Solutions to the final exam
TFY4210 – Applied quantum mechanics
May 23, 2007

Problem 1

a) The functional $F[n]$ is said to be *universal* because it is independent of the external potential v_{ext} and does not refer to a specific system. This implies that the same $F[n]$ is to be used for *all* electron structure problems, whether the calculation involves only a single atom or a molecule adsorbed on a metal surface.

b) Normalising:

$$\begin{aligned} N &= C \int \mathrm{d}\mathbf{r}\ \mathrm{e}^{-r/R} \\ &= 4\pi C \int_0^\infty \mathrm{d}r\, r^2\, \mathrm{e}^{-r/R} \\ &= 4\pi C R^3 \int_0^\infty \mathrm{d}t\, t^2\, \mathrm{e}^{-t} \\ &= 4\pi C R^3 \Gamma(3) \\ &= 8\pi C R^3 \end{aligned}$$

So $C = N/(8\pi R^3)$, and

$$n(r) = \frac{N}{8\pi R^3}\, \mathrm{e}^{-r/R}$$

It is a good idea to check the units: $[R] = \mathrm{m}$, so the electron (*number*) density has the correct unit $[n] = \mathrm{m}^{-3}$.

c) We first calculate E_{ext}:

$$\begin{aligned} E_{\text{ext}}(R) &= -\frac{Ze^2}{4\pi\varepsilon_0} \int \mathrm{d}\mathbf{r}\, \frac{n(r)}{r} \\ &= -\frac{NZe^2}{32\pi^2\varepsilon_0 R^3} 4\pi \int_0^\infty \mathrm{d}r\, r\, \mathrm{e}^{-r/R} \\ &= -\frac{e^2}{8\pi\varepsilon_0} \frac{NZ}{R^3} R^2 \int_0^\infty \mathrm{d}t\, t\, \mathrm{e}^{-t} \end{aligned}$$

$$= -\frac{e^2}{8\pi\varepsilon_0}\frac{NZ}{R}\Gamma(2)$$

$$= -\underbrace{\frac{e^2}{8\pi\varepsilon_0}}_{\equiv C_1}\frac{NZ}{R}$$

(Note that $[e^2/(\varepsilon_o R)] = \mathrm{C}^2/(\mathrm{C}^2\mathrm{J}^{-1}\mathrm{m}^{-1}\mathrm{m}) = \mathrm{J}$, so $[E_{\mathrm{ext}}] = \mathrm{J}$.)
Then the kinetic energy T_{TF}:

$$T_{\mathrm{TF}}(R) = A_s \int \mathrm{d}\mathbf{r}\, n^{5/3}(r)$$

$$= A_s \frac{N^{5/3}}{(8\pi)^{5/3}R^5} 4\pi \int_0^\infty \mathrm{d}r\, r^2\, \mathrm{e}^{-5r/3R}$$

$$= A_s \frac{N^{5/3}}{(8\pi)^{5/3}R^5} 4\pi \left(\frac{3}{5}R\right)^3 \int_0^\infty \mathrm{d}t\, t^2\, \mathrm{e}^{-t}$$

$$= A_s \frac{N^{5/3}}{(8\pi)^{5/3}R^5} 4\pi \left(\frac{3}{5}R\right)^3 \Gamma(3)$$

$$= \underbrace{\frac{27}{125}\frac{A_s}{(8\pi)^{2/3}}}_{\equiv C_2}\frac{N^{5/3}}{R^2}$$

(Units: $A_s \propto \hbar^2/m_e$ so $[A_s] = \mathrm{J}^2\mathrm{s}^2/\mathrm{kg} = \mathrm{Jm}^2$ and $[T_{\mathrm{TF}}] = \mathrm{Jm}^2\mathrm{m}^{-2} = \mathrm{J}$.)
We finally calculate the Hartree energy:

$$E_{\mathrm{H}}(R) = \frac{e^2}{8\pi\varepsilon_0}\int \mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2 \frac{n(r_1)n(r_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

$$= \frac{e^2}{(8\pi)^3\varepsilon_0}\frac{N^2}{R^6}\int \mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2 \frac{\mathrm{e}^{-(r_1+r_2)/R}}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

