigger.
- Set the ground-state phasor to various angles and make sure you understand the colour-coding of the wavefunction phase.
- Untick Stopped and observe how the wavefunction evolves in time.
- Double click on the 1st excited state phasor (only this one should be highlighted now) and repeat the observations of the previous two points.
- Compare the shape of the wavefunction with its mathematical formula; does it make sense?
- Set a superposition of the ground and 1st excited states and observe how it evolves in time (you may need to reduce Simulation Speed); would you expect such evolution from the mathematics?
- Explore other representations of the wavefunction at View, Wave Function.
- Use the mouse to create Gaussian wavepackets of various shapes, translate them to various positions and observe their evolution; recall that you are looking at superpositions of the time independent Schrödinger equation.
- Vary other settings of the program and pay attention to the numerical values being displayed – your aim is to understand the formalism of quantum mechanics by simulating various cases.
Problem sheet 2

Note: To solve the following problems you may use any information in the “Useful Formulae” sheet.

Units

1. A He-Ne laser emits radiation with wavelength $\lambda = 633$ nm. How many photons are emitted per second by a laser with a power of 1 mW?

2. The ionisation energy of the hydrogen atom in its ground state is $E_{\text{ion}} = 0.5 \, E_h$. Calculate the frequency and wavelength of the electromagnetic radiation that will just ionise the atom. Give the answers in SI units.

3. Atomic clocks are so stable that the second in now defined as the duration of 9 192 631 770 periods of oscillation of the radiation corresponding to a transition between two hyperfine levels of the caesium-133 atom. Calculate the energy difference between the two levels in eV and in atomic units.

4. Neutron diffraction may be used to determine crystal structures. Considering their de Broglie wavelength and assuming reasonable values of quantities that are not given, do the following:
   
   (a) Estimate a suitable value for the velocity of the neutrons.
   
   (b) Calculate the kinetic energy of the neutron in eV for this velocity.
   
   (c) It is common practice in this type of experiment to select a beam of monoenergetic neutrons from a gas of neutrons at temperature $T$. Estimate a suitable value for $T$.

Bragg’s law of diffraction

The scattering of electrons, X-rays and neutrons by crystals can be described as a reflection of the beams at planes of atoms (lattice planes), independent of the actual physical reason causing the diffraction event. If the incident plane wave hits the crystal at an arbitrary angle, the interference of the reflected waves can be either destructive or constructive.

To obtain constructive interference, the path difference between the two incident and the scattered waves, which is $2d \sin \theta$, has to be a multiple of the wavelength $\lambda$. For this case, the Bragg law then gives the relation between interplanar distance $d$ and diffraction angle $\theta$:

$$n\lambda = 2d \sin \theta$$

http://www.microscopy.ethz.ch/bragg.htm
Problem sheet 3

Note: To solve the following problems you may use any information in the “Useful Formulae” sheet.

Hydrogenic atom

1. Consider the probability density of an electron in a hydrogen atom in the ground state.
   (a) At which location is the electron most likely to be? Calculate the relevant probability density $P_a$ at this place.
   (b) At what distance from the nucleus the electron is most likely to be? Calculate the relevant probability density $P_b$.
   (c) Explain why $P_a$ and $P_b$ differ. Are their units the same?

2. The wavefunction of an electron in a hydrogen-like ion (i.e. an ion having just one electron) can be treated in the same way as in hydrogen, but with a different value of $Z$, where $Ze$ is the charge of the nucleus.
   (a) Calculate the probability density of finding electron at the centre of hydrogen-like uranium ion in the ground state, $U^{91+}$ 1s, in atomic units.
   The radius of an atomic nucleus is given approximately by $r_N = A^{1/3}r_0$ where $r_0 = 1.2 \times 10^{-15}$ m and $A$ is the mass number.
   (b) Find the nucleus radius of the U-238 isotope in atomic units.
   (c) Neglecting the variation of the probability density you found in part (a) across the nucleus, calculate the probability of finding the electron inside the uranium nucleus.
   (d) Estimate the order of magnitude of atoms which have an electron inside the nucleus in 1 g sample of uranium.

3. In Lecture 4, a qualitative method of solving the radial equation for a hydrogenic atom was presented. This problem should help you to understand the concepts leading to this solution.

A particle in one dimension is described by a real-valued wavefunction $\psi(x)$ shown here:

(a) You make a measurement to locate the particle. Which of the following is true?
   (i) You will always find the particle at point $B$.
   (ii) You are most likely to find the particle at point $A$ or $C$ and least likely to find the particle at point $B$.
   (iii) You are most likely to find the particle at points $A$, $B$ or $C$.

Explain your answer.
(b) Which of the following potentials $V(x)$ could give rise to this $\psi(x)$?

(i)

(ii)

(iii)

Explain your answer.

4. The Bohr model and the step-by-step method of solving the radial equation for the hydrogen atom are given in Handout 3. Do these calculations yourself:

(a) calculate the electron energies using the Bohr model;
(b) find the eigenfunctions and eigenenergies of the radial equation;
(c) check that the results of (a) and (b) agree.
Problem sheet 4

Note: To solve the following problems you may use any information in the “Useful Formulae” sheet.

Dirac notation

1. An atom is prepared in a superposition of two states:

   \[ |\psi\rangle = a_1 |1\rangle + a_2 |2\rangle. \]

   Normalise vector \( |\psi\rangle \), i.e. find the coefficients \( a_1 \) and \( a_2 \) knowing that \( a_1 = \text{Re} \ a_1 > 0 \), for the following cases:
   
   (a) the probability of finding the atom in state \( |1\rangle \) is two times higher than in state \( |2\rangle \);
   
   (b) the probability amplitude of finding the atom in state \( |1\rangle \) is two times higher than in state \( |2\rangle \);
   
   (c) \( a_2 = -a_1 \).

2. Functions \( r_{nlm} = u_{nlm}(r) = R_{nl}(\rho) Y_{lm}(\theta, \varphi) \) are the eigenfunctions of the hydrogen atom. Find out if the following functions (or vectors) are the eigenfunctions (or eigenvectors) of the parity operator, calculate the eigenvalue of this operator if applicable, and justify the answer:

   (a) \( |3 1 0\rangle \),
   
   (b) \( |3 1 0\rangle + 2 |2 1 1\rangle \),
   
   (c) \( (|2 1 1\rangle + |2 0 0\rangle) / \sqrt{2} \),
   
   (d) \( R_{31}(r) \),
   
   (e) \( Y_{10}(\theta, \varphi) \).

3. One-dimensional harmonic oscillator is in the state

   \[ |\psi\rangle = 0.6 |0\rangle + 0.8 |1\rangle, \]

   where \( |n\rangle \) with \( n = 0, 1 \) are the eigenvectors and the angular frequency of the oscillation is

   \[ \omega = 0.2 \ E_h / \hbar. \]

   What is the energy expectation in this state? Give the answer in atomic units.

4. A hydrogen atom is in the state

   \[ |\psi\rangle = A (0.5 |2 1 -1\rangle + i |2 1 0\rangle - 0.5 |2 1 1\rangle), \]

   where \( |nlm\rangle \) are the eigenvectors. Find the normalisation constant \( A \) and calculate the expectation values in this state of:

   (a) the energy,
   
   (b) the \( \hat{L}^2 \) operator,
   
   (c) the \( \hat{L}_z \) operator.
Problem sheet 5

Note: To solve the following problems you may use any information in the “Useful Formulae” sheet.

Radiation

1. The maximum of sunlight spectral intensity is at $\lambda = 500$ nm. Calculate in atomic and SI units the following physical quantities related to this wavelength:
   (a) the frequency, $\nu$, in SI and atomic units;
   (b) the angular frequency, $\omega$, in atomic units;
   (c) the photon energy, $E$, in atomic units and eV.

2. One-dimensional harmonic oscillator (HO) is a convenient model for many quantum systems because it is relatively easy to calculate matrix elements of operators commonly encountered in practical applications. Denoting the matrix element as $\langle j | Q | i \rangle$, where vectors $| i \rangle$ represent 1D HO wavefunctions $u_i(x)$, calculate the following elements of the position operator in terms of the HO angular frequency, $\omega$:
   (a) $\langle 1 | x | 0 \rangle$,
   (b) $\langle 2 | x | 0 \rangle$,
   (c) $\langle 3 | x | 0 \rangle$.

