Variational methods

- ~~guess~~ x^6 potential or x^4 potential with $N\exp(-\cancel{x^2/2})$ trial function. T 4 (1)
- LHO with $\frac{A}{1+Bx^2}$ trial function, local energy - H.A.
  LHO with $a(1+\cos bx)$ in $-\pi/b - \pi/b$ interval.-
- H atom with $\exp(-\alpha x^2)$
- 1st excited state of LHO with $\psi^{trial} = Ax\exp(-ax^2)$.

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1) $\hat{H} = \frac{p^2}{2m} + Ax^6$

$$\int_{-\infty}^{\infty} e^{-(Ax^2)} = \sqrt{\frac{\pi}{A}} \qquad \int_{-\infty}^{\infty} x^2 e^{-Ax^2} = \frac{1}{2A}\sqrt{\frac{\pi}{A}} \qquad \int_{-\infty}^{\infty} x^4 e^{-Ax^2} = \frac{3}{2A}\,\frac{1}{2A}\sqrt{\frac{\pi}{A}}$$

$$\int_{-\infty}^{\infty} x^6 e^{-Ax^2} = \frac{5}{2A}\,\frac{3}{2A}\,\frac{1}{2A}\sqrt{\frac{\pi}{A}}$$

- trial function $\psi = N\exp(-ax^2)$

normalisation: $1 = \int_{-\infty}^{\infty}\psi^*\psi = N^2\int_{-\infty}^{\infty}\exp(-2ax^2) = N^2\sqrt{\frac{\pi}{2a}}$

$$\to N = \sqrt[4]{\frac{2a}{\pi}} \qquad a>0\,;\ A>0$$

energy: $\langle\psi|\hat{H}|\psi\rangle = \int_{-\infty}^{\infty}\psi^*\left[\frac{p^2}{2m} + Ax^6\right]\psi = \cancel{\int_{-\infty}\sqrt{\frac{2a}{\pi}}\exp(-a}$

$$= \sqrt{\frac{2a}{\pi}}\int_{-\infty}^{\infty}\exp(-ax^2)\left[-\frac{\hbar^2 d^2}{2m\,dx^2} + Ax^6\right]\exp(-ax^2) =$$

$$= \sqrt{\frac{2a}{\pi}}\int_{-\infty}^{\infty} dx\,\exp(-ax^2)\left[-\frac{\hbar^2}{2m}\frac{d}{dx}\Big(-2ax\exp(-ax^2)\Big) + Ax^6\exp(-ax^2)\right]$$

$$= \sqrt{\frac{2a}{\pi}}\int dx\,\exp(-ax^2)\left[-\frac{\hbar^2}{2m}\Big(-2a\exp(-ax^2) + 4a^2x^2\exp(-ax^2)\Big) + Ax^6\exp(-ax^2)\right]$$

$$= \sqrt{\frac{2a}{\pi}}\int_{-\infty}^{\infty} dx\left[+\frac{\hbar^2}{2m}2a\exp(-2ax^2) - \frac{\hbar^2}{2m}4a^2x^2\exp(-2ax^2) + Ax^6\exp(-2ax^2)\right]$$

$$= \sqrt{\frac{2a}{\pi}}\left[\frac{\hbar^2}{2m}2a\sqrt{\frac{\pi}{2a}} - \frac{\hbar^2}{2m}4a^2\frac{1}{4a}\sqrt{\frac{\pi}{2a}} + A\frac{15}{8\cdot 8a^3}\sqrt{\frac{\pi}{2a}}\right]$$

$$= \frac{\hbar^2}{2m}2a - \frac{\hbar^2}{2m}a + A\frac{15}{64a^3} = \frac{\hbar^2 a}{2m} + A\frac{15}{64a^3}\ ; \quad \frac{dE(a)}{da} = \frac{\hbar^2}{2m} - \frac{45A}{64a^4} = 0 \to \left.\frac{d^2E}{da^2}\right|_{a_{min}} > 0$$

$$\cancel{\frac{dE(a)}{da} = 0 = \frac{2\hbar^2}{2m} - \frac{\hbar^2}{2m}8a - \frac{45A}{64a^4} \to \frac{\hbar^2}{m}a^4 - \frac{4\hbar^2}{m}a^3 - \frac{45A}{64} = 0}$$

$$\frac{\hbar^2}{2m} = \frac{45A}{64a^4} \Rightarrow a_0^4 = \frac{45A}{64}\,\frac{2m}{\hbar^2} \Rightarrow a_0 = \frac{1}{2}\sqrt{\frac{3}{\hbar}}\sqrt[4]{\frac{mA5}{2}}$$

