Hydrogen Atom in homogeneous Magnetic Vector Potential

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1 Deriving Schrödinger's Equation of the System

We start with the time-independant Schrödinger equation.

$$H\Psi = E\Psi$$

The Hamiltonian for a proton and electron in a Magnetic Vector Potential $\overrightarrow{A}$ is given by:

$$H = \frac{1}{2m_p}(\frac{\hbar}{i}\nabla_p - eA)^2 + \frac{1}{2m_e}(\frac{\hbar}{i}\nabla_e + eA)^2 - \frac{e^2}{4\pi\epsilon_0|\overrightarrow{r_p} - \overrightarrow{r_e}|}$$

We can now introduce the centre of mass

$$\overrightarrow{R} = \frac{m_p\overrightarrow{r_p} + m_e\overrightarrow{r_e}}{m_p + m_e} = \frac{m_p\overrightarrow{r_p} + m_e\overrightarrow{r_e}}{M} \tag{1}$$

and

$$\overrightarrow{r} = \overrightarrow{r_p} - \overrightarrow{r_e} \tag{2}$$

Since we choose to deal only with homogenious Vector Potentials:

$$\left(\frac{\hbar}{i}\nabla - eA\right)^2 = -\hbar^2\nabla^2 - \frac{2\hbar}{i}eA\nabla + e^2A^2$$

for the proton. And

$$\left(\frac{\hbar}{i}\nabla + eA\right)^2 = -\hbar^2\nabla^2 + \frac{2\hbar}{i}eA\nabla + e^2A^2$$

for the electron.
Now let us just focus on the terms involving the x component for a while.

$$\frac{\partial}{\partial x_p} = \frac{\partial R_x}{\partial x_p}\frac{\partial}{\partial R_x} + \frac{\partial r_x}{\partial x_p}\frac{\partial}{\partial r_x} = \frac{\partial}{\partial R_x}\frac{m_p}{M} + \frac{\partial}{\partial r_x} \tag{3}$$

$$\frac{\partial^2}{\partial x_p^2} = \frac{\partial^2}{\partial R_x^2}\left(\frac{m_p}{M}\right)^2 + \frac{\partial^2}{\partial R_x \partial r_x}\frac{2m_p}{M} + \frac{\partial^2}{\partial r_x^2} \tag{4}$$

and analogous for the electron:

$$\frac{\partial}{\partial x_e} = \frac{\partial R_x}{\partial x_e}\frac{\partial}{\partial R_x} + \frac{\partial r_x}{\partial x_e}\frac{\partial}{\partial r_x} = \frac{\partial}{\partial R_x}\frac{m_e}{M} - \frac{\partial}{\partial r_x} \tag{5}$$

$$\frac{\partial^2}{\partial x_e^2} = \frac{\partial^2}{\partial R_x^2}\left(\frac{m_e}{M}\right)^2 - \frac{\partial^2}{\partial R_x \partial r_x}\frac{2m_e}{M} + \frac{\partial^2}{\partial r_x^2} \tag{6}$$

Now the total Hamiltonian (only considering terms in x) of the system is given by:

$$\begin{aligned} H\Psi =& \frac{1}{2m_p}\Bigg(-\hbar^2\left(\frac{\partial^2}{\partial R_x^2}\left(\frac{m_p}{M}\right)^2 + \frac{\partial^2}{\partial R_x \partial r_x}\frac{2m_p}{M} + \frac{\partial^2}{\partial r_x^2} + \dots\right) \\ & - \frac{2eA\hbar}{i}\begin{pmatrix} \frac{\partial}{\partial R_x}\frac{m_p}{M} + \frac{\partial}{\partial r_x} \\ \vdots \end{pmatrix} + e^2A^2\Bigg)\Psi \\ & + \frac{1}{2m_e}\Bigg(-\hbar^2\left(\frac{\partial^2}{\partial R_x^2}\left(\frac{m_e}{M}\right)^2 - \frac{\partial^2}{\partial R_x \partial r_x}\frac{2m_e}{M} + \frac{\partial^2}{\partial r_x^2} + \dots\right) \\ & + \frac{2eA\hbar}{i}\begin{pmatrix} \frac{\partial}{\partial R_x}\frac{m_p}{M} - \frac{\partial}{\partial r_x} \\ \vdots \end{pmatrix} + e^2A^2\Bigg)\Psi \\ & - \frac{e^2}{4\pi\epsilon_0|\overrightarrow{r}|}\Psi = E\Psi \end{aligned} \tag{7}$$

Now $\frac{1}{2m_p}(-\hbar^2)\frac{\partial^2}{\partial R_x \partial r_x}\frac{2m_p}{M}$ cancels with $-\frac{1}{2m_e}(-\hbar^2)\frac{\partial^2}{\partial R_x \partial r_x}\frac{2m_e}{M}$ and $\frac{1}{2m_p}\left(-\frac{2eA\hbar}{i}\begin{pmatrix} \frac{\partial}{\partial R_x}\frac{m_p}{M} \\ \vdots \end{pmatrix}\right)$ cancels with $\frac{1}{2m_e}\left(\frac{2eA\hbar}{i}\begin{pmatrix} \frac{\partial}{\partial R_x}\frac{m_e}{M} \\ \vdots \end{pmatrix}\right)$

This leaves us with:

$$\begin{aligned} H\Psi =& \frac{1}{2m_p}\Bigg(-\hbar^2\left(\frac{\partial^2}{\partial R_x^2}\left(\frac{m_p}{M}\right)^2 + \frac{\partial^2}{\partial r_x^2} + \dots\right) - \frac{2eA\hbar}{i}\begin{pmatrix} \frac{\partial}{\partial r_x} \\ \vdots \end{pmatrix} + e^2A^2\Bigg)\Psi \\ & + \frac{1}{2m_e}\Bigg(-\hbar^2\left(\frac{\partial^2}{\partial R_x^2}\left(\frac{m_e}{M}\right)^2 + \frac{\partial^2}{\partial r_x^2} + \dots\right) - \frac{2eA\hbar}{i}\begin{pmatrix} \frac{\partial}{\partial r_x} \\ \vdots \end{pmatrix} + e^2A^2\Bigg)\Psi \\ & - \frac{e^2}{4\pi\epsilon_0|\overrightarrow{r}|}\Psi = E\Psi \end{aligned} \tag{8}$$