   Use the above results to:
   (d) deduce a selection rule for the $\langle j | x | i \rangle$ matrix elements,
   (e) check if they are consistent with the typical value of the transition electric dipole moment of an electron in an atom, assuming $\omega = E_h/\hbar$.

3. One of the lasers in the basement of the Blackett Laboratory emits pulses of 2 ps duration. The laser is tuned to a weak transition in a molecular system with the aim to transfer the system fully from the lower to the upper level, i.e. a $\pi/2$ pulse is required. Assuming the dipole moment of the transition is $\mu = -10^{-2} \, e a_0$, calculate the following:
   (a) the Rabi frequency, $\Omega$, in SI and atomic units;
   (b) the electric field amplitude required to produce the $\pi/2$ pulse, in SI and atomic units;
   (c) the laser intensity in the pulse, in SI units;
   (d) the ratio of the pulse intensity to the sunlight intensity.

4. An electron in a hydrogen atom is in a state $| \psi \rangle = | n l m \rangle = | 3 1 0 \rangle$.
   (a) State $\psi$ may decay to the ground state emitting a photon. Calculate the wavelength of the photon in nanometres with an accuracy of 3 significant figures. In which part of the electromagnetic spectrum this wavelength lies?
   (b) Between state $\psi$ and the ground state there are states 2s and 2p but a transition from $\psi$ is observed to only one of them. Explain this finding.
   (c) Calculate the wavelength of the photon emitted in part (b) in nanometres with an accuracy of 3 significant figures. If many such photons were emitted, could you observe them with an unaided eye?
   (d) Find out the polarization of the photon emitted in part (b).
5. This is 2010 exam question.

The solar interior is opaque to electromagnetic radiation. Atoms and ions in the interior are in thermal equilibrium with radiation, which has the spectral energy density distribution of a black body (Planck’s law).

Consider a hydrogen-like (i.e. having only one electron) carbon ion, \( \text{C}^{5+} \), in the ground state. This ion is in the solar interior at temperature \( T = 2\times10^6 \) K.

(a) Using the spectroscopic notation write down the electronic configuration of the electron. [2 marks]

(b) Show that the transition from the ground state to the 2s state by an absorption of a photon is not allowed by using the wavefunctions given in Useful Formulae to calculate the electric dipole moment between the two states for the polarization:

(i) parallel to the \( z \) axis, [3 marks]
(ii) parallel to the \( x \) axis, [3 marks]
(iii) parallel to the \( y \) axis. [3 marks]

(c) Consider excitation of the \( \text{C}^{5+} \) ion from the ground to the 2p state. Taking into account the interaction with the surrounding radiation calculate the following quantities for this transition with an accuracy of 3 significant figures:

(i) the energy in hartrees of the photon absorbed in the excitation process, [3 marks]

(ii) the ratio of the probability per unit time of a photon being spontaneously emitted from the 2p state to the probability per unit time of a photon being absorbed from the ground state. (Hint: see Useful Formulae) [3 marks]

(d) The de-excitation rate is in fact higher than calculated in part (c) (ii). Name the radiative process responsible for this increase and take it into account to calculate the combined de-excitation rate with an accuracy of 3 significant figures. [3 marks]

[Total 20 marks]
Problem sheet 6

Note: To solve the following problems you may use any information in the “Useful Formulae” sheet.

Helium atom and helium-like ions

1. The Experimental Storage Ring (ESR) near Darmstadt, Germany, can produce a very wide range of atomic ions, from singly-ionised helium to bare uranium nucleus. Consider an experiment with hydrogen-like uranium ions that have just one electron, which is in the ground state. One of these ions captures a second electron in the 5d state. This state decays to the 4p state of the helium-like uranium ion emitting a photon. We would like to estimate the energy of the photon, which can be done quite accurately assuming that the 1s electron moves in the potential of the bare nucleus, $U^{92+}$, and the electron on a higher orbital effectively “feels” the potential of one charge less, equivalent to the protactinium nucleus, $Pa^{91+}$. Using this assumption, find the following:
   
   (a) the energy of the $U^{91+} 1s$ state in atomic units;
   (b) the energy of the $U^{90+} 1s5d$ state in atomic units;
   (c) the energy of the $U^{90+} 1s4p$ state in atomic units;
   (d) the energy of the photon emitted during the $1s5d \rightarrow 1s4p$ transition, in eV.

2. In this question you will need to know the following energies of states of the helium atom. They are given as energies relative to the first ionisation energy (i.e. the state with one electron in the 1s state and the other electron just free of the nucleus).

<table>
<thead>
<tr>
<th>Electron configuration</th>
<th>Energy / eV</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Triplet</td>
</tr>
<tr>
<td>1s²</td>
<td>–</td>
</tr>
<tr>
<td>1s2s</td>
<td>–4.77</td>
</tr>
<tr>
<td>1s2p</td>
<td>–3.62</td>
</tr>
<tr>
<td>1s3s</td>
<td>–1.87</td>
</tr>
<tr>
<td>1s3p</td>
<td>–1.58</td>
</tr>
<tr>
<td>1s3d</td>
<td>–1.51</td>
</tr>
<tr>
<td>1s4s</td>
<td>–0.99</td>
</tr>
</tbody>
</table>

Investigate the origin of this structure in the following manner:

(a) Write down an expression for the binding energy (in eV) of the ‘outer’ electron (in the $nl$ orbital) of helium, including the first order energy shift (from perturbation theory) in terms of $J$ and $K$, the direct and exchange integrals.

(b) Explain why there is no entry in the table for the ground-state triplet?

(c) Given the energies of the various helium states listed above, infer the values of the $J$ and $K$ integrals for each of the states assuming the perturbation theory shifts match the experimental results exactly.

(d) Look at the way that $J$ and $K$ depend on the values of $n$ and $l$ for the valence electron in helium. Give reasons for the observed variation. For which of these states is the binding energy closest to that of hydrogen in the state with the same value of $n$? Why?
3. This problem is based on an exam question set in 2000 for the Atomic Physics course. The notation has been modified to match the current course.

(a) Write down a pair of normalised approximate wavefunctions for the excited states of helium that are acceptable when the indistinguishability of the electrons is taken into account.

(b) Explain how these wavefunctions could be used to find the energy of the excited states using perturbation theory.

(c) Show that each excited configuration splits into two terms.

We might have suggested using a simple product wavefunction of the form

$$\psi(r_1, r_2) = u_{1s}(r_1)u_{nlm}(r_2),$$

where one electron is taken to be in the ground (1s) state and the other is in an excited state ($n \neq 1$).

(d) Calculate the value of the joint probability function $|\psi(r_1, r_2)|^2$ for the situation where the excited electron is in the 2p($m = 0$) state at the ($r, \theta, \phi$) co-ordinates $(a_0, \pi/2, 0)$ for electron 1 and $(a_0, 0, 0)$ for electron 2.

(e) By exchanging the labels on the two electrons calculate $|\psi(r_2, r_1)|^2$, show that the simple product wavefunction given is not acceptable and explain why.

4. This problem is based on an exam question set in 2001 for the Atomic Physics course. It has been modified to match the current course.

(a) The individual spin states of two non-identical spin-1/2 particles $\alpha$ and $\beta$ can be written as $\alpha_+,$ $\alpha_0,$ $\beta_+,$ and $\beta_0,$ where the +/- indices represent, respectively, positive/negative value of the spin magnetic quantum number $m_s$. If $\alpha$ and $\beta$ are brought together, we can start constructing the spin state of the combined system as simple products of the individual spin states. Write down the four combined spin states for the system.

(b) What does the Pauli Exclusion Principle (PEP) say about the overall symmetry of electronic states in atoms? If both particles in (a) are electrons, explain why some of the two-particle states you wrote down in (a) are not all acceptable. Write down a set of four alternative two-particle spin states that are acceptable under the limitations imposed by the PEP. What is the symmetry of each of these states under the exchange operation?