Introducing the new parameters $\mathbf{s}_1 = R\mathbf{r}_1$ and $\mathbf{s}_2 = R\mathbf{r}_2$:

$$E_{\mathrm{H}}(R) = \frac{e^2}{(8\pi)^3\varepsilon_0}\frac{N^2}{R}\int \mathrm{d}\mathbf{s}_1\mathrm{d}\mathbf{s}_2 \frac{\mathrm{e}^{-(s_1+s_2)}}{|\mathbf{s}_1 - \mathbf{s}_2|}$$

Then we use the expansion (given on page 5 of the exam set):

$$\frac{1}{|\mathbf{s}_1 - \mathbf{s}_2|} = \frac{1}{s_1}\sum_{l,m}\left(\frac{4\pi}{2l+1}\right)\left(\frac{s_2}{s_1}\right)^l Y_{lm}(\theta_1,\phi_1)Y_{lm}(\theta_2,\phi_2)$$

when $s_2 > s_1$, and with s_1 and s_2 interchanged when $s_2 < s_1$. Our trial electron density $n(r)$ is independent of angles, so the integration over the angles is easy. Only the spherical harmonics depend on the angles, so

$$\int \mathrm{d}\Omega_1 \int \mathrm{d}\Omega_2 \frac{1}{|\mathbf{s}_1 - \mathbf{s}_2|} = \frac{1}{s_1} \sum_{l,m} \left(\frac{4\pi}{2l+1}\right) \left(\frac{s_2}{s_1}\right)^l \int \mathrm{d}\Omega_1 \, Y_{lm}(\theta_1, \phi_1) \int \mathrm{d}\Omega_2 \, Y_{lm}(\theta_2, \phi_2)$$

Since

$$\begin{aligned} \int \mathrm{d}\Omega_1 \, Y_{lm}(\theta_1, \phi_1) &= \sqrt{4\pi} \int \mathrm{d}\Omega_1 \, Y^*_{00}(\theta_1, \phi_1) Y_{lm}(\theta_1, \phi_1) \\ &= \sqrt{4\pi} \delta_{l,0} \delta_{m,0} \end{aligned}$$

we get

$$\int \mathrm{d}\Omega_1 \int \mathrm{d}\Omega_2 \frac{1}{|\mathbf{s}_1 - \mathbf{s}_2|} = \begin{cases} (4\pi)^2/s_1 & : \quad s_2 > s_1 \\ (4\pi)^2/s_2 & : \quad s_2 < s_1 \end{cases}$$

The radial integration must be split into two parts, one with $s_2 < s_1$ and one with $s_2 > s_1$:

$$\begin{aligned} E_{\mathrm{H}}(R) &= \frac{1}{(8\pi)^3 \varepsilon_0} \frac{e^2 N^2}{R} (4\pi)^2 \int_0^\infty \mathrm{d}s_2 \, s_2^2 \, \mathrm{e}^{-s_2} \left[\int_0^{s_2} \mathrm{d}s_1 \, \frac{s_1^2}{s_2} \, \mathrm{e}^{-s_1} + \int_{s_2}^\infty \mathrm{d}s_1 \, \frac{s_1^2}{s_1} \, \mathrm{e}^{-s_1} \right] \\ &= \frac{1}{32\pi\varepsilon_0} \frac{e^2 N^2}{R} \int_0^\infty \mathrm{d}s_2 \, s_2^2 \, \mathrm{e}^{-s_2} \left[\frac{2}{s_2} - \frac{1}{s_2}(2 + 2s_2 + s_2^2) \, \mathrm{e}^{-s_2} + (1 + s_2) \, \mathrm{e}^{-s_2} \right] \\ &= \frac{1}{32\pi\varepsilon_0} \frac{e^2 N^2}{R} \left[2 \int_0^\infty \mathrm{d}s_2 \, s_2 \, \mathrm{e}^{-s_2} - 2 \int_0^\infty \mathrm{d}s_2 \, s_2 \, \mathrm{e}^{-2s_2} - \int_0^\infty \mathrm{d}s_2 \, s_2^2 \, \mathrm{e}^{-2s_2} \right] \\ &= \frac{1}{32\pi\varepsilon_0} \frac{e^2 N^2}{R} \left[2\Gamma(2) - \frac{1}{2}\Gamma(2) - \frac{1}{8}\Gamma(3) \right] \\ &= \frac{5}{32} \left(\frac{e^2}{4\pi\varepsilon_0} \right) \frac{N^2}{R} \end{aligned}$$

