24 hr extension

5. Now let's confront our estimates in problem 4 (problem set 1) with experiment.

(a) Make a simple table comparing your variational bounds with the observed ground state energies for lithium, beryllium, and nitrogen. Note that a simple web search for "ionization potentials" will get you a multitude of tables of observed values, or you can look at a reference such as the CRC Press's *Handbook of Chemistry and Physics*. The table entries are typically of the form:

$$B(Z, N) - B(Z, N-1).$$

(b) Do your results make sense? If not, can you figure out what is wrong, and whether the calculation we did for He is to be trusted?

a.)

all in eV

Ry:	Lithium (Z=3)	N						
13.60569	3	3	2	1				
	Estimate	33.69534	74.08723	122.4512				
	Experimental Value	5.4	75.6	122				
	Berillium (Z=4)	N						
	4	4	3	2	1			
	Estimate	45.49403	94.92095	152.32	217.691			
	Experimental Value	9.3	18.2	154	218			
	Nitrogen (Z=7)	N						
	7	7	6	5	4	3	2	1
	Estimate	87.90551	164.4375	248.9416	341.4178	441.866	550.2864	666.6788
	Experimental Value	14.5	29.6	47.5	77.4	97.9	552	667

b.) The N=1,2 values are very accurate, but the rest tend to overestimate a lot. This makes sense because our approximate assumes the orbitals are all "s" orbitals. However, past N=2, the orbitals of an atom are no longer "s" orbitals. Moreover, the spacing between energy levels past N=2 is smaller in reality as a result. Therefore, these results are to be expected.

6.)

We use the WKB method to estimate the tunneling rate as follows: We imagine the α is bound in the nucleus, between $x = 0$ and $x = x_0$. Sometimes it bounces up

We use the WKB method to estimate the tunneling rate as follows: We imagine the α is bound in the nucleus, between $x = 0$ and $x = x_0$. Sometimes it bounces up against the potential barrier at $x = x_0$. When this occurs, there is some probability that it will escape the nucleus, where this probability is just $|\psi(x_e)/\psi(x_0)|^2$, where the wave function is estimated according to the WKB method in Eq. 2.

In the classically forbidden region between $x = x_0$ and $x = x_e$, the "phase" is imaginary, and the exponential factor damps the wave function according to $e^{-\Delta/2}$, where

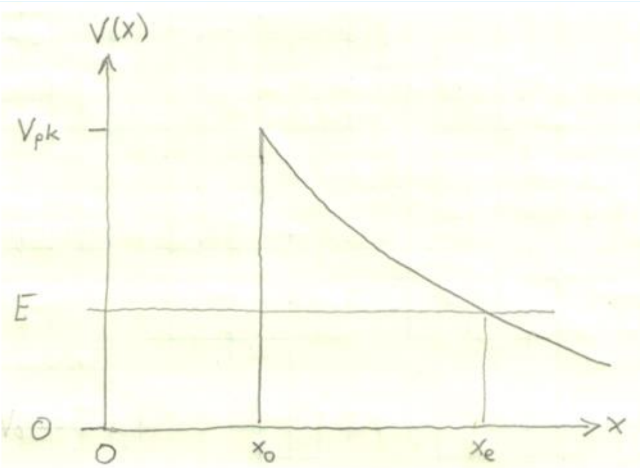
$$\Delta/2 = \int_{x_0}^{x_e} \sqrt{2m\left[V(x') - E\right]}dx'. \tag{3}$$

(a) Find an expression for Δ by evaluating this integral. It will be convenient to use the ratio $\rho \equiv x_0/x_e$. Try to simplify as much as you can. Note that you may find the discussion in the text on pages 444-445 helpful.

(b) Find an expression for x_e in terms of known quantities.

(c) To estimate the decay rate, we must multiply the tunneling probability by the rate at which the α strikes the potential barrier at x_0. Find an expression for this rate to strike the barrier by estimating the speed of the α and using the distance traveled between collisions.

