

(Griffiths 5.19) The ground state of dysprosium is given as 5I_8 .

What are the total spin, total orbital, and grand total angular momentum quantum numbers?

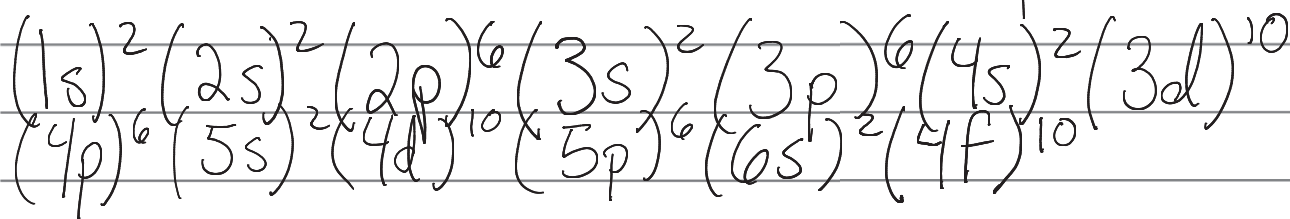
What is a likely electron configuration for dysprosium?

$$^5I_8 \Rightarrow 5 = 2S + 1 \rightarrow S = 2$$

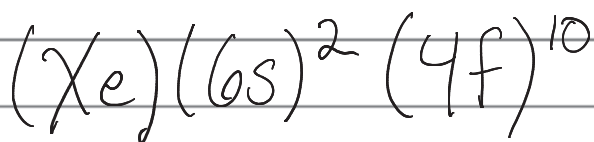
$$I \rightarrow L = 7$$

$$8 \rightarrow J = 8$$

For the electron configuration, we can read from the periodic table



or more compactly



You can see a discussion on $4s$ having lower energy than $3d$ in the 3rd paragraph of page 213 I asked you to read.

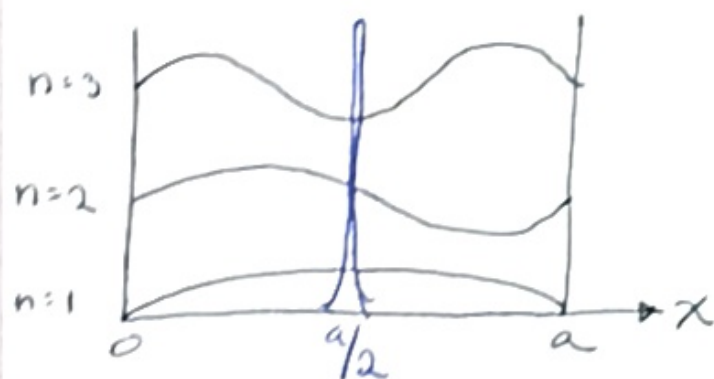
Homework 7

1. (Griff. Hs 7.1) Suppose we put a delta-fcn bump at the center of the square well:

$$H' = \alpha \delta(x - a/2)$$

- 2) Find the first order perturbed energies. Why are energies not perturbed for even n ?

The second part is straightforward: all even- n are zero at the center of the well so are unaffected by the $\delta(x - a/2)$.



Now to find the energy corrections:

$$E_n^{(1)} = \langle n | H' | n \rangle$$

$$= \int dx \sin\left(\frac{n\pi x}{a}\right) \alpha \delta(x - a/2) \sin\left(\frac{n\pi x}{a}\right) \cdot \left(\sqrt{\frac{2}{a}}\right)^2$$

$$= \frac{2}{a} \alpha \sin^2\left(\frac{n\pi}{2}\right) = \frac{2\alpha}{a} \sin^2\left(\frac{n\pi}{2}\right)$$

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b) Find the first 3 non-zero terms in $\psi_1^{(1)}$.

$$\psi_n^{(1)} = \sum_{m \neq n} \frac{\langle \psi_m^{(0)} | H' | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}} |\psi_m^{(0)}\rangle$$

with $n=1$

$$\psi_1^{(1)} = \sum_{m \neq 1} \frac{\langle \psi_m^{(0)} | H' | \psi_1^{(0)} \rangle}{E_1^{(0)} - E_m^{(0)}} |\psi_m^{(0)}\rangle$$