Since the same simplifications can be done with terms due to y and z components, the Hamiltonian can be simplified to:

$$H\Psi = \left(-\frac{\hbar^2}{2M}\nabla_R^2 - \frac{\hbar^2}{2\mu}\nabla_r^2 - \frac{eA\hbar}{i\mu}\nabla_r - \frac{e^2}{4\pi\epsilon_0|\overrightarrow{r}|}\right)\Psi = \left(E - \frac{e^2A^2}{2\mu}\right)\Psi \tag{9}$$

where $\mu = \frac{m_p m_e}{m_p + m_e}$

2 Applying degenerate Perturbation Theory

The Hamiltonian of the System can be split into two independant parts. One is the term $-\frac{\hbar^2}{2M}\nabla_R^2$ and second are the terms $-\frac{\hbar^2}{2\mu}\nabla_r^2 - \frac{eA\hbar}{i\mu}\nabla_r - \frac{e^2}{4\pi\epsilon_0|\overrightarrow{r}|}$. It is obvious that a Separationsansatz can be applied. This will result in a plane wave for the Centre of Mass and a solution to the latter part of the Hamiltonian.
To solve this, we notice that it can be expressed as a perturbed Hamiltonian of a Hydrogen Atom, where the perturbation part is $H' = -\frac{eA\hbar}{i\mu}\nabla_r$. Thus we now apply Perturbation Theory. The general result of Perturbation Theory is:

$$H^0\Psi' + H'\Psi^0 = E^0\Psi' + E'\Psi^0 \tag{10}$$

Now left-hand multiplying with $\Psi^0_{l'm'}$ and taking the scalar product:

$$\left\langle \Psi^0_{l'm'} \,\middle|\, H^0 \,\middle|\, \Psi' \right\rangle + \left\langle \Psi^0_{l'm'} \,\middle|\, H' \,\middle|\, \Psi^0 \right\rangle = E^0_{lm} \left\langle \Psi^0_{l'm'} \,\middle|\, \Psi' \right\rangle + E' \left\langle \Psi^0_{l'm'} \,\middle|\, \Psi^0 \right\rangle \tag{11}$$

Because H^0 is Hermitian the first term on the left cancels with the first term on the right. This leaves us with:

$$\left\langle \Psi^0_{l'm'} \,\middle|\, H' \,\middle|\, \Psi^0 \right\rangle = E' \left\langle \Psi^0_{l'm'} \,\middle|\, \Psi^0 \right\rangle \tag{12}$$

Since Ψ^0 is an eigenfunction of the Hydrogen Atom, it can be written as a linear combination of Eigenfunctions Ψ^0_{ij} of the Hydrogen Atom, where i and j are Quantum Numbers.

$$\Psi^0 = \sum_{i=0}^{n-1}\sum_{j=-i}^{i} \alpha_{ij}\Psi^0_{ij} \tag{13}$$

Thus we get:

$$\left\langle \Psi^0_{l'm'} \,\middle|\, H' \,\middle|\, \sum_{i=0}^{n-1}\sum_{j=-i}^{i} \alpha_{ij}\Psi^0_{ij} \right\rangle = E' \left\langle \Psi_{l'm'} \,\middle|\, \sum_{i=0}^{n-1}\sum_{j=-i}^{i} \alpha_{ij}\Psi^0_{ij} \right\rangle \tag{14}$$

$$\sum_{i=0}^{n-1}\sum_{j=-i}^{i} \alpha_{ij} \left\langle \Psi^0_{l'm'} \,\middle|\, H' \,\middle|\, \Psi^0_{ij} \right\rangle = \alpha_{l'm'}E \tag{15}$$

Where l' can vary from 0 to $n-1$ and m' from $-l'$ to l'.
Let us for example say that $n = 2$. Then direct expansion of the summation yields:

$$\begin{aligned} &\alpha_{00} \left\langle \Psi^0_{l'm'} \,\middle|\, H' \,\middle|\, \Psi^0_{00} \right\rangle + \alpha_{1,-1} \left\langle \Psi^0_{l'm'} \,\middle|\, H' \,\middle|\, \Psi^0_{1,-1} \right\rangle \\ &+ \alpha_{10} \left\langle \Psi^0_{l'm'} \,\middle|\, H' \,\middle|\, \Psi^0_{10} \right\rangle + \alpha_{11} \left\langle \Psi^0_{l'm'} \,\middle|\, H' \,\middle|\, \Psi^0_{11} \right\rangle = \alpha_{l'm'}E' \end{aligned} \tag{16}$$

Since l' varies from 0 to 1 and m' from -1 to 1, this can be written in matrix notation.

$$\begin{pmatrix} \langle \Psi^0_{0,0} \mid H' \mid \Psi^0_{0,0} \rangle & \langle \Psi^0_{0,0} \mid H' \mid \Psi^0_{1,-1} \rangle & \langle \Psi^0_{0,0} \mid H' \mid \Psi^0_{1,0} \rangle & \langle \Psi^0_{0,0} \mid H' \mid \Psi^0_{1,1} \rangle \\ \langle \Psi^0_{1,-1} \mid H' \mid \Psi^0_{00} \rangle & \langle \Psi^0_{1,-1} \mid H' \mid \Psi^0_{1,-1} \rangle & \langle \Psi^0_{1,-1} \mid H' \mid \Psi^0_{10} \rangle & \langle \Psi^0_{1,-1} \mid H' \mid \Psi^0_{11} \rangle \\ \langle \Psi^0_{1,0} \mid H' \mid \Psi^0_{00} \rangle & \langle \Psi^0_{1,0} \mid H' \mid \Psi^0_{1,-1} \rangle & \langle \Psi^0_{1,0} \mid H' \mid \Psi^0_{10} \rangle & \langle \Psi^0_{1,0} \mid H' \mid \Psi^0_{11} \rangle \\ \langle \Psi^0_{1,1} \mid H' \mid \Psi^0_{00} \rangle & \langle \Psi^0_{1,1} \mid H' \mid \Psi^0_{1,-1} \rangle & \langle \Psi^0_{1,1} \mid H' \mid \Psi^0_{10} \rangle & \langle \Psi^0_{1,1} \mid H' \mid \Psi^0_{11} \rangle \end{pmatrix} \begin{pmatrix} \alpha_{0,0} \\ \alpha_{1,-1} \\ \alpha_{1,0} \\ \alpha_{1,1} \end{pmatrix} =$$

$$E' \begin{pmatrix} \alpha_{0,0} \\ \alpha_{1,-1} \\ \alpha_{1,0} \\ \alpha_{1,1} \end{pmatrix}$$

