

CHEM 3PA3, Fall 2016 – Assignment #2 Solutions

- The hydrogenic atomic orbitals are comprised of the product of radial and angular functions (spherical harmonics), $R_{nl}(r)Y_{l,m_l}(\theta, \phi)$, which are eigenfunctions of the (separable) Hamiltonian for an electron in a Coulomb potential generated by a nucleus of charge Z ($=2$, for the He case under study in this problem; the orbitals can be thought of as those corresponding to an He^+ atom). The radial functions and spherical harmonics are tabulated on pages 190-191 of the text (n.b.: the normalization factors for the spherical harmonics, I_l , can be found on page 136 of the text). Linear combinations of the angular parts of these wavefunctions can be taken to ensure that the resulting orbitals are real; rather than labelling by the set of quantum numbers $\{n, l, m_l\}$, these real orbitals are labelled by the conventional nomenclature of n for the energy level, $s/p/d/f \dots$ for the angular momentum, and a directional orientation based on m_l .

The $2p$ and $3d$ orbitals of the He^+ for this problem, written in natural units of length (i.e. where length is in units of the Bohr radius a_0), are the following:

$$\begin{aligned}\psi_{2p_z} &= \frac{1}{4\sqrt{2\pi}} 2^{\frac{3}{2}} \rho e^{-\frac{\rho}{2}} \cos(\theta) = \frac{1}{4\sqrt{2\pi}} 2^{\frac{3}{2}} \rho e^{-\frac{\rho}{2}} \left(\frac{z}{r}\right) \\ \psi_{2p_x} &= \frac{1}{4\sqrt{2\pi}} 2^{\frac{3}{2}} \rho e^{-\frac{\rho}{2}} \sin(\theta) \cos(\phi) = \frac{1}{4\sqrt{2\pi}} 2^{\frac{3}{2}} \rho e^{-\frac{\rho}{2}} \left(\frac{x}{r}\right) \\ \psi_{2p_y} &= \frac{1}{4\sqrt{2\pi}} 2^{\frac{3}{2}} \rho e^{-\frac{\rho}{2}} \sin(\theta) \sin(\phi) = \frac{1}{4\sqrt{2\pi}} 2^{\frac{3}{2}} \rho e^{-\frac{\rho}{2}} \left(\frac{y}{r}\right) \\ \psi_{3d_{z^2}} &= \frac{1}{81\sqrt{6\pi}} 2^{\frac{3}{2}} \rho^2 e^{-\frac{\rho}{3}} (3 \cos^2(\theta) - 1) = \frac{1}{81\sqrt{6\pi}} 2^{\frac{3}{2}} \rho^2 e^{-\frac{\rho}{3}} \left(\frac{3z^2 - r^2}{r^2}\right) \\ \psi_{3d_{x^2-y^2}} &= \frac{1}{81\sqrt{2\pi}} 2^{\frac{3}{2}} \rho^2 e^{-\frac{\rho}{3}} \sin^2(\theta) \cos(2\phi) = \frac{1}{81\sqrt{2\pi}} 2^{\frac{3}{2}} \rho^2 e^{-\frac{\rho}{3}} \left(\frac{x^2 - y^2}{r^2}\right) \\ \psi_{3d_{xz}} &= \frac{\sqrt{2}}{81\sqrt{\pi}} 2^{\frac{3}{2}} \rho^2 e^{-\frac{\rho}{3}} \sin(\theta) \cos(\theta) \cos(\phi) = \frac{\sqrt{2}}{81\sqrt{\pi}} 2^{\frac{3}{2}} \rho^2 e^{-\frac{\rho}{3}} \left(\frac{xz}{r^2}\right) \\ \psi_{3d_{yz}} &= \frac{\sqrt{2}}{81\sqrt{\pi}} 2^{\frac{3}{2}} \rho^2 e^{-\frac{\rho}{3}} \sin(\theta) \cos(\theta) \sin(\phi) = \frac{\sqrt{2}}{81\sqrt{\pi}} 2^{\frac{3}{2}} \rho^2 e^{-\frac{\rho}{3}} \left(\frac{yz}{r^2}\right) \\ \psi_{3d_{xy}} &= \frac{1}{81\sqrt{2\pi}} 2^{\frac{3}{2}} \rho^2 e^{-\frac{\rho}{3}} \sin^2(\theta) \sin(2\phi) = \frac{1}{81\sqrt{2\pi}} 2^{\frac{3}{2}} \rho^2 e^{-\frac{\rho}{3}} \left(\frac{xy}{r^2}\right)\end{aligned}$$

1.1

with $\rho = Zr = 2r$ in these units, and $r = \sqrt{x^2 + y^2 + z^2}$.

To generate plots of the probability densities for each orbital in Excel, slices of the orbitals in **1.1** are taken in the xz -plane, with y set equal to zero. The orbitals associate a probability density value to each point in three-dimensional space, meaning that it would be necessary to represent a four-dimensional structure in the plot, which is challenging (hence the slices). Letting x and z cover $[-10, 10]$ provides a suitable range to reveal all of the features of the orbitals, and an increment of 0.1 provides suitable resolution for the contour plots. To set up the calculation, extend a series of x values along the top row* of the spreadsheet from column B onwards, and a series of z values in column A, starting from row 2. The formulas to generate the probability density of the orbital at each point in the grid are as follows (note that, because real linear combinations of the spherical harmonics are used, the probability density is obtainable by simply squaring the expressions in **1.1**):

