1. In Cartesian coordinates, the position vector is given by

$$\vec{r} = x\hat{\mathbf{x}} + y\hat{\mathbf{y}} + z\hat{\mathbf{z}}.$$

We start with this form because $\hat{\mathbf{x}}, \hat{\mathbf{y}}, \hat{\mathbf{z}}$ are constant, so their derivatives are zero. If we started with the spherical form $r\hat{\mathbf{r}}$, then we take a derivative we would need to know quantities such as $\partial\hat{\mathbf{r}}/\partial\theta$. Since we want to use this method to find quantities like $\hat{\mathbf{r}}$, we won't get very far if we need to know its derivative to proceed.

We can then rewrite the coefficients in terms of spherical coordinates,

$$\vec{r} = r\sin\theta\cos\phi\hat{\mathbf{x}} + r\sin\theta\sin\phi\hat{\mathbf{y}} + r\cos\theta\hat{\mathbf{z}},$$

as this is the form most suitable to taking derivatives in spherical coordinates. We then have

$$\frac{\partial\vec{r}}{\partial\theta} = r\cos\theta\cos\phi\hat{\mathbf{x}} + r\cos\theta\sin\phi\hat{\mathbf{y}} - r\sin\theta\hat{\mathbf{z}},$$

where we have used that the partial derivative holds r, ϕ constant and that $\hat{\mathbf{x}}, \hat{\mathbf{y}}, \hat{\mathbf{z}}$ are all constants. The norm of this vector is

$$\sqrt{\frac{\partial\vec{r}}{\partial\theta}\cdot\frac{\partial\vec{r}}{\partial\theta}} = \sqrt{r^2\cos^2\theta\cos^2\phi + r^2\cos^2\theta\sin^2\phi + r^2\sin^2\theta} = r.$$

The normalized unit vector is thus given by

$$\hat{\theta} = \cos\theta\cos\phi\hat{\mathbf{x}} + \cos\theta\sin\phi\hat{\mathbf{y}} - \sin\theta\hat{\mathbf{z}}.$$

2. (a) We know (from lecture) that n can be any positive integer. It is by construction one larger than the maximum value of ℓ, so ℓ can be at most $n-1$. ℓ is in general required to be a non-negative integer. m (as it does in general) takes on integer values from $-\ell$ to ℓ, inclusive.

   (b) To share the same energy, the orbitals must share the same n. We are requiring that they also share the same ℓ; this leaves m to range freely. As stated above, m can take integer values from $-\ell$ to ℓ; there are $2\ell+1$ of these integers and so $2\ell+1$ orbitals which share the same energy and all have the same angular momentum ℓ. From the allowed values of ℓ above, we know that for the energy level indexed by n, ℓ can vary from 0 to $n-1$. We thus have the degeneracy of this level as

$$\sum_{\ell=0}^{n-1} 2\ell + 1 = 2\frac{n(n-1)}{2} + n = n^2$$

   Note that this is the degeneracy considering only n, ℓ, m; it will turn out that there is one more quantum number with two possible values and the n^2 given above will become $2n^2$.

3. (a) We know that the spherical harmonic Y_1^0 is proportional to $\cos\theta$ with no ϕ dependence. We can thus write $z = bY_1^0$, where b is an r-dependent constant but independent of θ, ϕ.

   (b) The (squares of the) spherical harmonics all have no particular direction; along any given axis, they give equal weight to the positive and negative directions. You can see this, if skeptical, from both $\cos^2\theta$ and $\sin^2\theta$ being symmetric about $\pi/2$, while the θ integral runs from 0 to π. Since they have no particular direction, $\langle z\rangle$ can be neither positive nor negative and must be zero.

   If you would prefer a calculation to a symmetry argument, the appropriate tool to use is the orthonormality of the spherical harmonics. We saw above that z is proportional to Y_1^0. Multiplying any spherical harmonic Y_ℓ^m by Y_1^0 will take you to a different spherical harmonic, and since it is different it must be orthogonal to the original spherical harmonic.

(c) Since we have a linear combination, the expectation value will now involve cross terms with one factor of Y_0^0 and one of Y_1^0. Since these are different, the symmetry argument above fails. Y_0^0 is a positive constant everywhere, while Y_1^0 is positive for small θ (positive z) and negative for large θ (negative z). $\langle z \rangle$ will thus be non-zero (and positive).

Alternatively, following the calculation above, we can observe that since $Y_0^0 \cos\theta \propto Y_1^0$, orthonormality of the spherical harmonics means that we will get a non-zero result for $\langle z \rangle$ for the cross term $Y_0^0 Y_1^0$. The different spherical harmonic referenced in the previous part, when multiplying Y_0^0 by Y_1^0, is Y_1^0; since this does in fact appear in our state, we get a non-zero result.

Note that the non-zero $\langle z \rangle$ depends on the linear combination; it does not happen for all of them. $\left(1/\sqrt{2}\right)(\psi_{210} + \psi_{211})$, for example, does have $\langle z \rangle = 0$.

(d) In the previous part, we took an equal weight superposition of ψ_{100} (which has no θ, ϕ dependence) and ψ_{210}, whose θ, ϕ dependence is the same as z. Our desired state should thus replace ψ_{210} with a state whose θ, ϕ dependence matches x rather than z. We know that $x \propto \sin\theta\cos\phi$; looking at the spherical harmonics, we see that both Y_1^1 and Y_1^{-1} have the correct θ dependence. To get the ϕ dependence right, we use $\cos\phi = \left(e^{i\phi} + e^{-i\phi}\right)/2$. This tells us we need $\left(Y_1^1 - Y_1^{-1}\right)/\sqrt{2}$. The desired state is thus

$$\frac{1}{\sqrt{2}}\left(\psi_{100} + \frac{1}{\sqrt{2}}\left(\psi_{211} - \psi_{21-1}\right)\right)$$