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 1s³ 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. \[ \langle T \rangle = \alpha^2 \quad \text{and} \quad \langle V \rangle = -2Z\alpha + \frac{5}{8}\alpha \]
   For the optimized variational function, \( \alpha = Z - \frac{5}{16} \), so
   \[ \langle T \rangle = \left( Z - \frac{5}{16} \right)^2 \quad \text{and} \quad \langle V \rangle = -2 \left( Z - \frac{5}{16} \right)^2 \]
   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 \(-7.280 \text{ hartrees}\).

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,
   \[ \langle -\frac{1}{2} \nabla_i^2 \rangle = \frac{1}{2}\alpha^2, \quad \langle -\frac{Z}{r_i} \rangle = -Z\alpha, \quad \langle \frac{1}{r_{ij}} \rangle = \frac{5}{8}\alpha \]
   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 $\psi$ is an “illegal” wavefunction.