1. Write the electronic Hamiltonian for a Li atom under the BO approximation in atomic units.

$$\hat{H}_{el} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{1}{2}\nabla_3^2 - \frac{3}{r_1} - \frac{3}{r_2} - \frac{3}{r_3} + \frac{1}{r_{12}} + \frac{1}{r_{13}} + \frac{1}{r_{23}}$$

2. If electron-electron repulsion is neglected, what is the ground state energy of Li?

$$E_{Li} = 2E_1 + 1E_2 = 2\left(-\frac{3^2}{2(1)^2}\right) + 1\left(-\frac{3^2}{2(2)^2}\right) = -10.125\,Hartree$$

This energy is smaller compared to the exact energy because electron-electron repulsion is a positive contribution.

3. Write a possible Slater determinant for this system where e-e repulsion is ignored.

$$\Psi = \frac{1}{(3!)^{1/2}} \begin{bmatrix} \Psi_{1s}(\mathbf{r}_1)\alpha(1) & \Psi_{1s}(\mathbf{r}_1)\beta(1) & \Psi_{2s}(\mathbf{r}_1)\alpha(1) \\ \Psi_{1s}(\mathbf{r}_2)\alpha(2) & \Psi_{1s}(\mathbf{r}_2)\beta(2) & \Psi_{2s}(\mathbf{r}_2)\alpha(2) \\ \Psi_{1s}(\mathbf{r}_3)\alpha(3) & \Psi_{1s}(\mathbf{r}_3)\beta(3) & \Psi_{2s}(\mathbf{r}_3)\alpha(3) \end{bmatrix}$$

4. Using this wavefunction, and the complete Hamiltonian, how is the energy compared to te exact energy?

According to variational principle, the energy of a trial function would be higher than the ground state exact energy given by the exact ground state wavefunction.

5. What is the ground state energy of Be^{+2} if:

  • no electron electron repulsion is considered?

$$E = 2E_1 = 2\left(-\frac{3^2}{2(1)^2}\right) = -16\,Hartree$$

  • the e-e repulsion is treated as a first order perturbation?

$$E = -Z^2 + \frac{5}{8}Z = -13.5\,Hartree$$

  • the trial function is used to treat the problem variationally?
  Energy is given by $E(\zeta) = -\zeta^2 + \frac{5}{8}\zeta + 2\zeta^2 - 2\zeta Z$, and the value of ζ that minimizes energy is 3.6875, so $E(3.6875) = -13.598\,Hartree$.

6. What is the wavelength associated to the following transitions in the hydrogen atom?

   (a) $2p$-orbital to $3s$-orbital

   $$\Delta E = -\frac{1}{2(3)^2} - \left(-\frac{1}{2(2)^2}\right) = \frac{5}{72}\,Ha = 3.0276 \times 10^{-19}\,J = \frac{hc}{\lambda}$$

   $$\lambda = \frac{hc}{\Delta E} = 6.56 \times 10^{-7}\,m$$

   (b) $3s$-orbital to $3d$-orbital
       Energies are equal, so there is no photon associated with transition.

7. What is the ionization energy for the ground state hydrogen atom?

   $$\Delta E = 0 - \left(-\frac{1}{2(1)^2}\right) = 2.179872 \times 10^{-18}\,J$$

   $$IE = \Delta E \times N_A = (2.179872 \times 10^{-18}\,J)(6.022 \times 10^{23}\,J/mol) = 1312.7\,kJ/mol$$

8. Consider the ground state of a harmonic oscillator. As a trial function, try

   $$\phi(x) = \cos \lambda x \qquad -\frac{\pi}{2\lambda} < x < \frac{\pi}{2\lambda},$$

   where λ is a variational parameter. Use this trial function to calculate the ground-state energy of a harmonic oscillator. First, you must obtain the expression of the energy and then minimize with respect to λ. The Hamiltonian operator for this system is

   $$\hat{H} = -\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2} + \frac{k}{2}x^2.$$

   What is the error of using this trial function? Is the energy higher or lower than the exact value? Do your results agree with the variational principle?

   $$E(\lambda) = \frac{\left\langle \phi \left| \hat{H} \right| \phi \right\rangle}{\langle \phi | \phi \rangle}$$

   $$= \frac{\lambda^2 \hbar^2}{2\mu} + \frac{k}{4\lambda^2}\left[\frac{\pi^2}{6} - 1\right]$$

   $$\frac{dE}{d\lambda} = \frac{\hbar^2 \lambda}{\mu} - 2\frac{k}{4\lambda^3}\left[\frac{\pi^2}{6} - 1\right] = 0$$

   $$\lambda = \left(\left[\frac{\pi^2}{12} - 0.5\right]\frac{k\mu}{\hbar^2}\right)^{1/4}$$

   $$E(\lambda) = 1.14\left(\frac{\hbar\omega}{2}\right)$$

   $$\Delta E = 0.07\hbar\omega$$