(d) Finally put it all together and obtain a numerical prediction for the uranium decay rate, Γ. How does your result compare with the measured rate?



a.)

$$V(x) = \begin{cases} 0 & \text{if } x < x_0 \\ \underbrace{\frac{1}{4\pi\varepsilon_0}\frac{q_N}{x}}_{\text{electric potential (J/C)}} \cdot q_\alpha & \text{if } x \geq x_0 \end{cases}$$

charge of α particle.

where $q_N = (92 - 2)e = 90e$

where $q_N = (92-2)e = 90e$

$q_\alpha = 2e$

$$\rightarrow V(x) = \frac{1}{4\pi\varepsilon_0}\frac{180 e^2}{x} \equiv \frac{\beta}{x}$$

Notice $E = V(x_e) = \frac{\beta}{x_e} \rightarrow x_e = \frac{\beta}{E}$

Thus,

$$\Delta/2 = \int_{x_0}^{x_e}\left[2m\left(\frac{\beta}{x'} - E\right)\right]^{1/2} dx'$$

$-\sqrt{kg \cdot J}$ m

$= kg\, m \cdot m \cdot s^{-1}$

$$= \sqrt{2m}\int_{x_0}^{x_e}\underbrace{\sqrt{\frac{\beta}{x'} - E}}_{\beta^{1/2}\sqrt{\frac{1}{x'} - \frac{E}{\beta}} = \beta^{1/2}\sqrt{\frac{1}{x'} - \frac{1}{x_e}}}\, dx'$$

$$= \sqrt{2m}\,\beta^{1/2}\cdot\frac{1}{\sqrt{x_e}}\int_{x_0}^{x_e}\sqrt{\frac{1}{\left(\frac{x'}{x_e}\right)} - 1}\, dx'$$

let $z = \frac{x'}{x_e}$

$\rightarrow dx' = x_e dz$

$$= \sqrt{2m\beta}\cdot\sqrt{x_e}\int_0^1 \underbrace{\sqrt{\frac{1}{z} - 1}}_{\sqrt{\frac{1-z}{z}}}\, dz$$

Let $z = \cos^2\theta \rightarrow dz = -2\cos\theta\sin\theta\, d\theta$

$$\rightarrow \Delta/2 = \sqrt{2m\beta x_e}\int_a^b \sqrt{\frac{\sin^2\theta}{\cos^2\theta}}\cdot(-2)\cos\theta\sin\theta\, d\theta$$

$$= 2\sqrt{2m\beta x_c}\int_b^a \frac{\sin\theta}{\cos\theta}\cdot\cos\theta\sin\theta\,d\theta$$

$$= 2\underbrace{\sqrt{2m\beta x_c}}_{\equiv C_1}\int_b^a \sin^2\theta\,d\theta$$

$$= C_1 2\cdot\frac{1}{2}\left(\theta - \sin\theta\cos\theta\right)_b^a$$

where

$$\cos^2 a = \rho \to a = \cos^{-1}(\sqrt{\rho})$$

and

$$\cos^2 b = 1 \to b = 0$$

$\sin x = \sqrt{1-\cos^2 x}$

Thus,

$$\Delta/2 = C_1\cdot\left(a - \sin a\cos a\right)$$

$$= C_1\cdot\left(\cos^{-1}(\sqrt{\rho}) - \sqrt{1-\sqrt{\rho}^2}\cdot\sqrt{\rho}\right)$$

$$= C_1\left(\cos^{-1}(\sqrt{\rho}) - \sqrt{\rho(1-\rho)}\right)$$

Thus,

$$\boxed{\Delta = 2\sqrt{2m\beta x_c}\left(\cos^{-1}(\sqrt{\rho}) - \sqrt{\rho(1-\rho)}\right)} \left(\times\frac{1}{\hbar}\right)$$

where $\boxed{\beta = \frac{180e^2}{4\pi\varepsilon_0}}$ and $\boxed{x_c = \beta/E}$

$[\Delta] = \sqrt{kg\,(Jm)\cdot m} = kg\,m^2\,s^{-1}$
$= J/Hz$
$= [\hbar]$

b.)

$$\boxed{x_c = \frac{\beta}{E} = 60.7\text{ fm}}$$

c.) The decay rate is

$$r = r_s \cdot \left| \frac{\psi(x_e)}{\psi(x_0)} \right|^2 \approx r_s \left| \frac{\psi(x_0) e^{-\Delta/2}}{\psi(x_0)} \right|^2$$

$$= r_s \cdot e^{-\Delta}$$

where r_s is the rate at which the α particle strikes the potential barrier.