(c) The states you wrote down in (b) correspond to the quantum numbers $S = 1, M_S = 1, 0, -1$ and $S = 0, M_S = 0$. Identify without proof which states correspond to which quantum numbers.

(d) Write down an approximate spatial wavefunction for the ground state of helium in terms of single-particle hydrogenic wavefunctions $u_{nlm}(r_1)$ for electron $\alpha$ and $u_{nlm}(r_2)$ for electron $\beta$. What is the symmetry of this state?
5. This problem is based on a 2008 exam question. It has been modified to match the current course.

Within the independent particle approximation (IPA) the helium atom is approximated as two independent single-electron systems.

(a) Within the IPA how much energy, in eV, is required to remove both the electrons from a helium atom initially in its ground-state?

(b) Including both the spin and spatial parts write down the form of the wavefunction of the lowest energy state of helium accounting for the fact that electrons are fermions.

The additional electron-electron repulsion in the helium atom changes the ground-state energy by a large amount compared to the IPA value.

(c) Applying the perturbation calculus to the IPA wavefunction, show that to first order the energy shift is given by an expression of the form:

$$
\Delta E^{(1)} = \int_{\text{all space}} \frac{64}{\pi^2 a_0^6} \exp\left(-\frac{4(r_1 + r_2)}{a_0}\right) \frac{e^2}{4\pi\epsilon_0 |r_{12}|} d\tau_1 d\tau_2
$$

(d) If $\Delta E^{(1)} \approx 34$ eV, what is the energy required to remove both the electrons from helium?
Problem sheet 7

Various topics

1. The parity operator is defined by its action on an arbitrary function: \( \hat{P} \psi(r) = \psi(-r) \).

   (a) Verify that \( \hat{P}^2 = \hat{1} \).

   (b) Hence show that the possible eigenvalues of \( \hat{P} \) are \( \pm 1 \).

2. Quantum numbers:

   (a) The electron in a hydrogen atom is in the \( l = 1 \) state having the lowest possible energy and the highest possible value for \( m \). What are the \( n \), \( l \) and \( m \) quantum numbers?

   (b) A particle is moving in an unknown central potential. The wavefunction of the particle is spherically symmetric. What are the values of \( l \) and \( m \)?

   (c) A helium atom is in state \( \text{He} \ 1s2p^3P_0^o \).

      (i) Write down the principal, orbital and spin quantum numbers for the individual electrons and their combined spin, orbital and total angular momentum quantum numbers. Use the conventional symbols for these numbers.

      (ii) If the parity symbol was not given, how could you work it out?

      (iii) Which are the symbols standing for “configuration”, “term” and “level”?

3. The relation between the Einstein coefficients for spontaneous and stimulated emission, \( A_{21} \) and \( B_{21} \), can be derived by considering an ensemble of 2-level atoms in a thermal equilibrium with black-body radiation. In equilibrium the number of excitations and de-excitations per unit time must be equal, therefore

   \[
   N_1 W_{12} = N_2 (W_{21} + W_{21}') ,
   \]

   where \( N_i \) are the populations (occupation numbers) of the two states \( i = 1, 2 \), and \( W_{ij} \) are transition probability rates (i.e. per unit time) from level \( i \) to level \( j \). In thermal equilibrium the populations follow the Boltzmann distribution:

   \[
   \frac{N_2}{N_1} = \exp(-\hbar \omega / kT) ,
   \]

   while the transition probability rates can be related to the Einstein coefficients:

   \[
   W_{12} = B_{12} \rho(\omega) ,
   W_{21} = B_{21} \rho(\omega) ,
   W_{21}' = A_{21} ,
   \]

   where \( \rho(\omega) \) is the spectral density of the radiation given by the Planck formula.

   Knowing from lectures that there is a simple relation between the \( B_{12} \) and \( B_{21} \) coefficients complete the derivation of the relation between \( A_{21} \) and \( B_{21} \).
4. Derive the relation between the spectral intensity of incoherent light, \( I(\omega) \), and its spectral energy density \( \rho(\omega) \).

*Hint:* Consider a beam of light in a form of a long cuboid that moves with the speed of light; the length and the cross section of the cuboid should cancel out in your derivation. Check that the SI units are correct in your formula.

5. Alkali metals have only one electron in the outermost, valence shell. The shells beneath the valence shell are completely filled and efficiently screen most of the nuclear charge from the valence electron. As the result, the valence electron is weakly bound, which translates to low ionisation energies of the alkali atoms:

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Electron configuration</th>
<th>Ionisation energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>1s(^2)2s</td>
<td>5.392 eV</td>
</tr>
<tr>
<td>Na</td>
<td>1s(^2)2s(^2)2p(^6)3s</td>
<td>5.139 eV</td>
</tr>
<tr>
<td>K</td>
<td>1s(^2)2s(^2)2p(^5)3s(^2)3p(^6)4s</td>
<td>4.341 eV</td>
</tr>
<tr>
<td>Rb</td>
<td>1s(^2)2s(^2)2p(^6)3s(^2)3p(^6)3d(^10)4s(^2)4p(^6)5s</td>
<td>4.177 eV</td>
</tr>
<tr>
<td>Cs</td>
<td>1s(^2)2s(^2)2p(^6)3s(^2)3p(^6)3d(^10)4s(^2)4p(^6)4d(^10)5s(^2)5p(^6)6s</td>
<td>3.894 eV</td>
</tr>
</tbody>
</table>

Find the following:

(a) the alkali atom of the highest ionisation energy that can be ionised by the radiation emitted from mercury lamp at the wavelength \( \lambda = 254 \text{ nm} \);

(b) the velocity of the electron released in this ionisation process, in SI and atomic units;

(c) the de Broglie wavelength of this electron, in SI and atomic units.

6. The hydrogenic wavefunctions, \( u_{nlm}(r) \), are used extensively in a description of many-electron systems. One finds that complicated atoms, and even molecules, can be built up by considering the individual electrons to inhabit nearly independent hydrogen-like orbitals (i.e. the wavefunctions). It turns out that this approach explains many features of the periodic table, among them the chemical unreactivity of the noble gases, which have the sub-shells filled up, i.e. for given \( nl \) all values of \( m \) are fully occupied.

Consider the krypton atom with a sub-shell 3d:

(a) Write down all the possible combinations of the \( nlm \) quantum numbers for this particular sub-shell.

(b) Write down the electron probability per unit solid angle for the state \( |nlm\rangle \) in the direction \((\theta, \phi)\) in terms of a spherical harmonic.

(c) Using the formulae for the first few wavefunctions derive explicit expressions for the probability density you have found in part (b) for all the states considered in part (a).

(d) Calculate the sum of the probability densities you have found in part (c).

(e) How does the result in part (d) change if you consider also the spin projection quantum number, \( m_s \)?

(f) How does the result of part (e) relate to the unreactivity of krypton?

(g) Integrate the result of part (e) over all angles and explain the value you have obtained.
Problem sheet 2 – Solutions

Problem 1

\[ E = h \nu = \frac{hc}{\lambda} \]

\[ n = \frac{P}{E} = \frac{P \lambda}{hc} = \frac{1 \times 10^{-3} \text{W} \times 6.33 \times 10^{-9} \text{m}}{6.63 \times 10^{-34} \text{J} \cdot \text{s} \times 3 \times 10^8 \text{m/s}} = 3.19 \times 10^{15} \text{photons/s} \]

Problem 2

\[ h \nu = E_{ion} \]

\[ \nu = \frac{E_{ion}}{h} = \frac{0.5 \times 4.36 \times 10^{-18} \text{J}}{6.63 \times 10^{-34} \text{J} \cdot \text{s}} \]

\[ = \frac{3.29 \times 10^{15} \text{Hz}}{3.29 \text{PHz}} = 9.12 \times 10^{-8} \text{m} = 91.2 \text{nm} \]

Problem 3

\[ \Delta E = h \nu = \frac{h}{E_h} \rho \nu \quad \text{E}_h = \text{a.u. of energy} \]

\[ = 2 \pi \times 2.42 \times 10^{-18} \text{eVs} \times 9.13 \times 10^8 \text{Hz} \quad \text{E}_h = 1.39 \times 10^6 \text{eVs} \]

\[ = 1.39 \times 10^{-6} \times 27.2 \text{eV} = 38 \text{meV} \]
Problem 4

Bragg’s law \( n\lambda = 2d \sin \theta \)