This is clearly an eigenvalue equation. Therefore the first order correction in the Energy can be solved by finding the Eigenvalues of the matrix above. In order to do this we have to find the elements of the matrix by evaluating $\langle \Psi^0_{op} \mid H' \mid \Psi^0_{lm} \rangle$. However before we embark on evaluating $\langle \Psi^0_{op} \mid H' \mid \Psi^0_{lm} \rangle$, we can apply the following extended theorem:

Let A be a hermitian operator that commutes with H^0 and H'. If Ψ^0_{lm} and $\Psi^0_{l'm'}$ (the degenerate eigenfunction of H^0) are also eigenfunctions of A, with distinct eigenvalues,

$$A\Psi^0_{lm} = \alpha_{lm}\Psi^0_{lm}$$

$$A\Psi^0_{l'm'} = \alpha_{l'm'}\Psi^0_{l'm'}$$

then $\langle \Psi^0_{lm} \mid H' \mid \Psi^0_{l'm'} \rangle = 0$

In our case Ψ^0_{lm} is an Eigenfunction for fixed n of the Hamiltonian of the Hydrogen Atom:

$$\Psi^0_{lm} = \sqrt{\left(\frac{2}{na}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}} \exp\left(-\frac{r}{na}\right) \left(\frac{2r}{na}\right)^l L^{2l+1}_{n-l-1}\left(\frac{2r}{na}\right) Y^m_l(\theta, \phi) \tag{17}$$

Where L^{2l+1}_{n-l-1} is an associated Laguerre Polynomial with the Rodrigues formula:

$$L^p_{q-p}(x) = (-1)^p \frac{d^p}{dx^p}\left(e^x \frac{d^q}{dx^q}(e^{-x}x^q)\right) \tag{18}$$

and

$$Y^m_l(\theta, \phi) = \sqrt{\frac{2l+1}{4\pi}\frac{(l-m)!}{(l+m)!}} e^{im\theta} P^m_l(cos(\phi)) \tag{19}$$

where P^m_l is an associated Legendre Polynomial with the Rodrigues formula:

$$P^m_l(x) = (-1)^m (1-x^2)^{m/2} \frac{d^m}{dx^m}\left(\frac{1}{2^l l!}\frac{d^l}{dx^l}\left(x^2-1\right)^l\right) \tag{20}$$

Moreover for simplicity and without loss of generality we will choose

$$\overrightarrow{A} = \begin{pmatrix} 0 \\ 0 \\ A_z \end{pmatrix} \tag{21}$$

Therefore

$$H' = -\frac{e\hbar A_z}{i\mu}\frac{\partial}{\partial z} = -\frac{e\hbar A_z}{i\mu}\left(cos\left(\phi\right)\frac{\partial}{\partial r} - \frac{sin\left(\phi\right)}{r}\frac{\partial}{\partial \phi}\right) \tag{22}$$

One operator which fulfills the conditions of the theorem is the angular momentum operator in z direction $L_z = \frac{\hbar}{i}\frac{\partial}{\partial\theta}$ with eigenvalue $\hbar m$.Therefore all scalar products $\left\langle \Psi^0_{lm} \,\middle|\, H' \,\middle|\, \Psi^0_{l'm'} \right\rangle$ for which $m \neq m'$ vanish. Note that this is true for all l and l'. For illustration we can now write the simplified matrix for $n = 2$:

$$\begin{pmatrix} \left\langle \Psi^0_{0,0} \middle| H' \middle| \Psi^0_{0,0} \right\rangle & 0 & \left\langle \Psi^0_{0,0} \middle| H' \middle| \Psi^0_{1,0} \right\rangle & 0 \\ 0 & \left\langle \Psi^0_{1,-1} \middle| H' \middle| \Psi^0_{1,-1} \right\rangle & 0 & 0 \\ \left\langle \Psi^0_{1,0} \middle| H' \middle| \Psi^0_{00} \right\rangle & 0 & \left\langle \Psi^0_{1,0} \middle| H' \middle| \Psi^0_{10} \right\rangle & 0 \\ 0 & 0 & 0 & \left\langle \Psi^0_{1,1} \middle| H' \middle| \Psi^0_{11} \right\rangle \end{pmatrix}$$

$$= E' \begin{pmatrix} \alpha_{0,0} \\ \alpha_{1,-1} \\ \alpha_{1,0} \\ \alpha_{1,1} \end{pmatrix}$$

Note that it might be possible to simplify the matrix even further by eliminating the off diagonal elements. This would be possible if we could find a hermitian Operator, which satisfies the condition of the Theorem mentioned above and had distinct eigenvalues in l. However the author was not able to find such an operator. Now in order to evaluate the eigenvalues we must calculate $\left\langle \Psi^0_{lm} \,\middle|\, H' \,\middle|\, \Psi^0_{l'm} \right\rangle$.