Let's look at the numerator:

$$\begin{aligned} \langle \psi_m^{(0)} | H' | \psi_n^{(0)} \rangle &= \int dx \left(\frac{2}{a} \right)^2 \sin\left(\frac{m\pi x}{a}\right) \alpha \delta(x - \frac{a}{2}) \sin\left(\frac{n\pi x}{a}\right) \\ &= \frac{2\alpha}{a} \sin\left(\frac{m\pi}{2}\right) \sin\left(\frac{n\pi}{2}\right) \end{aligned}$$

$\sin(\pi/2) = 1$ so

$$\langle \psi_m^{(0)} | H' | \psi_n^{(0)} \rangle = \frac{2\alpha}{a} \sin\left(\frac{m\pi}{2}\right)$$

which is non-zero for odd n . Since $m=1$ is excluded, we have $m \in \{3, 5, 7\}$

Meanwhile, in the denominator, we have

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1C

$$E_n^{(0)} - E_m^{(0)} = \frac{\pi^2 \hbar^2 n^2}{2ma^2} - \frac{\pi^2 \hbar^2 m^2}{2ma^2}, \text{ but } n=1 \text{ so}$$

$$= \frac{\pi^2 \hbar^2}{2ma^2} (1 - m^2)$$

and

$$\frac{1}{E_n^{(0)} - E_m^{(0)}} = \frac{2ma^2}{\pi^2 \hbar^2 (1 - m^2)}$$

Putting it all together, and recognizing that $\sin(3\pi/2) = -1$, $\sin(5\pi/2) = +1$, $\sin(7\pi/2) = -1$, we have

$$\psi_1^{(1)} = \frac{2\alpha}{\alpha} \cdot \frac{2ma^2}{\pi^2 \hbar^2} \left[\frac{-1}{1-9} \psi_3^{(0)} + \frac{1}{1-25} \psi_5^{(0)} - \frac{1}{1-49} \psi_7^{(0)} + \dots \right]$$

$$\psi_1^{(1)} = \frac{4m\alpha a \sqrt{2}}{\pi^2 \hbar^2 \sqrt{a}} \left[\frac{1}{8} \sin\left(\frac{3\pi x}{a}\right) - \frac{1}{24} \sin\left(\frac{5\pi x}{a}\right) + \frac{1}{48} \sin\left(\frac{7\pi x}{a}\right) + \dots \right]$$

$$= \frac{m\alpha}{\pi^2 \hbar^2} \sqrt{\frac{a}{2}} \left[\sin\left(\frac{3\pi x}{a}\right) - \frac{1}{3} \sin\left(\frac{5\pi x}{a}\right) + \frac{1}{6} \sin\left(\frac{7\pi x}{a}\right) + \dots \right]$$

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2A

2. (Griffiths 7.2) For the 1-D QMHO,

$$H = \frac{p^2}{2m} + \frac{k}{2} x^2 \quad \text{with} \quad E_n = (n + \frac{1}{2}) \hbar \omega$$

$$\text{with } \omega = \sqrt{\frac{k}{m}}$$

Now perturb by $k \rightarrow (1 + \epsilon)k$.a) Find the exact solution and expand to 2nd order in ϵ .

$$\text{As } k \rightarrow (1 + \epsilon)k, \quad \omega \rightarrow \sqrt{\frac{(1 + \epsilon)k}{m}} = \omega'$$

so the energies are $E_n = (n + \frac{1}{2}) \hbar \omega'$, or, in terms of k & ϵ :

$$E_n = \hbar (n + \frac{1}{2}) \sqrt{\frac{k}{m} (1 + \epsilon)} = \hbar \omega (n + \frac{1}{2}) \sqrt{1 + \epsilon}$$

$$(1 + \epsilon)^n = 1 + n\epsilon + \frac{1}{2} n(n-1) \epsilon^2 + \dots$$

$$E_n = (n + \frac{1}{2}) \hbar \omega \left[1 + \frac{1}{2} \epsilon + \frac{1}{2} \left(\frac{1}{2} \right) \left(-\frac{1}{2} \right) \epsilon^2 + \dots \right]$$

$$E_n = (n + \frac{1}{2}) \hbar \omega \left[1 + \frac{1}{2} \epsilon - \frac{1}{8} \epsilon^2 + \dots \right]$$

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2B

b) Now use perturbation theory (without integrals!) to find $E_n^{(1)}$ and see that it agrees with part a.

$$E_n^{(1)} = \langle n | H' | n \rangle$$

What is H' ?

