— $\alpha - 1.61\beta$ — $\alpha - \sqrt{3}\beta$

— $\alpha - 0.61\beta$

1. Butadiene TMM + + α

$\alpha + 0.61\beta$

$\alpha + 1.61\beta$ # $\alpha + \sqrt{3}\beta$

$$E^{tot}(\text{butadiene}) = 2(\alpha + 1.61\beta) + 2(\alpha + .61\beta) = 4\alpha + 4.44\beta$$

$$E^{tot}(\text{TMM}) = 2(\alpha + \sqrt{3}\beta) + 2\alpha = 4\alpha + 3.46\beta$$

So butadiene is predicted to be appreciably more stable.

2. $H = -\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2} + \gamma x^4$

$$H^{(0)} = -\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2} + \frac{1}{2}kx^2, \quad H^{(1)} = \gamma x^4 - \frac{1}{2}kx^2$$

(a) $E^{(0)} = \frac{\hbar\omega}{2}$, $\langle \psi_0^{(0)} | \gamma x^4 - \frac{1}{2}kx^2 | \psi_0^{0} \rangle$

$$E^{(1)} = 3\left(\frac{\hbar}{2m\omega}\right)^2\gamma - \frac{1}{4}\hbar\omega$$

$$E^{(0)} + E^{(1)} = \frac{\hbar\omega}{4} + 3\left(\frac{\hbar}{2m\omega}\right)^2\gamma$$

(b) What is the 2nd order energy

$\langle 0 | x^2 | 2 \rangle$ is nonzero as are $\langle 0 | x^4 | 4 \rangle$ and $\langle 0 | x^4 | 2 \rangle$

So the 2nd order energy correction is

$$\frac{\langle 0 | -\frac{1}{2}kx^2 + \gamma x^4 | 2 \rangle \langle 2 | -\frac{1}{2}kx^2 + \gamma x^4 | 0 \rangle}{-2\hbar\omega} + \frac{\langle 0 | \gamma x^4 | 4 \rangle \langle 4 | \gamma x^4 | 0 \rangle}{-4\hbar\omega}$$

$$\langle 0 | x^4 | 4 \rangle = \left(\frac{\hbar}{2m\omega}\right)^2 (4 \cdot 3 \cdot 2 \cdot 1) = \left(\frac{\hbar}{m\omega}\right)^2 6$$

$$\frac{\gamma^2 |\langle 0 | x^4 | 4 \rangle|^2}{-4\hbar\omega} = \left(\frac{\hbar}{m\omega}\right)^4 \gamma^2 \frac{36}{-4\hbar\omega} = -9\frac{\hbar^3}{\omega^5}\gamma^2$$

$$\left.\begin{aligned} \langle 0 | x^2 | 2 \rangle &= \frac{\hbar}{2m\omega}\sqrt{2} \\ \langle 0 | x^4 | 2 \rangle &= \left(\frac{\hbar}{2m\omega}\right)^2 6\sqrt{2} \end{aligned}\right\} \quad \frac{|\langle 0 | \gamma x^4 - \frac{1}{2}kx^2 | 2 \rangle|^2}{-2\hbar\omega} = \frac{\left(-\frac{1}{2}k\left(\frac{\hbar}{2m\omega}\right)\sqrt{2} + \left(\frac{\hbar}{2m\omega}\right)^2 6\sqrt{2}\right)^2}{-2\hbar\omega}$$

So the contribution from coupling with $|2\rangle$ is

$$-\frac{1}{2\hbar\omega}\left[\frac{1}{2}k^2\left(\frac{\hbar}{2m\omega}\right)^2 - 12\left(\frac{\hbar}{2m\omega}\right)^3 k\gamma + 72\left(\frac{\hbar}{2m\omega}\right)^4\gamma^2\right]$$