2.1 Applying the perturbing Hamiltonian

Now we must apply the perturbing Hamiltonian on the wavefunction $\Psi^0_{lm}$for a Hydrogen Atom.

$$H'\Psi^0_{lm} = -\frac{e\hbar A_z}{i\mu}\left(cos\left(\phi\right)\frac{\partial}{\partial r} - \frac{sin\left(\phi\right)}{r}\frac{\partial}{\partial \phi}\right)\Psi^0_{lm} \tag{23}$$

$$\begin{aligned}\frac{\partial\Psi^0_{lm}}{\partial r} &= \frac{\partial}{\partial r}\left(\sqrt{\left(\frac{2}{na}\right)^3\frac{(n-l-1)!}{2n[(n+l)!]^3}}\exp\left(-\frac{r}{na}\right)\left(\frac{2r}{na}\right)^l L^{2l+1}_{n-l-1}\left(\frac{2r}{na}\right)Y^m_l(\theta,\phi)\right) \\ &= \sqrt{\left(\frac{2}{na}\right)^3\frac{(n-l-1)!}{2n[(n+l)!]^3}}Y^m_l(\theta,\phi)\frac{\partial}{\partial r}\left(\exp\left(-\frac{r}{na}\right)\left(\frac{2r}{na}\right)^l L^{2l+1}_{n-l-1}\left(\frac{2r}{na}\right)\right)\end{aligned}$$

$$\begin{aligned}\frac{\partial}{\partial r}\left(\exp\left(-\frac{r}{na}\right)\left(\frac{2r}{na}\right)^{l}L^{2l+1}_{n-l-1}\left(\frac{2r}{na}\right)\right)=&-\frac{1}{na}\exp\left(-\frac{r}{na}\right)\left(\frac{2r}{na}\right)^{l}L^{2l+1}_{n-l-1}\left(\frac{2r}{na}\right)\\&+\frac{2l}{na}\exp\left(-\frac{r}{na}\right)\left(\frac{2r}{na}\right)^{l-1}L^{2l+1}_{n-l-1}\left(\frac{2r}{na}\right)\\&+\exp\left(-\frac{r}{na}\right)\left(\frac{2r}{na}\right)^{l}\frac{\partial}{\partial r}\left(L^{2l+1}_{n-l-1}\left(\frac{2r}{na}\right)\right)\end{aligned}$$

Using the derivative formula for Associated Laguerre Polynomials[1]

$$\frac{\partial}{\partial r}\left(L^{2l+1}_{n-l-1}\left(\frac{2r}{na}\right)\right)=-\frac{2}{na}L^{2l+2}_{n-l-2}\left(\frac{2r}{na}\right)\tag{24}$$

Introducing $\kappa_l=\sqrt{\left(\frac{2}{na}\right)^3\frac{(n-l-1)!}{2n[(n+l)!]^3}}$

$$\begin{aligned}\frac{\partial\Psi^0_{lm}}{\partial r}=\kappa_l Y^m_l(\theta,\phi)\Bigg(&-\frac{1}{na}\exp\left(-\frac{r}{na}\right)\left(\frac{2r}{na}\right)^{l}L^{2l+1}_{n-l-1}\left(\frac{2r}{na}\right)\\&+\frac{2l}{na}\exp\left(-\frac{r}{na}\right)\left(\frac{2r}{na}\right)^{l-1}L^{2l+1}_{n-l-1}\left(\frac{2r}{na}\right)\\&+\exp\left(-\frac{r}{na}\right)\left(\frac{2r}{na}\right)^{l}\left(-\frac{2}{na}L^{2l+2}_{n-l-2}\left(\frac{2r}{na}\right)\right)\Bigg)\end{aligned}\tag{25}$$

Now we evaluate

$$\begin{aligned}\frac{\partial\Psi^0_{lm}}{\partial\phi}=&\frac{\partial}{\partial\phi}\left(\kappa_l\exp\left(-\frac{r}{na}\right)\left(\frac{2r}{na}\right)^{l}L^{2l+1}_{n-l-1}\left(\frac{2r}{na}\right)Y^m_l(\theta,\phi)\right)\\=&\kappa_l\exp\left(-\frac{r}{na}\right)\left(\frac{2r}{na}\right)^{l}L^{2l+1}_{n-l-1}\left(\frac{2r}{na}\right)\frac{\partial}{\partial\phi}\left(Y^m_l(\theta,\phi)\right)\end{aligned}$$

Using the derivative formula with respect to the polar angle ϕ for Spherical Harmonics for positive m:

$$\frac{\partial}{\partial\phi}\left(Y^m_l(\theta,\phi)\right)=mcot(\phi)Y^m_l(\theta,\phi)+\sqrt{(l+m+1)(l-m)}e^{-i\theta}Y^{m+1}_l(\theta,\phi)\tag{26}$$

And for negative indices:

$$\frac{\partial}{\partial\phi}\left(Y^{-m}_l(\theta,\phi)\right)=mcot(\phi)Y^{-m}_l(\theta,\phi)-\sqrt{(l+m+1)(l-m)}e^{i\theta}Y^{-(m+1)}_l(\theta,\phi)$$

$$\hat{m}=-m$$

[1] http://mathworld.wolfram.com/AssociatedLaguerrePolynomial.html

$$\frac{\partial}{\partial\phi}\left(Y_l^{\hat{m}}(\theta,\phi)\right) = -\hat{m}cot(\phi)Y_l^{\hat{m}}(\theta,\phi) - \sqrt{(l-\hat{m}+1)(l+\hat{m})}e^{i\theta}Y_l^{\hat{m}-1}(\theta,\phi) \tag{27}$$

These two equations can be combined into one equation:

$$\frac{\partial}{\partial\phi}\left(Y_l^{m}(\theta,\phi)\right) = \pm mcot(\phi)Y_l^{m}(\theta,\phi) \pm \sqrt{(l\pm m+1)(l\mp m)}e^{\mp i\theta}Y_l^{m\pm1}(\theta,\phi) \tag{28}$$

Introducing $\gamma_l^m = \sqrt{(l\pm m+1)(l\mp m)}$ we get:

$$\begin{aligned}\frac{\partial\Psi_{lm}^0}{\partial\phi} = \alpha_l \exp\left(-\frac{r}{na}\right)\left(\frac{2r}{na}\right)^l L_{n-l-1}^{2l+1}\left(\frac{2r}{na}\right)\Big(&\pm mcot(\phi)Y_l^m(\theta,\phi)\\ &\pm \gamma_l^m e^{\mp i\theta}Y_l^{m\pm1}(\theta,\phi)\Big)\end{aligned} \tag{29}$$

