1 The trial wave function for the ground state should be spherically symmetric and satisfy boundary conditions : $\psi(r=a)=0$ and $\psi(r=b)=0$. The simplest functional form that meets the criteria is a parabola :

$$\psi(r) = \begin{cases} C(r-a)(b-r) & , \quad a \le r \le b \\ 0 & , \quad \text{otherwise} \end{cases}$$

The value of C comes from normalization. Therefore, the trial wave function has no adjustable parameters that we could vary.

$$\langle\psi|\psi\rangle = 4\pi \int_a^b |\psi|^2 r^2 dr = 4\pi C^2 \int_a^b (r-a)^2(b-r)^2 r^2 dr =$$

$$= 4\pi C^2 \frac{2}{105} (b-a)^5 (2a^2+3ab+2b^2)$$

$$\langle\psi|H|\psi\rangle = 4\pi \int_a^b \psi\left(-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}\psi\right) r^2 dr = 4\pi C^2 \frac{\hbar^2}{2m}\int_a^b (r-a)(b-r)\cdot$$

$$\cdot\, 2(a+b-3r)r\, dr = 4\pi C^2 \frac{\hbar^2}{2m}\frac{4}{15}(b-a)^3(2a^2+ab+2b^2)$$

$$E = \frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle} = \frac{\hbar^2}{2m}\frac{4/15}{2/105}\frac{(2a^2+ab+2b^2)}{(b-a)^2(2a^2+3ab+2b^2)} =$$

$$= \frac{7\hbar^2}{m}\frac{(2a^2+ab+2b^2)}{(b-a)^2(2a^2+3ab+2b^2)}$$

(2) The eigenvalues and normalized eigenvectors of H_0 are

$$E_1 = 1 \quad \psi_1 = \frac{1}{\sqrt{2}}\begin{pmatrix}0\\-1\\1\end{pmatrix} \qquad E_2 = 1 \quad \psi_2 = \begin{pmatrix}1\\0\\0\end{pmatrix} \qquad E_3 = 3 \quad \psi_3 = \frac{1}{\sqrt{2}}\begin{pmatrix}0\\1\\1\end{pmatrix}$$

Because the energy level $E = 1$ is doubly degenerate we need to apply the degenerate perturbation theory for that level. Matrix V in basis $\{\psi_1, \psi_2\}$ looks as follows:

$$V_{11} = \langle\psi_1|V|\psi_1\rangle = \frac{\beta}{2}(0\ -1\ 1)\begin{pmatrix}0&1&0\\1&0&0\\0&0&1\end{pmatrix}\begin{pmatrix}0\\-1\\1\end{pmatrix} = \frac{\beta}{2}$$

$$V_{12} = \langle\psi_1|V|\psi_2\rangle = \frac{\beta}{\sqrt{2}}(0\ -1\ 1)\begin{pmatrix}0&1&0\\1&0&0\\0&0&1\end{pmatrix}\begin{pmatrix}1\\0\\0\end{pmatrix} = -\frac{\beta}{\sqrt{2}} \qquad V_{21} = V_{12}$$

$$V_{22} = \langle\psi_2|V|\psi_2\rangle = \beta(1\ 0\ 0)\begin{pmatrix}0&1&0\\1&0&0\\0&0&1\end{pmatrix}\begin{pmatrix}1\\0\\0\end{pmatrix} = 0$$

Solving the corresponding 2×2 eigenvalue problem yields

$$\beta\begin{pmatrix}\frac{1}{2} & -\frac{1}{\sqrt{2}}\\ -\frac{1}{\sqrt{2}} & 0\end{pmatrix}\begin{pmatrix}c_1\\c_2\end{pmatrix} = \varepsilon\begin{pmatrix}c_1\\c_2\end{pmatrix}$$

$$\varepsilon_1 = -\frac{\beta}{2} \quad \begin{pmatrix}c_1\\c_2\end{pmatrix} = \begin{pmatrix}\frac{1}{\sqrt{3}}\\ \sqrt{\frac{2}{3}}\end{pmatrix} \qquad \varepsilon_2 = \beta \quad \begin{pmatrix}c_1\\c_2\end{pmatrix} = \begin{pmatrix}\sqrt{\frac{2}{3}}\\ -\sqrt{\frac{1}{3}}\end{pmatrix}$$