$$H = \frac{p^2}{2m} + \frac{k(1+\epsilon)}{2} x^2. \text{ Now expand:}$$

$$H = \underbrace{\frac{p^2}{2m} + \frac{k}{2} x^2}_{H_0} + \underbrace{\frac{k\epsilon}{2} x^2}_{H'}$$

$$\begin{aligned} \therefore E_n^{(1)} &= \langle n | H' | n \rangle \\ &= \left\langle n \left| \frac{k\epsilon}{2} x^2 \right| n \right\rangle \end{aligned}$$

∃ 2 ways to do this:

- 1) The virial theorem $\langle T \rangle = \frac{n}{2} \langle V \rangle \xrightarrow{\text{for QMHO}} \langle T \rangle = \langle V \rangle$
as x^n with $n=2$
- 2) Operators

The virial theorem method is most straightforward

$$E_n^{(1)} = \epsilon \langle n | V | n \rangle = \epsilon \langle V \rangle$$

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Since $\langle V \rangle = \langle T \rangle$ and $\langle V \rangle + \langle T \rangle = E_n$,
 $\langle V \rangle = \frac{1}{2} E_n$. Thus

$$E_n^{(1)} = \frac{\epsilon}{2} E_n = \frac{\epsilon}{2} (n + \frac{1}{2}) \hbar \omega$$

a perfect match for the linear term highlighted
at the bottom of pg 2A.

The other option is to write $x = \sqrt{\frac{\hbar}{2m\omega}} (a + a^\dagger)$
and proceed that way.

Problem 3 (Griffiths 7.4)

Start by stating global assumptions for this notebook: that both energies are real and positive while $0 < \lambda < 1$.

```
In[1]:= $Assumptions = Ea ∈ Reals && Ea > 0 && Eb ∈ Reals && Eb > 0 && λ ∈ Reals && λ > 0 && λ < 1
Out[1]= Ea ∈ ℝ && Ea > 0 && Eb ∈ ℝ && Eb > 0 && λ ∈ ℝ && λ > 0 && λ < 1
```

Apply perturbation theory to the most general two-state system with unperturbed energies:

```
In[2]:= MatrixForm[H0 = {{Ea, 0}, {0, Eb}}]
Out[2]//MatrixForm=

$$\begin{pmatrix} Ea & 0 \\ 0 & Eb \end{pmatrix}$$

```

and perturbation

```
In[3]:= MatrixForm[H1 = λ {{Vaa, Vab}, {Vab, Vbb}}]
Out[3]//MatrixForm=

$$\begin{pmatrix} Vaa \lambda & Vab \lambda \\ Vab \lambda & Vbb \lambda \end{pmatrix}$$

```

(Note, I am using $Vab = Vba$. What is really true, however, $Vba^* = Vab$. However, this is simpler for Mathematica)

```
In[4]:= MatrixForm[H1]
Out[4]//MatrixForm=

$$\begin{pmatrix} Vaa \lambda & Vab \lambda \\ Vab \lambda & Vbb \lambda \end{pmatrix}$$

```

a) Find the exact energies

```
In[5]:= MatrixForm[H = H0 + H1]
Out[5]//MatrixForm=

$$\begin{pmatrix} Ea + Vaa \lambda & Vab \lambda \\ Vab \lambda & Eb + Vbb \lambda \end{pmatrix}$$

```

In[6]:= **Emp = Eigenvalues [H]**

$$\text{Out[6]} = \left\{ \frac{1}{2} \left(E_a + E_b + V_{aa} \lambda + V_{bb} \lambda - \sqrt{(-E_a - E_b - V_{aa} \lambda - V_{bb} \lambda)^2 - 4(E_a E_b + E_b V_{aa} \lambda + E_a V_{bb} \lambda - V_{ab}^2 \lambda^2 + V_{aa} V_{bb} \lambda^2)} \right), \right. \\ \left. \frac{1}{2} \left(E_a + E_b + V_{aa} \lambda + V_{bb} \lambda + \sqrt{(-E_a - E_b - V_{aa} \lambda - V_{bb} \lambda)^2 - 4(E_a E_b + E_b V_{aa} \lambda + E_a V_{bb} \lambda - V_{ab}^2 \lambda^2 + V_{aa} V_{bb} \lambda^2)} \right) \right\}$$