Now we have the perturbing Hamiltonian operating on the wavefunction of the Hydrogen Atom.

$$H'\Psi_{lm}^0 = -\frac{e\hbar A_z}{i\mu}\frac{\partial\Psi_{lm}^0}{\partial z} = -\frac{e\hbar A_z}{i\mu}\left(cos\,(\phi)\,\frac{\partial\Psi_{lm}^0}{\partial r} - \frac{sin\,(\phi)}{r}\frac{\partial\Psi_{lm}^0}{\partial\phi}\right)$$

2.2 Computing the Scalar Product

Now we need to calculate the scalar product $\left\langle\Psi_{op}^0\,\middle|\,H'\,\middle|\,\Psi_{lm}^0\right\rangle$. Due to the linearity this can be split into two scalar products, which can be split further:

$$\left\langle\Psi_{op}^0\,\middle|\,H'\,\middle|\,\Psi_{lm}^0\right\rangle = -\frac{e\hbar A_z}{i\mu}\left(\left\langle\Psi_{op}^0\,\middle|\,cos\,(\phi)\,\frac{\partial\Psi_{lm}^0}{\partial r}\right\rangle - \left\langle\Psi_{op}^0\,\middle|\,\frac{sin\,(\phi)}{r}\frac{\partial\Psi_{lm}^0}{\partial\phi}\right\rangle\right) \tag{30}$$

We can split the first scalar product into three sub scalar products.

$$\begin{aligned}&\left\langle\Psi_{op}^0\,\middle|\,cos\,(\phi)\,\frac{\partial\Psi_{lm}^0}{\partial r}\right\rangle =\\ &= \left\langle\Psi_{op}^0\,\middle|\,-cos\,(\phi)\,\frac{1}{na}\kappa_l Y_l^m(\theta,\phi)\exp\left(-\frac{r}{na}\right)\left(\frac{2r}{na}\right)^l L_{n-l-1}^{2l+1}\left(\frac{2r}{na}\right)\right\rangle\\ &+ \left\langle\Psi_{op}^0\,\middle|\,cos\,(\phi)\,\frac{2l}{na}\kappa_l Y_l^m(\theta,\phi)\exp\left(-\frac{r}{na}\right)\left(\frac{2r}{na}\right)^{l-1} L_{n-l-1}^{2l+1}\left(\frac{2r}{na}\right)\right\rangle\\ &+ \left\langle\Psi_{op}^0\,\middle|\,-cos\,(\phi)\,\frac{2}{na}\kappa_l Y_l^m(\theta,\phi)\exp\left(-\frac{r}{na}\right)\left(\frac{2r}{na}\right)^l L_{n-l-2}^{2l+2}\left(\frac{2r}{na}\right)\right\rangle\end{aligned} \tag{31}$$

And we can split the second scalar product into two sub scalar products.

$$\left\langle\Psi_{op}^0\,\middle|\,\frac{sin\,(\phi)}{r}\frac{\partial\Psi_{lm}^0}{\partial\phi}\right\rangle =$$

$$= \pm \left\langle \Psi^0_{op} \,\middle|\, \frac{sin\,(\phi)}{r} \alpha_l \exp\left(-\frac{r}{na}\right)\left(\frac{2r}{na}\right)^l L^{2l+1}_{n-l-1}\left(\frac{2r}{na}\right) mcot(\phi) Y^m_l(\theta,\phi) \right\rangle$$
$$\pm \left\langle \Psi^0_{op} \,\middle|\, \frac{sin\,(\phi)}{r} \alpha_l \exp\left(-\frac{r}{na}\right)\left(\frac{2r}{na}\right)^l L^{2l+1}_{n-l-1}\left(\frac{2r}{na}\right) \gamma^m_l e^{\mp i\theta} Y^{m\pm1}_l(\theta,\phi)\right) \right\rangle \quad (32)$$

where

$$\Psi^0_{op} = \kappa_o \exp\left(-\frac{r}{na}\right)\left(\frac{2r}{na}\right)^o L^{2o+1}_{n-o-1}\left(\frac{2r}{na}\right) Y^p_o(\theta,\phi) \quad (33)$$

and

$$\langle f(r,\theta,\phi)\,|\,g(r,\theta,\phi)\rangle = \int_{r=0}^{\infty}\int_{\phi=0}^{\pi}\int_{\theta=0}^{2\pi} r^2 sin(\phi)\overline{f(r,\theta,\phi)} g(r,\theta,\phi) d\theta d\phi dr \quad (34)$$

Introducing $\beta^m_l = \sqrt{\frac{2l+1}{4\pi}\frac{(l-m)!}{(l+m)!}}$, the first part of the first scalar product:

$$\left\langle \Psi^0_{op} \,\middle|\, -cos\,(\phi)\frac{1}{na}\kappa_l Y^m_l(\theta,\phi)\exp\left(-\frac{r}{na}\right)\left(\frac{2r}{na}\right)^l L^{2l+1}_{n-l-1}\left(\frac{2r}{na}\right)\right\rangle$$

$$= -\int_{r=0}^{\infty} \kappa_l\kappa_o \frac{1}{na} r^2 \exp\left(-\frac{2r}{na}\right)\left(\frac{2r}{na}\right)^{l+o} L^{2o+1}_{n-o-1}\left(\frac{2r}{na}\right) L^{2l+1}_{n-l-1}\left(\frac{2r}{na}\right) dr$$
$$\int_{\phi=0}^{\pi} \beta^m_l \beta^p_o sin(\phi) cos(\phi) P^m_l(cos(\phi)) P^p_o(cos(\phi)) d\phi \int_{\theta=0}^{2\pi} e^{im\theta} e^{-ip\theta} d\theta$$

$$= -2\pi \int_{r=0}^{\infty} \kappa_l\kappa_o \frac{1}{na} r^2 \exp\left(-\frac{2r}{na}\right)\left(\frac{2r}{na}\right)^{l+o} L^{2o+1}_{n-o-1}\left(\frac{2r}{na}\right) L^{2l+1}_{n-l-1}\left(\frac{2r}{na}\right) dr$$
$$\int_{\phi=0}^{\pi} \delta_{mp}\beta^m_l \beta^p_o sin(\phi) cos(\phi) P^m_l(cos(\phi)) P^p_o(cos(\phi)) d\phi \quad (35)$$

