8.1 M10Q.1

a) The Hamiltonian, neglecting electron-electron repulsion, is given by,

$$\boxed{H = \sum_{j=1}^{N} \left(-\frac{\hbar^2}{2m} \nabla_j^2 - \frac{Ze^2}{4\pi\epsilon_0 r_j} \right)}$$

where $N = Z$ and ∇_j^2 is the Laplacian with respect to the $\mathbf{r}_j$ coordinate. The energy of the nth electronic orbital is given by,

$$\boxed{E_n = -\frac{Z^2 E_0}{n^2}, \quad E_0 = \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \frac{m}{2\hbar^2}}$$

b) The degeneracy of the nth orbital is $g(n) = 2n^2$. Therefore,

$$E(Z_n) = \sum_{j=1}^{n} g(n) E_n = -2Z^2 E_0 n$$

The number of closed shells, n, is related to Z_n by,

$$Z_n = 2 \sum_{j=1}^{n} j^2$$

The sum of first n squares has a closed form expression that I can never remember, so we need to derive it. Thinking about the term geometrically, we can write

$$\sum_{j=1}^{n} j^2 = \sum_{j=1}^{n} \sum_{k=j}^{n} k = \sum_{j=1}^{n} \left(\sum_{k=1}^{n} k - \sum_{k=1}^{j-1} k \right)$$

The sum of the first n natural numbers are given by $n(n+1)/2$ (easy to remember as triangular numbers). Therefore, the above expression becomes,

$$\sum_{j=1}^{n} j^2 = \frac{1}{2} \sum_{j=1}^{n} [n(n+1) - j(j-1)] \Rightarrow 3 \sum_{j=1}^{n} j^2 = n^2(n+1) + \sum_{j=1}^{n} j$$

$$\Rightarrow \sum_{j=1}^{N} j^2 = \frac{1}{6} n(n+1)(2n+1)$$

For $n \gg 1$, we find that

$$Z_n \approx \frac{2}{3} n^3 + \mathcal{O}(n^2)$$

Thus, the asymptotic expression for the energy is,

$$\boxed{E(Z) \sim -12^{1/3} E_0 Z^{7/3}}$$

c) Using the Virial theorem, given by $2\langle K \rangle = \alpha \langle V \rangle$ for $V \sim r^\alpha$, we find that

$$\langle K \rangle = -\frac{1}{2} \langle V \rangle$$

In terms of the expectation value of the energy, we have,

$$\boxed{\langle V \rangle = 2\langle E \rangle, \quad \langle K \rangle = -\langle E \rangle}$$

d) The expression for the average distance is given in the problem as,

$$\frac{1}{r_{\rm av}} = \left\langle \frac{1}{N}\sum_{j=1}^{N}\frac{1}{r_j}\right\rangle = \frac{1}{N}\sum_{j=1}^{N}\left\langle\frac{1}{r_j}\right\rangle = \frac{2}{N}\sum_{j=1}^{n} j^2\left\langle\frac{1}{\tilde{r}_j}\right\rangle$$

where r_j is the distance from the nucleus of the jth electron and $\tilde{r}_j$ is the distance of the electron in the jth orbital. Note that the last equality assumes the atom is in the ground state. From part (c), we know that $\langle V\rangle = 2\langle E\rangle$ (which is also true for each orbital energy individually). Therefore,

$$\frac{Ze^2}{4\pi\epsilon_0}\left\langle\frac{1}{\tilde{r}_n}\right\rangle = \frac{2Z^2E_0}{n^2} \Rightarrow \left\langle\frac{1}{\tilde{r}_n}\right\rangle = \frac{mZ^2e^2}{4\pi\epsilon_0\hbar^2 n^2}$$

Substituting into the expression for $r_{\rm av}$ yields,

$$\frac{1}{r_{\rm av}} = \frac{me^2}{2\pi\epsilon_0\hbar^2}n \sim \frac{3^{1/3}me^2}{2^{4/3}\pi\epsilon_0\hbar^2}Z^{1/3} \Rightarrow r_{\rm av} \sim Z^{-1/3}$$

where the asymptotic expression for n from (b) was used.