To have diffraction we need \( n\lambda < 2d \)

Let us take \( n=1 \) (1st order)

and \( \lambda = d = 0.2 \text{ nm} \) (typical interatomic spacing)

\[
d\text{e} \text{ de Broglie } \lambda = \frac{h}{p} = \frac{h}{mv}
\]

(a) \( v = \frac{h}{m\lambda} = \frac{6.63 \times 10^{-34} \text{ J} \cdot \text{s}}{1.67 \times 10^{-27} \text{ kg} \times 0.2 \times 10^{-9} \text{ m}} = 2.0 \text{ km/s} \)

(b) \[
E = \frac{mv^2}{2} = \frac{1.67 \times 10^{-27} \text{ kg} \times (2.0 \times 10^3 \text{ m/s})^2}{2}
\]

\[
= 3.3 \times 10^{-21} \text{ J} = \frac{3.3 \times 10^{-21}}{1.6 \times 10^{-19}} \text{ eV} = 20 \text{ meV}
\]

(c) \( E = kT \)

\[
T = \frac{E}{k} = \frac{3.3 \times 10^{-21} \text{ J}}{1.38 \times 10^{-23} \text{ J/K}} = 240 \text{ K} \approx \text{ room temperature}
\]

\( \Rightarrow \) thermal neutrons from a nuclear reactor are suitable
Problem sheet 3 – Solutions

Problem 1

From Useful Formulae (UF):

\[ u_{100}(r) = \sqrt{\frac{1}{4\pi}} \left( \frac{2}{a_0} \right)^{3/2} e^{-2r/a_0} \]

\[ \Rightarrow \int_{-a_0}^{a_0} e^{-r/a_0} \, d\theta = 1 \]

(a) \( P_a \) is given by the modulus squared of the wave function:

\[ P_a(r) = |u_{100}(r)|^2 = \frac{1}{a_0^3} e^{-2r/a_0} \]

\[ P_a(r) = \max \text{ for } r = 0, \quad P_a(0) = \frac{1}{a_0^3} \]

(b) \( P_b \) is \( P_a \) integrated over a sphere of a radius \( r \):

\[ P_b(r) = \int_0^{2\pi} d\theta \sin \theta \int_0^{2\pi} d\varphi r^2 P_a(r) = 4\pi r^2 P_a(r) = \frac{4r^2}{a_0^2} e^{-2r/a_0} \]

\[ \frac{d}{dr} P_b(r) = \frac{2 \times 4r}{a_0^2} e^{-2r/a_0} - \frac{2}{a_0} \frac{4r^2}{a_0^2} e^{-2r/a_0} = 0 \]

\[ \frac{2 \times 4r}{a_0^2} e^{-2r/a_0} \left( 1 - \frac{r}{a_0} \right) = 0 \]

\[ P_b(a_0) = \frac{4a_0^2}{a_0^2} e^{-2} = \frac{4}{e^2a_0} \]

(c) In (a) the electron position is uniquely defined in 3D space. In (b) the electron can be anywhere on a sphere of radius \( a_0 \).

The units of \( P_a \) and \( P_b \) are different: \( P_a \) is per unit of volume and \( P_b \) is per unit of distance (from the nucleus).

Note: \( P_a(r) d^3r \) is the probability of finding the electron in volume \( d^3r \) at a particular point on the sphere of radius \( r \). If we ask about the most likely distance, however, we do not care where exactly the electron is on the sphere. Therefore we need to integrate \( P_a(r) \) over the surface of the sphere, which gives \( P_b(r) \). \( P_b(r) dr \) is the probability of finding the electron anywhere in a shell of radius \( r \) and thickness \( dr \).
Problem 2

From $U_F$:
\[ U_{1s}(r) = U_{1s0}(r) = \frac{\hbar^2}{2m} \frac{2}{(a_o)^3} e^{-2r/a_o} = \frac{1}{\pi} \left( \frac{2}{a_o} \right)^{3/2} e^{-2r/a_o} \]

(a) $U_{91+}$: $\Sigma = 92$
\[ \psi(r=0) = U_{1s}^2 = \frac{1}{\pi} \left( \frac{92}{a_o} \right)^{3/2} = \frac{248 \times 10^3}{a_o^3} \]

(b) $K_N = \frac{A^{1/3}}{a_o} a_o = 2.38^{1/3} \times \frac{1.2 \times 10^{-15}}{52.9 \times 10^{-12}} a_o = 0.141 \times 10^{-3} a_o$

(c) $P = \frac{4}{3} \pi r_N^3 \psi(r=0) = \frac{4}{3} \pi \left( 0.141 \times 10^{-3} \right)^3 a_o^3 \times 248 \times 10^3 / a_o^3 = 2.88 \times 10^{-6}$

(d) The number of atoms in 1g sample is Avogadro's number (see Mathematical Formulae) divided by atomic mass:
\[ N = N_A / 238 = 6 \times 10^{23} / 238 = 2.5 \times 10^{21} \]
\[ PN = 10^{16} \text{ atoms will have an electron inside the nucleus. Quite a lot!} \]

Problem 3

(a) The correct answer is (iii). You are most likely to find the particle at points $A, B$ or $C$ because $|\psi(x)|^2$ is approximately equal at these three points.

(b) The correct answer is (i). Answer (iii) is incorrect because the potential is not bound and it cannot support a stationary state, i.e. an energy eigenfunction, which is real-valued. Answer (ii) is incorrect because an energy eigenfunction of this potential cannot have a probability maximum in the middle (point $B$).

Problem 4

The detailed answers are in Handout 3.
Problem sheet 4 – Solutions

Problem 1

\[ \langle \psi | \psi \rangle = a_1^2 + a_2^2 = 1 \quad P_1 = |\langle 1 | \psi \rangle|^2 = a_1^2 \]
\[ P_2 = |\langle 2 | \psi \rangle|^2 = a_2^2 \]

(a) \[ a_1^2 = 2 a_2^2 \]
\[ a_2 = 1/\sqrt{3} \]
\[ a_1 = \sqrt{2/3} \]

(b) \[ a_1^2 = 2 a_2^2 \]
\[ 4 a_2^2 + a_2^2 = 5 a_2^2 = 1 \]
\[ a_2 = 1/\sqrt{5} \]
\[ a_1 = 2/\sqrt{5} \]

(c) \[ a_1 = -a_2 \]
\[ a_2^2 + a_2^2 = 2 a_2^2 = 1 \]
\[ a_2 = -1/\sqrt{2} \]
\[ a_1 = 1/\sqrt{2} \]

Problem 2

\[ \hat{P} |nlm\rangle = (-1)^L |nlm\rangle \]

\( \uparrow \text{ eigenvalue} \)

(a) \[ \hat{P} |310\rangle = -1 |310\rangle , \text{ Yes} \]

(b) \[ \hat{P} \left( |310\rangle + 2 |211\rangle \right) = -1 \left( |310\rangle + 2 |211\rangle \right) , \text{ Yes} \]

(c) \[ \hat{P} \left( |211\rangle + |200\rangle \right)/\sqrt{2} = \left( -1 |211\rangle + 1 |200\rangle \right)/\sqrt{2} , \text{ No} \]

(d) \[ \hat{P} R_{n\ell}(\tau) = 1 R_{n\ell}(\tau) \text{- even function, Yes} \]

(e) \[ \hat{P} y_{\ell m}(\theta, \phi) = (-1)^L y_{\ell m}(\theta, \phi) , \text{ Yes} \]
\[ =-1 , \ell = 1 \]
Problem 3

\[
\langle \hat{H} \rangle = \frac{\langle 0 | 0.6^2 \frac{1}{2} \hbar \omega | 0 \rangle + \langle 1 | 0.8^2 \frac{3}{2} \hbar \omega | 1 \rangle}{0.2E_h + 0.2E_h} = (0.6^2 + 3 \times 0.8^2) \times 0.1E_h = 0.228E_h
\]