If the α particle has energy E, then its momentum is

$$p = \sqrt{2mE}$$

Thus, its velocity is

$$v = \sqrt{\frac{2E}{m}}$$

Thus, $r_s = \frac{v}{2x_0} \Rightarrow \boxed{r_s = \frac{\sqrt{2E/m}}{2x_0}}$

Thus,

$$r = \frac{v}{2x_0} e^{-\Delta}.$$

d.) $r = \frac{v}{2x_e} e^{-\Delta}$

7. Let's do a very simple calculation using the Ritz method, in order to make sure we understand the idea. Suppose we are interested in the energy levels of a particle of mass m in the one dimensional potential:

$$V(x) = \begin{cases} 0 & x \in (-L/2, L/2) \\ \infty & \text{otherwise} \end{cases} \tag{4}$$

Of course, we know the exact answer to both the eigenstates and eigenvalues for this system. However, let us pretend that we don't, and try using the Ritz method to estimate the two lowest energy levels. Thus, let us pick two trial wave functions.

We might by accident in this simple case actually pick the exact functions, but we'll avoid that. Let us make an "educated guess", and choose:

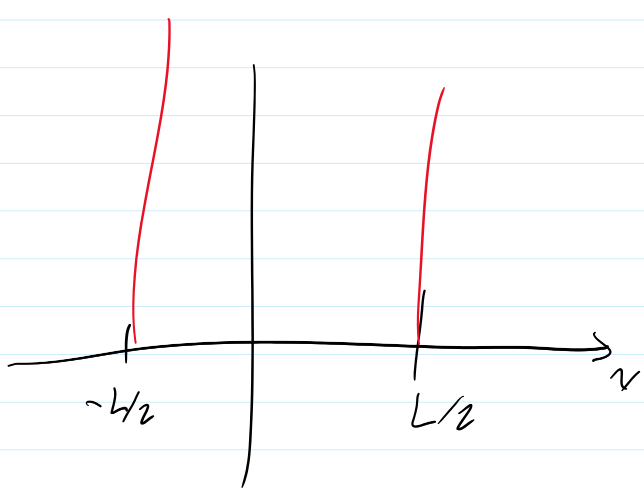
$$|1\rangle = A_1\left[(L/2)^2 - x^2\right] \tag{5}$$
$$|2\rangle = A_2 x\left[(L/2)^2 - x^2\right], \tag{6}$$

where A_1 and A_2 are normalization constants and it is understood that these functions are taken to be zero when $|x| \geq L/2$. I encourage you to consider why this might be a good guess, even if we avoided the exact answers.

(a) Carry out the Ritz procedure using these two trial wave functions, and estimate the two lowest energy levels. Along the way, try to note how we really did make some good choices.

(b) Compare your results with the exact eigenvalues for the two lowest levels.

a.)



$$\langle m|(H - \lambda I)\sum_n a_n|n\rangle = 0, \quad \forall m.$$

Note:

Note:

$$\frac{d^2}{dx^2}\langle x|1\rangle = \frac{d}{dx}\left[A_1\left[0-2x\right]\right]$$

$$= -2A_1$$

and

$$\frac{d^2}{dx^2}\langle x|2\rangle = \frac{d}{dx}\left[\frac{A_2}{A_1}|1\rangle + \frac{A_2 x}{A_1}\left(\frac{d}{dx}|1\rangle\right)\right]$$

$$= \frac{A_2}{A_1}\left(-2xA_1\right) + \frac{A_2}{A_1}\left(-2A_1 x\right) + \frac{A_2 x}{A_1}\left(-2A_1\right)$$

