1. We consider the quantum mechanics of a particle in the earth's gravitational field:

$$V(r) = -G\frac{Mm}{r} \tag{1}$$
$$= -G\frac{Mm}{R+z} \tag{2}$$
$$\approx -G\frac{Mm}{R} + mgz \tag{3}$$

where

$$M = \text{mass of earth} \tag{4}$$
$$m = \text{mass of particle} \tag{5}$$
$$r = \text{distance from center of earth} \tag{6}$$
$$G = \text{Newton's gravitational constant} \tag{7}$$
$$R = \text{radius of earth} \tag{8}$$
$$z = \text{height of particle above surface of earth} \tag{9}$$
$$g = GM/R^2. \tag{10}$$

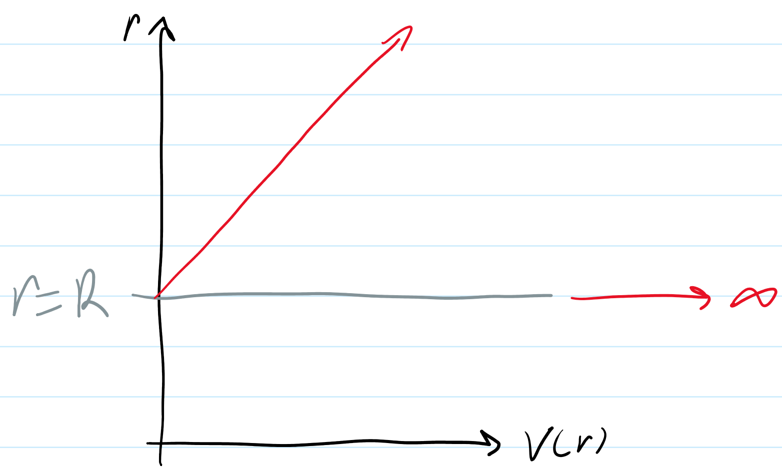
Let $x = z$

We may drop the constant term in our discussion, and consider only the mgz piece, with $z \ll R$. We further assume that no angular momentum is involved, and treat this as a one dimensional problem. Finally, assume that the particle is unable to penetrate the earth's surface.

(a) Make a WKB calculation for the energy spectrum of the particle.

(b) If the particle is an atom of atomic weight $A \sim 100$, use the result of part (a) to estimate the particle's ground state energy (in eV). Is sunlight likely to move the particle into excited states?

$$V(x) = \begin{cases} mgx & \text{if } x > 0 \\ \infty & \text{if } x \le 0 \end{cases} \qquad (x = 0 \Leftrightarrow r = R) \quad (x = z)$$



a.) First, we solve for the classical turning points. Clearly, there is a turning point at r=R ($x=x_1=0$). The other is found by equating the energy of the particle with its potential energy so that it has no KE:

$$E = mgx \rightarrow x_2 = \frac{E}{mg} \qquad (E = mgx_2)$$

Then, solve for the function of E:

Then, solve for the function of E:

$[kg^{1/2} \cdot m \cdot J^{1/2}] = [kg \cdot m^2 \cdot s^{-1}] \longleftrightarrow \hbar$

$$f(E) = \int_{x_1(E)}^{x_2(E)} dx \sqrt{2m(E - V(x))}$$

$x = x_2 \sin^2\theta$

$\rightarrow dx = 2x_2 \sin\theta\cos\theta \, d\theta$

$$= \int_0^{x_2} dx \sqrt{2m(mgx_2 - mgx)} = m\sqrt{2g}\int_0^{x_2} dx\sqrt{x_2 - x}$$

$$= m\sqrt{2g}\int_0^{\pi/2} 2x_2 \sin\theta\cos\theta \sqrt{x_2}\,(1-\sin^2\theta)^{1/2} d\theta$$

$$= m\sqrt{2g}\int_0^{\pi/2} 2x_2^{3/2} \sin\theta\cos^2\theta \, d\theta$$

$= 0 - (-\frac{2}{3}) = \frac{2}{3}$

$$= m\sqrt{2g}\, x_2^{3/2} \cdot \left[-\frac{2}{3}\cos^3\theta\right]_0^{\pi/2}$$

$$\rightarrow f(E) = \frac{2\sqrt{2}}{3} m g^{1/2} x_2^{3/2}$$

$\frac{kg^{3/2}\,\frac{m^3}{s^3}}{mg^{1/2}\,\frac{m}{s^2}} = kg\,m^2 s^{-1}$ ✓

$$= \frac{2\sqrt{2}}{3} m g^{1/2} \frac{E^{3/2}}{m^{3/2} g^{3/2}} = \frac{2\sqrt{2}}{3}\frac{E^{3/2}}{m^{1/2} g}$$