$\rightarrow \psi = N \exp(-ax^2) \quad ; N = \sqrt[4]{\frac{2a}{\pi}} \quad ; \quad a = \frac{1}{2}\sqrt{\frac{3}{\hbar}}\sqrt[4]{\frac{5mA}{2}}$ $\qquad$ T4(2)

$$E = \frac{\hbar^2 a}{2m} + A\frac{15}{64a^3} = \frac{\hbar^2}{2m}\frac{1}{2}\sqrt{\frac{3}{\hbar}}\sqrt[4]{\frac{5mA}{2}} + \frac{15A}{64}\frac{8\hbar}{3}\sqrt{\frac{\hbar}{3}}\sqrt[4]{\left(\frac{2}{5mA}\right)^3}$$

$$= \frac{\hbar^2}{4m}\sqrt{\frac{3}{\hbar}}\sqrt[4]{\frac{5mA}{2}} + \frac{5A\hbar}{8}\sqrt{\frac{\hbar}{3}}\sqrt[4]{\frac{8}{125m^3A^3}}$$

$$E = \langle\psi|\hat{H}|\psi\rangle = \sqrt{\frac{2a}{\pi}}\int_{-\infty}^{\infty}\exp(-ax^2)\left[-\frac{\hbar^2 d^2}{2m\,dx^2} + Ax^6\right]\exp(-ax^2) =$$

$$= \sqrt{\frac{2a}{\pi}}\int_{-\infty}^{\infty}\exp(-ax^2)\left[-\frac{\hbar^2}{2m}\left(-2a\exp(-ax^2) + a^2x^2\exp(-ax^2)\right) + Ax^6\right]\exp(-ax^2)$$

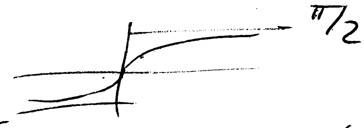
$$= \sqrt{\frac{2a}{\pi}}\int_{-\infty}^{\infty}\left[\frac{2\hbar^2 a}{2m}\exp(-2ax^2) - \frac{4\hbar^2 a^2x^2}{2m}\exp(-2ax^2) + Ax^6\exp(-2ax^2)\right]$$

$$= \sqrt{\frac{2a}{\pi}}\left[\frac{2\hbar^2 a}{2m}\sqrt{\frac{\pi}{2a}} - \frac{4\hbar^2 a^2}{2m}\sqrt{\frac{\pi}{2a}}\frac{1}{4a} + A\frac{5}{4a}\frac{3}{4a}\frac{1}{4a}\sqrt{\frac{\pi}{2a}}\right]$$

$$= \frac{\hbar^2 a}{2m} + \frac{15A}{64a^3} \quad \text{OK} \ldots$$

$$\frac{\hbar^{3/2}A^{1/4}}{m^{3/4}}\cdot\frac{\sqrt{3}}{4\sqrt{2}}\frac{\sqrt[4]{5}}{4} + \frac{\hbar^{3/2}A^{1/4}}{m^{3/4}}\cdot\frac{\sqrt[4]{5}}{\sqrt{3}\,4\,2^{3/4}}$$

LHO with $\frac{A}{1+Bx^2}$ trial function



$$\hat{H} = \frac{p^2}{2m} + \frac{1}{2}m\omega^2x^2 = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2x^2$$

$$\psi = \frac{A}{1+Bx^2} \qquad \int_{-\infty}^{\infty}\psi^*\psi\,dx = \int_{-\infty}^{\infty}\frac{A^2}{(1+Bx^2)^2} = A^2\left(\frac{x}{2(Bx^2+1)} + \frac{\arctan(\sqrt{B}x)}{2\sqrt{B}}\right)\Bigg|_{-\infty}^{\infty}$$

$$= \frac{A^2\arctan(\sqrt{B}x)}{2\sqrt{B}}\Bigg|_{-\infty}^{\infty} = \frac{A^2}{2\sqrt{B}}\left(\frac{\pi}{2} + \frac{\pi}{2}\right) = \frac{\pi}{2}\frac{A^2}{\sqrt{B}} = 1 \quad \cancel{\Rightarrow A = \sqrt{B}}$$

$$\Rightarrow A^2 = \frac{\sqrt{B}\,2}{\pi}$$

$$\Rightarrow \psi = \sqrt{\frac{2\sqrt{B}}{\pi}}\frac{1}{1+Bx^2} \qquad A = \sqrt{\frac{2\sqrt{B}}{\pi}}$$

$$\langle\psi|H|\psi\rangle = \int_{-\infty}^{\infty}\frac{2\sqrt{B}}{\pi}\frac{1}{1+Bx^2}\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2x^2\right)\frac{1}{1+Bx^2} \qquad = \sqrt{\frac{2\sqrt{B}}{\pi}}$$

$$= \frac{2\sqrt{B}}{\pi}\int_{-\infty}^{\infty}\frac{1}{1+Bx^2}\left(-\frac{\hbar^2}{2m}\frac{d}{dx}\frac{-1}{(1+Bx^2)^2}2Bx + \frac{1}{2}m\omega^2\frac{x^2}{1+Bx^2}\right)dx$$

$$= \frac{2\sqrt{B}}{\pi}\int_{-\infty}^{\infty}\frac{1}{1+Bx^2}\left(-\frac{\hbar^2}{2m}\left[\frac{2\cdot(2Bx)^2}{(1+Bx^2)^3} - \frac{2B}{(1+Bx^2)^2}\right] + \frac{1}{2}m\omega^2\frac{x^2}{1+Bx^2}\right)dx$$

$$= \frac{2\sqrt{B}}{\pi}\int_{-\infty}^{\infty}dx\left[-\frac{8\hbar^2B^2x^2}{2m(1+Bx^2)^4} + \frac{2B\hbar^2}{2m(1+Bx^2)^3} + \frac{1}{2}m\omega^2\frac{x^2}{(1+Bx^2)^2}\right]$$