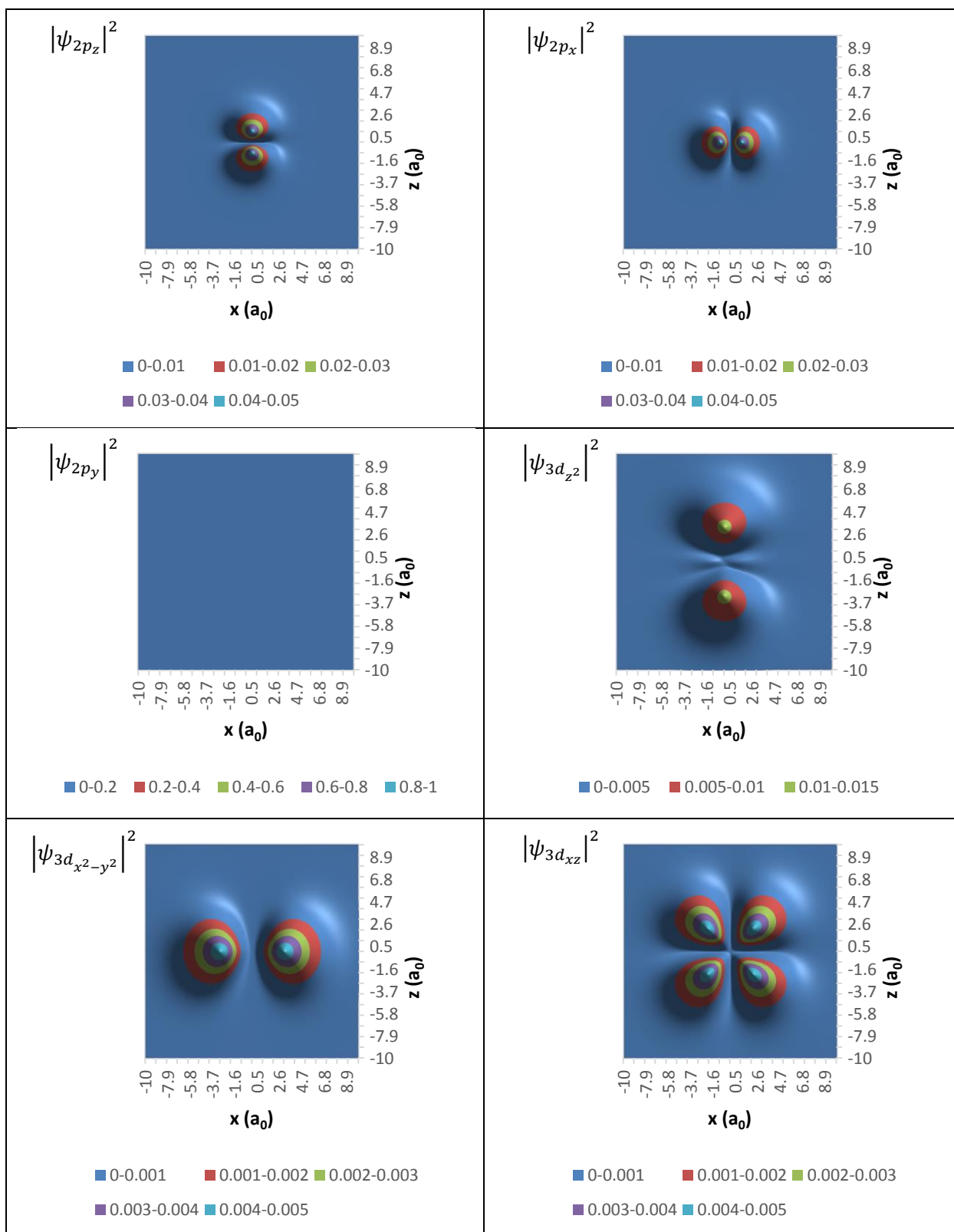
$ \psi_{2p_z} ^2$	$=((1/(4*\text{SQRT}(2*\text{PI}())))*2^{(3/2)}*\$A3^2*\text{SQRT}(\$B\$2^2+\$A3^2)*\text{EXP}(-0.5*2*\text{SQRT}(\$B\$2^2+\$A3^2)))/\text{IF}(\$B\$2=0,\text{IF}(\$A3=0,1,\text{SQRT}(\$B\$2^2+\$A3^2)),\text{SQRT}(\$B\$2^2+\$A3^2)))^2$
$ \psi_{2p_x} ^2$	$=((1/(4*\text{SQRT}(2*\text{PI}())))*2^{(3/2)}*\$B\$2^2*\text{SQRT}(\$B\$2^2+\$A3^2)*\text{EXP}(-0.5*2*\text{SQRT}(\$B\$2^2+\$A3^2)))/\text{IF}(\$B\$2=0,\text{IF}(\$A3=0,1,\text{SQRT}(\$B\$2^2+\$A3^2)),\text{SQRT}(\$B\$2^2+\$A3^2)))^2$
$ \psi_{3d_{z^2}} ^2$	$=((1/(81*\text{SQRT}(6*\text{PI}())))*2^{(3/2)}*(3*\$A3^2-\text{SQRT}(\$B\$2^2+\$A3^2))*(2*\text{SQRT}(\$B\$2^2+\$A3^2))^2*\text{EXP}(-2*\text{SQRT}(\$B\$2^2+\$A3^2)/3))/\text{IF}(\$B\$2=0,\text{IF}(\$A3=0,1,\text{SQRT}(\$B\$2^2+\$A3^2)),\text{SQRT}(\$B\$2^2+\$A3^2)))^2$
$ \psi_{3d_{x^2-y^2}} ^2$	$=((1/(81*\text{SQRT}(2*\text{PI}())))*2^{(3/2)}*\$B\$2^2*(2*\text{SQRT}(\$B\$2^2+\$A3^2))^2*\text{EXP}(-2*\text{SQRT}(\$B\$2^2+\$A3^2)/3))/\text{IF}(\$B\$2=0,\text{IF}(\$A3=0,1,\text{SQRT}(\$B\$2^2+\$A3^2)),\text{SQRT}(\$B\$2^2+\$A3^2)))^2$
$ \psi_{3d_{xz}} ^2$	$=((\text{SQRT}(2)/(81*\text{SQRT}(\text{PI}())))*2^{(3/2)}*\$A3*\$B\$2*(2*\text{SQRT}(\$B\$2^2+\$A3^2))^2*\text{EXP}(-2*\text{SQRT}(\$B\$2^2+\$A3^2)/3))/\text{IF}(\$B\$2=0,\text{IF}(\$A3=0,1,\text{SQRT}(\$B\$2^2+\$A3^2)),\text{SQRT}(\$B\$2^2+\$A3^2)))^2$

*The formulas assume that the actual top row of the spreadsheet is left empty, and the row of values defining x is placed in the second row of the spreadsheet.