Solve for energy spectrum by applying WKB approx:

$$f(E) = (n+\tfrac{1}{2})\pi^{(\times\hbar)} = \frac{\sqrt{8}}{3}\frac{E_n^{3/2}}{m^{1/2} g}$$

$$\rightarrow (n+\tfrac{1}{2})^{2/3}\pi^{2/3} = \frac{8^{1/3}}{3^{2/3}}\frac{E_n}{m^{1/3} g^{2/3}}$$

$$\rightarrow E_n = \left(\frac{9}{8} m g^2 (n+\tfrac{1}{2})^2 \pi^2 \underset{\times\hbar^2}{}\right)^{1/3}$$

$\hookrightarrow kg \cdot m^2 \cdot s^{-4} \cdot kg^2 \cdot m^4 \cdot s^{-2}$

– if not

$\rightarrow kg \cdot m \cdot s^{-1} \cdot \quad kg \cdot m \cdot s^{-2}$

$$\rightarrow \boxed{E_n = \frac{\sqrt[3]{9}}{2} \pi^{2/3} m^{1/3} g^{2/3} \left(n+\frac{1}{2}\right)^{2/3} (\times \hbar^{2/3})}$$

if not using natural units

b.) The ground state energy of the particle is given by

$$E_0 = \left(\frac{9}{8} \pi^2 m g^2 \cdot \hbar^2\right)^{1/3} \left(0+\frac{1}{2}\right)^{2/3}$$

$eV^2 \cdot s^2$

where

$$m = A \cdot 9.31 \cdot 10^8 eV/c^2$$

$eV\ m^{-2} s^2$

$$g^2 \leftrightarrow [m^2 s^{-4}]$$

$$\Rightarrow \boxed{E_0 = 5.12 \cdot 10^{-12} eV}$$

Yes, sunlight is likely to move the particle into excited states since it is of the energy ~0.1eV whereas the ground state is more than a billion times smaller than this.

2. Continuing with the gravitational problem in problem 1, now make a variational calculation for the ground state energy (*i.e.*, an upper bound thereon). Pick a "sensible" trial wave function, at least in the sense that it satisfies the right boundary conditions. Compare your result with the ground state level from the WKB approximation.

First, notice that the wave function must have a node at z=0, and it must go to zero as z→∞. Since the potential is increasing, we choose the first excited state of the QHO as the trial solution, with a variable coefficient of decay:

Let $x \equiv \sqrt{\frac{m\omega}{\hbar}} z$. Then, our trial wave f^n is

$$\psi(z) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{1}{\sqrt{2\cdot 1}} \cdot 2x \cdot e^{-x^2/2}$$

$$\equiv B\, x e^{-x^2/2}$$

$$\left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \cdot \sqrt{2}$$

where ω is the variational parameter ~~Notice that we must have~~

$$1 = \int_0^\infty |\psi(z)|^2\, dz = \frac{1}{2}\int_{-\infty}^\infty B^2 x^2 e^{-\alpha x^2}\, dz$$

$$= \frac{B^2}{2}\left(\frac{\hbar}{m\omega}\right)^{1/2} \int_{-\infty}^{\infty} x^2 e^{-\alpha x^2}\, dx \qquad dx = \sqrt{\frac{m\omega}{\hbar}}\, dz$$

$$= \left(A^2 \cdot \frac{1}{\sqrt{\pi}}\right)\cdot\left(\frac{\sqrt{\pi}}{2\alpha^{3/2}}\right) = \frac{A^2}{2\alpha^{3/2}}$$

$$\rightarrow A^2 = 2\alpha^{3/2} \rightarrow A = \sqrt{2}\,\alpha^{3/4}$$

$$\rightarrow \psi(z) = \left(\frac{m\omega\,\alpha^3}{\pi\hbar}\right)^{1/4} x e^{-\alpha x^2/2} \cdot 2 \cdot \sqrt{2}$$

$$= 2\left(\frac{m\omega\,\alpha^3}{\pi\hbar}\right)^{1/4} x e^{-\alpha x^2/2}$$

Now, we minimize the expected energy w.r.t. ω:

$$0 = \frac{\delta\left(\frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle}\right)}{\delta\omega} = \frac{\delta\langle\psi|H|\psi\rangle}{\delta\omega}$$