LHO with $\frac{A}{1+Bx^2}$ trial function cont'd $\qquad$ T4(3)

$$\langle\psi|H|\psi\rangle = \frac{2\cancel{8}\sqrt{B}}{\pi}\int_{-\infty}^{\infty}\left[-\frac{8\hbar^2B^2x^2}{2m(1+Bx^2)^4}+\frac{2B\hbar^2}{2m(1+Bx^2)^3}+\frac12 m\omega^2\frac{x^2}{(1+Bx^2)^2}\right]$$

$$\cancel{\frac{8B}{\pi}}\int_{-\infty}^{\infty}\frac{x^2}{(1+Bx^2)^4} = \frac{\sqrt{B}x(3B^2x^4+8Bx^2-3)+3(Bx^2+1)^3\arctan(\sqrt{B}x)}{48B^{3/2}(Bx^2+1)^3}\Bigg|_{-\infty}^{\infty}$$

$$= \frac{3\arctan(\sqrt{B}x)}{48B^{3/2}}\Bigg|_{-\infty}^{\infty} = \frac{\arctan(\sqrt{B}x)}{16B^{3/2}} = \frac{1}{16B^{3/2}}\left(\frac{\pi}{2}+\frac{\pi}{2}\right) = \frac{\pi}{16B^{3/2}}$$

$$\int_{-\infty}^{\infty}\frac{1}{(1+Bx^2)^3} = \frac18\left[\frac{x(3Bx^2+5)}{(Bx^2+1)^2}+\frac{3\arctan(\sqrt{B}x)}{\sqrt{B}}\right]_{-\infty}^{\infty} = \frac{3}{8\sqrt{B}}\arctan(\sqrt{B}x)\Big|_{-\infty}^{\infty}$$

$$= \frac{3\pi}{8\sqrt{B}}$$

$$\int_{-\infty}^{\infty}\cancel{\tfrac12 m\omega^2}\frac{x^2}{(1+Bx^2)^2} = \frac{\arctan(\sqrt{B}x)}{2B^{3/2}} - \frac{x}{2B(Bx^2+1)}\Bigg|_{-\infty}^{\infty} = \frac{\pi}{2B^{3/2}}$$

$$\langle\psi|H|\psi\rangle = \frac{2\cancel{8}\sqrt{B}}{\pi}\left[-\frac{8\hbar^2B^2\pi}{2m\,16B^{3/2}}+\frac{2B\hbar^2\,3\pi}{2m\,8\sqrt{B}}+\frac12 m\omega^2\frac{\pi}{2B^{3/2}}\right]$$

$$-\tfrac12+\tfrac34 = -\tfrac34+\tfrac34 = \tfrac14$$

$$= 2\cancel{8}\sqrt{B}\left[-\frac{\hbar^2B^{1/2}}{2\cdot 2m}+\frac{3B^{1/2}\hbar^2}{4\cdot 2m}+\frac14\frac{m\omega^2}{B^{3/2}}\right]$$

$$= 2B^{3/2}\hbar^2 + 2\frac{m\omega^2}{B^{1/2}}$$

$$\frac{dE(B)}{dB} = \frac32\,2B^{1/2}\hbar^2 - 2m\omega^2\,\frac12\,\frac{1}{B^{3/2}} = 0$$

$$3B^{1/2}\hbar^2 - m\omega^2\frac{1}{B^{3/2}} = 0$$

$$B^2 = \frac{m\omega^2}{3\hbar^2}$$

$$\Rightarrow B = \frac{\omega}{\hbar}\sqrt{\frac{m}{3}}$$

$$E = 2\hbar^2\left(\frac{\omega}{\hbar}\sqrt{\frac{m}{3}}\right)^{3/2} + 2m\omega^2\left(\sqrt[4]{\frac{3}{m}}\sqrt{\frac{\hbar}{\omega}}\right)$$

$$\psi = A\sqrt{\frac{2}{\pi}}\sqrt[4]{\frac{m\omega}{\hbar}}\sqrt[8]{2}\,\frac{1}{1+\frac{m\omega\sqrt{2}}{\hbar}x^2}$$

$$\psi_{LHO} = \sqrt[4]{\frac{m\omega}{\pi\hbar}}\exp\left(-\frac{m\omega}{\hbar}\frac{x^2}{2}\right)$$

$$\langle\psi|H|\psi\rangle = 2\sqrt{B}\left[\frac{B^{1/2}\hbar^2}{4\cdot 2m}+\frac14\frac{m\omega^2}{B^{3/2}}\right] = \frac{2B\hbar^2}{4\cdot 2m}+\frac{\cancel{2}m\omega^2}{2B} = \frac{B\hbar^2}{4m}+\frac{\cancel{2}m\omega^2}{2B}$$

$$\cancel{\frac{dE(B)}{dB} = 2\hbar^2 - \frac{2m\omega^2}{B^2} = 0} \qquad \cancel{B = \frac{\omega}{\hbar}\sqrt{m}}$$

$$\cancel{E = 2\frac{\omega}{\hbar}\sqrt{m}\,\hbar^2}$$

$$\frac{dE(B)}{dB} = \frac{\hbar^2}{4m} - \frac{\cancel{2}m\omega^2}{2B^2} = 0$$

$$B = \frac{m\omega\sqrt{2}}{\hbar}$$

$$E = \frac{B\hbar^2}{4m}+\frac{\cancel{2}m\omega^2}{2B} = \frac{m\omega}{\hbar}\sqrt{2}\,\frac{\hbar^2}{m\,4}+\frac{2m\omega^2}{4}\,\frac{\hbar}{m\omega\sqrt{2}} =$$

$$= \frac{\omega\hbar\sqrt{2}}{4}+\frac{\omega\hbar\sqrt{2}}{4} = \frac{\sqrt{2}}{2}\omega\hbar = \omega\hbar\frac{1}{\sqrt{2}} \text{ or } \omega\hbar\frac{\sqrt{2}}{2} \text{ or } 0.707\,\omega\hbar$$

↑ virial holds!!!