(Units: $[E_{\mathrm{H}}] = [e^2/(\varepsilon_o R)] = \mathrm{C}^2/(\mathrm{C}^2\mathrm{J}^{-1}\mathrm{m}^{-1}\mathrm{m}) = \mathrm{J}$)

d) We can find an approximation for the ground state energy by minimising

$$\begin{aligned} E(R) &= E_{\mathrm{ext}}(R) + T_{\mathrm{TF}}(R) + E_{\mathrm{H}}(R) \\ &= -C_1 \frac{NZ}{R} + C_2 \frac{N^{5/3}}{R^2} + C_k \frac{N^2}{R} \\ &= -\left(C_1 Z - C_k N\right) \frac{N}{R} + C_2 \frac{N^{5/3}}{R^2} \end{aligned} \tag{1}$$

Here I have introduced

$$C_k = \frac{5}{32}\frac{1}{4\pi\varepsilon_0}\ .$$

We first find the value $R_{\min}$ that minimise $E(R)$:

$$\left.\frac{\partial E(R)}{\partial R}\right|_{R=R_{\min}} = 0 = (C_1 Z - C_k N)\,\frac{N}{R_{\min}^2} - 2C_2\frac{N^{5/3}}{R_{\min}^3}$$

which gives us:

$$R_{\min} = \frac{2C_2 N^{2/3}}{C_1 Z - C_k N}$$

Substituting this value in equation (1), we get our approximation for the ground state energy as a function of N and Z:

$$\begin{aligned}
E(N,Z) &= -(C_1 Z - C_k N)\,\frac{N}{R_{\min}} + C_2\frac{N^{5/3}}{R_{\min}^2} \\
&= -\left[(C_1 Z - C_k N) - C_2 N^{2/3}\frac{1}{R_{\min}}\right]\frac{N}{R_{\min}} \\
&= -\left[(C_1 Z - C_k N) - \frac{1}{2}(C_1 Z - C_k N)\right] N^{1/3}\frac{(C_1 Z - C_k N)}{2C_2} \\
&= -\frac{1}{4}N^{1/3}\frac{(C_1 Z - C_k N)^2}{C_2}
\end{aligned}$$

The approximation for the ground state electron density is:

$$\begin{aligned}
n(r,N,Z) &= \frac{N}{8\pi R_{\min}^3}\,\mathrm{e}^{-r/R_{\min}} \\
&= \frac{(C_1 Z - C_k N)^3}{64\pi N C_2^3}\,\mathrm{e}^{-r(C_1 Z - C_k N)/(2C_2 N^{2/3})}
\end{aligned}$$

e) Neutral atom, $N = Z$:

$$\begin{aligned}
E_{\mathrm{GS}}(Z,Z) &= -\frac{1}{4}Z^{1/3}\frac{(C_1 Z - C_k Z)^2}{C_2} \\
&= -\underbrace{\frac{1}{4}\frac{(C_1 - C_k)^2}{C_2}}_{\equiv C_3} Z^{7/3}
\end{aligned}$$

Our value for C_3 is

$$\begin{aligned} C_3 &= \frac{1}{4}\frac{(C_1 - C_k)^2}{C_2} \\ &= \frac{1}{4}\frac{e^4}{16\pi^2\varepsilon_0^2}\left(\frac{1}{2} - \frac{5}{32}\right)^2 \frac{125}{27}\frac{(8\pi)^{2/3}}{A_s} \\ &= \frac{5^4 11^2}{2^{15}3^4}\left(\frac{8}{3\pi}\right)^{2/3}\frac{e^4 m_e}{\pi^2\varepsilon_0^2\hbar^2} \\ &\approx 1.7818 \cdot 10^{-18}\ \mathrm{J} \end{aligned}$$