$\partial \omega$

Notice

$$\delta \langle \psi | H | \psi \rangle = \langle \psi | \frac{p^2}{2m} \psi \rangle + \langle \psi | mgz \psi \rangle$$

Moreover,

$$\langle \psi | \frac{p^2}{2m} | \psi \rangle = -\frac{\hbar^2}{2m} \int_0^\infty \psi^* \frac{d^2\psi}{dz^2} \, dz$$

- $$\frac{d^2\psi}{dz^2} = \frac{d^2\psi}{dx^2}\left(\frac{dx}{dz}\right)^2 \quad \frac{d\psi}{dx}\left(\frac{d^2 z}{dx^2}\right) \to 0$$

$$= \frac{m\omega}{\hbar} \frac{d^2\psi}{dx^2}$$

$$= -\frac{\hbar^2}{2m} \cdot \frac{m\omega}{\hbar} \int_0^\infty \psi(x) \frac{d^2\psi}{dx^2} \, dx$$

$$= -\frac{\hbar\omega}{2} \int_0^\infty \psi(x) \frac{d^2\psi}{dx^2} \, dx$$

$$\frac{d^2\psi}{dx^2} = \frac{d}{dx}\left(B e^{-x^2/2} - B x^2 e^{-x^2/2}\right)$$

$$= B \frac{d}{dx}\left((1 - x^2) e^{-x^2/2}\right)$$

$$= B \frac{d}{dx}\left(\left[-2x + (1 - x^2) \cdot (-x)\right] e^{-x^2/2}\right)$$

$$= \beta \frac{d}{dx}\left(\left[-2x + (1-x^2)\cdot(-x)\right]e^{-x^2/2}\right)$$

$$= \beta \frac{d}{dx}\left(\left[\right.\right.$$

$$p = i\sqrt{\frac{\hbar m\omega}{2}}\,(a_+ - a_-)$$

$$\frac{1}{2m}\langle n|p^2|n\rangle = \langle n\,|\,a_+^2 - a_+a_- - a_-a_+ + a_-^2|n\rangle \cdot \frac{1}{2m}$$

$$= -(2n+1)\cdot -\frac{\hbar m\omega}{2}\cdot\frac{1}{2m}$$

$$= \left(n+\frac{1}{2}\right)\hbar\omega \cdot \frac{1}{2}$$

$$\rightarrow \langle\psi|\,\frac{p^2}{2m}\,|\psi\rangle = \frac{3}{2}\cdot\hbar\omega\cdot\frac{1}{2} = \frac{3\hbar\omega}{4}$$

Moreover,

$$\langle\psi\,|\,V(z)\,|\,\psi\rangle = \langle\psi\,|\,mgz\,\psi\rangle$$

$$= \int_0^\infty dz\,\psi^*(x)\,mg\sqrt{\frac{\hbar}{m\omega}}\,x\,\psi(x)$$

$$= mg\sqrt{\frac{\hbar}{m\omega}}\cdot\sqrt{\frac{\hbar}{m\omega}}\,\underbrace{\int_0^\infty dx\,x\,|\psi(x)|^2}_{4\sqrt{\frac{m\omega}{\pi\hbar}}\underbrace{\int_0^\infty x^3 e^{-x^2}dx}_{1/2}}$$

$= 2mg\sqrt{\frac{\hbar}{\cdots}}$ [illegible]

$$= 2mg\sqrt{\frac{\hbar}{\pi m \omega}}$$

$$kg \cdot \frac{m}{s^2} \cdot \left(L^2 \cdot s^{-1/2}\right) \cdot s^{1/2} = \frac{kg\, m^2}{s^2}$$

Thus

$$\langle \psi | H | \psi \rangle = \underbrace{\frac{3\hbar}{4}}_{\equiv a}\omega + \underbrace{2mg\sqrt{\frac{\hbar}{\pi m}}}_{\equiv b}\omega^{-1/2}$$

$$0 = \frac{d\langle \psi | H | \psi \rangle}{d\omega} = a + b\cdot\left(-\frac{1}{2}\right)\omega^{-3/2}$$

$$\rightarrow \frac{1}{2} b\omega^{-3/2} = a \rightarrow \omega^{3/2} = \frac{b}{2a} \rightarrow \omega = \left(\frac{b}{2a}\right)^{2/3}$$