($0.5\omega\hbar$ $1.5\omega\hbar$ $2.5\omega\hbar$ …)

1st excited state of LHO with $\psi^{trial} = A x \exp(-ax^2)$

$$H = \frac{p^2}{2m} + \frac{1}{2} m\omega^2 x^2$$

normalisation $\langle \psi | \psi \rangle = \int_{-\infty}^{\infty} A^2 x^2 \exp(-2ax^2) = A^2 \frac{1}{4a}\sqrt{\frac{\pi}{2a}} = 1$

$$A = 2\sqrt{a\sqrt{\frac{2a}{\pi}}} = 2\sqrt{a}\,\sqrt[4]{\frac{2a}{\pi}}$$

energy $\langle \psi | H | \psi \rangle = 4a\sqrt{\frac{2a}{\pi}} \int_{-\infty}^{\infty} x \exp(-ax^2)\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2} m\omega^2 x^2\right] x \exp(-ax^2)\, dx$

$$= 4a\sqrt{\frac{2a}{\pi}} \int_{-\infty}^{\infty} x \exp(-ax^2)\left[\left(-\frac{\hbar^2}{2m}\right)\frac{d}{dx}\left(\exp(-ax^2) - x^2 2a \exp(-ax^2)\right) + \frac{1}{2} m\omega^2 x^3 \exp(-ax^2)\right]$$

$$= 4a\sqrt{\frac{2a}{\pi}} \int_{-\infty}^{\infty} x \exp(-ax^2)\left[\left(-\frac{\hbar^2}{2m}\right)\left(-2ax\exp(-ax^2) - 4ax\exp(-ax^2) + 4a^2x^3\exp(-ax^2)\right) + \frac{1}{2} m\omega^2 x^3 \exp(-ax^2)\right]$$

$$= \frac{4a\sqrt{2a}}{\sqrt{\pi}} \int_{-\infty}^{\infty} dx\, \frac{2ax^2\hbar^2}{2m}\exp(-2ax^2) + \frac{4ax^2\hbar^2}{2m}\exp(-2ax^2) - \frac{4a^2x^4\hbar^2}{2m}\exp(-2ax^2) + \frac{1}{2} m\omega^2 x^4 \exp(-2ax^2)$$

$$= \frac{4a\sqrt{2a}}{\sqrt{\pi}} \int_{-\infty}^{\infty} \frac{3ax^2\hbar^2}{m}\exp(-2ax^2) - \frac{2a^2\hbar^2 x^4}{m}\exp(-2ax^2) + \frac{1}{2} m\omega^2 x^4 \exp(-2ax^2)$$

$$= \frac{4a\sqrt{2a}}{\sqrt{\pi}}\left[\frac{3a\hbar^2}{m}\frac{1}{4a}\sqrt{\frac{\pi}{2a}} - \frac{2a^2\hbar^2}{m}\frac{3}{4a\,4a}\sqrt{\frac{\pi}{2a}} + \frac{1}{2} m\omega^2 \frac{3}{4a\,4a}\sqrt{\frac{\pi}{2a}}\right]$$

$$= \frac{3a\hbar^2}{m} - \frac{2a^2\hbar^2}{m}\frac{3}{4a} + \frac{1}{2} m\omega^2 \frac{3}{4a} = \frac{3a\hbar^2}{m} - \frac{3}{2}\frac{a\hbar^2}{m} + \frac{1}{2} m\omega^2 \frac{3}{4a}$$

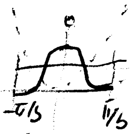
$$= \frac{3a\hbar^2}{2m} + \frac{1}{2} m\omega^2 \frac{3}{4a}$$

$$\frac{dE(a)}{da} = \frac{3\hbar^2}{2m} - \frac{1}{2} m\omega^2 \frac{3}{4a^2} \qquad \frac{3a^2\hbar^2}{2m} = \frac{3}{2}\frac{m\omega^2}{4}$$

$$a^2 = \frac{3m^2\omega^2}{4\hbar^2} \qquad a = \frac{m\omega}{2\hbar}$$

$$E = \frac{3a\hbar^2}{2m} + \frac{1}{2} m\omega^2 \frac{3}{4a} = \frac{3\hbar^2}{2m}\cdot\frac{m\omega}{2\hbar} + \frac{1}{2} m\omega^2 \frac{3}{4}\frac{2\hbar}{m\omega} = \frac{3}{4}\hbar\omega + \frac{3\hbar\omega}{4}$$

$$= \frac{3}{2}\hbar\omega \checkmark$$

- LHO with  $\psi = a(1+\cos bx)$ $\int [\cos(bx)]^2 = \frac{2bx + \sin(2bx)}{4b}$ T4(5)