Problem 4

\[
\langle \psi | \psi \rangle = 1
\]

\[
\langle \psi | \psi \rangle = A \left( 0.5 \langle 21-1 | -i \langle 210 | -0.5 \langle 211 | \right) \times
\]

\[
x A \left( 0.5 | 21-1 \rangle + i | 210 \rangle - 0.5 | 211 \rangle \right) = A^2 \left( 0.5^2 - i^2 + 0.5^2 \right) = 1.5A^2 = 1
\]

\[
A = \frac{1}{\sqrt{1.5}} = 0.816
\]

(a) All eigenvectors have \( n = 2 \)

\[
\langle E \rangle = E_2 = - \frac{E_h}{2} \frac{1}{2^2} = - \frac{E_h}{8}
\]

(b) Similarly all \( L = 1 \)

\[
\langle \psi | \hat{L}^2 | \psi \rangle = L(L+1) \hbar^2 = 2\hbar^2
\]

(c) \[
\langle \psi | \hat{L}_z^2 | \psi \rangle = \left( \langle 21-1 | 0.5^2 \times (-i) \hbar | 21-1 \rangle + \langle 210 | (-i)i \times 0 \hbar | 210 \rangle + \langle 211 | 0.5^2 \times 1 \hbar | 211 \rangle \right) A^2 = (-0.5^2 \hbar + 0.5^2 \hbar) A^2 = 0
\]
Problem 1

(a) \( \nu = \frac{c}{\lambda} = \frac{c}{\lambda} \frac{E_h}{h} = \frac{c/\alpha_0 E_h}{\lambda/\alpha_0} \frac{E_h}{h} = \frac{137}{500 \times 10^{-9} m/5.29 \times 10^{-11} m} \frac{E_h}{h} = 0.0145 \frac{E_h}{h} \)

This should be a pure number; calculate it checking that units cancel out.

(b) \( \omega = 2\pi \text{ rad} \nu = 2\pi \times 0.0145 \text{ rad} \frac{E_h}{h} = 0.0911 \text{ rad} \frac{E_h}{h} \)

(c) \( E = h \omega = 0.0911 E_h \) (radians are dimensionless)

\[ E = 1240 \text{ nm} \cdot \text{eV}/\lambda = 1240 \text{ eV}/500 = 2.48 \text{ eV} \]

See U.F.
Problem 2

(a) \[ \langle 1 \mid x \mid 0 \rangle = \int_{-\infty}^{\infty} u_1^*(x) x u_0(x) \, dx = \]

\[ = \int_{-\infty}^{\infty} \left( \frac{m \omega}{\pi \hbar} \right)^{1/4} \sqrt{\frac{2 m \omega}{\hbar}} x e^{-m \omega x^2/2 \hbar} \left( \frac{m \omega}{\pi \hbar} \right)^{1/4} e^{-m \omega x^2/2 \hbar} \, dx \]

\[ y^2 = \frac{m \omega}{\hbar} x^2, \quad dx = \frac{\hbar}{m \omega} \, dy \]

\[ = \sqrt{\frac{2 \hbar}{\pi m \omega}} \int_{-\infty}^{\infty} y^2 e^{-y^2} \, dy = \sqrt{\frac{\hbar}{2 m \omega}} \]

From U.F. \[ = \sqrt{\pi/2} \]

(b) \[ \langle 2 \mid x \mid 0 \rangle = \int_{-\infty}^{\infty} u_2^*(x) x u_0(x) \, dx = 0 \]

\[ \text{even} \quad \text{odd} \quad \text{even} \]

(c) \[ \langle 3 \mid x \mid 0 \rangle = \int_{-\infty}^{\infty} u_3^*(x) x u_0(x) \, dx = \]

\[ = \sqrt{\frac{m \omega}{\pi \hbar}} \sqrt{\frac{m \omega}{3 \hbar}} \int_{-\infty}^{\infty} x^2 \left( 2 \frac{m \omega}{\hbar} x^2 - 3 \right) e^{-m \omega x^2/2 \hbar} \, dx = \]

\[ = \frac{1}{\sqrt{3 \pi}} \sqrt{\frac{\hbar}{m \omega}} \int_{-\infty}^{\infty} y^2 \left( 2 y^2 - 3 \right) e^{-y^2} \, dy = 0 \]

\[ 2 \int_{-\infty}^{\infty} y^4 e^{-y^2} \, dy - 3 \int_{-\infty}^{\infty} y^2 e^{-y^2} \, dy \]

From U.F. \[ = 2 \times 3 \sqrt{\pi/4} \quad 3 \sqrt{\pi/2} \]
Problem 2 continued

(d) the selection rule is \( \langle j | x | i \rangle = 0 \) for \( |j-i| \neq 1 \)

Extra:
the non-zero values are

\[
\langle j | x | i \rangle = \begin{cases} 
\frac{\hbar}{\sqrt{\mu j}} \sqrt{\frac{j}{2}} & \text{for } j = i + 1 \\
\frac{\hbar}{\sqrt{\mu i}} \sqrt{\frac{i}{2}} & \text{for } i = j + 1 
\end{cases}
\]

(e) applying (a) to an electron
when \( \omega = \frac{E_b}{\hbar} = \frac{\hbar^2}{\hbar} = \frac{\hbar}{\mu e a_0^2} = \frac{\hbar}{m_e a_0^2} \)
gives \( \mu = -e \langle 1 | x | 0 \rangle = -e \sqrt{\frac{\hbar}{2m_e \omega}} = -\frac{1}{\sqrt{2}} e a_0 \)

which is consistent with the typical value for an electron in an atom \( \mu = -e a_0 \)
Problem 3

(a) Population oscillation: \( P_2 = \sin^2(\Omega t) \)  
\( P_2 = 1, \quad \Omega t = \pi/2, \quad t = 2 \text{ ps} \)

\[
\Omega = \frac{\pi}{2t} = \frac{\pi \text{ rad}}{2 \times 2 \times 10^{-12} \text{ s}} = 7.85 \times 10^{11} \text{ rad/s}
\]

\[
= \frac{\pi \text{ rad}}{2t/E_h} \frac{E_h}{h} = \frac{\pi \times 2.42 \times 10^{-18}}{2 \times 2 \times 10^{-12}} \text{ rad} \frac{E_h}{h} = 19.0 \times 10^{-6} \text{ rad} \frac{E_h}{h}
\]

(6) From UF: \( \Delta \Sigma = -\frac{mF_o}{2\hbar} \)

\[
F_o = -\frac{2\hbar \Omega}{m} = \frac{2 \times 19.0 \times 10^{-6} E_h}{10^{-2} e \alpha_0} = 3.80 \times 10^{-3} \frac{E_h}{e \alpha_0}
\]

\[
= 3.80 \times 10^{-3} \times 5.14 \times 10^{10} \text{ V/m} = 1.95 \times 10^9 \text{ V/m} = 19.5 \text{ MV/cm}
\]

(7) From UF: \( F_o/V_{cm} = 27.48 \sqrt{I_o/W_{cm^2}} \)

\[
I_o = \left( \frac{F_o/V_{cm}}{27.48} \right)^2 \frac{W}{cm^2} = \left( \frac{19.5 \times 10^6}{27.48} \right)^2 \frac{W}{cm^2} = 5.04 \times 10^{11} \frac{W}{cm^2}
\]

(8) From UF: \( I_{\text{sunlight}} \approx 1 \text{ kW/m}^2 = 0.1 \text{ W/cm}^2 \)

\[
\frac{I_o}{I_{\text{sunlight}}} \approx 5 \times 10^{12}
\]
Problem 4

\[ |3\text{p}\rangle = |3\text{p}\rangle \]

\[ \frac{E_n}{2} = \frac{E_h}{n^2} = -\frac{E_h}{2} \frac{1}{n^2} \]

\[ E(1\text{s}) = E_1 = -\frac{E_h}{2} \]

\[ E(2\text{s}, 2\text{p}) = E_2 = -\frac{E_h}{18} \]

\[ E(3\text{p}) = E_3 = -\frac{E_h}{18} \]