To apply these formulas in a spreadsheet, simply paste them into the top-left corner of the grid constructed as above, which would correspond to cell B3 (assuming that the top row is left empty). Clearly, since the focus is on the xz -plane, the orbitals ψ_{2p_y} , $\psi_{3d_{yz}}$, and $\psi_{3d_{xy}}$ will have trivial formulas (i.e. zero for all values of the grid). Also, note that the 'IF' statement in denominator is simply to prevent division by zero, which Excel will flag with a non-numeric value. Additionally, it is important to make sure that when filling the axis values to form the edge of the grid, that you check that the values which are supposed to correspond to zero actually have a zero in them, rather than simply a very small number (a numerical error stemming from how Excel proceeds with the 'fill' operation), as this can also cause problems. An example of the appearance of the spreadsheet for the $2p_z$ orbital is as follows:

z --v	x -->				
	-10	-9.9	-9.8	-9.7	-9.6
-10	1.66E-11	1.91E-11	2.19E-11	2.52E-11	1.66E-11
-9.9	1.87E-11	2.15E-11	2.48E-11	2.85E-11	1.87E-11
-9.8	2.11E-11	2.43E-11	2.80E-11	3.23E-11	2.11E-11

The results of the orbital computations are plotted on the following page, using the 'overhead' contour option under Chart Types in Excel. Note how the orientation of the orbital lobes corresponds to the label each is given, which indicate a sort of 'directionality' to the orbital, and the relative size difference of the p and d orbitals. Also, as mentioned above, the xz -plane is a nodal plane for the ψ_{2p_y} , $\psi_{3d_{yz}}$, and $\psi_{3d_{xy}}$ orbitals, so the empty plot for the ψ_{2p_y} orbital represents the lack of probability density in this particular slice of space. Similarly, the $\psi_{3d_{x^2-y^2}}$ orbital, whose lobes are directed along the axes in the xy -plane, appears to only have two instead of four lobes, because the lobes along the y -axis have no probability density contribution on the xz -plane. Finally, close inspection of the plot for the $\psi_{3d_{z^2}}$ probability density reveals a faint contribution from the characteristic ring around the z -axis which is centred in the xy -plane.



2. Given the rate expression for the transitions between excited states of hydrogenic atoms via spontaneous emission:

$$\text{rate} = \frac{4\alpha\omega_{j',j}^3}{3c^2} \left(|\langle\psi_{j'}|x|\psi_j\rangle|^2 + |\langle\psi_{j'}|y|\psi_j\rangle|^2 + |\langle\psi_{j'}|z|\psi_j\rangle|^2 \right) \quad 2.1$$

a) To determine the selection rules, it is necessary to assess the brackets (integrals) between the two states with the position operator that comes from the dipole moment, $\vec{\mu}$ (which is how, to lowest order, the electrons interact with the spontaneous fluctuations – zero point energy density – of the electromagnetic field).

One selection rule is immediately evident from the frequency scale of the transition, $\omega_{j',j}$: since this term depends on the energy difference between the orbitals, as $(E_{j'} - E_j)/\hbar$, the principle quantum number n , which exclusively governs the energy of the orbitals, must be different between the orbitals undergoing the transition – a $2p \rightarrow 2s$ transition is forbidden at this level of approximation, since the frequency, and hence, the rate, is identically zero. Because the second part of the problem concerns transitions from the $2p$ orbitals, and spontaneous emission must lower the energy of the electron from that of its j' state, the j orbital in that part of the question must be $1s$.

Inserting the general expressions for the hydrogenic atomic orbitals into the overlap integrals (brackets) in 2.1 gives, with $q = x, y, z$:

$$|\langle\psi_{j'}|q|\psi_j\rangle|^2 = \int_0^\infty r^2 dr \int_0^\pi \sin(\theta) d\theta \int_0^{2\pi} d\phi q(r, \theta, \phi) R_{n',l}^*(r) R_{n,l}(r) Y_{l',m_l'}^*(\theta, \phi) Y_{l,m_l}(\theta, \phi) \quad 2.2$$

Considering each component $q = x, y, z$ separately, and separating the spherical harmonics into θ and ϕ functions (note that the radial functions are real, as are the $\Theta(\theta)$):

$$|\langle\psi_{j'}|x|\psi_j\rangle|^2 = \int_0^\infty r^2 dr r R_{n',l}(r) R_{n,l}(r) \int_0^\pi \sin(\theta) d\theta \sin(\theta) \Theta_{l',m_l'}(\theta) \Theta_{l,m_l}(\theta) \int_0^{2\pi} d\phi \cos(\phi) \Phi_{m_l'}^*(\phi) \Phi_{m_l}(\phi) \quad 2.3$$

$$|\langle\psi_{j'}|y|\psi_j\rangle|^2 = \int_0^\infty r^2 dr r R_{n',l}(r) R_{n,l}(r) \int_0^\pi \sin(\theta) d\theta \sin(\theta) \Theta_{l',m_l'}(\theta) \Theta_{l,m_l}(\theta) \int_0^{2\pi} d\phi \sin(\phi) \Phi_{m_l'}^*(\phi) \Phi_{m_l}(\phi) \quad 2.4$$

$$|\langle\psi_{j'}|z|\psi_j\rangle|^2 = \int_0^\infty r^2 dr r R_{n',l}(r) R_{n,l}(r) \int_0^\pi \sin(\theta) d\theta \cos(\theta) \Theta_{l',m_l'}(\theta) \Theta_{l,m_l}(\theta) \int_0^{2\pi} d\phi \Phi_{m_l'}^*(\phi) \Phi_{m_l}(\phi) \quad 2.5$$

The first thing evident from these integrals is that they don't specify a selection rule on n ; the extra factor of r breaks the orthonormality of the radial functions in the general case, so the aforementioned stipulation that $n' \neq n$ evident from the prefactor in 2.1 is the only restriction on n . Focusing on the θ integral in 2.5 for $\mu \propto z$, the orthonormality condition for the $\Theta(\theta)$ functions, which are Legendre polynomials of $\cos(\theta)$, is that:

$$\int_0^\pi \sin(\theta) d\theta \Theta_{l',m_l'}(\theta) \Theta_{l,m_l}(\theta) = \delta_{l',l} \delta_{m_l',m_l} \quad 2.6$$

The $\cos(\theta)$ factor in **2.5** renders this condition unsatisfied, as it can be viewed as raising the degree of one of the Legendre polynomials in $\cos(\theta)$ represented by the $\Theta(\theta)$ functions. It is possible to show, but beyond the scope of this course, that a recursion relation exists among the Legendre polynomials, wherein one of degree l multiplied by a factor of $\cos(\theta)$ can be written as a linear combination of one of degree $l + 1$ and one of degree $l - 1$. Consequently, the orthonormality condition **2.6** will be restored if the other Legendre polynomial is of one of those two degrees, and the integral will be nonzero. Hence, $\Delta l = \pm 1$ for the selection rule on l when $\mu \propto z$. Returning to **2.5**, in the $\mu \propto z$ case there is the strict orthonormality condition on the $\Phi(\phi)$ functions, as there is no function of ϕ to lift it, so it must be that $\Delta m_l = 0$.