$H = \frac{p^2}{2m} + \frac{1}{2} m\omega^2 x^2$ between $0 \le |x| \le \pi/b$

- normalise $\to \int_{-\pi/b}^{\pi/b} \psi^* \psi \, dx = a^2 \int_{-\pi/b} dx\, (1+\cos bx)^2 = a^2 \int_{-\pi/b}^{\pi/b} dx \left[1 + 2\cos bx + \cos^2 bx\right]$

$$= \frac{2\pi a^2}{b} + \frac{2a^2 \sin bx}{b}\Big|_{-\pi/b}^{\pi/b} + \frac{a^2}{4b}\left(2bx + \sin(2bx)\right)\Big|_{-\pi/b}^{\pi/b} =$$

$$= \frac{2\pi a^2}{b} + 0 + \frac{a^2}{4b}\left[4\pi + 0\right] = \frac{2\pi a^2}{b} + \frac{\pi a^2}{b} = 1$$

$$a^2 = \frac{b}{3\pi} \qquad a = \sqrt{\frac{b}{3\pi}}$$

$$\to \psi = \sqrt{\frac{b}{3\pi}}(1 + \cos bx)$$

$$\langle \psi | H | \psi \rangle = \frac{b}{3\pi} \int_{-\pi/b}^{\pi/b} (1+\cos bx)\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2} m\omega^2 x^2\right](1+\cos bx) =$$

$$= \frac{b}{3\pi}\int_{-\pi/b}^{\pi/b} (1+\cos bx)\left[+\frac{\hbar^2 b^2}{2m}\cos(bx) + \frac{1}{2} m\omega^2 x^2 + \frac{1}{2} m\omega^2 x^2 \cos bx\right]$$

$$= \frac{b}{3\pi}\int_{-\pi/b}^{\pi/b} dx\, \frac{\hbar^2 b^2}{2m}\cos(bx) + \frac{1}{2} m\omega^2 x^2 + \frac{1}{2} m\omega^2 x^2 \cos(bx) + \frac{\hbar^2 b^2}{2m}\cos^2(bx) + \frac{1}{2} m\omega^2 x^2 \cos(bx) + \frac{1}{2} m\omega^2 x^2 \cos^2(bx)$$

$$= \frac{b}{3\pi}\Bigg(\cancel{\frac{\hbar^2 b^2}{2m}\frac{\sin(bx)}{b}}\Big|_{-\pi/b}^{\pi/b} + \frac{1}{6} m\omega^2 x^3\Big|_{-\pi/b}^{\pi/b} + m\omega^2 \frac{2x\cos(bx)}{b^2}\Big|_{-\pi/b}^{\pi/b} + m\omega^2\frac{(b^2x^2 - 2)\sin(bx)}{b^3}\Big|_{-\pi/b}^{\pi/b} + \frac{\hbar^2 b^2}{2m}\frac{2bx + \sin(2bx)}{4b}\Big|_{-\pi/b}^{\pi/b}$$

$$+ \frac{1}{2} m\omega^2 \frac{x\cos(2bx)}{4b^2}\Big|_{-\pi/b} + \frac{1}{2} m\omega^2\frac{(2b^2x^2 - 1)\sin(2bx)}{8b^3}\Big|_{-\pi/b}^{\pi/b} + \frac{1}{2} m\omega^2\frac{x^3}{6}\Big|_{-\pi/b}^{\pi/b}\Bigg)$$

$$= \frac{b}{3\pi}\left[\frac{1}{6} m\omega^2 x^3\Big|_{-\pi/b}^{\pi/b} + m\omega^2 \frac{2x\cos(bx)}{b^2}\Big|_{-\pi/b}^{\pi/b} + \frac{\hbar^2 b^2}{2m}\frac{2bx}{4b}\Big|_{-\pi/b}^{\pi/b} + \frac{1}{2} m\omega^2 \frac{x\cos(2bx)}{4b^2}\Big|_{-\pi/b}^{\pi/b} + \frac{1}{2} m\omega^2 \frac{2x^3}{6}\Big|_{-\pi/b}^{\pi/b}\right]$$

$$= \frac{b}{3\pi}\left[\frac{1}{4} m\omega^2\left[\frac{\pi^3}{b^3} + \frac{\pi^3}{b^3}\right] + \frac{2m\omega^2}{b^2}\left[-\frac{\pi}{b} - \frac{\pi}{b}\right] + \frac{\hbar^2 b^2}{4m}\left[\frac{\pi}{b} + \frac{\pi}{b}\right] + \frac{1}{2}\frac{m\omega^2}{4b^2}\left[\pi/b + \pi/b\right]\right]$$

$$= \frac{m\omega^2\pi^2}{6b^2} - \frac{4m\omega^2}{3b^2} + \frac{\hbar^2 b^2}{6m} + \frac{m\omega^2}{12b^2} = \frac{m\omega^2}{b^2}\left(\frac{2\pi^2}{12} - \frac{16}{12} + \frac{1}{12}\right) + \frac{\hbar^2 b^2}{6m}$$

$$= \frac{m\omega^2}{b^2}\left(\frac{\pi^2}{6} - \frac{5}{4}\right) + \frac{\hbar^2 b^2}{6m}$$

$$\frac{dE(b)}{db} = -2\frac{m\omega^2}{b^3}\left(\frac{\pi^2}{6} - \frac{5}{4}\right) + 2\frac{\hbar^2 b}{6m} = 0$$