(a) \[ \Delta E = E_3 - E_1 = -\frac{E_h}{18} (\frac{3}{2} - \frac{1}{2}) = E_h \left( \frac{9}{18} - \frac{1}{18} \right) = \frac{8}{18} E_h = \frac{8}{18} \times 27.2 \text{eV} = 12.1 \text{eV} \]

\[ \lambda = \frac{1240 \text{eV} \cdot \text{nm}}{12.1 \text{eV}} = 103 \text{nm} \], which is in UV (vacuum UV)

(b) \[ L = 1 \text{ for } 3\text{p} \]

\[ L = 0 \text{ for } 2\text{s} \]

\[ L = 1 \text{ for } 2\text{p} \]

\[ \Rightarrow 3\text{p} \rightarrow 2\text{p} \text{ is forbidden and transitions only to } 2\text{s} \text{ and } 1\text{s} (\text{the ground state}) \text{ are observed} \]

(c) \[ \Delta E = E_3 - E_2 = -\frac{E_h}{18} (\frac{3}{2} - \frac{1}{2}) = E_h \left( \frac{9}{22} - \frac{1}{22} \right) = \frac{8}{22} E_h = \frac{8}{22} \times 27.2 \text{eV} = 1.89 \text{eV} \]

\[ \lambda = \frac{1240 \text{eV} \cdot \text{nm}}{1.89 \text{eV}} = 656 \text{nm} \], which is red, can be observed

(d) only \( m = 0 \) is possible for \( 2\text{s} \) \[ \Rightarrow |2\text{s}\rangle = |200\rangle \]

\[ \Delta \text{m} = 0 \text{ in transition } |3\text{p}\rangle \rightarrow |200\rangle \]

\[ \Rightarrow \text{polarization is parallel to the } z \text{ axis} \]
Problem 5

(a) $C^5_1 S$

(b) $\mu = -e \langle 2S | \hat{E} \cdot \hat{r} | S \rangle$

(i) $\hat{E} \parallel z \quad \hat{E} \cdot \hat{r} = r \cos \theta$

$\mu = -e \int_0^\infty r^2 R_{20}(r) R_{10}(r) \int_0^\pi d\theta \sin \theta Y_{00}(\theta, \phi) \cos \theta Y_{00}(\theta, \phi) \int_0^{2\pi} dp \frac{d\varphi}{\sqrt{4\pi}}$

$\mu \propto \int_0^\pi d\theta \sin \theta \cos \theta = \int_0^\pi d\theta \frac{1}{2} \sin (2\theta) = 0$

(ii) $\hat{E} \parallel x \quad \hat{E} \cdot \hat{r} = r \sin \theta \cos \phi$

$\mu \propto \int_0^\pi d\theta \sin^2 \theta \int_0^{2\pi} dp \cos \phi = 0$

(iii) $\hat{E} \parallel y \quad \hat{E} \cdot \hat{r} = r \sin \theta \sin \phi$

$\mu \propto \int_0^{2\pi} dp \sin \phi = 0$

(c) $E_n = -\frac{E_h \Delta^2}{2n^2}$

$1S: n=1 \quad 2P: n=2$

$\hbar \omega = E_2 - E_1 = -E_h \frac{6^2}{2} \left( \frac{1}{2^2} - \frac{1}{1^2} \right) = \frac{3 \times 36 \hbar}{8} E_h = \frac{27}{2} E_h = 13.5 E_h$
Problem 5 continued

(c) (ii)

\[
W_{21}^{'} = W_{12}^{'} = \frac{A_{21}}{B_{12} S(\omega)} = \frac{\frac{\hbar}{\pi^2 c^3} B_{12}}{B_{12} \frac{\hbar}{\pi^2 c^3} e^{\frac{\hbar \omega}{kT}} - 1} = \frac{B_{12}}{B_{12} \frac{\hbar}{\pi^2 c^3} e^{\frac{\hbar \omega}{kT}} - 1} = e^{\frac{\hbar \omega}{kT}} - 1 = e^{\exp\left(\frac{13.5 E_h}{k \times 2 \times 10^6}\right)} - 1 = e^{2.132} - 1 = 7.43
\]

(d) Stimulated emission

\[
\frac{W_{21}^{'} + W_{21}}{W_{12}^{'} + W_{12}} = \frac{A_{21} + B_{21} S(\omega)}{B_{12} S(\omega)} = \frac{W_{21}}{W_{12}} + 1 = 7.43 + 1 = 8.43
\]
Problem sheet 6 – Solutions

Problem 1

1s electron "feels" the charge of the bare nucleus, \(+92e\); the system is \(U^{91+1s}\)

5d electron "feels" a lower charge of \(+31e\) because the 1s electron screens the nucleus; the system is equivalent to \(Pa^{90+5d}\)

\[
\begin{align*}
\text{From } U F: \quad E_n &= -\frac{Z^2}{2n^2} E_h \\
(a) \quad E(U^{91+1s}) &= -\frac{92^2}{2} E_h = -4,232 \ E_h \\
\text{see the diagram} \\
(b) \quad E(U^{90+1s\ 5d}) &= E(U^{91+1s}) + E(Pa^{90+5d}) = \\
&= \left(-\frac{92^2}{2} - \frac{91^2}{2 \times 5^2}\right) E_h = -43,976 \ E_h \\
\text{similar to the diagram} \\
(c) \quad E(U^{90+1s\ 4p}) &= E(U^{91+1s}) + E(Pa^{90+4p}) = \\
&= \left(-\frac{92^2}{2} - \frac{91^2}{2 \times 4^2}\right) E_h = -44,908 \ E_h \\
\text{(d) } \Delta E &= E(Pa^{90+5d}) - E(Pa^{90+4p}) = \\
&= \left(-\frac{91^2}{2 \times 5^2} + \frac{91^2}{2 \times 4^2}\right) E_h = \left(\frac{1}{16} - \frac{1}{25}\right) \frac{91^2}{2} E_h = \\
&= 93.2 \ E_h = 93.2 \times 27.2 \text{ eV} = 2.53 \text{ keV}
\end{align*}
\]
Problem 2

(a) From Lecture 10:
\[ E^\pm = E^0 + J_{nl} \pm K_{nl} \]

Independent Particle Approximation
(\text{IPA} \equiv \text{0th order})

1st order correction from perturbation theory

(b) In the ground state the spatial wavefunctions of both electrons are the same, \( u_{1s}(\vec{r}_1) \) and \( u_{1s}(\vec{r}_2) \). Therefore an antisymmetric spatial wavefunction is not possible because it would be
\[ u_{1s}(\vec{r}_1) u_{1s}(\vec{r}_2) - u_{1s}(\vec{r}_2) u_{1s}(\vec{r}_1) = 0. \]

Therefore there is no \( \pm K_{nl} \) splitting of the ground state.

Because electrons are fermions, the full wavefunction must be antisymmetric. As the spatial part of the ground state must be symmetric, the spin part must be antisymmetric, which is a singlet.

Triplet is not allowed because its spin part is symmetric, which would make the full wavefunction also symmetric.

(c) Adding and subtracting the two equations in (a):
\[ E^+ + E^- = 2E^0 + 2J_{nl} \]
\[ E^+ - E^- = 2K_{nl} \]

\[ J_{nl} = \frac{E^+ + E^-}{2} - E^0 \]
\[ K_{nl} = \frac{E^+ - E^-}{2} \]

Using IPA:
\[ E^0 = E^0_{\text{He} 1s_{nl}} = \frac{E \left( \text{He}^+ 1s \right) + E \left( \text{He}^+ n\ell \right)}{2} \]

\[ = 0 \text{ by the convention used in the table, } E_n = \frac{E_n}{2} \frac{\ell^2}{n^2}, \ell = 2 \text{ for He} \]
Problem 2 continued

(c) continued...

\[ E^0 = -\frac{2E_h}{n^2} = -\frac{54.4\,\text{eV}}{n^2}, \quad E^- = E(\text{Triplet}), \quad E^+ = E(\text{Singlet}) \]

Now the J and K integrals can be computed:

