

1. For the trial function

$$\psi(x) = \begin{cases} N(A^2 - x^2) & -A < x < A, \\ 0 & \text{otherwise,} \end{cases}$$

a) The normalized wavefunction is obtained by requiring

$$\begin{aligned} \langle \psi | \psi \rangle &= \int dx |\psi|^2 = \int_{-A}^A dx N^2 (A^2 - x^2)^2 = N^2 \int_{-A}^A dx (A^4 - 2A^2x^2 + x^4) \\ &= N^2 \left[A^4x - \frac{2}{3}A^2x^3 + \frac{1}{5}x^5 \right]_{-A}^A = N^2 A^5 \cdot 2 \left(1 - \frac{2}{3} + \frac{1}{5} \right) = \frac{16}{15} N^2 A^5 = 1, \end{aligned}$$

such that

$$N = \sqrt{\frac{15}{16A^5}}.$$

b) Using the Hamiltonian inside a 1D box, the variational energy is

$$\begin{aligned} \varepsilon &= \langle \psi | \hat{H} | \psi \rangle = \int_{-A}^A dx \frac{15}{16A^5} (A^2 - x^2) \left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \right) (A^2 - x^2) \\ &= 2 \frac{\hbar^2}{2m} \frac{15}{16A^5} \int_{-A}^A dx (A^2 - x^2) = \frac{15\hbar^2}{16mA^5} dx \left[A^2x - \frac{1}{3}x^3 \right]_{-A}^A \\ &= \frac{15\hbar^2}{16mA^5} \frac{4A^3}{3} = \frac{5\hbar^2}{4mA^2} = 1.25 \frac{\hbar^2}{mA^2}. \end{aligned}$$

The exact ground-state energy for a box of length $L = 2A$ is

$$E = \frac{h^2 1^2}{8mL^2} = \frac{4\pi^2 \hbar^2}{8m \cdot 4A^2} = \frac{\pi^2 \hbar^2}{8mA^2} \approx 1.23 \frac{\hbar^2}{mA^2} < \varepsilon.$$

So, the variational principle holds and the approximation is quite good.

c) Replacing the box Hamiltonian with that of a harmonic oscillator,

$$\begin{aligned} \varepsilon &= \langle \psi | \hat{H} | \psi \rangle = \int_{-A}^A dx \frac{15}{16A^5} (A^2 - x^2) \left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \frac{1}{2} kx^2 \right) (A^2 - x^2) \\ &= \frac{5\hbar^2}{4mA^2} + \frac{1}{2} k \frac{15}{16A^5} \overbrace{\int_{-A}^A dx (A^2 - x^2) x^2 (A^2 - x^2)}^{\frac{16A^7}{105}} \\ &= \frac{5\hbar^2}{4mA^2} + \frac{1}{2} k \frac{A^2}{7}. \end{aligned}$$

Minimizing this gives

$$\frac{\partial \varepsilon(A)}{\partial A} = -\frac{10\hbar^2}{4mA^3} + k \frac{A}{7} = 0 \Rightarrow A_{\min} = \left(\frac{70\hbar^2}{4mk} \right)^{\frac{1}{4}}.$$

d) The minimum energy from the previous calculation is

$$\varepsilon(A_{\min}) = \frac{5\hbar^2}{4m\sqrt{\frac{70\hbar^2}{4mk}}} + \frac{1}{2} k \frac{\sqrt{\frac{70\hbar^2}{4mk}}}{7} = \sqrt{\frac{5}{14}} \hbar \sqrt{\frac{k}{m}} \approx 0.59 \hbar \sqrt{\frac{k}{m}},$$

while the exact answer is (note $k = m\omega^2 \Rightarrow \omega = \sqrt{\frac{k}{m}}$)

$$E_0 = \boxed{\frac{1}{2}\hbar\sqrt{\frac{k}{m}} < \varepsilon}.$$

The variational principle therefore holds.

2. For the potential

$$V(x) = -\operatorname{sech}^2(x) = -\left(\frac{2}{e^x + e^{-x}}\right)^2,$$

a) The Schrödinger equation in atomic units ($\hbar = m = 1$) is

$$\boxed{\left(-\frac{1}{2}\frac{\partial^2}{\partial x^2} - \left(\frac{2}{e^x + e^{-x}}\right)^2\right)\psi(x) = E\psi(x)}.$$

b) At $x \rightarrow \infty$, the positive exponent diverges while the negative exponent goes to zero; at $x \rightarrow -\infty$ the opposite of this happens. Therefore, at each of these limits the denominator diverges and the potential approaches zero.