$$\frac{m^2\omega^2}{\hbar^2}\left(\frac{\pi^2}{3} - \frac{5}{2}\right) = \frac{b^4}{3}$$

$$b = \sqrt{\frac{m\omega}{\hbar}}\sqrt[4]{\pi^2 - \frac{15}{2}}$$

$$E = \frac{m\omega^2\hbar}{m\omega\sqrt{\pi^2 - \frac{15}{2}}}\left(\frac{\pi^2}{6} - \frac{5}{4}\right) + \frac{\hbar^2 m\omega}{6m}\sqrt{\pi^2 - \frac{15}{2}}$$

$$= \frac{\omega\hbar}{6}\sqrt{\pi^2 - 15/2} + \frac{\omega\hbar}{6}\sqrt{\pi^2 - \frac{15}{2}} = \frac{\omega\hbar}{3}\sqrt{\pi^2 - \frac{15}{2}}$$

$$= 0.51312\,\hbar\omega$$

[seems too good to be true :)]

H-atom with Gaussian basis fction

$$\psi = N \exp(-\alpha r^2)$$

$$\hat{H} = \frac{p^2}{2m} - \frac{e^2}{4\pi\varepsilon_0 |r|}$$

$$\int_0^\infty x^2 \exp(-Ax^2) = \frac{1}{4A}\sqrt{\frac{\pi}{A}}$$

$$\int_0^\infty x^4 \exp(-Ax^2) = \frac{3}{2A}\,\frac{1}{2A}\sqrt{\frac{\pi}{A}}\cdot \frac{1}{2}$$

1) $$\langle\psi|\psi\rangle = N^2\int d^3r\, \exp(-2\alpha r^2) = N^2\, 4\pi \int dr\, r^2 \exp(-2\alpha r^2) =$$
$$= N^2\, 4\pi \sqrt{\frac{\pi}{2\alpha}}\,\frac{1}{8\alpha} = N^2\left(\frac{\pi}{2\alpha}\right)^{3/2} \qquad N = \left(\frac{2\alpha}{\pi}\right)^{3/4}$$

2) $$\langle\psi|\frac{p^2}{2m}|\psi\rangle = \left(\frac{2\alpha}{\pi}\right)^{3/2}\int dr\, 4\pi r^2 \exp(-\alpha r^2)\left(-\frac{\hbar^2}{2m r^2}\right)\frac{d}{dr}\, r^2\, \frac{d \exp(-\alpha r^2)}{dr}$$
$$= -\left(\frac{2\alpha}{\pi}\right)^{3/2}\frac{\hbar^2}{2m}\int d^3r \exp(-\alpha r^2)\,\frac{1}{r^2}\frac{d}{dr}\, r^2(-2\alpha r)\exp(-\alpha r^2)$$
$$= +\left(\frac{2\alpha}{\pi}\right)^{3/2}\frac{\hbar^2\pi 2}{m}\int dr \exp(-\alpha r^2)\,\frac{d}{dr}\,(+2\alpha r^3)\exp(-\alpha r^2)$$
$$= 2\left(\frac{2\alpha}{\pi}\right)^{3/2}\frac{\hbar^2\pi}{m}\int dr\exp(-\alpha r^2)\left[6\alpha r^2\exp(-\alpha r^2) + 2\alpha r^3(-2\alpha r)\exp(-\alpha r^2)\right]$$
$$= 2\left(\frac{2\alpha}{\pi}\right)^{3/2}\frac{\hbar^2\pi}{m}\int_0^\infty dr\,\left\{\exp(-2\alpha r^2)\left[6\alpha r^2 - 4\alpha^2 r^4\right]\right\}$$
$$= 2\left(\frac{2\alpha}{\pi}\right)^{3/2}\frac{\hbar^2\pi}{m}\left[6\alpha\,\frac{1}{8\alpha}\sqrt{\frac{\pi}{2\alpha}} - \frac{3}{4\alpha}\,\frac{1}{8\alpha}\sqrt{\frac{\pi}{2\alpha}}\cdot 4\alpha^2\right]$$
$$= 2\,\frac{2\alpha}{\pi}\,\frac{\hbar^2\pi}{m}\left[\frac{3}{4} - \frac{3}{8}\right] = \frac{4\alpha\hbar^2}{m}\,\frac{3}{8} = \frac{3}{2}\frac{\alpha\hbar^2}{m}$$

$$\langle\psi|V_c|\psi\rangle = -\left(\frac{2\alpha}{\pi}\right)^{3/2}\int_0^\infty dr\, 4\pi r^2\,\frac{1}{r}\exp(-2\alpha r^2)\,\frac{e^2}{4\pi\varepsilon_0} = -\left(\frac{2\alpha}{\pi}\right)^{3/2}\frac{e^2}{4\pi\varepsilon_0}\,4\pi\int_0^\infty dr\, r\, \exp^{-(2\alpha r^2)}$$
$$= -\left(\frac{2\alpha}{\pi}\right)^{3/2}\frac{e^2}{4\pi\varepsilon_0}\,4\pi\int_0^\infty du\,\frac{1}{4\alpha}\exp^{-u} = -\left(\frac{2\alpha}{\pi}\right)^{3/2}\frac{e^2}{4\pi\varepsilon_0}\,\frac{\pi}{\alpha} = -\sqrt{\frac{\alpha}{\pi}}\,2\sqrt{2}\,\frac{e^2}{4\pi\varepsilon_0} \qquad u = 2\alpha r^2,\ du = 4\alpha r\,dr$$