The energy is

$$E_0 = a\left(\frac{b}{2a}\right)^{2/3} + b\left(\frac{2a}{b}\right)^{1/3}$$

$$= a^{1/3} b^{2/3} 2^{-2/3} + b^{2/3} a^{1/3} 2^{1/3}$$

$$= \left(2^{1/3} + 2^{-2/3}\right)\left(ab^2\right)^{1/3}$$

$$= \left(2^{1/3} + 2^{-2/3}\right)\left(\frac{3\hbar}{4} \cdot 4m^2 g^2 \cdot \frac{\hbar}{\pi m}\right)^{1/3}$$

$$= (\cdots)\left(\frac{3\hbar^2 m g^2}{\pi}\right)^{1/3} \qquad \frac{kg^3 m^4}{s^2} \quad m^2/s^4$$

$$= \boxed{6.52 \cdot 10^{-12}\, eV}$$

3. We can find other inequalities in the same spirit as our inequality on the ground state energy. For example, if we can find a lower bound on $E_1 - \langle\psi|H|\psi\rangle$, where E_1 is first excited energy, and ψ is a trial wave function, the theorem below might be used to obtain a lower bound on E_0. Prove the theorem:

1

$\langle H \rangle$

Theorem: If we have a normalized function $|\psi\rangle$ such that

$$E_0 \leq \langle\psi|H|\psi\rangle \leq E_1, \tag{11}$$

then

$$E_0 \geq \langle\psi|H|\psi\rangle - \frac{\langle H\psi|H\psi\rangle - \langle\psi|H|\psi\rangle^2}{E_1 - \langle\psi|H|\psi\rangle}. \tag{12}$$

$$A \equiv \langle H \rangle - \frac{\langle H^2 \rangle - \langle H \rangle^2}{E_1 - \langle H \rangle}$$

Let

$$|\psi\rangle = \sum_{n=0}^{\infty} c_n |n\rangle$$

Thus,

$$\langle H \rangle = \sum_{n=0}^{\infty} |c_n|^2 E_n \qquad \left(\langle\psi|H|\psi\rangle = \sum_{n=0}^{\infty} c_n^2 \langle n|H|n\rangle \right)$$

$$\langle H^2 \rangle = \sum_{n=0}^{\infty} |c_n|^2 E_n^2$$

Notice that $E_0 \geq 0$. Thus, we can prove the theorem by showing that $A \leq 0$.

Thus, let $E_0 = 0$.

Notice that

$$\langle H^2 \rangle = \sum |c_n|^2 E_n^2$$

Notice that

$$\langle H^2 \rangle = \sum_{n=0}^{\infty} |c_i|^2 E_n^2$$

$$= E_1 \sum_{n=0}^{\infty} |c_i|^2 E_n \cdot \frac{E_n}{E_1}$$

$$= E_1 \sum_{n=1}^{\infty} |c_i|^2 E_n \cdot \frac{E_n}{E_1}$$

$$\geq E_1 \sum_{n=1}^{\infty} |c_i|^2 E_n$$

$$= E_1 \sum_{n=0}^{\infty} |c_i|^2 E_n$$

$$= E_1 \langle H \rangle$$

$$\rightarrow \langle H^2 \rangle \geq E_1 \langle H \rangle$$

$$\rightarrow \langle H^2 \rangle - \langle H \rangle^2 \geq E_1 \langle H \rangle - \langle H \rangle^2$$

$$\rightarrow \langle H^2 \rangle - \langle H \rangle^2 \geq (E_1 - \langle H \rangle) \langle H \rangle$$

$$\rightarrow \langle H \rangle - \frac{\langle H^2 \rangle - \langle H \rangle^2}{E_1 - \langle H \rangle} \leq 0$$

Thus we have shown the theorem is true

$\square$

4. Let us pursue our variational approach to the estimation of ground state energy levels of atoms for the "general" case. We consider an atom with nuclear charge Z, and N electrons. The Hamiltonian of interest is:

$$H(Z,N) = H_{\text{kin}} - ZV_c + V_e \quad (13)$$
$$H_{\text{kin}} = \sum_{n=1}^{N} \frac{\mathbf{p}_n^2}{2m}, \quad \equiv Z_0 \quad (14)$$
where (15)
$$V_c = \alpha \sum_{n=1}^{N} \frac{1}{|\mathbf{x}_n|} \quad (16)$$
$$V_e = \alpha \sum_{N \geq j > k \geq 1} \frac{1}{|\mathbf{x}_k - \mathbf{x}_j|} \quad (17)$$
$$m = \text{electron mass} \quad (18)$$
$$\alpha = \text{fine structure constant.} \quad (19)$$

Denote the ground state energy of $H(Z,N)$ by $-B(Z,N)$, with $B(Z,0)=0$.