The same logic can be applied to the θ integrals in **2.3** and **2.4** for x and y , by simply noting that $\sin(\theta) = \cos(\theta \pm \pi/2)$, which is $\cos(\theta)$ up to a sign change when the trigonometric addition formulae are employed. However, in this case, there is either a $\cos(\phi)$ or $\sin(\phi)$ factor in the ϕ integral, so the orthonormality condition on the $\Phi(\phi)$ functions is lifted here. Using the Euler formula for complex exponential representations of trigonometric functions, and working with $\cos(\phi)$ (the derivation is exactly analogous with $\sin(\phi)$, but the Euler formula has a different sign and an additional factor of i):

$$\begin{aligned} \int_0^{2\pi} d\phi \cos(\phi) e^{-im'_l\phi} e^{im_l\phi} &= \int_0^{2\pi} d\phi \left(\frac{e^{i\phi} + e^{-i\phi}}{2} \right) e^{i(m_l - m'_l)\phi} \\ &= \frac{1}{2} \int_0^{2\pi} d\phi e^{i(m_l - m'_l + 1)\phi} + \frac{1}{2} \int_0^{2\pi} d\phi e^{i(m_l - m'_l - 1)\phi} \end{aligned}$$

These integrals will be nonzero only if $m'_l = m_l + 1$ in the first case, or $m'_l = m_l - 1$ in the second, since complex exponentials are oscillatory functions, and an integer multiple of ϕ in the argument will have a period either equal to or commensurate with 2π , so the integral will be zero unless the integer multiple of ϕ is zero (in which case, the function is obviously just 1, and the integral will yield π).

Thus, the selection rules can be summarized as:

$$\Delta n < 0, \quad \Delta l = \pm 1 \begin{cases} \Delta m_l = 0, & \mu \propto \cos(\theta) \\ \Delta m_l = \pm 1, & \mu \propto \sin(\theta) \end{cases} \quad 2.7$$

b) Drawing on the fact elaborated in **a)** that n must change in the transition, and that the initial state is a $2p$ orbital, most of the quantum numbers in **2.1** can be assigned by default; it remains to be calculated what the effect of having different values of m_l for the $2p$ orbital (i.e. changing its orientation) will be on the integrals. The rate expression becomes:

$$\text{rate}_{1s \leftarrow 2p} = \frac{4\alpha\omega_{2,1}^3}{3c^2} \left(|\langle \psi_{21m_l} | x | \psi_{100} \rangle|^2 + |\langle \psi_{21m_l} | y | \psi_{100} \rangle|^2 + |\langle \psi_{21m_l} | z | \psi_{100} \rangle|^2 \right) \quad 2.8$$

Each of the 3 integrals in **2.8** is composed of separable spatial integrals for the 3 spherical polar coordinates, so there are 9 integrals in total for each value of m_l . Many can be evaluated trivially by

appealing to the orthogonality conditions for the various components (i.e. the selection rules elucidated above), but written explicitly using **2.3-2.5**, equation **2.8** has the form:

$$\begin{aligned} \text{rate}_{1s \leftarrow 2p} = \frac{4\alpha\omega_{2,1}^3}{3c^2} & \left[\int_0^\infty r^2 dr r R_{2,1}(r) R_{1,0}(r) \int_0^\pi \sin(\theta) d\theta \sin(\theta) \Theta_{1,m_l}(\theta) \Theta_{0,0}(\theta) \int_0^{2\pi} d\phi \cos(\phi) \Phi_{m_l}^*(\phi) \Phi_0(\phi) \right. \\ & + \int_0^\infty r^2 dr r R_{2,1}(r) R_{1,0}(r) \int_0^\pi \sin(\theta) d\theta \sin(\theta) \Theta_{1,m_l}(\theta) \Theta_{0,0}(\theta) \int_0^{2\pi} d\phi \sin(\phi) \Phi_{m_l}^*(\phi) \Phi_0(\phi) \\ & \left. + \int_0^\infty r^2 dr r R_{2,1}(r) R_{1,0}(r) \int_0^\pi \sin(\theta) d\theta \cos(\theta) \Theta_{1,m_l}(\theta) \Theta_{0,0}(\theta) \int_0^{2\pi} d\phi \Phi_{m_l}^*(\phi) \Phi_0(\phi) \right] \end{aligned} \quad 2.9$$

Note that $\Phi_0(\phi) = 1$ and $\Theta_{0,0}(\theta) = (4\pi)^{-\frac{1}{2}}$ under this nomenclature. The radial integral is common to all three terms, and is also independent of m_l , so it will be the same for all three cases:

$$\begin{aligned} \int_0^\infty r^2 dr r R_{2,1}(r) R_{1,0}(r) &= \int_0^\infty dr r^3 \left[\frac{1}{\sqrt{3}} \left(\frac{Z}{2a_0} \right)^{\frac{3}{2}} \rho e^{-\frac{\rho}{2}} \right] \left[2 \left(\frac{Z}{a_0} \right)^{\frac{3}{2}} e^{-\rho} \right] = \sqrt{\frac{1}{6}} \left(\frac{Z}{a_0} \right)^3 \int_0^\infty \left(\frac{a_0}{Z} \right) d\rho \left(\frac{a_0 \rho}{Z} \right)^3 \rho e^{-\frac{3\rho}{2}} \\ &= \sqrt{\frac{1}{6}} \frac{a_0}{Z} \int_0^\infty d\rho \rho^4 e^{-\frac{3\rho}{2}} \end{aligned} \quad 2.10$$

The substitution $\rho = Zr/a_0$ is made on going to the final step in the first line. The result **2.10** can be computed using a spreadsheet, taking an increment of 0.01 and a range of $[0,10]$, with the Bohr radius $a_0 = 5.292 \times 10^{-11}$ m, and $Z = 1$ for hydrogen. To compute the integral itself, the trapezoidal rule can be employed:

$$\int_a^b dx f(x) \cong \frac{b-a}{N} \left[\frac{f(a)}{2} + \sum_{k=1}^{N-1} f\left(a + k \frac{(b-a)}{N}\right) + \frac{f(b)}{2} \right] \quad 2.11$$

Here, $b - a = 10$ and $N = 1000$, with f as the integrand in **2.10**, which can be represented in Excel via the formula $= 5.291\text{E-}11/(1)*1/\text{SQRT}(6)*\text{A1}^4*\text{EXP}(-3*\text{A1}/2)$, where the grid $[0,10]$ is located in column A, and the formula would be dragged out along another column (e.g. B). To apply **2.11** to this filled out column, use $=(\text{SUM}(\text{B1:B1001})-0.5*(\text{B1}+\text{B1001}))*(10/(1001-1))$ The result should be approximately 6.82×10^{-11} m.