The only minimum of the function is at $\boxed{x = 0}$, where $\boxed{V = -1}$:

$$\begin{aligned}\frac{\partial V(x)}{\partial x} &= \frac{8(e^x - e^{-x})}{(e^{-x} + e^x)^3} = 0. \\ &\Downarrow \\ e^x &= e^{-x} \\ &\Downarrow \\ x &= \boxed{0}.\end{aligned}$$

c) To perform the Taylor expansion, we need the second derivative of the potential at the minimum:

$$\left.\frac{\partial^2 V(x)}{\partial x^2}\right|_{x=0} = \left[8\left(\frac{1}{(e^x + e^{-x})^2} - 3\frac{(e^x - e^{-x})^2}{(e^x + e^{-x})^4}\right)\right]\Bigg|_{x=0} = 2.$$

With this,

$$V(x) \simeq \overbrace{V(0)}^{=-1} + x \overbrace{\left(\frac{\partial V(x)}{\partial x}\right)\Big|_{x=0}}{=0} + \frac{1}{2}x^2 \overbrace{\left(\frac{\partial^2 V(x)}{\partial x^2}\right)\Big|_{x=0}}{=2} = \boxed{-1 + x^2}.$$

The result is the Hamiltonian of a harmonic oscillator with $\frac{1}{2}m\omega^2 = 1 \Rightarrow \omega = \sqrt{2}$, and the zero point energy is $\frac{1}{2}\hbar\omega = \frac{\sqrt{2}}{2}$ (in atomic units, where $\hbar = m = 1$). This must be added to the constant energy -1 , giving

$$\boxed{E_0 \approx \frac{\sqrt{2}}{2} - 1 \approx -0.29}.$$

d) We replace the given function into the Schrödinger equation:

$$\begin{aligned}
 \left(-\frac{1}{2} \frac{\partial^2}{\partial x^2} - \left(\frac{2}{e^x + e^{-x}} \right)^2 \right) \frac{2}{e^x + e^{-x}} &\stackrel{?}{=} E \frac{2}{e^x + e^{-x}} \\
 \Downarrow \\
 -\frac{1}{2} \frac{\partial^2}{\partial x^2} \frac{2}{e^x + e^{-x}} - \left(\frac{2}{e^x + e^{-x}} \right)^2 \frac{2}{e^x + e^{-x}} &\stackrel{?}{=} E \frac{2}{e^x + e^{-x}} \\
 \Downarrow \\
 -\frac{1}{2} \frac{2}{e^x + e^{-x}} \left(\frac{2(e^x - e^{-x})^2}{(e^x + e^{-x})^2} - 1 \right) - \left(\frac{2}{e^x + e^{-x}} \right)^3 \frac{2}{e^x + e^{-x}} &\stackrel{?}{=} E \frac{2}{e^x + e^{-x}} \\
 \Downarrow \\
 -\frac{(e^x - e^{-x})^2}{(e^x + e^{-x})^2} + \frac{1}{2} - \left(\frac{2}{e^x + e^{-x}} \right)^2 &\stackrel{?}{=} E \\
 \Downarrow \\
 -\frac{\overbrace{e^{2x} - 2 + e^{-2x} + 4}^{(e^x + e^{-x})^2}}{(e^x + e^{-x})^2} + \frac{1}{2} &\stackrel{?}{=} E
 \end{aligned}$$

So, this is an eigenfunction with $E = -\frac{1}{2}$. This differs from the harmonic approximation by over 40%.

3. For the box with the mobile inner wall,

a) The Hamiltonian is

$$\hat{H} = \frac{\hat{p}^2}{2m},$$

with the boundary conditions

$$\psi(\ell) = \psi(L) = 0.$$

b) The eigenfunction and energies are those of a 1D box:

$$\begin{aligned}
 \psi_n(x) &= \sqrt{\frac{2}{L-\ell}} \sin\left(\frac{n\pi(x-\ell)}{L-\ell}\right), \\
 E_n &= \frac{h^2 n^2}{8m(L-\ell)^2}.
 \end{aligned}$$

c) We need only set n to 1:

$$\begin{aligned}
 \psi_1(x) &= \sqrt{\frac{2}{L-\ell}} \sin\left(\frac{\pi(x-\ell)}{L-\ell}\right), \\
 E_1 &= \frac{h^2}{8m(L-\ell)^2}.
 \end{aligned}$$