<table>
<thead>
<tr>
<th>Electron configuration</th>
<th>Energy (eV)</th>
<th>n</th>
<th>(E^0) (eV)</th>
<th>J (eV)</th>
<th>K (eV)</th>
<th>L</th>
</tr>
</thead>
<tbody>
<tr>
<td>1s^2</td>
<td>-24.58</td>
<td>1</td>
<td>-54.40</td>
<td>29.82</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>1s2s</td>
<td>-4.77</td>
<td>2</td>
<td>-13.60</td>
<td>9.23</td>
<td>0.40</td>
<td></td>
</tr>
<tr>
<td>1s2p</td>
<td>-3.62</td>
<td>2</td>
<td>-13.60</td>
<td>10.11</td>
<td>0.13</td>
<td></td>
</tr>
<tr>
<td>1s3s</td>
<td>-1.87</td>
<td>3</td>
<td>-6.04</td>
<td>4.27</td>
<td>0.10</td>
<td></td>
</tr>
<tr>
<td>1s3p</td>
<td>-1.58</td>
<td>3</td>
<td>-6.04</td>
<td>4.50</td>
<td>0.04</td>
<td></td>
</tr>
<tr>
<td>1s3d</td>
<td>-1.51</td>
<td>3</td>
<td>-6.04</td>
<td>4.53</td>
<td>0.00</td>
<td></td>
</tr>
<tr>
<td>1s4s</td>
<td>-0.99</td>
<td>4</td>
<td>-3.40</td>
<td>2.45</td>
<td>0.04</td>
<td></td>
</tr>
</tbody>
</table>

(d) For an increasing \(n\) the values of the \(J\) and \(K\) integrals are decreasing. This is because the \(nl\) electron is further and further away from the He^+ 1s core, which makes the electron-electron repulsion potential factored in the integrals less and less significant. For a given \(n\) and an increasing \(l\) the \(K\) integral is decreasing. The explanation is similar: an electron that has a high orbital angular momentum penetrates the core less than an electron of a lower orbital angular momentum.

The hydrogen atom energy \(E_H = \frac{-E_h}{2n^2} = E\). From the table we see that -1.51 eV = -6.04 eV/4 for the 1s3d state. This state is almost hydrogenic because the two electrons are well separated and the 1s electron screens the nucleus from the 3d one almost perfectly. There are two reasons for it:

1. a significant difference in \(n=1\) and \(n=3\) numbers;
2. the large angular momentum of the d electron.
Problem 3

See Lecture 10.

(a) The full wavefunction \( \Psi \) must be antisymmetric. If we approximate it as a product of spatial and spin parts then we have two possibilities:

\[
\Psi_A^0 = \Psi_s \Psi_A \quad \text{or} \quad \Psi_A^0 = \Psi_A \Psi_s
\]

the simplest acceptable (0th) approximation

The spatial part can be constructed from hydrogenic orbitals, \( \psi_{nl} \) (\( m \) can be any allowed):

\[
\psi_s \left( \frac{r_1}{r_2} \right) = \frac{1}{\sqrt{2}} \left( \psi_{1s} \left( \frac{r_1}{r_2} \right) \psi_{nl} \left( r_2 \right) + \psi_{nl} \left( \frac{r_1}{r_2} \right) \psi_{1s} \left( r_2 \right) \right)
\]

\[
\psi_A \left( \frac{r_1}{r_2} \right) = \frac{1}{\sqrt{2}} \left( \psi_{1s} \left( \frac{r_1}{r_2} \right) \psi_{nl} \left( r_2 \right) - \psi_{nl} \left( \frac{r_1}{r_2} \right) \psi_{1s} \left( r_2 \right) \right)
\]

(b) We apply the perturbation calculus (see Prof. Dauncey’s Lecture 20):

\[
E^1 = E^0 + \int \psi_s^* \left( \frac{r_1}{r_2} \right) \frac{e^2}{4 \pi \epsilon_0 \left| \frac{r_1}{r_2} - \frac{r_2}{r_1} \right|} \psi \left( \frac{r_1}{r_2} \right) \frac{d^3 r_1}{d^3 r_2} V \left( \frac{r_1}{r_2} \right) \frac{d^3 r_1}{d^3 r_2} \frac{d^3 r_1}{d^3 r_2}
\]

0th approximation (IPA)

1st approximation

V - electron-electron repulsion potential, which perturbs \( \Psi \)

(c) as we have two possible wavefunctions, \( \psi_s \) and \( \psi_A \), the energy \( E^1 \) is split into two terms. This can be shown explicitly.

Denoting \( \psi_{1s} = a \), \( \psi_{nl} = b \) with indices 1 and 2 corresponding to arguments \( \frac{r_1}{r_2} \) and \( \frac{r_2}{r_1} \), we have

\[
E^\pm = E^0 + \int \frac{d^3 r_1}{d^3 r_2} \left( a^* b \pm a^* b^* \right) V \left( \frac{r_1}{r_2} \right) \left( a b^* \pm a b \right) \frac{d^3 r_1}{d^3 r_2} \frac{d^3 r_1}{d^3 r_2}
\]

\[
= E^0 + \frac{1}{2} \int a^* b^* V a b^* + \frac{1}{2} \int a^* b^* V a b^* = \ ... \\
\]

these two integrals are equal because we can swap \( \frac{r_1}{r_2} \leftrightarrow \frac{r_2}{r_1} \)
Problem 3 continued

\[ \cdots \pm \frac{1}{2} \int a_2^{*} b_2^{*} V_a b_2 \, d\tau \pm \frac{1}{2} \int a_1^{*} b_2^{*} V_a b_1 \, d\tau = \]

these two integrals are equal for the same reason

\[ = E^0 + \int a_1^{*} b_2^{*} V_a b_2 \, d\tau \pm \int a_1^{*} b_2^{*} V_a b_1 \, d\tau = \]

\[ = E^0 + J \pm K \]

(d) From U.F.: 

\[ A_1 = |u_{11}(\vec{r}_1)|^2 = R_{10}^2(\alpha_0) Y_{00}^2 = \frac{1}{2} (\frac{2}{\pi a_0^3})^2 e^{-2r_1^2/4a_0^2} = \frac{8}{\pi a_0^2} \]  

\[ B_2 = |u_{21}(\vec{r}_2)|^2 = R_{21}^2(\alpha_0) Y_{10}^2(0,0) = \frac{1}{3} (\frac{1}{\pi a_0^3})^2 e^{-2r_2^2/4a_0^2} = \frac{1}{3a_0^3} \]

\[ |\psi(\vec{r}_1, \vec{r}_2)|^2 = A_1 B_2 = \frac{8}{\pi a_0^2} e^{-2} \]

(E) evaluating \[ |\psi(\vec{r}_1, \vec{r}_2)|^2 = A_2 B_1 \] in a similar way we notice that

\[ B_1 \propto Y_{10}^2 (\frac{\pi}{2}, 0) \propto \cos^2 \frac{\pi}{2} = 0, \]

i.e. now \[ |\psi|^2 = 0 \], which is unacceptable because it must be \[ = A_1 B_2 \] i.e. the same as in part (d).
Problem 4

(a) \( \alpha_- \beta_-, \alpha_+ \beta_+, \alpha_- \beta_+, \alpha_+ \beta_- \)

(b) The electronic states must be antisymmetric because electrons are fermions. The last two states in (a) are not acceptable because they do not have symmetry when exchanging the particles \( \alpha \leftrightarrow \beta \). The acceptable states are:

\[
\begin{aligned}
\alpha_+ \beta_+ \\
\frac{1}{\sqrt{2}} (\alpha_+ \beta_- + \alpha_- \beta_+) \\
\alpha_- \beta_-\\
\frac{1}{\sqrt{2}} (\alpha_+ \beta_- - \alpha_- \beta_+)
\end{aligned}
\]

\[
\begin{array}{l}
\text{symmetric} \\
\text{antisymmetric}
\end{array}
\]

(c) In the same order as above

\( S = 1 \), \( M_S = \begin{cases} 1 \\ 0 \\ -1 \end{cases} \)

\( S' = 0 \), \( M_{S'} = 0 \)

(d) From lecture 10:

\( \psi (\text{He } 1s^2) = \psi_{100}(\vec{r}_1) \psi_{100}(\vec{r}_2) \)