Using the selection rules established in **a)**, the angular integrals for all three m_l cases can be readily assessed as being zero or finite:

$m_l = 0$	θ term	ϕ term	$m_l = 1$	θ term	ϕ term	$m_l = -1$	θ term	ϕ term
x	0	0	x	$\neq 0$	$\neq 0$	x	$\neq 0$	$\neq 0$
y	0	0	y	$\neq 0$	$\neq 0$	y	$\neq 0$	$\neq 0$
z	$\neq 0$	$\neq 0$	z	0	0	z	0	0

It is instructive to nevertheless calculate the zero integrals numerically, and confirm that (within numerical error) they are indeed the zero value required by the selection rules, although this is left as an

exercise. The nonzero terms in the table above are as follows (using the tabulated spherical harmonics on pg. 191 in the text, and a grid of 100 points in the $[0, \pi]$ interval for the θ integrals):

$$\langle \Theta_{1,0} | z | \Theta_{0,0} \rangle = \frac{\sqrt{3}}{4\pi} \int_0^\pi d\theta \sin(\theta) \cos^2(\theta) \approx 0.092, \quad \langle \Phi_0 | z | \Phi_0 \rangle = \int_0^{2\pi} d\phi (1)(1) = 2\pi,$$

$$\langle \Theta_{1,\pm 1} | x | \Theta_{0,0} \rangle = \langle \Theta_{1,\pm 1} | y | \Theta_{0,0} \rangle = \mp \frac{1}{4\pi} \sqrt{\frac{3}{2}} \int_0^\pi d\theta \sin^3(\theta) \approx \mp 0.130,$$

$$\langle \Phi_{\pm 1} | x | \Phi_0 \rangle = \int_0^{2\pi} d\phi e^{\mp i\phi} \cos(\phi) = \pi, \quad \langle \Phi_{\pm 1} | y | \Phi_0 \rangle = \int_0^{2\pi} d\phi e^{\mp i\phi} \sin(\phi) = \mp i\pi$$

Multiplying out the corresponding values of these integrals according to the columns of each m_l section of the table above, and incorporating the radial integral in **2.10**, complex-conjugating, and then summing over the rows in each section of the table (i.e. computing **2.9**) gives the result up to the prefactor:

$$\frac{4\alpha\omega_{j',j}^3}{3c^2} = \frac{4(7.29735 \times 10^{-3})}{3(2.99792458 \times 10^8 \text{ m} \cdot \text{s}^{-1})^2} \left[\frac{(-13.606 \text{ eV})}{(6.58212 \times 10^{-16} \text{ eV} \cdot \text{s})} \left(\frac{1}{(2)^2} - \frac{1}{(1)^2} \right) \right]^3 = 4.0338 \times 10^{29} \text{ m}^{-2} \cdot \text{s}^{-1} \quad \mathbf{2.12}$$

(Dimension-wise, note that the integrals have units of m^2 , from the position operator in the bracket, which is ultimately squared.)

Combining the integrals obtained via the method described above with the prefactor in **2.12**, the resulting transition rates and lifetimes ($\tau = \text{rate}^{-1}$) for the three $2p$ orbitals of hydrogen undergoing spontaneous emission are all $\text{rate}_{1s \leftarrow 2p} = 6.25 \times 10^8 \text{ s}^{-1}$ and $\tau_{2p} = 1.60 \text{ ns}$. They should all be the same because the zero-point fluctuations of the electromagnetic field which induce the transition will have no preferred orientation. (This can also be intuitively deduced on symmetry grounds; since the destination orbital is spherically symmetric, the rate should not depend on which way the $2p$ orbital is oriented, which is what m_l determines.)

c) The selection rule on l immediately indicates that – up to first order in perturbation, which is a dipole-mediated transition – the $1s \leftarrow 2s$ transition is forbidden. To see this explicitly, expression **2.9** for the rate can be modified accordingly:

$$\begin{aligned} \text{rate}_{1s \leftarrow 2s} = \frac{4\alpha\omega_{2,1}^3}{3c^2} & \left[\int_0^\infty r^2 dr r R_{2,0}(r) R_{1,0}(r) \int_0^\pi \sin(\theta) d\theta \sin(\theta) \Theta_{0,0}(\theta) \Theta_{0,0}(\theta) \int_0^{2\pi} d\phi \cos(\phi) \Phi_0^*(\phi) \Phi_0(\phi) \right. \\ & + \int_0^\infty r^2 dr r R_{2,0}(r) R_{1,0}(r) \int_0^\pi \sin(\theta) d\theta \sin(\theta) \Theta_{0,0}(\theta) \Theta_{0,0}(\theta) \int_0^{2\pi} d\phi \sin(\phi) \Phi_0^*(\phi) \Phi_0(\phi) \\ & \left. + \int_0^\infty r^2 dr r R_{2,0}(r) R_{1,0}(r) \int_0^\pi \sin(\theta) d\theta \cos(\theta) \Theta_{0,0}(\theta) \Theta_{0,0}(\theta) \int_0^{2\pi} d\phi \Phi_0^*(\phi) \Phi_0(\phi) \right] \quad \mathbf{2.13} \end{aligned}$$

The radial integral is still nonzero, and the θ integrals for the x and y components are nonzero (the integral of $\sin^2(\theta)$ over $[0, \pi]$ is $\pi/2$), as will clearly be the case for the ϕ integral of the z component. However, the ϕ integrals for the x and y components are obviously zero (integrals of sine and cosine over a full period), and it is straightforward to show that the θ integral for the z component is also zero:

$$\int_0^\pi \sin(\theta) d\theta \cos(\theta) \Theta_{0,0}(\theta) \Theta_{0,0}(\theta) = \frac{1}{4\pi} \int_0^\pi d\theta \sin(\theta) \cos(\theta) = \frac{1}{4\pi} \int_0^\pi d\theta \frac{\sin(2\theta)}{2} = 0$$

Thus, to first order, the transition is forbidden, and the $2s$ state will not decay by spontaneous emission. The key phrase in the previous statement is ‘to first order.’ It turns out that there is a two-photon process whereby that decay can happen (aside from other more complicated physics which can weaken the selection rule on l or n by altering the relative energy levels of the states), but this is a second-order effect, and as might be intuitively predicted, the transition rate is correspondingly much lower as a result. This is why the measured lifetime for the $2s$ state is larger than those of the $2p$ states by 8 orders of magnitude.