Converted to the Rydberg unit:

$$C_3 = 0.81740\ \mathrm{Ry}$$

So, with our choice of trial electron density we are almost 50% in error compared to the exact value. At least we have found an upper limit to the ground state energy (as expected for a variational approximation):

$$E_{\mathrm{GS}}^{\mathrm{approx}} = -0.81740\, Z^{7/3}\ \mathrm{Ry}$$

g) For a neutral atom our approximation to the electron density is:

$$n(r, Z) = \frac{Z^2\gamma^3}{8\pi}\,\mathrm{e}^{-\gamma r Z^{1/3}}$$

where

$$\gamma = (C_1 - C_k)/(2C_2) = \frac{1375}{1728}\frac{e^2}{4\pi\varepsilon_0}\frac{(8\pi)^{2/3}}{A_s} \approx 4.4936 \cdot 10^{10}\,\mathrm{m}^{-1}$$

which is larger than zero, so our approximate electron density is a exponentially decreasing function of r. Figure 1 shows plots of the electron density (more precisely the radial distribution of electrons $4\pi r^2 n(r)$) for Xe. The plot on the left hand side shows the result of a (much) more precise LDA (local density approximation) calculation (Note that they have used atomic units, so the values along the r-axis differ in the two plots) and on the right hand side is a plot of our electron density. As you can see, our electron density lacks the shell structure seen in the LDA-plot.

h) In our approximation we have

- *not* included the exchange energy-contribution to the total energy.

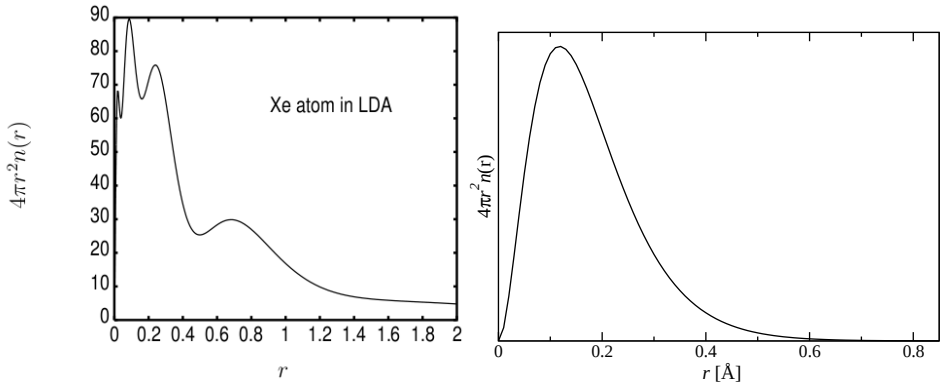

Figure 1:

– *not* included the electron correlation-contribution to the total energy.
– used a rather crude approximation for the kinetic energy (assumed that it is equal to the kinetic energy of a non-interacting electron gas (ideal Fermi gas).

Problem 2

a) Our starting point is

$$\mathrm{i}\hbar\frac{\partial\Psi}{\partial t} = H\Psi$$

where $H = c\sqrt{\mathbf{p}^2}$ for a massless particle. Can the square root be linearised?

$$\sqrt{\mathbf{p}^2} = \alpha_1 p_1 + \alpha_2 p_2 + \alpha_3 p_3$$

where α_i (with $i = 1, 2, 3$) are unknown quantities to be determined. Take the square of each side of this equation:

$$p_1^2 + p_2^2 + p_3^2 = \alpha_1^2 p_1^2 + \alpha_2^2 p_2^2 + \alpha_3^2 p_3^2 +$$
$$+(\alpha_1\alpha_2 + \alpha_2\alpha_1)p_1p_2 + (\alpha_1\alpha_3 + \alpha_3\alpha_1)p_1p_3 + (\alpha_3\alpha_2 + \alpha_2\alpha_3)p_2p_3$$

The right and left hand side are equal if the quantities α_i satisfy the *anti*-commutator relations

$$\alpha_i\alpha_j + \alpha_j\alpha_i \equiv \{\alpha_i, \alpha_j\} = 2\delta_{ij}$$

where δ_{ij} is the Kroenecker delta. In addition α_i must be hermitian $\alpha_i^\dagger = \alpha_i$ (so that H is hermitian). Other properties:

1. $\alpha_i^2 = 1$ so the eigen values of α_i must be ± 1.
2. $\mathrm{Tr}\,\alpha_i = 0$
   Proof: (shown only for α_1)

$$\mathrm{Tr}\,\alpha_1 = \mathrm{Tr}(\alpha_1\alpha_2^2) = \mathrm{Tr}(\alpha_2\alpha_1\alpha_2) = -\,\mathrm{Tr}(\alpha_2^2\alpha_1) = -\,\mathrm{Tr}\,\alpha_1$$

   which implies that $\mathrm{Tr}\,\alpha_1 = 0$. Here I have used the fact that α_1 and α_2 anti-commute, and that the trace is cyclic (i.e., $\mathrm{Tr}(ABC) = \mathrm{Tr}(BCA) = \mathrm{Tr}(CAB)$, etc, for matrices A, B and C).
3. The dimension of α_i must be *even*, i.e. $D = 2n$ where $n = 1, 2, 3, \ldots$ This follows from the property $\mathrm{Tr}\,\alpha_i = 0$ and the fact that the eigen values to α_i are ± 1 (the trace of a matrix is equal to the sum of its eigen values).

Thus, we get the following equation

$$\mathrm{i}\hbar\frac{\partial\Psi}{\partial t} = H\Psi = c\boldsymbol{\alpha}\cdot\hat{\mathbf{p}}\Psi = \frac{c\hbar}{\mathrm{i}}\boldsymbol{\alpha}\cdot\nabla\Psi$$

where $\boldsymbol{\alpha} = (\alpha_1, \alpha_2, \alpha_3)$ are $2n$-dimensional matrices with the above mentioned properties. This is of course exactly the same equation as we get if we put $m = 0$ in the Dirac equation.

b) We need *three* hermitian and mutually anti-commuting matrices. The Pauli matrices are three such matrices, so in this case we can choose $\alpha = \sigma$. We then get the following two equations (when we do not forget both signs $E = \pm c\sqrt{\mathbf{p}}$):

$$\frac{\partial\Psi}{\partial t} = \pm c\boldsymbol{\sigma}\cdot\nabla\Psi$$

We *cannot* use the Pauli matrices when $m \neq 0$, because we then need *four* hermitian, anti-commuting matrices. Assume to the contrary that there is such a fourth matrix:

$$\tilde{\sigma} = \begin{pmatrix} a & b^* \\ b & -a \end{pmatrix}$$

This matrix is hermitian and $\mathrm{Tr}\,\tilde{\sigma} = 0$. It must anti-commute with σ_z:

$$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} a & b^* \\ b & -a \end{pmatrix} = -\begin{pmatrix} a & b^* \\ b & -a \end{pmatrix}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

By multiplying the matrices we get

$$\begin{pmatrix} a & b^* \\ -b & a \end{pmatrix} = \begin{pmatrix} -a & b^* \\ -b & -a \end{pmatrix}$$

thus $a = 0$:

$$\tilde{\sigma} = \begin{pmatrix} 0 & b^* \\ b & 0 \end{pmatrix}$$

Our matrix must also anti-commute with σ_x. It is easy to show that this demand implies $b^* = -b$, so

$$\tilde{\sigma} = \text{constant} \times \begin{pmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix} = \text{constant} \times \sigma_y$$

and so $\tilde{\sigma}$ will *not* anti-commute with σ_y. It is therefore not possible to find four mutually anti-commuting, hermitian 2×2-matrices, and we can therefore not use the Pauli matrices when $m \neq 0$.

c) Assume a plane-wave solution:

$$\Psi = u\, \mathrm{e}^{-\frac{\mathrm{i}}{\hbar}(Et - \mathbf{p}\cdot\mathbf{r})}$$

where u is a two-component spinor. Then we find from on of the Weyl equations:

$$Eu = c\boldsymbol{\sigma} \cdot \mathbf{p}u$$

Written on matrix form:

$$\begin{pmatrix} E + cp_z & c(p_x + \mathrm{i}p_y) \\ c(p_x - \mathrm{i}p_y) & E - cp_z \end{pmatrix} \begin{pmatrix} u_1 \\ u_2 \end{pmatrix} = 0$$

This equation has non-trivial solutions only if the determinant of the system's matrix is zero:

$$(E + cp_z)(E - cp_z) - c^2(p_x + \mathrm{i}p_y)(p_x - \mathrm{i}p_y) = 0$$

which yields:

$$E^2 - c^2\mathbf{p}^2 = 0$$

or equivalently $E = \pm pc$.

