

1. Given  $\hat{H} = -\frac{1}{2}\frac{d^2}{dx^2} + \frac{1}{2}x^2 + \frac{1}{5}x$ ,

a)  $\hat{H}_0 = -\frac{1}{2}\frac{d^2}{dx^2} + \frac{1}{2}x^2$  describes an HO with  $\hbar = m = \omega = \alpha = 1$ , so:

$$\varepsilon_0 = \frac{1}{2}, \varepsilon_1 = \frac{3}{2},$$

$$\psi_0(x) = \left(\frac{1}{\pi}\right)^{\frac{1}{4}} e^{-\frac{x^2}{2}}, \psi_1(x) = \left(\frac{4}{\pi}\right)^{\frac{1}{4}} x e^{-\frac{x^2}{2}}.$$

b) There are three matrix elements to calculate:

$$H_{00} = \langle \psi_0 | \hat{H} | \psi_0 \rangle = \varepsilon_0 + \frac{1}{5\sqrt{\pi}} \overbrace{\int dx x e^{-x^2}}^{=0} = \boxed{\frac{1}{2}},$$

$$H_{11} = \langle \psi_1 | \hat{H} | \psi_1 \rangle = \varepsilon_1 + \frac{2}{5\sqrt{\pi}} \overbrace{\int dx x^3 e^{-x^2}}^{=0} = \boxed{\frac{3}{2}},$$

$$H_{01} = H_{10}^* = \langle \psi_0 | \hat{H} | \psi_1 \rangle = \overbrace{\langle \psi_0 | \varepsilon_1 | \psi_1 \rangle}^{=0} + \sqrt{\frac{2}{\pi}} \frac{1}{5} \overbrace{\left( \int dx x^2 e^{-x^2} \right)}^{=\frac{\sqrt{\pi}}{2}} = \boxed{\frac{1}{5\sqrt{2}}}.$$

The overlap matrix is  $S_{ij} = \delta_{ij}$ , since the states are orthogonal.

c) For  $\phi = c_0\psi_0 + c_1\psi_1$ , we must solve

$$\sum_j (H_{ij} - \varepsilon \delta_{ij}) (c_j) = 0 \Rightarrow \begin{vmatrix} \frac{1}{2} - \varepsilon & \frac{1}{5\sqrt{2}} \\ \frac{1}{5\sqrt{2}} & \frac{3}{2} - \varepsilon \end{vmatrix} = 0 \Rightarrow \left(\frac{1}{2} - \varepsilon\right) \left(\frac{3}{2} - \varepsilon\right) - \frac{1}{50} = 0,$$

or

$$\boxed{\varepsilon_{0,1} = 1 \pm \frac{3\sqrt{3}}{10}}.$$

d) These are both  $\boxed{0}$  (as we have seen in the earlier calculation).

e) The results are:

	Variational	Perturbation	Exact
$\varepsilon_0$	0.480385	$\frac{1}{2}$	0.48
$\varepsilon_1$	1.51962	$\frac{3}{2}$	1.48
$\varepsilon_1 - \varepsilon_0$	$\frac{3\sqrt{3}}{5} \approx 1.039$	1	1

So, variation gives a better ground state but worse excitation energy.

2. For the Lorentzian wavefunction  $\psi(x) = \frac{1}{\pi} \frac{\alpha}{x^2 + \alpha^2}$ ,

a) The potential must be even and have a minimum at zero, which is also the most probable position for the electron to be measured in and its expectation value. This is the ground state, since it has no nodes.

b) The Schrödinger equation is:

$$\left( \frac{\hat{p}^2}{2m} + V(x) \right) \frac{1}{\pi} \frac{\alpha}{x^2 + \alpha^2} = \varepsilon \frac{1}{\pi} \frac{\alpha}{x^2 + \alpha^2}.$$

c) Applying the definition of the momentum operator gives:

$$\begin{aligned}
 -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \frac{1}{\pi} \frac{\alpha}{x^2 + \alpha^2} &= (\varepsilon - V(x)) \frac{1}{\pi} \frac{\alpha}{x^2 + \alpha^2} \\
 &\Downarrow \\
 \frac{\hbar^2}{2m} \frac{1}{\pi} \frac{\partial}{\partial x} \frac{2x\alpha}{(x^2 + \alpha^2)^2} &= (\varepsilon - V(x)) \frac{1}{\pi} \frac{\alpha}{x^2 + \alpha^2} \\
 &\Downarrow \\
 \frac{\hbar^2}{2m} \frac{1}{\pi} \frac{2\alpha}{(x^2 + \alpha^2)^2} - \frac{\hbar^2}{2m} \frac{1}{\pi} \frac{2\alpha x \cdot 2 \cdot 2x}{(x^2 + \alpha^2)^3} &= (\varepsilon - V(x)) \frac{1}{\pi} \frac{\alpha}{x^2 + \alpha^2} \\
 &\Downarrow \\
 V(x) &= \boxed{\varepsilon - \frac{\hbar^2}{m} \frac{1}{x^2 + \alpha^2} + \frac{4\hbar^2}{m} \frac{x^2}{(x^2 + \alpha^2)^2}}.
 \end{aligned}$$

The constant determines the energy of the state.

d) The shifted wavefunction is  $\boxed{\psi = \frac{1}{\pi} \frac{\alpha}{(x - x_0)^2 + \alpha^2}}$ , no change in energy.

3. For the box with the mobile wall,

a) The single particle Hamiltonians are:

$$\hat{H}_1 = \frac{\hat{p}_1^2}{2m}, \quad \hat{H}_2 = \frac{\hat{p}_2^2}{2m},$$

The boundary conditions are

$$\begin{aligned}
 \psi_1(0) &= \psi_1(\ell) = 0, \\
 \psi_2(\ell) &= \psi_2(L) = 0.
 \end{aligned}$$

This describes particles in a box, so:

$$\begin{aligned}
 \psi_{1n}(x_1) &= \sqrt{\frac{2}{\ell}} \sin \frac{n\pi x_1}{\ell}, \quad E_{1n} = \frac{h^2}{8m} \frac{n^2}{\ell^2}, \\
 \psi_{2n}(x_2) &= \sqrt{\frac{2}{L-\ell}} \sin \frac{n\pi(x_2 - \ell)}{L-\ell}, \quad E_{2n} = \frac{h^2}{8m} \frac{n^2}{(L-\ell)^2}.
 \end{aligned}$$

The assumption is similar to the one behind the Born-Oppenheimer approximation: the wall is much more massive, therefore its motion can be neglected when solving for the electronic wavefunction.

b) The full Hamiltonian is

$$\boxed{\hat{H} = \hat{H}_1 + \hat{H}_2},$$

and it has the eigenfunctions

$$\boxed{\Psi_{nm}(x_1, x_2) = \psi_{1n}(x_1) \psi_{2m}(x_2)}$$

and energies

$$\boxed{E_{nm} = E_{1n} + E_{2m}}.$$

c) The ground state is

$$\Psi_{11}(x_1, x_2) = \psi_{11}(x_1) \psi_{21}(x_2) = \boxed{\frac{2}{\sqrt{\ell(L-\ell)}} \sin\left(\frac{\pi x_1}{\ell}\right) \sin\left(\frac{\pi(x_2 - \ell)}{L-\ell}\right)}.$$

(with the understanding that each wavefunction is nonzero only within the appropriate box.) Its energy is

$$E_0(\ell) = E_{11}(\ell) + E_{21}(\ell) = \frac{\hbar^2}{8m} \left( \frac{1}{\ell^2} + \frac{1}{(L-\ell)^2} \right) = \boxed{\frac{\hbar^2}{8m} \frac{(L-\ell)^2 + \ell^2}{\ell^2(L-\ell)^2}}.$$

d) We need to minimize the energy with respect to  $\ell$ :

$$\begin{aligned} \frac{\partial E_0(\ell)}{\partial \ell} &= \frac{\hbar^2}{8m} \left( -\frac{2}{\ell^3} + \frac{2}{(L-\ell)^3} \right) = 0 \\ &\Downarrow \\ \frac{2}{\ell^3} &= \frac{2}{(L-\ell)^3} \\ &\Downarrow \\ (L-\ell)^3 &= \ell^3. \end{aligned}$$