3. Given the Coulomb and exchange overlap integrals for the $1s^1 2s^1$ triplet configuration of He (with development given in the problem statement to reach these expressions omitted for brevity):

$$J_{1s,2s} = \int_0^\infty r_1^2 dr_1 \int_0^\infty r_2^2 dr_2 \frac{1}{r_{>}} R_{1,0}^2(r_1) R_{2,0}^2(r_2) \quad 3.1$$

$$K_{1s,2s} = \int_0^\infty r_1^2 dr_1 \int_0^\infty r_2^2 dr_2 \frac{1}{r_{>}} R_{1,0}(r_1) R_{2,0}(r_2) R_{1,0}(r_2) R_{2,0}(r_1) \quad 3.2$$

a) The integrals are effectively two-dimensional, since while the radial functions separate between the radial coordinates for each electron, the coordinates are coupled by $r_{>}$, which means ‘the larger of the two coordinates, r_1 and r_2 , at the point (r_1, r_2) where the integrand is being evaluated.’ To evaluate them numerically in Excel, the trapezoidal formula **2.11** can be employed, with the spreadsheets configured similarly to those in Problem 1, where one coordinate was arrayed along the top row, and the other arrayed along the first column. To evaluate $r_{>}$, it suffices to use the MAX function, which gives as its output the largest of the arguments it is supplied.

The radial functions necessary for the evaluation of **3.1** and **3.2** are tabulated on pg. 191 of the text. The calculation can be performed in so-called ‘natural units’ by using these functions as-is, which will return the energy corrections J and K in units of Hartrees. A grid of $[0.01, 10]$ for both r_1 and r_2 with increment of 0.01 is more than sufficient to accurately compute the values. The formulae necessary for populating the coordinate grid in the spreadsheet are given below:

$J_{1s,2s}$	=B\$2^2*\$A3^2*(1/(MAX(B\$2,\$A3)))*(2*(2/1)^(3/2)*EXP(-2*B\$2))^2*((2/2)^(3/2)*(2-2*\$A3)*EXP(-\$A3))^2
$K_{1s,2s}$	=B\$2^2*\$A3^2*(1/(MAX(B\$2,\$A3)))*(2*(2/1)^(3/2)*EXP(-2*B\$2))*(2*(2/1)^(3/2)*EXP(-2*\$A3))*((2/2)^(3/2)*(2-2*\$A3)*EXP(-\$A3))*((2/2)^(3/2)*(2-2*B\$2)*EXP(-B\$2))

(Note that, as in Problem 1, the formulae assume that the top row of the spreadsheet is empty, to leave room for subsequent calculations.)

The first few rows and columns of the spreadsheet for $J_{1s,2s}$ are given below as an example of how the spreadsheet can be constructed:

r2 --v	r1 -->		J	0.420582
	0.01	0.02	0.03	0.04
0.01	0.000118	0.000227	0.000327	0.000419
0.02	0.000227	0.000872	0.001257	0.00161
0.03	0.000327	0.001256	0.002716	0.003479

The trapezoidal integration formula (assuming the grid is laid out as described above), would be:

$$=(\text{SUM}(\text{B3:ALM1002})-0.5*(\text{SUM}(\text{C3:ALM3})+\text{SUM}(\text{ALM4:ALM1001})+\text{SUM}(\text{C1002:ALM1002})+\text{SUM}(\text{B4:B1001}))-0.25*(\text{B3+ALM3+B1002+ALM1002}))* (10/(1002-3))^2$$

with $(b - a)/N = 10/999$ for both axes (hence the square in the formula), and the edges and corners of the grid treated as specified in **2.11**, since the rule is based around the midpoints of the discrete grid used for the integration. The final calculated results for the $J_{1s,2s}$ and $K_{1s,2s}$ expressions in **3.1** and **3.2** are ≈ 0.421 Hartree and ≈ 0.044 Hartree, respectively. This gives a triplet energy for the configuration, correct to the first order approximations made, and within numerical error, of:

$$E_{1s,2s,\text{triplet}} = E_{1s} + E_{2s} + J_{1s,2s} - K_{1s,2s} = \left(-\frac{2^2}{1^2} - \frac{2^2}{2^2} + 0.421 - 0.044 \right) \text{Hartree} = -2.123 \text{ Hartree} \quad 3.3$$

where $E_n = -Z^2/n^2$ in units of Hartree, and $K_{1s,2s}$ enters with a minus sign because a triplet state is specified, which is antisymmetric under exchange of the orbital part of the wavefunction (the spin part is symmetric, with both spins the same for a triplet spin state with $S = S_1 + S_2 = 1/2 + 1/2 = 1$).

b) In order to compute $J_{1s,2p}$ and $K_{1s,2p}$, it is necessary to return to the general expressions for these energy corrections, and work out which terms in the expansion of r_{12}^{-1} contribute to the integrals. On the basis that the electronic repulsion will be the same regardless of which $2p$ orbital is used in the calculation, it is simplest to proceed (as granted in the question statement) with the $m_l = 0$ case. The general expressions are as follows:

$$J_{1s,2p} = \int_{-\infty}^{\infty} d\vec{x}_1 \int_{-\infty}^{\infty} d\vec{x}_2 \frac{(1s)^2(\vec{x}_1)(2p)^2(\vec{x}_2)}{r_{12}} \quad 3.4$$

$$K_{1s,2p} = \int_{-\infty}^{\infty} d\vec{x}_1 \int_{-\infty}^{\infty} d\vec{x}_2 \frac{(1s)(\vec{x}_1)(1s)(\vec{x}_2)(2p)(\vec{x}_1)(2p)(\vec{x}_2)}{r_{12}} \quad 3.5$$

The spherical harmonic expansion of r_{12}^{-1} , which parcels its dependence on the coordinates of both electrons into separate spherical harmonic functions which independently depend on one set of coordinates or the other, is as follows:

$$\frac{1}{r_{12}} = \sum_{l=0}^{\infty} \frac{4\pi}{2l+1} \sum_{m_l=-l}^l (-1)^{m_l} \frac{r_{<}^l}{r_{>}^{l+1}} Y_{l,m_l}^*(\theta_1, \phi_1) Y_{l,m_l}(\theta_2, \phi_2) \quad 3.6$$