Now

$$\int_{\phi=0}^{\pi} \delta_{mp}\beta^m_l \beta^p_o sin(\phi) cos(\phi) P^m_l(cos(\phi)) P^p_o(cos(\phi)) d\phi$$
$$= \int_{-1}^{1} \delta_{mp}\beta^m_l \beta^m_o cos(\phi) P^m_l(cos(\phi)) P^m_o(cos(\phi)) d(cos(\phi))$$

Applying integration by parts and using[2]

$$\int_{-1}^{1} P^m_l(x) P^m_o(x) dx = \frac{2(l\pm m)!}{(2l+1)(l\mp m)!}\delta_{lo} \quad (36)$$

$$\int_{-1}^{1} \beta^m_l \beta^m_o cos(\phi) P^m_l(cos(\phi)) P^m_o(cos(\phi)) d(cos(\phi))$$

[2] http://mathworld.wolfram.com/AssociatedLegendrePolynomial.html

$$= \beta_l^m \beta_o^m \delta_{mp}\delta_{lo}\left[\left[\frac{2(l\pm m)!}{(2l+1)(l\mp m)!}cos(\phi)\right]_{cos(\phi)=-1}^{1} + \frac{2(l\pm m)!}{(2l+1)(l\mp m)!}\int_{-1}^{1} sin(\phi)d(cos(\phi))\right]$$

$$= \beta_l^m \beta_o^m \frac{2(l\pm m)!}{(2l+1)(l\mp m)!}\left(2+\frac{\pi}{2}\right)\delta_{mp}\delta_{lo}$$

So substituting into equation (35)

$$-2\pi\int_{r=0}^{\infty}\kappa_l\kappa_o\frac{1}{na}r^2\exp\left(-\frac{2r}{na}\right)\left(\frac{2r}{na}\right)^{l+o}L_{n-o-1}^{2o+1}\left(\frac{2r}{na}\right)L_{n-l-1}^{2l+1}\left(\frac{2r}{na}\right)dr$$
$$\int_{\phi=0}^{\pi}\delta_{mp}\beta_l^m\beta_o^p sin(\phi)cos(\phi)P_l^m(cos(\phi))P_o^p(cos(\phi))d\phi$$

$$= -2\pi\int_{r=0}^{\infty}\delta_{lo}\kappa_l\kappa_o\frac{1}{na}r^2\exp\left(-\frac{2r}{na}\right)\left(\frac{2r}{na}\right)^{l+o}L_{n-o-1}^{2o+1}\left(\frac{2r}{na}\right)L_{n-l-1}^{2l+1}\left(\frac{2r}{na}\right)dr$$
$$\frac{2(l\pm m)!}{(2l+1)(l\mp m)!}\delta_{mp}\beta_l^m\beta_o^m\left(2+\frac{\pi}{2}\right)$$

$$= -2\pi\int_{r=0}^{\infty}\left(\frac{na}{2}\right)^2(\kappa_l)^2\exp\left(-\frac{2r}{na}\right)\left(\frac{2r}{na}\right)^{2l+2}L_{n-l-1}^{2l+1}\left(\frac{2r}{na}\right)L_{n-l-1}^{2l+1}\left(\frac{2r}{na}\right)d\left(\frac{2r}{na}\right)$$
$$\frac{(l\pm m)!}{(2l+1)(l\mp m)!}\delta_{mp}(\beta_l^m)^2\left(2+\frac{\pi}{2}\right)$$

This time we can use[3]

$$\int_{x=0}^{\infty}\exp(-x)x^{k+1}\left[L_n^k(x)\right]^2 dx = n!(n+k)!(2n+k+1) \tag{37}$$

Therefore the first scalar product:

$$\begin{aligned} &= -2\pi\frac{(l\pm m)!}{(2l+1)(l\mp m)!}(\beta_l^m)^2\left(2+\frac{\pi}{2}\right)\left(\frac{na}{2}\right)^2 \\ &\quad (\kappa_l)^2(n-l-1)!(n+l)!(2n+1)\delta_{mp}\delta_{lo} \end{aligned} \tag{38}$$

The second scalar product:

$$\left\langle \Psi_{op}^0 \left| cos\left(\phi\right)\frac{2l}{na}\kappa_l Y_l^m(\theta,\phi)\exp\left(-\frac{r}{na}\right)\left(\frac{2r}{na}\right)^{l-1}L_{n-l-1}^{2l+1}\left(\frac{2r}{na}\right)\right.\right\rangle \tag{39}$$

[3]http://mathworld.wolfram.com/AssociatedLaguerrePolynomial.html

$$
\begin{aligned}
&= \int_{r=0}^{\infty} \kappa_l \kappa_o \frac{2l}{na} r^2 \exp\left(-\frac{2r}{na}\right) \left(\frac{2r}{na}\right)^{l+o-1} L_{n-o-1}^{2o+1}\left(\frac{2r}{na}\right) L_{n-l-1}^{2l+1}\left(\frac{2r}{na}\right) dr \\
&\int_{\phi=0}^{\pi} \beta_l^m \beta_o^p sin(\phi) cos(\phi) P_l^m(cos(\phi)) P_o^p(cos(\phi)) d\phi \int_{\theta=0}^{2\pi} e^{im\theta} e^{-ip\theta} d\theta
\end{aligned} \tag{40}
$$