While this is a third-order equation, we can safely assume that both  $\ell$  and  $L-\ell$  are real and positive such that we can take the third root of both sides, giving  $L-\ell = \ell \Rightarrow \boxed{\ell = \frac{L}{2}}$ . Another way is to guess from symmetry that the answer must be either  $\ell = 0, L$  (which doesn't solve the above equation) or  $\ell = \frac{L}{2}$  (which does). Therefore,

$$E_0 = E_0(\ell)|_{\ell=\frac{L}{2}} = \frac{\hbar^2}{8m} \left( \frac{4}{L^2} + \frac{4}{L^2} \right) = \boxed{\frac{\hbar^2}{mL^2}}.$$

This is four times the energy for two particles in an  $L$ -sized box. If the wall is treated classically, it lies at the bottom of the particle potential and has no further energy.

e) We expand the potential in a Taylor series around its minimum. First,

$$\left. \frac{\partial^2 E_0(\ell)}{\partial \ell^2} \right|_{\ell=\frac{L}{2}} = \left[ \frac{\hbar^2}{8m} \left( \frac{6}{\ell^4} + \frac{6}{(L-\ell)^4} \right) \right] \Big|_{\ell=\frac{L}{2}} = \frac{24\hbar^2}{mL^4}.$$

With this, comparing to a harmonic oscillator,

$$E_0(\ell) \simeq \frac{\hbar^2}{mL^2} + \frac{\overbrace{1 \ 24\hbar^2}^{\equiv \frac{1}{2}M\omega^2}}{2 \ mL^4} \left( \ell - \frac{L}{2} \right)^2,$$

and we can find

$$\omega = \sqrt{\frac{24\hbar^2}{MmL^4}},$$

such that the correction to the energy is

$$\frac{1}{2}\hbar\omega = \boxed{\frac{1}{4\pi} \sqrt{\frac{24\hbar^4}{MmL^4}} = \sqrt{\frac{3\hbar^4}{2\pi^2 MmL^4}}}.$$

4. For  $\text{Na}_3$ ,

- $1S^2 2S^2 2P^6 3S^1$ . Only the  $3S$  orbitals will be used in the approximation.
- For the linear configuration,

i. The secular determinant:

$$\begin{vmatrix} \alpha - \epsilon & \beta & 0 \\ \beta & \alpha - \epsilon & \beta \\ 0 & \beta & \alpha - \epsilon \end{vmatrix}.$$

ii. We need to solve

$$(\alpha - \epsilon) (\alpha^2 - 2\alpha\epsilon - 2\beta^2 + \epsilon^2) = 0.$$

The answers, in decreasing order of size, are

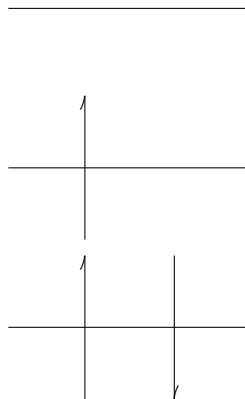
$$\begin{aligned} \epsilon_3 &= \alpha - \sqrt{2}\beta, \\ \epsilon_2 &= \alpha, \\ \epsilon_1 &= \alpha + \sqrt{2}\beta. \end{aligned}$$

iii. The molecular orbitals are given by:

$$\begin{aligned} \epsilon_3 &\rightarrow \sqrt{2}c_1 = \sqrt{2}c_3 = -c_2, \oplus \ominus \oplus \\ \epsilon_2 &\rightarrow c_2 = 0, c_1 = -c_3, \oplus \circ \ominus \\ \epsilon_1 &\rightarrow \sqrt{2}c_1 = \sqrt{2}c_3 = c_2, \oplus \oplus \oplus \end{aligned}$$

(the central one should be “bigger” in the first and last cases...)

iv. The ground state has two electrons in  $\epsilon_1$  and one in  $\epsilon_2$ . The electron in the higher orbit will be in the *doublet* state, since the total spin in the unfilled orbital is  $1/2$ .



v. The degeneracy is 2 (due to the spin).