3. Sloped particle in box problem

$$\left.\begin{aligned} H_{11} &= \langle 1|-\tfrac{1}{2}\tfrac{d^2}{dx^2}+ax|1\rangle \\ H_{22} &= \langle 2|-\tfrac{1}{2}\tfrac{d^2}{dx^2}+ax|2\rangle \\ H_{12} &= \langle 1|-\tfrac{1}{2}\tfrac{d^2}{dx^2}+ax|2\rangle \end{aligned}\right\}\ \text{using atomic units}$$

$$H_{11} = \frac{\pi^2\hbar^2}{2mL^2}+a\frac{L}{2},\quad H_{22} = \frac{4\pi^2\hbar^2}{2mL^2}+a\frac{L}{2},\quad H_{12} = a\langle 1|x|2\rangle$$

$$H_{12} = \frac{2}{L}\int_0^L x\sin\left(\frac{\pi x}{L}\right)\sin\left(\frac{2\pi x}{L}\right)dx = \frac{2}{L}\left(-\frac{8L^2}{9\pi^2}\right) = -\frac{16L}{9\pi^2}$$

$$E = \frac{H_{11}+H_{22}}{2} - \frac{1}{2}\sqrt{(H_{22}-H_{11})^2+4H_{12}^2}$$

$$E = \frac{\pi^2\hbar^2}{2mL^2}\frac{5}{2} - \frac{1}{2}\sqrt{\left(\frac{3\pi^2\hbar^2}{2mL^2}\right)^2+4\left(\frac{256L^2}{81\pi^4}\right)} + aL$$

switch back to a.u. and let $L = 10$ a.u.

$$E = \frac{5\pi^2}{4(100)} - \frac{1}{2}\sqrt{\frac{9\pi^2}{4(10)^4}+4\,\frac{256\cdot 100}{81\pi^4}} + aL$$

4. (a) with xy, one can reach all d_{xy} states

(b) with $z + z^2$, one can reach all p_z and d_{z^2} states

(c) What is the average of $1/r$.

One knows from the virial theorem that $E_{KE} = -\frac{1}{2}E_{PE}$

So $\langle 0|-\frac{1}{r}|0\rangle = -27.2\text{eV}$. But because the question asks about $1/r$, the answer is $+27.2\text{ eV}$

(d) Maxima of radial distribution function of the 2s orbital of He^{+2}

$$r^2 N^2 Z \quad r^2\left(2-\frac{Zr}{a_0}\right)^2 e^{-Zr/a_0}$$

differentiate wrt r, and set $=0$

obtain $8r - \frac{32}{a_0} r^2 + \frac{32 r^3}{a_0^2} - \frac{8r^4}{a_0^3} = 0$

factor out $8r$, $1 - 4\frac{r}{a_0} + 4\left(\frac{r}{a_0}\right)^2 - \left(\frac{r}{a_0}\right)^3 = 0$

$\rightarrow r = 1, \frac{1}{2}(3-\sqrt{5}), \frac{1}{2}(3+\sqrt{5})$, all multiplied by a_0

$r = 1 a_0, 0.38 a_0, 2.62 a_0$

$0.38 a_0$ and $2.62 a_0$ are maxima; $1 a_0$ is a minimum

(5) $\psi = \frac{1}{\sqrt{2}}(\psi_0 - \psi_1)$, where ψ_0 and ψ_1 are HO efs.

$\langle \psi | H^2 | \psi \rangle = \frac{1}{2} \langle \psi_0 - \psi_1 | H^2 | \psi_0 - \psi_1 \rangle = \langle \psi_0 - \psi_1 | E_0^2 \psi_0 - E_1^2 \psi_1 \rangle \frac{1}{2}$

$= \frac{1}{2} (E_0^2 + E_1^2)$

$|\langle \psi | H | \psi \rangle|^2 = \frac{1}{4} \{ E_0 - E_1 \}^2 = \frac{1}{4} (E_0^2 + E_1^2 - 2 E_0 E_1)$

$\langle \psi | H^2 | \psi \rangle - \langle \psi | H | \psi \rangle^2 = \frac{1}{4}(E_0^2 + E_1^2) - \frac{1}{2} E_0 E_1$

$= \frac{1}{4} [E_0 - E_1]^2$

$\sigma_H = \sqrt{\frac{1}{4}(E_0 - E_1)^2} = \frac{1}{2} |E_0 - E_1| = \frac{1}{2}\hbar\omega$