Chapter 8. Exercises

1. For the optimized helium variational wavefunction

$$\psi(r_1, r_2) = e^{-\alpha(r_1+r_2)}$$

calculate the expectation values of total kinetic and potential energies. Do these satisfy the virial theorem?

2. Using the same form of an optimized variational wavefunction

$$\psi(r_1, r_2) = e^{-\alpha(r_1+r_2)}$$

estimate the ground-state energy of Li^+.

3. Calculate the energy of the hypothetical $1s^3$ state of the Li atom using the optimized variational wavefunction

$$\psi(1, 2, 3) = e^{-\alpha(r_1+r_2+r_3)}$$

Neglect electron spin, of course. Compare with the experimental ground-state energy, $E_0 = -7.478$ hartrees. Comment on the applicability of the variational theorem.

Chapter 8. Solutions

1.
$$\langle T\rangle = \alpha^2 \qquad \text{and} \qquad \langle V\rangle = -2Z\alpha + \frac{5}{8}\alpha$$

For the optimized variational function, $\alpha = Z - 5/16$, so

$$\langle T\rangle = \left(Z - \frac{5}{16}\right)^2 \qquad \text{and} \qquad \langle V\rangle = -2\left(Z - \frac{5}{16}\right)^2$$

Thus $\langle V\rangle = -2\langle T\rangle$, in agreement with the virial theorem.

2. Li^+ is He-like with $Z = 3$. Just as for He,

$$E(\alpha) = \alpha^2 - 2Z\alpha + \frac{5}{8}\alpha$$

with optimal $\alpha = Z - \frac{5}{16} = 2.6875$ and

$$E = -\left(Z - \frac{5}{16}\right)^2 = -7.223 \text{ hartrees}$$

A more accurate value is -7.280 hartrees.

3. For the Li atom with 3 electrons,

$$\hat{H} = \sum_{i=1}^{3}\left(-\frac{1}{2}\nabla_i^2 - \frac{Z}{r_i}\right) + \frac{1}{r_{12}} + \frac{1}{r_{23}} + \frac{1}{r_{31}}$$

Assuming $\psi(1,2,3) = e^{-\alpha(r_1+r_2+r_3)}$, we find in analogy with helium results,

$$\left\langle -\frac{1}{2}\nabla_i^2\right\rangle = \frac{1}{2}\alpha^2, \quad \left\langle -\frac{Z}{r_i}\right\rangle = -Z\alpha, \quad \left\langle\frac{1}{r_{ij}}\right\rangle = \frac{5}{8}\alpha$$

The total energy is given by

$$E(\alpha) = \frac{3}{2}\alpha^2 - 3Z\alpha + \frac{15}{8}\alpha$$

with $Z = 3$. To optimize,

$$E'(\alpha) = 3\alpha - 9 + \frac{15}{8} = 0, \quad \alpha = 2.375, \quad E = -8.4609 \text{ hartrees}$$

This is *less than* the exact ground state energy -7.478, in apparent violation of the variational principle. But ψ is an "illegal" wavefunction.