The classical spring energy is

$$E_S = \frac{1}{2} k (L - \ell)^2$$

d) The equilibrium position will be the one having minimal energy, such that

$$\begin{aligned}\frac{dE(\ell)}{d\ell} &= \frac{d}{d\ell} \left(\frac{h^2}{8m(L-\ell)^2} + \frac{1}{2}k(L-\ell)^2 \right) \\ &= \frac{2h^2}{8m(L-\ell)^3} - k(L-\ell) = 0 \\ &\Downarrow \\ \ell_0 &= \boxed{L - \left(\frac{2h^2}{8mk} \right)^{\frac{1}{4}}}.\end{aligned}$$

Using this,

$$\boxed{E_g = \frac{h^2}{8m\sqrt{\frac{2h^2}{8mk}}} + \frac{1}{2}k\sqrt{\frac{2h^2}{8mk}}}.$$

e) We expand the potential in a Taylor series around the minimum:

$$\begin{aligned}\left. \frac{d^2E(\ell)}{d\ell^2} \right|_{\ell=\ell_0} &= \left. \frac{d}{d\ell} \left(\frac{2h^2}{8m(L-\ell)^3} - k(L-\ell) \right) \right|_{\ell=\ell_0} \\ &= \frac{6h^2}{8m(L-\ell_0)^4} + k \\ &= \boxed{4k}.\end{aligned}$$

So,

$$V(\ell) \simeq E_g + \frac{1}{2}(4k)(\ell - \ell_0)^2$$

and with $M\omega^2 = 4k$ we have

$$\Delta E = \frac{1}{2}\hbar\omega = \boxed{\frac{1}{2}\hbar\sqrt{\frac{4k}{M}}}.$$

4. For the LiH molecule,

a) According to the hydrogen-like atom model from class, using the fact that in atomic units $e = 1$ and $a_0 = 1$,

$$\alpha_{1S}^H = -\frac{1^2 e^2}{2a_0} \frac{1}{1^2} = \boxed{-\frac{1}{2}}, \quad \alpha_{2S}^{Li} = -\frac{3^2 e^2}{2a_0} \frac{1}{2^2} = \boxed{-\frac{9}{8}}.$$

b) With $\beta = \frac{1}{2} \left(-\frac{1}{2} - \frac{9}{8} \right) = -\frac{13}{16}$, the secular equation reads

$$\begin{pmatrix} \alpha_{1S}^H - \lambda & \beta \\ \beta & \alpha_{2S}^{Li} - \lambda \end{pmatrix} \begin{pmatrix} a_H \\ a_{Li} \end{pmatrix} = \boxed{\begin{pmatrix} -\frac{1}{2} - \lambda & -\frac{13}{16} \\ -\frac{13}{16} & -\frac{9}{8} - \lambda \end{pmatrix} \begin{pmatrix} a_H \\ a_{Li} \end{pmatrix} = 0}.$$

c) The determinant gives

$$\left(-\frac{1}{2} - \lambda \right) \left(-\frac{9}{8} - \lambda \right) - \left(\frac{13}{16} \right)^2 = 0 \Rightarrow \boxed{\lambda_{1,2} = \frac{1}{16} \left(-13 \pm \sqrt{194} \right) = -1.68, 0.058}.$$

The corresponding eigenvectors are

$$(0.56, 0.82), (-0.82, 0.56),$$

Such that the molecular orbitals will be

$$\begin{aligned} |\psi_1\rangle &\approx \boxed{0.56 |1S_H\rangle + 0.82 |2S_{Li}\rangle}, \oplus \oplus \\ |\psi_2\rangle &\approx \boxed{-0.82 |1S_H\rangle + 0.56 |2S_{Li}\rangle}, \odot \oplus \end{aligned}$$

In the ground state we will have two electrons in ψ_1 and a total energy of $2\lambda_1$.

d) The charge density is twice the square of the amplitudes:

$$n_H \approx 2 \times 0.56^2 \approx \boxed{0.62}, n_{Li} \approx 2 \times 0.82^2 \approx \boxed{1.34}.$$

e) In the second excited state, the particles have different spins and the wavefunction must have the symmetric form:

$$\psi(1,2) = \psi_2(1)\psi_1(2)$$

Once again, the charge density is twice the square of the amplitudes:

$$n_H \approx 2 \times 0.82^2 \approx \boxed{1.34}, n_{Li} \approx 2 \times 0.56^2 \approx \boxed{0.62}.$$