c) For the cyclic configuration,

i. The determinant is

$$\begin{vmatrix} \alpha - \epsilon & \beta & \beta \\ \beta & \alpha - \epsilon & \beta \\ \beta & \beta & \alpha - \epsilon \end{vmatrix}.$$

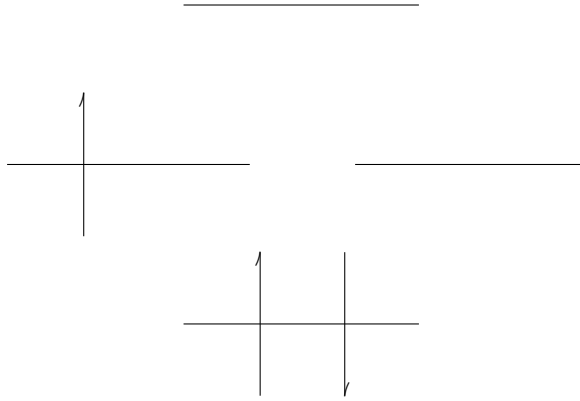
ii. Shown by substitution (it's easy to see that the first two rows are all  $\beta$ ). Factor the determinant to show that  $\alpha - \beta$  is degenerate.

$$\begin{aligned} \epsilon_{2,3} &= \alpha - \beta, \\ \epsilon_1 &= \alpha + 2\beta. \end{aligned}$$

iii. The molecular orbitals are given by:

$$\begin{aligned} \epsilon_3 &\rightarrow \sqrt{2}c_1 = \sqrt{2}c_3 = -c_2, \oplus \ominus \oplus \\ \epsilon_2 &\rightarrow c_2 = 0, c_1 = -c_3, \oplus \circ \ominus \\ \epsilon_1 &\rightarrow \sqrt{2}c_1 = \sqrt{2}c_3 = c_2, \oplus \oplus \oplus \end{aligned}$$

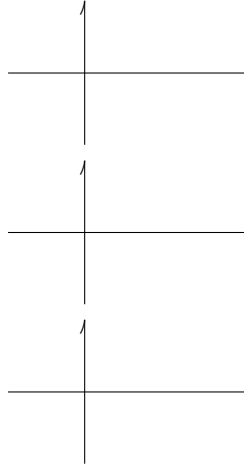
iv. The spin state is still a *doublet*, since the total spin in the unfilled orbitals is  $1/2$ .



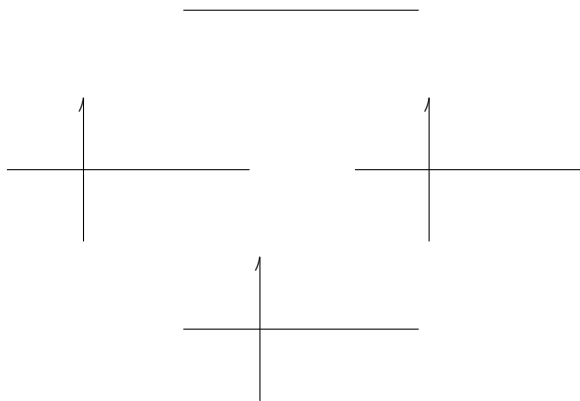
v. The degeneracy is 4.

d) The linear configuration has energy  $2 \cdot (\alpha + \sqrt{2}\beta) + 1 \cdot \alpha = 3\alpha + 2\sqrt{2}\beta$ , while the cyclic configuration has the energy  $2 \cdot (\alpha + 2\beta) + 1 \cdot (\alpha - \beta) = 3\alpha + 3\beta$ . Therefore, the cyclic configuration (which has the lower energy) is more stable.

e) In the linear case, we have the following configuration:



This has total spin 1.5, and is therefore a *quadruplet* with energy  $(\alpha + \sqrt{2}\beta) + \alpha + (\alpha - \sqrt{2}\beta) = 3\alpha$ . In the cyclic case, the configuration is:



This is also a *quadruplet*, and has energy  $\alpha + 2\beta + 2 \cdot (\alpha - \beta) = 3\alpha$ . Therefore, both isomers are equally stable in this case.