The radial function for the $2p$ state is $R_{2,1}(r)$, and the spherical harmonic for the $m_l = 0$ case is $Y_{1,0}(\theta, \phi)$. Applying these, along with **3.6**, in **3.4** for $J_{1s,2p}$ and explicitly writing out the integrals in spherical coordinates for both sets of electron coordinates gives:

$$\begin{aligned} J_{1s,2p} &= \int_0^{\infty} r_1^2 dr_1 \int_0^{\pi} \sin(\theta_1) d\theta_1 \int_0^{2\pi} d\phi_1 \int_0^{\infty} r_2^2 dr_2 \int_0^{\pi} \sin(\theta_2) d\theta_2 \int_0^{2\pi} d\phi_2 \\ &\quad \times \sum_{l=0}^{\infty} \frac{4\pi}{2l+1} \sum_{m_l=-l}^l (-1)^{m_l} \frac{r_{<}^l}{r_{>}^{l+1}} Y_{l,m_l}^*(\theta_1, \phi_1) Y_{l,m_l}(\theta_2, \phi_2) R_{1,0}^2(r_1) R_{2,1}^2(r_2) Y_{0,0}^2(\theta_1, \phi_1) Y_{1,0}^2(\theta_2, \phi_2) \\ &= \sum_{l=0}^{\infty} \frac{4\pi}{2l+1} \sum_{m_l=-l}^l (-1)^{m_l} \int_0^{\infty} r_1^2 dr_1 \int_0^{\infty} r_2^2 dr_2 \frac{r_{<}^l}{r_{>}^{l+1}} R_{1,0}^2(r_1) R_{2,1}^2(r_2) \\ &\quad \times \underbrace{\int_0^{\pi} \sin(\theta_1) d\theta_1 \int_0^{2\pi} d\phi_1 Y_{l,m_l}^*(\theta_1, \phi_1) Y_{0,0}^2(\theta_1, \phi_1)}_{\langle Y_{l,m_l} Y_{0,0} | Y_{0,0} \rangle} \underbrace{\int_0^{\pi} \sin(\theta_2) d\theta_2 \int_0^{2\pi} d\phi_2 Y_{l,m_l}(\theta_2, \phi_2) Y_{1,0}^2(\theta_2, \phi_2)}_{\langle Y_{1,0}^2 | Y_{l,m_l} \rangle} \end{aligned} \quad 3.7$$

The (angular) brackets are written with $Y_{0,0}$ and $Y_{1,0}$ complex conjugated in the (θ_1, ϕ_1) and (θ_2, ϕ_2) integrals, respectively, by taking advantage of the fact that both are real, so complex conjugation of them is trivial. Working with the first bracket:

$$\langle Y_{l,m_l} Y_{0,0} | Y_{0,0} \rangle = (4\pi)^{-\frac{1}{2}} \langle Y_{l,m_l} | Y_{0,0} \rangle = (4\pi)^{-\frac{1}{2}} \delta_{l,0} \delta_{m_l,0} \quad 3.8$$

where the fact that $Y_{0,0}(\theta, \phi) = (4\pi)^{-\frac{1}{2}}$ is a constant has been employed to move one factor of $Y_{0,0}$ outside of the integral, and then the orthonormality of the $Y_{l,m_l}(\theta, \phi)$ has been employed on the second step. [The Kronecker delta notation is mathematical shorthand for ‘select only those terms whose index – l or m_l in this case – match the given value.’]

The second bracket is more complicated, because $Y_{1,0}(\theta, \phi)$ is not a constant, and so cannot be simply taken outside of the integral. Note that $Y_{1,0}^2(\theta, \phi) = (4\pi/3)^{-1} \cos^2(\theta)$, and that $Y_{2,0} = (16\pi/5)^{-\frac{1}{2}}(3 \cos^2(\theta) - 1)$, such that:

$$\cos^2(\theta) = \frac{1}{3} \left[\left(\frac{5}{16\pi} \right)^{\frac{1}{2}} Y_{2,0} + 1 \right] \Rightarrow Y_{1,0}^2(\theta, \phi) = \left(\frac{4\pi}{3} \right)^{-1} \frac{1}{3} \left[\left(\frac{5}{16\pi} \right)^{\frac{1}{2}} Y_{2,0}(\theta, \phi) + 1 \right] = \sqrt{\frac{5}{256\pi^3}} Y_{2,0}(\theta, \phi) + \frac{1}{(4\pi)^{\frac{1}{2}} Y_{0,0}(\theta, \phi)} \quad 3.9$$

Applying this result in the second bracket of **3.7**:

$$\langle Y_{1,0}^2 | Y_{l,m_l} \rangle = \sqrt{\frac{5}{256\pi^3}} \langle Y_{2,0} | Y_{l,m_l} \rangle + (4\pi)^{-\frac{1}{2}} \langle Y_{0,0} | Y_{l,m_l} \rangle = \sqrt{\frac{5}{256\pi^3}} \delta_{l,2} \delta_{m_l,0} + (4\pi)^{-\frac{1}{2}} \delta_{l,0} \delta_{m_l,0} \quad 3.10$$

Inserting the results **3.8** and **3.10** for the spherical harmonic brackets into **3.7**, the result is that:

$$J_{1s,2p} = \sum_{l=0}^{\infty} \frac{4\pi}{2l+1} \sum_{m_l=-l}^l (-1)^{m_l} \int_0^{\infty} r_1^2 dr_1 \int_0^{\infty} r_2^2 dr_2 \frac{r_1^l}{r_2^{l+1}} R_{1,0}^2(r_1) R_{2,1}^2(r_2) \left[(4\pi)^{-\frac{1}{2}} \delta_{l,0} \delta_{m_l,0} \right] \left[\sqrt{\frac{5}{256\pi^3}} \delta_{l,2} \delta_{m_l,0} + (4\pi)^{-\frac{1}{2}} \delta_{l,0} \delta_{m_l,0} \right] \quad 3.11$$

The Kronecker δ 's in the second of the terms in the final square bracket are redundant when everything is multiplied out, since they specify the same indices in the sum. On the other hand, they are in conflict in first term – the $\delta_{l,0}$ and the $\delta_{l,2}$ cannot be simultaneously satisfied by the same term in the sum (each term only carries one solitary l value, after all), which means that if the angular integrations over each coordinate were carried out sequentially, those terms would be zero in the end via orthogonality of the spherical harmonics. Thus, **3.11** becomes:

$$\begin{aligned} J_{1s,2p} &= (4\pi)^{-\frac{1}{2}} (4\pi)^{-\frac{1}{2}} \sum_{l=0}^{\infty} \frac{4\pi}{2l+1} \sum_{m_l=-l}^l (-1)^{m_l} \delta_{l,0} \delta_{m_l,0} \int_0^{\infty} r_1^2 dr_1 \int_0^{\infty} r_2^2 dr_2 \frac{r_1^l}{r_2^{l+1}} R_{1,0}^2(r_1) R_{2,1}^2(r_2) \\ &= (4\pi)^{-1} \frac{4\pi}{2(0)+1} (-1)^{(0)} \int_0^{\infty} r_1^2 dr_1 \int_0^{\infty} r_2^2 dr_2 \frac{r_1^{(0)}}{r_2^{(0)+1}} R_{1,0}^2(r_1) R_{2,1}^2(r_2) \\ &= \int_0^{\infty} r_1^2 dr_1 \int_0^{\infty} r_2^2 dr_2 \frac{1}{r_2} R_{1,0}^2(r_1) R_{2,1}^2(r_2) \end{aligned} \quad 3.12$$