$$= -6A_2 x$$

We know $H = \frac{p^2}{2m} = -\partial_x^2/2m$

$$\langle 1|H|1\rangle = A_1^2\int_D \left((L/2)^2 - x^2\right)\frac{-2}{-2m}\,dx$$

$$= \frac{A_1^2}{m}\int_{-L/2}^{L/2} (L/2)^2 - x^2\,dx$$

$$= \frac{A_1^2}{m}\left[(L/2)^2 x - \frac{x^3}{3}\right]_{-L/2}^{L/2}$$

$$= \frac{A_1^2}{m}\left(2(L/2)^3 - \frac{2}{3}(L/2)^3\right)$$

$$\hookrightarrow \frac{1}{2}(\;\;-2\;)(L/2)^3$$

$$\hookrightarrow \frac{1}{3}(6-2)(L/2)^3$$

$$\to \langle 1|H|1\rangle = \frac{1}{6}\frac{A_1^2 L^3}{m}$$

Notice

$$1 = \langle 1|1\rangle = A_1^2 \int [\underbrace{(L/2)^2}_{\equiv \alpha} - x^2]^2 dx$$

$$= A_1^2 \int_{-L/2}^{L/2} \alpha^2 - 2\alpha x^2 + x^4 \, dx$$

$$= A_1^2 \left[\alpha^2 x - \frac{2}{3}\alpha x^3 + \frac{1}{5}x^5\right]_{-L/2}^{L/2}$$

$$= A_1^2 \left[2\alpha^2 (L/2) - \frac{4}{3}\alpha (L/2)^3 + \frac{2}{5}(L/2)^5\right]$$

$$= A_1^2 \left(\overset{30/15}{2} - \overset{20/15}{\frac{4}{3}} + \overset{6/15}{\frac{2}{5}}\right)(L/2)^5$$

$$= A_1^2 \left(\frac{16}{15}\right)(L/2)^5$$

$$= A_1^2 \frac{1}{30} L^5 \to A_1 = \sqrt{\frac{30}{L^5}}$$

$$\to \langle 1|H|1\rangle = \frac{1}{6}\cdot\frac{30}{L^5}\cdot\frac{L^3}{m}$$

$$= \frac{5}{\ldots}$$

$$= \frac{5}{L^2 m}$$

Moreover,

$$\langle 2|H|2\rangle = A_2^2 \int_D x\left[(L/2)^2 - x^2\right] \cdot \frac{-6x}{-2m}$$

$$= \frac{3A_2^2}{m}\int_D x^2\left[(L/2)^2 - x^2\right] dx$$

$$= \frac{3A_2^2}{m}\left[\frac{1}{3}(L/2)^2 x^3 - \frac{1}{5}x^5\right]_{-L/2}^{L/2}$$

$$= \frac{6A_2^2}{m}\left[\overset{5/15}{\frac{1}{3}}(L/2)^5 - \overset{3/15}{\frac{1}{5}}(L/2)^5\right]$$

$$= \frac{6A_2^2}{m}\cdot\frac{2}{15}(L/2)^5$$

Notice

$$1 = \langle 2|2\rangle = A_2^2\int_D x^2(\alpha - x^2)^2$$

$$= A_2^2\int_D \alpha^2 x^2 - 2\alpha x^4 + x^6\, dx$$

$$= A_2^2\left[\frac{1}{3}\alpha^2 x^3 - \frac{2}{5}\alpha x^5 + \frac{1}{7}x^7\right]_{-L/2}^{L/2}$$

$$= A_2^2 \cdot \frac{2}{105}\left[35 - 42 + 15\right](L/2)^7$$

$$= A_2^{\,2} \cdot \frac{16}{105} (L/2)^7$$

$$\rightarrow A_2^{\,2} = \frac{105}{16} (L/2)^{-7}$$

Thus,

$$\langle 2|H|2\rangle = \frac{12}{15} \cdot \frac{105}{16} \cdot \frac{1}{m} (L/2)^{-2}$$

$$= \frac{21}{mL^2}$$

Also, notice

$$\langle 1|H|2\rangle^* = \langle 2|H|1\rangle = A_1 A_2 \int_D x\left((L/2)^2 - x^2\right) \cdot \frac{-2}{-2m} dx$$

is an odd integral. Thus,

$$\begin{pmatrix} \langle 1| \\ \langle 2| \end{pmatrix} H \begin{pmatrix} |1\rangle & |2\rangle \end{pmatrix} = \frac{1}{mL^2} \begin{pmatrix} 5 & 0 \\ 0 & 21 \end{pmatrix}$$