The integrations with respect to θ and ϕ are the same as in the first scalar product, so:

$$
\begin{aligned}
&= 2\pi \int_{r=0}^{\infty} \delta_{lo} \kappa_l \kappa_o \frac{2l}{na} r^2 \exp\left(-\frac{2r}{na}\right) \left(\frac{2r}{na}\right)^{l+o-1} L_{n-o-1}^{2o+1}\left(\frac{2r}{na}\right) L_{n-l-1}^{2l+1}\left(\frac{2r}{na}\right) dr \\
&\qquad \frac{2(l \pm m)!}{(2l+1)(l \mp m)!} \delta_{mp} (\beta_l^m)^2 \left(2 + \frac{\pi}{2}\right)
\end{aligned}
$$

$$
\begin{aligned}
&= 2\pi \int_{r=0}^{\infty} \delta_{lo} (\kappa_l)^2 l \left(\frac{na}{2}\right)^2 \exp\left(-\frac{2r}{na}\right) \left(\frac{2r}{na}\right)^{2l+1} L_{n-l-1}^{2l+1}\left(\frac{2r}{na}\right) L_{n-l-1}^{2l+1}\left(\frac{2r}{na}\right) d\left(\frac{2r}{na}\right) \\
&\qquad \frac{2(l \pm m)!}{(2l+1)(l \mp m)!} \delta_{mp} (\beta_l^m)^2 \left(2 + \frac{\pi}{2}\right)
\end{aligned}
$$

Now we use[4]

$$
\int_0^{\infty} \exp(-x) x^k \left[L_n^k(x)\right]^2 dx = n!(n+k)! \tag{41}
$$

Therefore the second scalar product:

$$
\begin{aligned}
&= 2\pi \frac{2(l \pm m)!}{(2l+1)(l \mp m)!} (\beta_l^m)^2 \left(2 + \frac{\pi}{2}\right) \left(\frac{na}{2}\right)^2 \\
&\quad (\kappa_l)^2 l (n-l-1)!(n+l)! \delta_{mp} \delta_{lo}
\end{aligned} \tag{42}
$$

The third scalar product:

$$
\left\langle \Psi_{op}^0 \middle| -cos\,(\phi) \frac{2}{na} \kappa_l Y_l^m(\theta,\phi) \exp\left(-\frac{r}{na}\right) \left(\frac{2r}{na}\right)^l L_{n-l-2}^{2l+2}\left(\frac{2r}{na}\right) \right\rangle \tag{43}
$$

$$
\begin{aligned}
&= -\int_{r=0}^{\infty} \kappa_l \kappa_o \frac{2}{na} r^2 \exp\left(-\frac{2r}{na}\right) \left(\frac{2r}{na}\right)^{l+o} L_{n-o-1}^{2o+1}\left(\frac{2r}{na}\right) L_{n-l-2}^{2l+2}\left(\frac{2r}{na}\right) dr \\
&\int_{\phi=0}^{\pi} \beta_l^m \beta_o^p sin(\phi) cos(\phi) P_l^m(cos(\phi)) P_o^p(cos(\phi)) d\phi \int_{\theta=0}^{2\pi} e^{im\theta} e^{-ip\theta} d\theta
\end{aligned} \tag{44}
$$

The integrations with respect to θ and ϕ are the same as in the first and second scalar product, so:

$$
\begin{aligned}
&= -2\pi \int_{r=0}^{\infty} \delta_{lo} (\kappa_l)^2 \left(\frac{na}{2}\right)^2 \exp\left(-\frac{2r}{na}\right) \left(\frac{2r}{na}\right)^{2l+2} L_{n-l-1}^{2l+1}\left(\frac{2r}{na}\right) L_{n-l-2}^{2l+2}\left(\frac{2r}{na}\right) d\left(\frac{2r}{na}\right) \\
&\qquad \frac{2(l \pm m)!}{(2l+1)(l \mp m)!} \delta_{mp} (\beta_l^m)^2 \left(2 + \frac{\pi}{2}\right) = 0
\end{aligned}
$$

[4] http://mathworld.wolfram.com/AssociatedLaguerrePolynomial.html

The fourth scalar product:

$$= \pm \left\langle \Psi^0_{op} \left| \frac{sin\,(\phi)}{r} \kappa_l \exp\left(-\frac{r}{na}\right) \left(\frac{2r}{na}\right)^l L^{2l+1}_{n-l-1}\left(\frac{2r}{na}\right) mcot(\phi) Y^m_l(\theta,\phi) \right.\right\rangle \tag{45}$$

$$= \pm \int_{r=0}^{\infty} \kappa_l \kappa_o r \exp\left(-\frac{2r}{na}\right) \left(\frac{2r}{na}\right)^{l+o} L^{2o+1}_{n-o-1}\left(\frac{2r}{na}\right) L^{2l+1}_{n-l-1}\left(\frac{2r}{na}\right) dr$$
$$\int_{\phi=0}^{\pi} \beta^m_l \beta^p_o m sin^2(\phi) cot(\phi) P^m_l(cos(\phi)) P^p_o(cos(\phi)) d\phi \int_{\theta=0}^{2\pi} e^{im\theta} e^{-ip\theta} d\theta$$

Once again the integrations with respect to θ and ϕ are the same as in the first and second scalar product up to a constant factor m, so:

$$= \pm 2\pi \int_{r=0}^{\infty} \delta_{lo} \kappa_l \kappa_o r \exp\left(-\frac{2r}{na}\right) \left(\frac{2r}{na}\right)^{l+o} L^{2o+1}_{n-o-1}\left(\frac{2r}{na}\right) L^{2l+1}_{n-l-1}\left(\frac{2r}{na}\right) dr$$
$$\frac{2m(l \pm m)!}{(2l+1)(l \mp m)!} \delta_{mp} \left(\beta^m_l\right)^2 \left(2 + \frac{\pi}{2}\right)$$

$$= \pm 2\pi \int_{r=0}^{\infty} \delta_{lo} (\kappa_l)^2 \left(\frac{na}{2}\right)^2 \exp\left(-\frac{2r}{na}\right) \left(\frac{2r}{na}\right)^{2l+1} L^{2l+1}_{n-l-1}\left(\frac{2r}{na}\right) L^{2l+1}_{n-l-1}\left(\frac{2r}{na}\right) d\left(\frac{2r}{na}\right)$$
$$\frac{2m(l \pm m)!}{(2l+1)(l \mp m)!} \delta_{mp} \left(\beta^m_l\right)^2 \left(2 + \frac{\pi}{2}\right)$$