Problem 3

a)
- $\mathbf{e}_{\mathbf{k},\lambda}$ are two ($\lambda = 1, 2$) unit polarisation vectors normal to each other.
- $a^\dagger_{\mathbf{k},\lambda}$ and $a_{\mathbf{k},\lambda}$ are creation and annihilation operators. $a^\dagger_{\mathbf{k},\lambda}$ creates a photon in the mode $(\mathbf{k}, \lambda)$, while $a_{\mathbf{k},\lambda}$ destroys a photon in the mode $(\mathbf{k}, \lambda)$.

Coulomb gauge

$$0 = \nabla \cdot \mathbf{A} = \mathrm{i} \sum_{\mathbf{k},\lambda} (\mathbf{k} \cdot \mathbf{e}_{\mathbf{k},\lambda}) \sqrt{\frac{\hbar}{2V\varepsilon_0\omega_{\mathbf{k}}}} \left(a_{\mathbf{k},\lambda}\, \mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{r}} - a^\dagger_{\mathbf{k},\lambda}\, \mathrm{e}^{-\mathrm{i}\mathbf{k}\cdot\mathbf{r}} \right)$$

which implies

$$\mathbf{k} \cdot \mathbf{e}_{\mathbf{k},\lambda} = 0$$

so the polarisation vectors $\mathbf{e}_{\mathbf{k},1}$ and $\mathbf{e}_{\mathbf{k},2}$ are normal to the wave vector $\mathbf{k}$.

b) Now

$$\nabla \cdot (\mathbf{A}(\mathbf{r}) f(\mathbf{r})) = (\nabla \cdot \mathbf{A}(\mathbf{r})) f(\mathbf{r}) + \mathbf{A}(\mathbf{r}) \cdot \nabla f(\mathbf{r})$$

so choosing Coulomb gauge ($\nabla \cdot \mathbf{A} = 0$) we get

$$\nabla \cdot (\mathbf{A}(\mathbf{r}) f(\mathbf{r})) = \mathbf{A}(\mathbf{r}) \cdot \nabla f(\mathbf{r})$$

thus $\mathbf{p}$ and $\mathbf{A}$ *commute* when we use the Coulomb gauge, so

$$\begin{aligned} V &= \frac{e}{2m} (\mathbf{A} \cdot \mathbf{p} + \mathbf{p} \cdot \mathbf{A}) + \frac{e^2}{2m} \mathbf{A}^2 \\ &= \frac{e}{2m} (2\mathbf{A} \cdot \mathbf{p}) + \frac{e^2}{2m} \mathbf{A}^2 \\ &= \frac{e}{m} \mathbf{A} \cdot \mathbf{p} + \frac{e^2}{2m} \mathbf{A}^2 \end{aligned}$$

c) In the case of spontaneous emission there is one extra photon in the final state compared to the initial state. To *lowest* order we therefore must include the term which is linear in the creation operator $a^\dagger_{\mathbf{k},\lambda}$, i.e. $e/m\mathbf{A} \cdot \mathbf{p}$:

$$\begin{aligned} M &\propto \langle \psi_f | \langle \dots, n_{\mathbf{k},\lambda} + 1, \dots | \frac{e}{m} \mathbf{A} \cdot \mathbf{p} | \dots, n_{\mathbf{k},\lambda}, \dots \rangle | \psi_i \rangle \\ &\propto \underbrace{\langle \dots, n_{\mathbf{k},\lambda} + 1, \dots | a^\dagger_{\mathbf{k},\lambda} | \dots, n_{\mathbf{k},\lambda}, \dots \rangle}_{\sqrt{n_{\mathbf{k},\lambda}+1} \langle \dots, n_{\mathbf{k},\lambda}+1, \dots | \dots, n_{\mathbf{k},\lambda}+1, \dots \rangle = \sqrt{n_{\mathbf{k},\lambda}+1}} \end{aligned}$$

d) In the electric dipole approximation we have the selection rule $\Delta l = \pm 1$, thus the transitions

$$\begin{aligned} 4p &\rightarrow 3d \\ &\rightarrow 3s \\ &\rightarrow 2s \\ &\rightarrow 1s \end{aligned}$$

are allowed.