Generalize the variational calculation we performed for the ground state of helium to the general Hamiltonian $H(Z,N)$. Thus, select your "trial function" to be a product of N identical "hydrogen atom ground state" functions. Determine the resulting lower bound $\hat{B}(Z,N)$ on $B(Z,N)$ (*i.e.*, an upper limit on the ground state energies).

We select the "trial wavefunction" to be a product of N identical "hydrogen atom ground state" functions, with effective parameter Z:

$$\psi = \prod_{i=1}^{N} \psi_{100}(r_i) = \prod_{i=1}^{N} \underbrace{\left(\frac{Z^3}{\pi a_0^3}\right)^{1/2}}_{=c_0} e^{-Zr_i/a_0}$$

$$= \underbrace{\left(\frac{Z^3}{\pi a_0^3}\right)^{N/2}}_{=c_1} \cdot \exp\left[-\frac{Z}{a_0}\left(\sum_{i=1}^{N} r_i\right)\right]$$

We must first normalize this:

$$1 = A \int \cdots \int |\psi|^2 \, d^3\vec{r}_1 \cdots d^3\vec{r}_N$$

Notice

$$\int_0^{2\pi} d\theta \int_0^{\pi} d\phi \int_0^{\infty} dr \left(e^{-\frac{Z}{a_0}r}\right)^2 r^2 \sin\phi$$

$$\int_0^{\pi} \sin\phi \, d\phi = -\cos\phi \Big|_0^{\pi} = 2$$

$$= 4\pi \int_0^{\infty} dr \, r^2 e^{-\frac{2Z}{a_0}r} = 4\pi \frac{2}{\left(\frac{2Z}{a_0}\right)^3}$$

$$= 4\pi \int_0 dr\, r^2 e^{-\frac{2Z}{a_0} r} = 4\pi \frac{}{\left(\frac{2Z}{a_0}\right)^3}$$

$$= \pi \cdot Z^{-3} \cdot a_0^{3} = \frac{\pi a_0^3}{Z^3}$$

Thus,

$$1 = A \cdot \left(\frac{\pi a_0^3}{Z^3}\right)^N \cdot \left(\frac{Z^3}{\pi a_0^3}\right)^N = A$$

$\Rightarrow$ Already normalized.

We now compute the expectation value of the Hamiltonian. First, notice that

$$E(Z) = \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} = \langle \psi | H | \psi \rangle$$

$$= \left\langle \sum_{i=1}^{N} \frac{\vec{p}_n^{\,2}}{2m} \right\rangle - \alpha Z \left\langle \sum_{i=1}^{N} \frac{1}{|\vec{x}_n|} \right\rangle$$

$$+ \alpha \left\langle \sum_{N \geq i > k \geq 1} \frac{1}{|\vec{x}_k - \vec{x}_i|} \right\rangle$$

We see that

$$\left\langle \frac{\vec{p}_1^{\,2}}{2m} \right\rangle = \int \cdots \int_{(\infty)} d^3(\vec{x}_1) \cdots d^3(x_N)\, c_1 \exp\left[-\frac{Z}{r_0} \sum_{i=1}^{N} r_i\right] \frac{p_1^2}{2m} c_1 \exp\left[-\frac{Z}{r_0} \sum r_i\right]$$

$$= \int_{(\infty)} d^3(\vec{x}_1)\, c_0\, e^{-\frac{Z}{r_0} r_1} \frac{p_1^2}{2m} c_0\, e^{-\frac{Z}{r_0} r_1}$$

$$\cdot \underbrace{\int \cdots \int_{(\infty)} d^3(\vec{x}_2) \cdots d^3(\vec{x}_N)\, c_0^{2(N-1)} \exp\left[-\frac{2Z}{r_0} \sum_{i=1}^{N} r_i\right]}_{1}$$

$$= Z^2 \cdot \langle \psi_{100} | \frac{\vec{p}_1^{\,2}}{2m} | \psi_{100} \rangle$$ (as shown in lecture)

$$= Z^2 \cdot \frac{1}{2} m \alpha^2$$

Thus, by symmetry,

$$\langle H_{kin} \rangle = \frac{N}{2} m \alpha^2 Z^2$$

Moreover, (as shown in lecture)

$$-Z_0 \langle \frac{\alpha}{r_1} \rangle = -Z_0 \cdot Z \times \langle \psi_{100} | V_c | \psi_{100} \rangle$$

$$= -Z_0 Z m \alpha^2$$

Thus, by symmetry,

$$-Z_0 \langle V_c \rangle = -N Z_0 Z m \alpha^2$$

$N = 2$, $Z_0 = 2$

Therefore,

$$\langle \psi | H_{kin} - Z_0 V_c | \psi \rangle = \underbrace{\frac{1}{2} m \alpha^2 (N Z^2 - 2 N Z_0 Z)}_{\text{agrees with He case}}$$