With that the proper basis for our problem is

$$\phi_1 = \frac{1}{\sqrt{3}}\psi_1 + \sqrt{\frac{2}{3}}\psi_2 = \begin{pmatrix}\sqrt{\frac{2}{3}}\\ -\sqrt{\frac{1}{6}}\\ \sqrt{\frac{1}{6}}\end{pmatrix} \qquad \phi_2 = \sqrt{\frac{2}{3}}\psi_1 - \sqrt{\frac{1}{3}}\psi_2 = \begin{pmatrix}-\sqrt{\frac{1}{3}}\\ -\sqrt{\frac{1}{3}}\\ \sqrt{\frac{1}{3}}\end{pmatrix}$$

$$\phi_3 = \psi_3 = \frac{1}{\sqrt{2}}\begin{pmatrix}0\\1\\1\end{pmatrix}$$

The first order corrections to the energy are:

$$E_1^{(1)} = \varepsilon_1 = -\frac{\beta}{2} \qquad E_2^{(1)} = \varepsilon_2 = \beta$$

$$E_3^{(1)} = \langle\phi_3|V|\phi_3\rangle = \frac{\beta}{2}(0\ 1\ 1)\begin{pmatrix}0&1&0\\1&0&0\\0&0&1\end{pmatrix}\begin{pmatrix}0\\1\\1\end{pmatrix} = \frac{\beta}{2}$$

The first order corrections to the eigenstates are given by

$$\phi_n^{(1)} = \sum_{m\neq n} \frac{\langle \phi_m^{(0)} | V | \phi_n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}} \phi_m^{(0)}$$

Note that in our case $\langle \phi_1^{(0)} | V | \phi_2^{(0)} \rangle = \langle \phi_2^{(0)} | V | \phi_1^{(0)} \rangle = 0$

and

$$V_{13} = V_{31} = \langle \phi_1^{(0)} | V | \phi_3^{(0)} \rangle = \beta \begin{pmatrix} \sqrt{\frac{2}{3}} & -\frac{1}{\sqrt{6}} & \frac{1}{\sqrt{6}} \end{pmatrix} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 0 \\ \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{pmatrix} = \frac{\sqrt{3}}{2} \beta$$

$$V_{23} = V_{32} = \langle \phi_2^{(0)} | V | \phi_3^{(0)} \rangle = \beta \begin{pmatrix} -\frac{1}{\sqrt{3}} & -\frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}} \end{pmatrix} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 0 \\ \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{pmatrix} = 0$$

So we have

$$\phi_1^{(1)} = \frac{V_{31}}{E_1^{(0)} - E_3^{(0)}} \phi_3^{(0)} = \frac{\frac{\sqrt{3}}{2}\beta}{-2} \frac{1}{\sqrt{2}} \begin{pmatrix} 0 \\ 1 \\ 1 \end{pmatrix} = -\frac{\sqrt{3}\beta}{4\sqrt{2}} \begin{pmatrix} 0 \\ 1 \\ 1 \end{pmatrix}$$

$$\phi_2^{(1)} = \frac{V_{32}}{E_2^{(0)} - E_3^{(0)}} \phi_3^{(0)} = 0$$

$$\phi_3^{(1)} = \frac{V_{13}}{E_3^{(0)} - E_1^{(0)}} \phi_1^{(0)} + \frac{V_{23}}{E_3^{(0)} - E_2^{(0)}} \phi_2^{(0)} = \frac{\frac{\sqrt{3}}{2}\beta}{2} \begin{pmatrix} \sqrt{\frac{2}{3}} \\ -\sqrt{\frac{1}{6}} \\ \sqrt{\frac{1}{6}} \end{pmatrix} = \frac{\beta}{4\sqrt{2}} \begin{pmatrix} 2 \\ -1 \\ 1 \end{pmatrix}$$

(3) The ground state of this system is non-degenerate

$n_x = n_y = 1 \qquad \psi^{(0)} = \frac{2}{a}\sin\frac{\pi x}{a}\sin\frac{\pi y}{a}$

The first order correction to the energy is

$$E^{(1)} = \langle\psi^{(0)}|V|\psi^{(0)}\rangle = \gamma \underbrace{\int_0^{a/2}\left(\frac{2}{a}\sin\frac{\pi x}{a}\right)^2 dx}_{1/2}\ \underbrace{\int_0^{a/2}\left(\frac{2}{a}\sin\frac{\pi y}{a}\right)^2 dy}_{1/2} = \frac{\gamma}{4}$$

The first excited energy level is doubly degenerate:

$n_x = 1 \quad n_y = 2 \qquad \psi_1^{(0)} = \frac{2}{a}\sin\frac{\pi x}{a}\sin\frac{2\pi y}{a}$

$n_x = 2 \quad n_y = 1 \qquad \psi_2^{(0)} = \frac{2}{a}\sin\frac{2\pi x}{a}\sin\frac{\pi y}{a}$