We are very lucky with our guesses b/c the matrix is already diagonalized.

Thus, the eigenvalues are

$$\boxed{E^{(1)} = \frac{5}{mL^2} (\times \hbar^2) \qquad E^{(2)} = \frac{21}{mL^2} (\times \hbar^2)}$$

b.) The actual energies are

$$E_n = \frac{\hbar^2 \rho^2}{2mL^2} \quad (\times \hbar^2)$$

We find

$$\frac{E^{(1)}}{E_1} = 1.013 \qquad \frac{E^{(2)}}{E_2} = 1.064$$

The approximated and true energies are very close together - both are within 10% of each other. Moreover, both estimates are **overestimates**.

8. Consider an "anharmonic" oscillator, in which we add a perturbation

$$V = -\rho\omega\hat{X}^3. \tag{7}$$

to the one-dimension harmonic oscillator Hamiltonian. Here, we define $\hat{X} \equiv \sqrt{m\omega}X$ and the unperturbed Hamiltonian is

$$H_0 = \frac{P^2}{2m} + \frac{m\omega^2 X^2}{2}. \tag{8}$$

The parameter $0 < \rho \ll 1$ is a small dimensionless parameter giving the strength of the perturbation. [We assume that the perturbation is sufficiently small that we needn't worry about what happens at very large values of x.]

(a) Write the perturbation in terms of the raising and lowering operators a and $a^\dagger$. Compute all of the non-zero matrix elements of V in the basis of the unperturbed eigenstates.

(b) Compute the perturbed energy levels to the lowest non-trivial order in the perturbation.

(c) Compute the perturbed energy eigenfunctions to the lowest non-trivial order in the perturbation. Express in terms of the unperturbed energy eigenfunctions.

a.) We know

$$X = \left(\frac{\hbar}{2m\omega}\right)^{1/2}(a + a^\dagger) \qquad = \left(\frac{\hbar^3 \rho^2}{\dots}\right)^{1/2}$$

$$X = \left(\frac{\hbar}{2m\omega}\right)(a+a^\dagger)$$

Thus,

$$c_1 = \left(\frac{\hbar^3\rho^2}{8m^3\omega}\right)$$

$$V = -\rho\omega\, \hat{X}^3 = -\underbrace{\left(\rho^2\omega^2 \cdot \frac{\hbar^3}{8m^3\omega^3}\right)^{1/2}}_{c_1}(a+a^\dagger)^3$$

$$= -c_1\left[a^3 + \left(a^2a^\dagger + aa^\dagger a + a^\dagger aa\right) + \left(a^{\dagger 2}a + a^\dagger a a^\dagger + aa^{\dagger 2}\right) + a^{\dagger 3}\right]$$

$$\langle m|\, a^2a^\dagger |n\rangle$$

Note

$$V_{nm} = \langle m|V|n\rangle$$

Notice $V_{nm} \neq 0$ iff $m = n\pm 3$ or $m = n\pm 1$.