Which simplifies into E- (Em) and E+ (Ep) via

In[7]:= **Simplify[(a + b)^2 - 4 a * b]**

$$\text{Out[7]} = (a - b)^2$$

In[8]:= **Em = 1 / 2 * ((Ea + Eb + Vaa * λ + Vbb * λ) - Sqrt[(Ea + λ * Vaa - Eb - λ * Vbb)^2 + 4 * λ^2 * Vab^2])**

$$\text{Out[8]} = \frac{1}{2} \left(E_a + E_b + V_{aa} \lambda + V_{bb} \lambda - \sqrt{4 V_{ab}^2 \lambda^2 + (E_a - E_b + V_{aa} \lambda - V_{bb} \lambda)^2} \right)$$

In[9]:= **Ep = 1 / 2 * ((Ea + Eb + Vaa * λ + Vbb * λ) + Sqrt[(Ea + λ * Vaa - Eb - λ * Vbb)^2 + 4 * λ^2 * Vab^2])**

$$\text{Out[9]} = \frac{1}{2} \left(E_a + E_b + V_{aa} \lambda + V_{bb} \lambda + \sqrt{4 V_{ab}^2 \lambda^2 + (E_a - E_b + V_{aa} \lambda - V_{bb} \lambda)^2} \right)$$

b) Expand your results from (a) to second order in λ. Show that the results are the same as what we obtained in perturbation theory.

In[10]:= **Series[Em, {λ, 0, 2}]**

$$\text{Out[10]} = \frac{1}{2} (E_a + E_b - \text{Abs}[E_a - E_b]) + \frac{1}{2} \left(V_{aa} + V_{bb} - \frac{(V_{aa} - V_{bb}) \text{Abs}[E_a - E_b]}{E_a - E_b} \right) \lambda - \frac{V_{ab}^2 \text{Abs}[E_a - E_b] \lambda^2}{(E_a - E_b)^2} + O[\lambda]^3$$

This, of course, simplifies to (Ea-Eb)^2 = (Eb - Ea)^2

In[11]:= **Em = 1 / 2 (2 * Eb - Ea + Ea) + 1 / 2 (Vaa + Vbb - Vaa + Vbb) * λ + (Vab^2 * λ^2) / (Eb - Ea)**

$$\text{Out[11]} = E_b + V_{bb} \lambda + \frac{V_{ab}^2 \lambda^2}{-E_a + E_b}$$

Similarly for Ep

In[12]:= **Series[Ep, {λ, 0, 2}]**

$$\text{Out[12]} = \frac{1}{2} (E_a + E_b + \text{Abs}[E_a - E_b]) + \frac{1}{2} \left(V_{aa} + V_{bb} + \frac{(V_{aa} - V_{bb}) \text{Abs}[E_a - E_b]}{E_a - E_b} \right) \lambda + \frac{V_{ab}^2 \text{Abs}[E_a - E_b] \lambda^2}{(E_a - E_b)^2} + O[\lambda]^3$$

Simplifies to

In[13]:=
$$E_p = \frac{1}{2} (2 * E_a - E_b + E_b) + \frac{1}{2} (V_{aa} + V_{aa} - V_{bb} + V_{bb}) \lambda + \frac{(V_{ab}^2 * \lambda^2)}{(E_b - E_a)}$$

Out[13]=

$$E_a + V_{aa} \lambda + \frac{V_{ab}^2 \lambda^2}{-E_a + E_b}$$

Both of which match our results from perturbation theory!

c) Setting $V_{aa} = V_{bb} = 0$, show that the series only converges if $|V_{ab} / (E_b - E_a)| < 1/2$