The integral with respect to $\frac{2r}{na}$ is the same as in the second scalar product. Therefore the fourth scalar product is:

$$\begin{aligned} &= \pm 2\pi \frac{2m(l \pm m)!}{(2l+1)(l \mp m)!} \left(\beta^m_l\right)^2 \left(2 + \frac{\pi}{2}\right) \left(\frac{na}{2}\right)^2 \\ &\quad (\kappa_l)^2 (n-l-1)!(n+l)! \delta_{mp} \delta_{lo} \end{aligned} \tag{46}$$

And finally the fifth and last scalar product:

$$\pm \left\langle \Psi^0_{op} \left| \frac{sin\,(\phi)}{r} \kappa_l \exp\left(-\frac{r}{na}\right) \left(\frac{2r}{na}\right)^l L^{2l+1}_{n-l-1}\left(\frac{2r}{na}\right) \gamma^m_l e^{\mp i\theta} Y^{m\pm1}_l(\theta,\phi) \right) \right.\right\rangle \tag{47}$$

$$= \pm \int_{r=0}^{\infty} \kappa_l \kappa_o r \exp\left(-\frac{2r}{na}\right) \left(\frac{2r}{na}\right)^{l+o} L^{2o+1}_{n-o-1}\left(\frac{2r}{na}\right) L^{2l+1}_{n-l-1}\left(\frac{2r}{na}\right) dr$$
$$\int_{\phi=0}^{\pi} \gamma^m_l \beta^{m\pm1}_l \beta^p_o sin(\phi) P^{m\pm1}_l(cos(\phi)) P^p_o(cos(\phi)) d\phi \int_{\theta=0}^{2\pi} e^{im\theta} e^{-ip\theta} d\theta$$

$$\begin{aligned} &= \pm 2\pi \int_{r=0}^{\infty} \kappa_l \kappa_o r \exp\left(-\frac{2r}{na}\right) \left(\frac{2r}{na}\right)^{l+o} L^{2o+1}_{n-o-1}\left(\frac{2r}{na}\right) L^{2l+1}_{n-l-1}\left(\frac{2r}{na}\right) dr \\ &\quad \int_{\phi=0}^{\pi} \delta_{mp} \gamma^m_l \beta^{m\pm1}_l \beta^p_o sin(\phi) P^{m\pm1}_l(cos(\phi)) P^p_o(cos(\phi)) d\phi = 0 \end{aligned} \tag{48}$$

2.3 Combining the Integrals

$$\left\langle \Psi^0_{op} \,\middle|\, H' \,\middle|\, \Psi^0_{lm} \right\rangle = -\frac{e\hbar A_z}{i\mu}\left(\left\langle \Psi^0_{op} \,\middle|\, cos\,(\phi)\,\frac{\partial \Psi^0_{lm}}{\partial r} \right\rangle - \left\langle \Psi^0_{op} \,\middle|\, \frac{sin\,(\phi)}{r}\frac{\partial \Psi^0_{lm}}{\partial \phi} \right\rangle\right)$$

$$\begin{aligned} \left\langle \Psi^0_{op} \,\middle|\, cos\,(\phi)\,\frac{\partial \Psi^0_{lm}}{\partial r} \right\rangle = &-2\pi\frac{(l\pm m)!}{(2l+1)(l\mp m)!}(\beta^m_l)^2\left(2+\frac{\pi}{2}\right)\left(\frac{na}{2}\right)^2 \\ &(\kappa_l)^2(n-l-1)!(n+l)!(2n+1)\delta_{mp}\delta_{lo} \\ &+2\pi\frac{2(l\pm m)!}{(2l+1)(l\mp m)!}(\beta^m_l)^2\left(2+\frac{\pi}{2}\right)\left(\frac{na}{2}\right)^2 \\ &(\kappa_l)^2 l(n-l-1)!(n+l)!\delta_{mp}\delta_{lo} \end{aligned} \tag{49}$$

$$\begin{aligned} \left\langle \Psi^0_{op} \,\middle|\, \frac{sin\,(\phi)}{r}\frac{\partial \Psi^0_{lm}}{\partial \phi} \right\rangle = &\pm 2\pi\frac{2m(l\pm m)!}{(2l+1)(l\mp m)!}(\beta^m_l)^2\left(2+\frac{\pi}{2}\right)\left(\frac{na}{2}\right)^2 \\ &(\kappa_l)^2(n-l-1)!(n+l)!\delta_{mp}\delta_{lo} \end{aligned} \tag{50}$$

Therefore the Scalar Product is

$$\begin{aligned} \left\langle \Psi^0_{op} \,\middle|\, H' \,\middle|\, \Psi^0_{lm} \right\rangle = &-\frac{e\hbar A_z}{i\mu}\frac{2\pi(l\pm m)!}{(2l+1)(l\mp m)!}(\beta^m_l)^2\left(2+\frac{\pi}{2}\right)\left(\frac{na}{2}\right)^2(\kappa_l)^2(n-l-1)!(n+l)! \\ &(-(2n+1)+2l\mp 2m)\,\delta_{mp}\delta_{lo} \\ &=\frac{e\hbar A_z}{i\mu}\frac{2\pi(l\pm m)!}{(2l+1)(l\mp m)!}(\beta^m_l)^2\left(2+\frac{\pi}{2}\right)\left(\frac{na}{2}\right)^2(\kappa_l)^2(n-l-1)!(n+l)! \\ &((2n+1)-2l\pm 2m)\,\delta_{mp}\delta_{lo} \\ &=\frac{e\hbar A_z}{i\mu}\frac{2\pi(l\pm m)!}{(2l+1)(l\mp m)!}(\beta^m_l)^2\left(2+\frac{\pi}{2}\right)\left(\frac{na}{2}\right)^2(\kappa_l)^2(n-l-1)!(n+l)! \\ &(2(n-l\pm m)+1)\,\delta_{mp}\delta_{lo} \end{aligned}$$