Notice

$$\sqrt{\frac{(n+3)!}{n!}}$$

$$\boxed{\langle n+3|V|n\rangle = -c_1\sqrt{(n+1)(n+2)(n+3)}}$$

$$\sqrt{\frac{n!}{(n-3)!}}$$

$$\boxed{\langle n-3|V|n\rangle = -c_1\sqrt{n(n-1)(n-2)}}$$

Also

$$\langle n+1|V|n\rangle = -c_1\left[\overset{\downarrow\uparrow\uparrow}{\sqrt{n\cdot n\cdot(n+1)}} + \overset{\uparrow\uparrow\downarrow}{\sqrt{(n+1)(n+2)(n+2)}} + \overset{\uparrow\downarrow\uparrow}{\sqrt{(n+1)(n+1)(n+1)}}\right]$$

$$\Rightarrow \langle n+1|V|n\rangle = -c_1\left[n\sqrt{n+1} + (n+2)\sqrt{n+1} + (n+1)\sqrt{n+1}\right]$$

$$= -c_1\,(n+n+2+n+1)\sqrt{n+1}$$

$$\Rightarrow \boxed{\langle n+1|V|n\rangle = -3c_1(n+1)^{3/2}}$$

Let $n \to n-1$. Then, we see that

$$\boxed{\langle n-1|V|n\rangle = -3c_1 n^{3/2}}$$

b.) We know that

$$E_n = \varepsilon_n + \langle n|V|n\rangle + \sum_{m\neq n} \frac{|\langle m|V|n\rangle|^2}{\varepsilon_n - \varepsilon_m} + \ldots$$

Thus,

$$E_n = \varepsilon_n + 0 + \frac{|\langle n+3|V|n\rangle|^2}{\varepsilon_{n+3}-\varepsilon_n} + \ldots$$

$$E_n \approx \varepsilon_n + c_1^2\left(\frac{\frac{(n+3)!}{n!}}{\underbrace{\varepsilon_{n+3}-\varepsilon_n}_{3\hbar\omega}} + \frac{\frac{n!}{(n-3)!}}{\underbrace{\varepsilon_{n-3}-\varepsilon_n}_{-3\hbar\omega}} + 9\,\frac{(n+1)^3}{\underbrace{\varepsilon_{n+1}-\varepsilon_n}_{\hbar\omega}} + 9\,\frac{n^3}{\underbrace{\varepsilon_{n-1}-\varepsilon_n}_{-\hbar\omega}}\right)$$

$\quad\quad_{n-1} \quad\quad\quad \approx -\hbar\omega$

We know $E_n = (n+\frac{1}{2})\hbar\omega$.

$$\to E_n^{(2)} = \frac{c_1^2}{\hbar\omega}\left[\frac{1}{3}\left(\frac{(n+3)!}{n!} - \frac{n!}{(n-3)!}\right) + 9\left((n+1)^3 - n^3\right)\right]$$
$$+ (n+\tfrac{1}{2})\hbar\omega \quad ; \quad c_1^2 = \frac{\hbar^3\rho^2}{8m^3\omega}$$

Mathematica

$$\boxed{E_n \approx -\frac{\hbar^2\rho^2}{8m^3\omega^2}\left(30n^2 + 30n + 11\right) + (n+\tfrac{1}{2})\hbar\omega}$$

c.) We know that

$$|N\rangle = |n\rangle + \sum_{m\neq n} |m\rangle \frac{\langle m|V|n\rangle}{E_n - E_m} + \cdots$$

Thus,

$$|N^{(1)}\rangle = \frac{c_1}{\hbar\omega}\left[\frac{1}{3}\left(\sqrt{\frac{(n+3)!}{n!}}\,|n+3\rangle - \sqrt{\frac{n!}{(n-3)!}}\,|n-3\rangle\right)\right.$$
$$\left. + 3\left(\sqrt{(n+1)!}\,|n+1\rangle + \sqrt{n!}\,|n\rangle\right)\right]$$

$$\boxed{|N\rangle \approx |n\rangle + \frac{c_1}{\hbar\omega}\left[\frac{1}{3}\left(\sqrt{\frac{(n+3)!}{n!}}\,|n+3\rangle - \sqrt{\frac{n!}{(n-3)!}}\,|n-3\rangle\right) + 3\left(\sqrt{(n+1)!}\,|n+1\rangle + \sqrt{n!}\,|n\rangle\right)\right];\ c_1 = \sqrt{\frac{\hbar^3 \rho^2}{8m^3\omega}}}$$