The series only converge if

In[14]:=

$$4 V_{ab}^2 / (E_b - E_a)^2 < 1$$

Out[14]=

$$\frac{4 V_{ab}^2}{(-E_a + E_b)^2} < 1$$

or equivalently

In[15]:= $|V_{ab} / (E_b - E_a)| < 1/2$

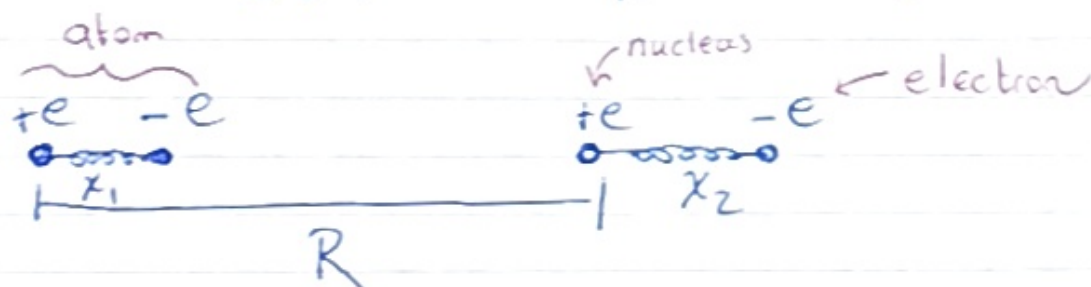
HW#7

4A

4 (Griff.Hhs 7.39) Van der Waals

$$H^0 = \frac{p_1^2}{2m} + \frac{1}{2} k x_1^2 + \frac{p_2^2}{2m} + \frac{1}{2} k x_2^2$$

$$H' = \frac{1}{4\pi\epsilon_0} \left(\frac{e^2}{R} - \frac{e^2}{(R-x_1)} - \frac{e^2}{(R+x_2)} + \frac{e^2}{(R-x_1+x_2)} \right)$$



a) Explain the perturbation.

The first term is the nuclear repulsion: $+e^2/R$

The second term is the attraction between the electron on the left and the nucleus on the right: $-e^2/(R-x_1)$

The third term is the attraction between the electron on the right and the left nucleus: $-e^2/(R+x_2)$

The final term is the repulsion of the two electrons: $+e^2/(R-x_1+x_2)$

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Also, assuming $|x_1| \ll R$ & $|x_2| \ll R$, show

$$H' \approx \frac{-e^2 x_1 x_2}{2\pi\epsilon_0 R^3}$$

$\frac{1}{R-x}$ appears in all terms but the first in some form. We want $(1+\epsilon)^n$

$$\frac{1}{R-x} = \frac{1}{R} \left(1 - \frac{x}{R}\right)^{-1}$$

$$\sim \frac{1}{R} \left(1 - \frac{x}{R} + \frac{1}{2}(-1)(-1-1)\left(\frac{x}{R}\right)^2 + \dots\right)$$

$$\sim \frac{1}{R} \left(1 - \frac{x}{R} + \left(\frac{x}{R}\right)^2 + \dots\right)$$

$$H' \approx \frac{e^2}{4\pi\epsilon_0 R} \left[\cancel{1} - \left(\cancel{1} + \frac{x_1}{R} + \frac{x_1^2}{R^2} \right) - \left(\cancel{1} - \frac{x_2}{R} + \frac{x_2^2}{R^2} \right) + \left(\cancel{1} + \frac{(x_1 - x_2)}{R} + \frac{(x_1 - x_2)^2}{R^2} \right) \right]$$

$$\approx \frac{e^2}{4\pi\epsilon_0 R} \left[\cancel{\frac{-x_1}{R}} + \cancel{\frac{x_2}{R}} + \cancel{\frac{(x_1 - x_2)}{R}} - \cancel{\frac{x_1^2}{R}} - \cancel{\frac{x_2^2}{R}} + \cancel{\frac{x_1^2}{R}} + \cancel{\frac{x_2^2}{R}} - \frac{2x_1 x_2}{R} \right]$$

$$\approx -\frac{e^2 x_1 x_2}{2\pi\epsilon_0 R^2} \quad \text{o.e.d.}$$

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4C

b) Show that H_0 plus the simplified H' separates into 2 QMHO's:

$$H = \left[\frac{p_+^2}{2m} + \frac{1}{2} \left(k - \frac{e^2}{2\pi\epsilon_0 R^3} \right) x_+^2 \right] + \left[\frac{p_-^2}{2m} + \frac{1}{2} \left(k + \frac{e^2}{2\pi\epsilon_0 R^3} \right) x_-^2 \right]$$

$$\text{With } x_{\pm} = \frac{1}{\sqrt{2}} (x_1 \pm x_2) \quad p_{\pm} = \frac{1}{\sqrt{2}} (p_1 \mp p_2)$$

The easiest way to do this is to work backwards and expand the result

$$p_+^2 = (p_1^2 + p_2^2 + 2p_1 p_2) \cdot \frac{1}{2}$$

(since 1 & 2 are independent particles, p_1 & p_2 commute!)