Additionally,

$$\langle \psi | \frac{\alpha}{r_{12}} | \psi \rangle = \alpha C_0^4 \int_{(\infty)} \int_{(\infty)} d^3(\vec{x})\, d^3(\vec{y})\, \frac{e^{-\frac{2Z}{a_0}(|\vec{x}| + |\vec{y}|)}}{|\vec{x} - \vec{y}|}$$

$$\cdot \underbrace{C_0^{2(N-2)} \int_{(\infty)} \cdots \int_{(\infty)} d^3(\vec{x}_3) \cdots d^3(\vec{x}_N)\, e^{-\frac{2Z}{a_0}\left(\sum_{i=3}^{N} x_i\right)}}_{=1 \text{ (same logic as before)}}$$

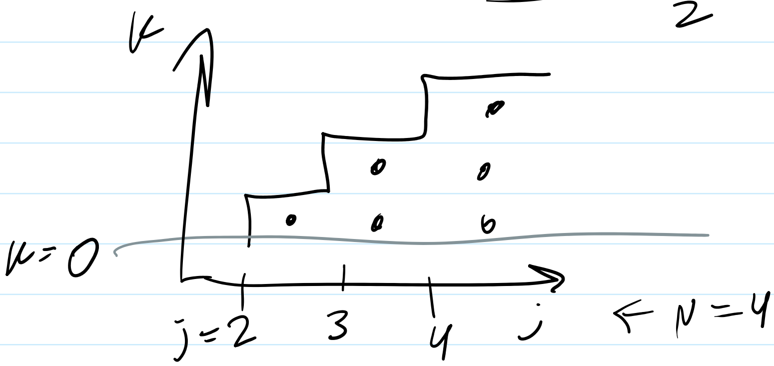
$$= \frac{1}{2} m \alpha^2 \frac{5}{4} Z$$

as shown in lecture. Notice that the number as shown in lecture. Notice that the number of terms in the sum defining V_e is

$$\sum_{N \geq j > k \geq 1} 1 = \sum_{j=1}^{N} \sum_{k=1}^{j-1} 1 = \sum_{j=1}^{N} (j-1)$$

$$= \left(\sum_{j=1}^{N} j \right) - N = \frac{N(N+1)}{2} - N$$

$$= \frac{N(N+1) - 2N}{2} = \frac{N(N-1)}{2}$$



Thus, by symmetry, we have

$$\langle V_e \rangle = \frac{N(N-1)}{2} \cdot \frac{1}{2} m \alpha^2 \frac{5}{4} Z$$

Thus,

$$\langle H \rangle = \frac{1}{2} m \alpha^2 \left(N Z^2 - 2 N Z_0 Z + \frac{5N(N-1)}{8} Z \right)$$

$$= \frac{N}{2} m \alpha^2 \left(Z^2 - 2 Z_0 Z + \frac{5(N-1)}{8} Z \right)$$

We now find an upper bound for the ground state energy:

$$0 = \frac{d\langle H \rangle}{dZ} \Rightarrow 2Z - 2Z_0 + \frac{5(N-1)}{8} = 0$$

$$\rightarrow Z = Z_0 - \frac{5(N-1)}{16} \quad \leftarrow \text{agrees w/ He} \checkmark\checkmark$$

This gives an energy of

$$\hat{B}(Z,N) = -\frac{N}{2} m\alpha^2 \left[\left(Z_0 - \frac{5(N-1)}{16} \right)^2 + \left(\frac{5(N-1)}{8} - 2Z_0 \right) \cdot \left(Z_0 - \frac{5(N-1)}{16} \right) \right]$$

$$= +\frac{N}{2} m\alpha^2 \left[Z_0 - \frac{5(N-1)}{16} \right]^2$$

$$\rightarrow \boxed{\hat{B}(Z,N) = N \left[Z_0 - \frac{5(N-1)}{16} \right]^2 \cdot R_y}$$