$$E(\alpha) = \frac{3}{2}\alpha\frac{\hbar^2}{m} - \sqrt{\frac{\alpha}{\pi}}\,2\sqrt{2}\,\frac{e^2}{4\pi\varepsilon_0}$$

$$\frac{dE(\alpha)}{d\alpha} = \frac{3}{2}\frac{\hbar^2}{m} - \cancel{\frac{1}{2}}\,\frac{1}{\sqrt{\alpha}}\,\cancel{2}\sqrt{\frac{2}{\pi}}\,\frac{e^2}{4\pi\varepsilon_0} = 0$$

$$\frac{3}{2}\frac{\hbar^2}{m} = \frac{1}{\sqrt{\alpha}}\sqrt{\frac{2}{\pi}}\,\frac{e^2}{4\pi\varepsilon_0}$$

$$\sqrt{\alpha} = \frac{2\sqrt{2}}{3}\,\frac{m e^2}{4\pi\varepsilon_0}\,\frac{1}{\hbar^2}\,\frac{1}{\sqrt{\pi}}$$

$$E(\alpha) = \frac{3}{2}\frac{\hbar^2}{m}\left[\frac{8}{9}\, m^2\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2\frac{1}{\hbar^4\pi}\right] - \cancel{\sqrt{\frac{2}{\pi}}\,\frac{e^2}{4\pi\varepsilon_0}\,\frac{3}{2\sqrt{2}}\,\frac{4\pi\varepsilon_0}{m e^2}\,\frac{\hbar^2}{\sqrt{\pi}}}$$
$$- \frac{2\sqrt{2}}{\sqrt{\pi}}\,\frac{e^2}{4\pi\varepsilon_0}\,\frac{2\sqrt{2}}{3}\,m\,\frac{e^2}{4\pi\varepsilon_0}\,\frac{1}{\hbar^2\sqrt{\pi}}$$
$$= \frac{4}{3\pi}\,\frac{m}{\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2 - \frac{8}{3\pi}\,\frac{m}{\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2 = -\frac{4}{3\pi}\underbrace{\frac{m}{\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2}_{\text{Ha} \,=\, 2R_y} = -\frac{8}{3\pi}R_y$$

$$2\langle T\rangle = -\langle V\rangle$$

(Virial theorem again here...)

$$= 0.8488\, R_y$$

with $\cos^2\phi$ & rotator – 1^{st} excited state from $|1\rangle$ & $|-1\rangle$ (7)

$$V = a\cos^2\phi = a\frac{1}{4}(e^{i\phi}+e^{-i\phi})(e^{i\phi}+e^{-i\phi}) = a\frac{1}{4}(2+e^{2i\phi}+e^{-2i\phi}) =$$

$$= \frac{a}{2}(1+\cos 2\phi)$$

$$\langle n|V|m\rangle = \frac{1}{2\pi}\int_0^{2\pi} d\phi\, e^{-in\phi}\frac{a}{4}(2+e^{2i\phi}+e^{-2i\phi})\, e^{im\phi} =$$

$$= \frac{1}{2\pi}\int_0^{2\pi} d\phi \left[e^{-in\phi}\frac{a}{2}e^{im\phi} + e^{-in\phi}\frac{a}{4}e^{2i\phi}e^{im\phi} + e^{-in\phi}\frac{a}{4}e^{-2i\phi}e^{im\phi}\right] =$$

$$= \frac{1}{2\pi}\cancel{\int_0^{2\pi} d\phi}\left[\frac{a}{2}\delta_{n,m}2\pi + \frac{a}{4}2\pi\delta_{m+2,n} + \frac{a}{4}2\pi\delta_{m-2,n}\right]$$

$$= \frac{a}{2}\delta_{n,m} + \frac{a}{4}\delta_{m+2,n} + \frac{a}{4}\delta_{m-2,n}$$

$$V = \begin{pmatrix} \frac{a}{2} & 0 & \frac{a}{4} & 0 & 0 \\ 0 & \frac{a}{2} & 0 & \frac{a}{4} & 0 \\ \frac{a}{4} & 0 & \frac{a}{2} & 0 & \frac{a}{4} \\ 0 & \frac{a}{4} & 0 & \frac{a}{2} & 0 \\ 0 & 0 & \frac{a}{4} & 0 & \frac{a}{2} \end{pmatrix}$$

$$\langle 0|H|0\rangle = 0 + \frac{a}{2}$$

$$\langle 1|H|1\rangle = +\frac{\hbar^2}{2I} + \frac{a}{2} = \langle -1|H|-1\rangle$$

$$|1\rangle + A|-1\rangle \quad \to \quad N' = \frac{1}{\sqrt{2\pi}}\frac{1}{\sqrt{1+A^2}}$$

$$\frac{1}{1+A^2}\left[\langle 1| + A\langle -1|\right]\left(-\frac{\hbar^2}{2I}\right)\frac{d^2}{d\phi^2}\left[|1\rangle + A|-1\rangle\right] =$$