At this point, equation **3.12** must be integrated, and it is most straightforward to do so numerically, as in **a)**. In fact, copying the spreadsheet from **a)** and simply replacing the $R_{2,0}^2(r_2)$ with $R_{2,1}^2(r_2)$ will accomplish this calculation, as the integral is otherwise identical. This was a significant amount of analytical work to change a single index compared with the $J_{1s,2s}$ expression! As will be demonstrated below, the change in going from $K_{1s,2s}$ to $K_{1s,2p}$ is not as straightforward. Numerically integrating **3.12** using the trapezoidal method as in **a)** will yield a value of $J_{1s,2p} \approx 0.486$ Hartree. The Excel formula to fill the grid, laid out as in **a)**, is as follows:

$J_{1s,2p}$	=B\$2^2*\$A3^2*(1/MAX(B\$2,\$A3))*((2*(2/1)^(3/2)*EXP(-2*B\$2))^2*((1/(SQRT(3))))*(2/2)^(3/2)*2*\$A3*EXP(-\$A3))^2
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To calculate $K_{1s,2p}$, starting from **3.5** and inserting the relevant radial functions and the expansion of r_{12}^{-1} gives:

$$\begin{aligned} K_{1s,2p} &= \sum_{l=0}^{\infty} \frac{4\pi}{2l+1} \sum_{m_l=-l}^l (-1)^{m_l} \int_0^{\infty} r_1^2 dr_1 \int_0^{\infty} r_2^2 dr_2 \frac{r_1^l}{r_2^{l+1}} R_{1,0}(r_1) R_{1,0}(r_2) R_{2,1}(r_1) R_{2,1}(r_2) \\ &\quad \times \underbrace{\int_0^{\pi} \sin(\theta_1) d\theta_1 \int_0^{2\pi} d\phi_1 Y_{l,m_l}^*(\theta_1, \phi_1) Y_{0,0}(\theta_1, \phi_1) Y_{1,0}(\theta_1, \phi_1)}_{\langle Y_{l,m_l} Y_{0,0} | Y_{1,0} \rangle} \underbrace{\int_0^{\pi} \sin(\theta_2) d\theta_2 \int_0^{2\pi} d\phi_2 Y_{l,m_l}(\theta_2, \phi_2) Y_{0,0}(\theta_2, \phi_2) Y_{1,0}(\theta_2, \phi_2)}_{\langle Y_{1,0} | Y_{l,m_l} Y_{0,0} \rangle} \end{aligned} \quad 3.13$$

In this case, it turns out that both spherical harmonic brackets are complex conjugates of each other (where use has once again been made of the fact that $Y_{0,0}(\theta, \phi)$ and $Y_{1,0}(\theta, \phi)$ are real), so both will have the same outcome as far as decimating the summation is concerned. To evaluate the bracket, note that:

$$\langle Y_{l,m_l} Y_{0,0} | Y_{1,0} \rangle = (4\pi)^{-\frac{1}{2}} \langle Y_{l,m_l} | Y_{1,0} \rangle = (4\pi)^{-\frac{1}{2}} \delta_{l,1} \delta_{m_l,0} \quad 3.14$$

similar to the result **3.8** above. Applying this result in **3.13** yields:

$$\begin{aligned}
 K_{1s,2p} &= \sum_{l=0}^{\infty} \frac{4\pi}{2l+1} \sum_{m_l=-l}^l (-1)^{m_l} \int_0^{\infty} r_1^2 dr_1 \int_0^{\infty} r_2^2 dr_2 \frac{r_{<}^l}{r_{>}^{l+1}} R_{1,0}(r_1) R_{1,0}(r_2) R_{2,1}(r_1) R_{2,1}(r_2) \left[(4\pi)^{-\frac{1}{2}} \delta_{l,1} \delta_{m_l,0} \right] \left[(4\pi)^{-\frac{1}{2}} \delta_{l,1} \delta_{m_l,0} \right] \\
 &= (4\pi)^{-1} \frac{4\pi}{2(1)+1} (-1)^{(0)} \int_0^{\infty} r_1^2 dr_1 \int_0^{\infty} r_2^2 dr_2 \frac{r_{<}^{(1)}}{r_{>}^{(1)+1}} R_{1,0}(r_1) R_{1,0}(r_2) R_{2,1}(r_1) R_{2,1}(r_2) \\
 &= \frac{1}{3} \int_0^{\infty} r_1^2 dr_1 \int_0^{\infty} r_2^2 dr_2 \frac{r_{<}}{r_{>}^2} R_{1,0}(r_1) R_{1,0}(r_2) R_{2,1}(r_1) R_{2,1}(r_2)
 \end{aligned}$$

3.15

Proceeding to numerically integrate **3.15** as above will yield a value for $K_{1s,2p} \approx 0.034$ Hartree, via the following Excel syntax (where the grid layout of **a**) is assumed):

$K_{1s,2p}$	<code>= (1/3)*B\$2^2*\$A3^2*(MIN(B\$2,\$A3)/(MAX(B\$2,\$A3))^2)*(2*(2/1)^(3/2)*EXP(-2*B\$2))*(2*(2/1)^(3/2)*EXP(-2*\$A3))*((1/(SQRT(3))))*(2/2)^(3/2)*2*B\$2*EXP(-B\$2))*((1/(SQRT(3))))*(2/2)^(3/2)*2*\$A3*EXP(-\$A3))</code>
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This gives a triplet energy for the $1s2p$ configuration, correct to the first order approximations made, and within numerical error, of:

$$E_{1s,2p,\text{triplet}} = E_{1s} + E_{2p} + J_{1s,2p} - K_{1s,2p} = \left(-\frac{2^2}{1^2} - \frac{2^2}{2^2} + 0.487 - 0.034 \right) \text{Hartree} = -2.048 \text{Hartree}$$

3.16

Contrasting with the value of -2.125 Hartree obtained for the $1s2s$ configuration, it is clear that the $1s2p$ configuration has the greater energy of the two excited states, once the energy corrections for inter-electron repulsion and exchange are incorporated (they are degenerate in energy otherwise). This is consistent with the familiar Aufbau principle, which suggests that adding an electron into a $2p$ state should occur only if the $2s$ orbitals (both spin-up and spin-down) are already occupied, since Pauli exclusion only permits one electron per unique set of quantum numbers. Further, triplet configurations will be lower in energy than singlet configurations, because of the sign difference on the K correction between triplet and singlet states, which demonstrates the first of Hund's rules, wherein configurations with maximal spin are most favourable.