Here we need to apply the degenerate perturbation theory:

$$V_{11} = \gamma \underbrace{\int_0^{a/2}\left(\frac{2}{a}\sin\frac{\pi x}{a}\right)^2 dx}_{1/2}\ \underbrace{\int_0^{a/2}\left(\frac{2}{a}\sin\frac{2\pi y}{a}\right)^2 dy}_{1/2} = \frac{\gamma}{4}$$

$$V_{12} = \gamma \underbrace{\int_0^{a/2}\left(\frac{2}{a}\sin\frac{\pi x}{a}\sin\frac{2\pi x}{a}\right) dx}_{4/3\pi}\ \underbrace{\int_0^{a/2}\left(\frac{2}{a}\sin\frac{\pi y}{a}\sin\frac{2\pi y}{a}\right) dy}_{4/3\pi} = \frac{16\gamma}{9\pi^2} \qquad V_{21} = V_{12}$$

$$V_{22} = \gamma \underbrace{\int_0^{a/2}\left(\frac{2}{a}\sin\frac{2\pi x}{a}\right)^2 dx}_{1/2}\ \underbrace{\int_0^{a/2}\left(\frac{2}{a}\sin\frac{\pi y}{a}\right)^2 dy}_{1/2} = \frac{\gamma}{4}$$

Solving the secular equation gives:

$$\gamma\begin{pmatrix} \frac{1}{4} & \frac{4}{3\pi} \\ \frac{4}{3\pi} & \frac{1}{4}\end{pmatrix}\begin{pmatrix} c_1 \\ c_2\end{pmatrix} = \varepsilon\begin{pmatrix} c_1 \\ c_2\end{pmatrix} \qquad \left(\frac{\gamma}{4}-\varepsilon\right)^2 - \frac{16\gamma}{9\pi^2} = 0 \qquad E_{1,2}^{(0)} = \varepsilon_{1,2} = \gamma\left(\frac{1}{4} \pm \frac{4}{3\pi}\right)$$

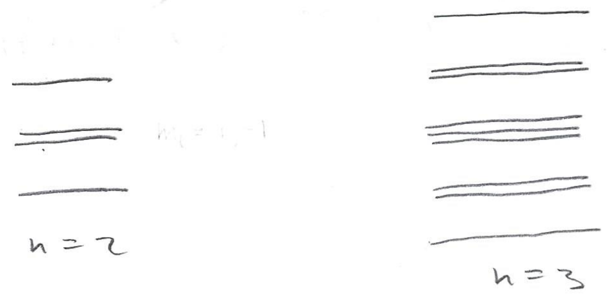
$$\phi_1^{(0)} = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\1\end{pmatrix} = \frac{1}{\sqrt{2}}\psi_1^{(0)} + \frac{1}{\sqrt{2}}\psi_2^{(0)} \qquad \phi_2^{(0)} = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\-1\end{pmatrix} = \frac{1}{\sqrt{2}}\psi_1^{(0)} - \frac{1}{\sqrt{2}}\psi_2^{(0)}$$

④ a) For a state with the principal quantum number n we have $n-1$ possible values of angular momentum quantum number l. For each l, the magnetic quantum number m_l can take $2l+1$ values (from $-l$ to $+l$). So the degeneracy is given by

$$g = \sum_{l=0}^{n-1} (2l+1) = n^2$$

If we take into account the spin of the electron then it gets doubled: $g = 2n^2$

b) Uniform external electric field partially lifts the degeneracy. For example for $n=2$ and 3 we have



c) If we neglect the electron spin the degeneracy is lifted partially (the splitting is proportional to Δm_l). However if we include the spin then the degeneracy is completely lifted.

d) The spin-orbit interaction lifts the degeneracy partially. The energy levels depend on j, but not on m_j

e) $p^2c^2 + m^2c^4 = E_{tot}^2$ where $E_{tot} = \underbrace{T}_{\text{kinetic energy}} + mc^2$

So

$$T = \sqrt{p^2c^2 + m^2c^4} - mc^2 = mc^2\left(\sqrt{1+\frac{p^2}{m^2c^2}} - 1\right) = mc^2\left(\frac{1}{2}\frac{p^2}{m^2c^2} - \frac{1}{8}\frac{p^4}{m^4c^4} + \dots\right) = \frac{p^2}{2m} - \underbrace{\frac{p^4}{8m^3c^2}}_{\text{leading correction}} + \dots$$

The mass-velocity correction, $-\frac{p^4}{8m^3c^2}$ partially lifts the degeneracy in hydrogen. The expectation values of $-\frac{p^4}{8m^3c^2}$ depend on l.