$$= \left(-\frac{\hbar^2}{2I}\right)\frac{1}{1+A^2}\left(\langle 1| + A\langle -1|\right)\left[-|1\rangle - A|-1\rangle\right] = \frac{\hbar^2}{2I}\frac{1+A^2}{1+A^2} = \frac{\hbar^2}{2I}$$

$$\frac{1}{1+A^2}\left[\langle 1| + A\langle -1|\right]\frac{a}{4}(2+e^{2i\phi}+e^{-2i\phi})\left[|1\rangle + A|-1\rangle\right] =$$

$$= \frac{1}{1+A^2}\frac{1}{2\pi}\int_0^{2\pi} d\phi\,(e^{-i\phi}+Ae^{+i\phi})\frac{a}{4}(2+e^{2i\phi}+e^{-2i\phi})(e^{i\phi}+Ae^{-i\phi}) =$$

$$= \frac{1}{1+A^2}\frac{1}{2\pi}\frac{a}{4}\int_0^{2\pi} d\phi\,\Big(e^{-i\phi}\cdot 2\cdot e^{i\phi} + e^{-i\phi}\cdot e^{2i\phi}\cdot Ae^{-2i\phi} +$$

$$+ Ae^{i\phi}\cdot 2\cdot Ae^{-i\phi} + Ae^{i\phi}\cdot e^{-2i\phi}\cdot e^{i\phi}\Big) =$$

$$= \frac{1}{1+A^2}\frac{1}{2\pi}\frac{a}{4}\left[2\cdot 2\pi + A\cdot 2\pi + A\cdot 2\pi + A^2\cdot 2\cdot 2\pi\right]$$

$$= \frac{1}{1+A^2}\frac{a}{4}\,2\cdot(1+A+A^2)$$

$$\frac{dE}{dA} = \frac{d}{dA}\frac{a}{2}\frac{A^2+A+1}{1+A^2} = \frac{a}{2}\cdot\left(\frac{2A+1}{1+A^2} - \frac{A^2+A+1}{(1+A^2)^2}\cdot 2A\right) = 0$$

$$\frac{a}{2}\frac{(2A+1)(1+A^2) - (A^2+A+1)\cdot 2A}{(1+A^2)^2} = 0$$

$$2A + 2A^3 + \cancel{1} + \cancel{A^2} - \cancel{A^2} - A - 1 = 0$$

$$2A^3 + A = 0$$

$$A(2A^2+1) = 0$$

$$A = 0 \qquad 2A^2 = -1$$

$$(2A+1)(1+A^2) - 2A^3 - 2A^2 - 2A = 0$$

$$= \cancel{2A^3} + \cancel{2A} + A^2 + 1 - \cancel{2A^3} - 2A^2 - \cancel{2A} =$$

$$= -A^2 + 1 = 0$$

$$A^2 = 1$$

$$\cancel{A = \sqrt{\tfrac{1}{2}}}$$

$$\to A = \pm 1 \text{ ok}$$

$$\begin{pmatrix} \frac{a}{2}-\lambda & a/4 \\ a/4 & a/2-\lambda \end{pmatrix} \qquad E = a/2 \pm a/4 \; \begin{cases} \frac{3a}{4} \\ \frac{a}{4} \end{cases}$$

$$\cancel{\frac{a^2}{4}} - \frac{a^2}{16} \to \left(\frac{a}{2}-\lambda\right)^2 - \left(\frac{a}{4}\right)^2 = 0 \qquad D = a^2 - \frac{3}{4}a^2 = \frac{a^2}{4}$$

$$\frac{a^2}{4} - \lambda a + \lambda^2 - \frac{a^2}{16} = 0 \qquad \lambda_{1,2} = \frac{a \pm \sqrt{\frac{a^2}{4}}}{2} = \frac{a}{2} \pm \frac{a}{4}$$

$$\lambda^2 - a\lambda + \frac{3a^2}{16} = 0$$

$E = \frac{a}{4}$

$$\begin{pmatrix} \frac{a}{4} & a/4 \\ a/4 & a/4 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0 \qquad c_1 = -c_2 = \frac{1}{\sqrt{2}}$$

OK

$E = \frac{3a}{4}$

$$\begin{pmatrix} -a/4 & a/4 \\ a/4 & -a/4 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0 \to c_1 = c_2 = \frac{1}{\sqrt{2}}$$

$$E(A) = \frac{a}{2} \cdot \frac{A^2+A+1}{1+A^2} \leftarrow \text{OK}$$

$$\frac{dE(A)}{dA} = \frac{a}{2}\left[\frac{2A+1}{1+A^2} - \frac{A^2+A+1}{(1+A^2)^2} \cdot 2A \right]$$

$$H = T + V = \frac{\hbar^2}{2I}\begin{pmatrix} 9 & & & & & \\ & 4 & & & & \\ & & 1 & & & \\ & & & 0 & & \\ & & & & 1 & \\ & & & & & 4 \\ & & & & & & \ddots \end{pmatrix} + \frac{a}{2}\begin{pmatrix} 1 & 0 & 1/2 & & & \\ 0 & 1 & 0 & 1/2 & & \\ 1/2 & 0 & 1 & 0 & 1/2 & \\ & 1/2 & 0 & 1 & 0 & \\ & & 1/2 & 0 & 1 & \\ & & & 1/2 & & \ddots \end{pmatrix}$$