It is symmetric.
Problem 5

(a) \( E_{IPA} (He \ 1s^2) = 2 E(He^+ \ 1s) = 2 E_1 (Z=2) = \frac{h^2}{2m} \)

From UF: \( E_n = -\frac{E_h}{2} \left( \frac{Z^2}{n^2} \right) \)

\( \frac{h^2}{2} - 2 \frac{E_h}{2} \frac{2^2}{1^2} = -4E_h = -4 \times 2.772 \text{ eV} = -108.8 \text{ eV} \)

(b) see Lecture 10:
\( \Psi = \Psi \chi \) (spatial x spin)

From problem 4d: \( \Psi = U_{100} (r_1) U_{100} (r_2) \)

\( \Psi \) is symmetric \( \Rightarrow \chi \) must be antisymmetric to make \( \Psi \) antisymmetric, thus \( \chi = \chi_{sp} = \chi_{100} \)

\( \Psi (He \ 1s^2) = U_{100} (r_1) U_{100} (r_2) \chi_{100} \)

(c) This is the direct integral, \( J \) (see problem 3):
\[ \Delta E^{(1)} = J_{1s^2} = \int U_{100}^{\star} (r_1) U_{100}^{\star} (r_2) \frac{e^2}{4\pi \varepsilon_0 |r_{12}|} U_{100} (r_1) U_{100} (r_2) \, d\tau_1 \, d\tau_2 \]

From UF: \( U_{100} (r) = R_{10} (r) Y_0^0 = 2 \left( \frac{2}{\alpha_0} \right)^{3/2} e^{-2r/\alpha_0} \sqrt{\frac{1}{\pi}} \left( \frac{2}{\alpha_0} \right)^{3/2} e^{-2r/\alpha_0} \)

\( \Delta E^{(1)} = \frac{Ze^4}{\alpha_0^2} \int e^{-4(r_1+r_2)/\alpha_0} \frac{e^2}{4\pi \varepsilon_0 |r_{12}|} \, d\sigma_1 \, d\sigma_2 \) \( \text{QED} \)

(d) The required energy is the absolute value of the shifted IPA energy:
\[ |E_{IPA} + \Delta E^{(1)}| \approx |-108.8 \text{ eV} + 34 \text{ eV}| = 75 \text{ eV} \]
Problem sheet 7 – Solutions

Problem 1

(a) for any \( \psi(\vec{r}) \): \( \hat{P}^2 \psi(\vec{r}) = \hat{P} \psi(-\vec{r}) = \psi(\vec{r}) = \hat{1} \psi(\vec{r}) \)
   \[ \therefore \hat{P}^2 = \hat{1} \]

(b) \( \hat{P} \psi = \lambda \psi \), \( \lambda = ? \)
   \[ \hat{P}^2 \psi = \hat{P} \lambda \psi = \lambda^2 \psi \]
   but \( \hat{P}^2 \psi = \hat{1} \psi = \psi \)
   \[ \Rightarrow \lambda^2 \psi = \psi \]
   hence \( \lambda^2 = 1 \) and \( \lambda = \pm 1 \)

Problem 2

(a) \( \ell = 1 \), min. \( n = 2 \)
    max. \( m = 1 \)

(6) \( Y_{lm}(\theta, \phi) \) independent of \( \theta, \phi \) \( \Rightarrow \) \( Y_{lm} = Y_{00} \)

(c) \( \text{He is } 2p \)

(i) \( n_1 = 1 \)
    \( n_2 = 2 \)
    \( l_1 = 0 \)
    \( l_2 = 1 \)
    \( s_1 = \frac{1}{2} \)
    \( s_2 = \frac{1}{2} \)
    \[ \beta = 1 \]
    \( l = 1 \)
    \( J = 2 \)

(ii) parity: \( (-1) \frac{\hbar}{2} l \beta i = (-1)^{1} = -1 \) odd = symbol "o"

(iii) configuration: \( 1s 2p \)
    term: \( 3p \)
    level: \( 3p_2 \)
Problem 3

Substituting (3) into (1)

\[ \frac{N_1}{N_2} B_{12} g(\omega) = B_{21} g(\omega) + A_{21} \]

\[ B_{12} = B_{21}, \quad \text{from the symmetry of eq. (7.1), Lecture 7} \]

\[ A_{21} = \left( \frac{N_1}{N_2} - 1 \right) B_{21} g(\omega) = \left( e^{\frac{\hbar \omega}{kT}} - 1 \right) \frac{\hbar \omega^3}{2! c^3} B_{21} \frac{1}{e^{\frac{\hbar \omega}{kT}} - 1} \]

\[ \uparrow \quad \uparrow \quad \text{from (2)} \quad \text{from } UF \]

\[ A_{21} = \frac{\hbar \omega^3}{2! c^3} B_{21} \]

Problem 4

Energy in the beam: \[ E = gAL \]

Radiation intensity: \[ I = \frac{E}{At} \quad \left\{ I = \frac{gAL}{AL/c} \right\} \]

Time for E to pass through A: \[ t = L/c = gC \]

or for spectral quantities: \[ I(\omega) = g(\omega)C \]

Units: \[ \frac{W}{m^2(\text{rad}/s)} = \frac{J}{m^3(\text{rad}/s)} \frac{m}{s} \]

agree as \( W = J/s \)
Problem 5

(a) Hg lamp photon energy (see UF)
\[ E_p = \frac{1240 \text{eV} \cdot \text{nm}}{1} = \frac{1240}{254} \text{eV} = 4.882 \text{eV} \]
\[ \therefore \text{potassium will be ionised but not sodium} \]

(b) electron energy
\[ E = E_p - E_I = (4.882 - 4.341) \text{eV} = 0.541 \text{eV} = \frac{0.541 \text{eV}}{2.72 \text{eV}/E_h} = 0.0199 E_h \]
\[ E = \frac{m_e v^2}{2} \quad v = \sqrt{\frac{2E}{m_e}} = \sqrt{2 \times 0.0199 \frac{a_0 E_h}{\hbar}} = 0.199 \frac{a_0 E_h}{\hbar} = 0.199 \times 2.19 \times 10^6 \text{ m/s} = 0.437 \text{ m/µs} \]

(c) \[ \lambda = \frac{\hbar}{P} = \frac{2\pi k}{m_e v} = \frac{2\pi}{0.199} a_0 = 31.6 a_0 = 1.67 \text{ nm} \]
Problem 6

(a) \( n = 3, \ L = 2, \ m = -2, -1, 0, 1, 2 \)

(b) \( P_{lm}(\theta, \phi) = |Y_{lm}(\theta, \phi)|^2 \)

(c) \( P_{20} = \frac{5}{16\pi} (3 \cos^2 \theta - 1)^2 \)

\[
P_{2 \pm 1} = \frac{15}{8\pi} \sin^2 \theta \cos^2 \theta
\]

\[
P_{2 \pm 2} = \frac{15}{32\pi} \sin^4 \theta
\]

(d) \( P_2 = P_{20} + 2P_{2 \pm 1} + 2P_{2 \pm 2} = \)

\[
= \frac{5}{16\pi} \left( (3 \cos^2 \theta - 1)^2 + 12 \frac{\sin^2 \theta \cos^2 \theta}{1 - \cos^2 \theta} + 3 \sin^4 \theta \right) =\]

\[
= \frac{5}{16\pi} \left( 9 \cos^4 \theta - 6 \cos^2 \theta + 1 + 12 \cos^2 \theta - 12 \cos^4 \theta + 3 - 6 \cos^2 \theta + 3 \cos^4 \theta \right) = \frac{5}{4\pi}
\]

(e) \( m_s = \pm \frac{1}{2} \Rightarrow 2 \) nlmm states for each nlm state

\( \Rightarrow P_2' = 2P_2 = \frac{5}{2\pi} \)

(f) \( P_2' \) is spherically symmetrical because the 3d sub-shell is fully occupied. There is neither charge concentration nor a hole that could support a chemical bond.

(g) \( P_2' \times 4\pi = 10 \)

The spherical harmonics are normalised \( \left( \int Y_{lm}(\Omega) d\Omega = 1 \right) \) and there are 10 nlmm states that have been added up in part (e). There are 10 electrons on the 3d subshell.