(a) Over the range $\theta \in [0, \pi)$, $\sin\theta$ is symmetric about $\theta = \pi/2$ and $\cos\theta$ is antisymmetric about $\theta = \pi/2$. Hence,

$$\begin{aligned}
E^1_{1,0,0} &= \int_0^{\pi} \int_0^{2\pi} \int_0^{\infty} \frac{1}{a^3\pi} e^{-2r/a} e E_{\text{ext}} r \cos\theta r^2 \sin\theta \, dr \, d\theta \, d\phi \\
&= \frac{2\pi}{\pi a^3} \int_0^{\pi} \cos\theta \sin\theta \, d\theta \int_0^{\infty} r^3 e^{-2r/a} dr = 0.
\end{aligned}$$

(b) Diagonals:

$$\begin{aligned}
W_{11} &= \ldots \int_0^{\pi} \cos\theta \sin\theta \, d\theta = 0 \\
W_{22} &= \ldots \int_0^{\pi} \cos\theta \sin^2\theta \sin\theta \, d\theta = 0 \\
W_{33} &= \ldots \int_0^{\pi} \cos\theta \cos^2\theta \sin\theta \, d\theta = 0 \\
W_{44} &= \ldots \int_0^{\pi} \cos\theta \sin^2\theta \sin\theta \, d\theta = 0
\end{aligned}$$

Off-diagonals (smart way): Noting that the the perturbation has no ϕ dependence, only W_{13} will be non-zero as this is the only one where the m quantum number is the same (meaning the ϕ dependence is the same, so that integrating over ϕ doesn't automatically lead to 0). Essentially $\psi_{nlm} = R_{nl}(r)\Theta_{lm}(\theta)\Phi_m(\phi)$, and $\int_0^{2\pi} \psi_{nlm} H'(r,\theta)\psi_{nl'm'} \, d\phi \propto \delta_{mm'}$.

Off diagonals (long way):

$$\begin{aligned}
W_{12} &= \ldots \int_0^{2\pi} e^{i\phi} d\phi = 0 \\
W_{14} &= \ldots \int_0^{2\pi} e^{-i\phi} d\phi = 0 \\
W_{23} &= \ldots \int_0^{2\pi} e^{-i\phi} d\phi = 0 \\
W_{24} &= \ldots \int_0^{2\pi} e^{-2i\phi} d\phi = 0 \\
W_{34} &= \ldots \int_0^{2\pi} e^{-2i\phi} d\phi = 0 \\
W_{13} &= \frac{eE_{\text{ext}}}{16\pi a^4} \iiint \left(1 - \frac{r}{2a}\right) r^4 e^{-r/a} \cos^2\theta \sin\theta \, dr \, d\theta \, d\phi \\
&= 2\pi \frac{eE_{\text{ext}}}{16\pi a^4} \iint \left(1 - \frac{r}{2a}\right) r^4 e^{-r/a} \cos^2\theta \sin\theta \, dr \, d\theta \\
&= \frac{eE_{\text{ext}}}{8a^4} \frac{2}{3} \int \left(1 - \frac{r}{2a}\right) r^4 e^{-r/a} \, dr \\
&= \frac{eE_{\text{ext}}}{12a^4} \left(\int r^4 e^{-r/a} \, dr - \frac{1}{2a} \int r^5 e^{-r/a} \, dr \right) \\
&= \frac{eE_{\text{ext}}}{12a^4} \left[\frac{4!}{(1/a)^5} - \frac{1}{2a} \frac{5!}{(1/a)^6} \right] = \frac{eaE_{\text{ext}}}{12}(24 - 60) = -3eaE_{\text{ext}}
\end{aligned}$$

and all $W_{jk} = W^*_{kj}$.

(c) We therefore have

$$-3aeE_{\mathrm{ext}}\begin{pmatrix}0&0&1&0\\0&0&0&0\\1&0&0&0\\0&0&0&0\end{pmatrix}\begin{pmatrix}\alpha\\\beta\\\gamma\\\delta\end{pmatrix}=E^1\begin{pmatrix}\alpha\\\beta\\\gamma\\\delta\end{pmatrix}.$$

Let $\lambda=-E^1/3aeE_{\mathrm{ext}}$, and so we have

$$\begin{pmatrix}-\lambda&0&1&0\\0&-\lambda&0&0\\1&0&-\lambda&0\\0&0&0&-\lambda\end{pmatrix}\begin{pmatrix}\alpha\\\beta\\\gamma\\\delta\end{pmatrix}=\begin{pmatrix}0\\0\\0\\0\end{pmatrix}.$$

Set the determinant $=0$ and solve:

$$-\lambda\begin{vmatrix}-\lambda&0&0\\0&-\lambda&0\\0&0&-\lambda\end{vmatrix}-0+\begin{vmatrix}0&-\lambda&0\\1&0&0\\0&0&-\lambda\end{vmatrix}-0=0$$
$$\Rightarrow \lambda^4-\lambda^2=\lambda^2(\lambda^2-1).$$

Hence we have values $\lambda=0,0,1,-1$ so it splits into 3 separate levels with energy shift $E_2^1=0,-3aeE_{\mathrm{ext}},3aeE_{\mathrm{ext}}$.

(d) Eigenvectors with $E_2^1=0$ are $|\varphi_2\rangle$ and $|\varphi_4\rangle$. The eigenvector with $\lambda=1$ (hence $E_2^1=-3aeE_{\mathrm{ext}}$) has

$$\begin{pmatrix}-1&0&1&0\\0&-1&0&0\\1&0&-1&0\\0&0&0&-1\end{pmatrix}\begin{pmatrix}\alpha\\\beta\\\gamma\\\delta\end{pmatrix}=\begin{pmatrix}0\\0\\0\\0\end{pmatrix}.$$

Hence, $-\alpha+\gamma=0$ or $\alpha=\gamma$ and the normalised eigenvector $\chi=(|\varphi_1\rangle+|\varphi_3\rangle)/\sqrt{2}$.

For $\lambda=-1$ (hence $E_2^1=3aeE_{\mathrm{ext}}$)

$$\begin{pmatrix}1&0&1&0\\0&1&0&0\\1&0&1&0\\0&0&0&1\end{pmatrix}\begin{pmatrix}\alpha\\\beta\\\gamma\\\delta\end{pmatrix}=\begin{pmatrix}0\\0\\0\\0\end{pmatrix},$$

and so $\alpha+\gamma=0$ or $\gamma=-\alpha$ and the normalised eigenvector $\chi=(|\varphi_1\rangle-|\varphi_3\rangle)/\sqrt{2}$.