8.1 M10Q.1

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

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

where \( N = Z \) and \( \nabla_j^2 \) is the Laplacian with respect to the \( r_j \) coordinate. The energy of the \( n \)th electronic orbital is given by,

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

b) The degeneracy of the \( n \)th 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

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

Thus, the asymptotic expression for the energy is,

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

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,

$$ \langle V \rangle = 2\langle E \rangle, \quad \langle K \rangle = -\langle E \rangle $$
d) The expression for the average distance is given in the problem as,

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

where \( r_j \) is the distance from the nucleus of the \( j \)th electron and \( \tilde{r}_j \) is the distance of the electron in the \( j \)th 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,

\[
\frac{Ze^2}{4\pi\varepsilon_0} \left\langle \frac{1}{\tilde{r}_n} \right\rangle = \frac{2Z^2E_0}{n^2} \Rightarrow \left\langle \frac{1}{\tilde{r}_n} \right\rangle = \frac{mZ^2e^2}{4\pi\varepsilon_0\hbar^2n^2}
\]

Substituting into the expression for \( r_{av} \) yields,

\[
\frac{1}{r_{av}} = \frac{me^2}{2\pi\varepsilon_0\hbar^2n} \sim \frac{3^{1/3}me^2}{2^{4/3}\pi\varepsilon_0\hbar^2} Z^{1/3} \Rightarrow r_{av} \sim Z^{-1/3}
\]

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