Similarly:

$$p_-^2 = \frac{1}{2} (p_1^2 + p_2^2 - 2p_1 p_2)$$

$$x_+^2 = \frac{1}{2} (x_1^2 + x_2^2 + 2x_1 x_2)$$

$$x_-^2 = \frac{1}{2} (x_1^2 + x_2^2 - 2x_1 x_2)$$

$$p_+^2 + p_-^2 = p_1^2 + p_2^2$$

$$x_+^2 + x_-^2 = x_1^2 + x_2^2 \quad x_-^2 - x_+^2 = -2x_1 x_2 \quad \text{o.e.d.}$$

HW #7

c) Assuming $k \gg \left(\frac{e^2}{2\pi\epsilon_0 R^3} \right)$ show that

$$\Delta V = E - E_0 \cong -\frac{\hbar}{8m^2\omega_0^3} \left(\frac{e^2}{2\pi\epsilon_0} \right)^2 \frac{1}{R^6}$$

with $\omega_0 = \sqrt{k/m}$ & $E_0 = (n_+ + n_- + 1)\hbar\omega = \hbar\omega$

The energies, in this case, are

$$E_0 = (n_+ + \frac{1}{2})\hbar\omega_+ + (n_- + \frac{1}{2})\hbar\omega_- = \frac{1}{2}\hbar(\omega_+ + \omega_-)$$

for $n_+ = n_- = 0$.

$$\omega_{\pm} = \sqrt{\frac{k \mp (e^2/2\pi\epsilon_0 R^3)}{m}}$$

$$\omega_{\pm} = \sqrt{\frac{k}{m}} \left(1 \mp \frac{e^2}{2\pi\epsilon_0 R^3 k} \right)^{1/2}$$

$$\begin{aligned} \omega_{\pm} &\approx \sqrt{\frac{k}{m}} \left[1 \mp \frac{1}{2} \left(\frac{e^2}{2\pi\epsilon_0 R^3 k} \right) + \frac{1}{2} \left(\frac{1}{2} \right) \left(\frac{1}{2} \right) \left(\frac{e^2}{2\pi\epsilon_0 R^3 k} \right)^2 + \dots \right] \\ &\approx \sqrt{\frac{k}{m}} \left[1 \mp \frac{1}{2} \left(\frac{e^2}{2\pi\epsilon_0 R^3 k} \right) - \frac{1}{8} \left(\frac{e^2}{2\pi\epsilon_0 R^3 k} \right)^2 + \dots \right] \end{aligned}$$

$$\Delta V = \frac{1}{2}\hbar(\omega_+ + \omega_-) - \hbar\omega_0$$

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4E

$$\Delta V \approx \frac{1}{2} \hbar \omega_0 \left\{ \left[1 - \frac{1}{2} \left(\frac{e^2}{2\pi\epsilon_0 R^3 \hbar} \right) - \frac{1}{8} \left(\frac{e^2}{2\pi\epsilon_0 R^3 \hbar} \right)^2 \right] + \left[1 + \frac{1}{2} \left(\frac{e^2}{2\pi\epsilon_0 R^3 \hbar} \right) - \frac{1}{8} \left(\frac{e^2}{2\pi\epsilon_0 R^3 \hbar} \right)^2 \right] \right\} - \hbar \omega_0$$

$$\Delta V \approx \frac{1}{2} \hbar \omega_0 \left\{ \cancel{1} - \cancel{\frac{1}{2}} \left(\frac{e^2}{2\pi\epsilon_0 R^3 \hbar} \right)^2 \right\} - \cancel{\hbar \omega_0}$$

$$\Delta V \approx - \frac{\hbar \omega_0}{8} \frac{e^2}{(2\pi\epsilon_0 R^3 \hbar)^2} \quad k = m\omega_0^2$$

$$\approx - \frac{1}{8} \frac{\hbar}{m^2 \omega_0^3} \left(\frac{e^2}{2\pi\epsilon_0} \right)^2 \frac{1}{R^6}$$

d) Now repeat using 2nd order P.T.

At first order, things go to zero

$$E_0^{(1)} = \langle 00 | H' | 00 \rangle \quad \text{using } |x_1, x_2\rangle \text{ notation}$$

$$= - \frac{e^2}{2\pi\epsilon_0 R^3} \langle 00 | x_1 x_2 | 00 \rangle$$

Since $x_1 = \sqrt{\frac{\hbar}{2m\omega}} (a_1 + a_1^\dagger)$, we see that

the result is zero: a_1 by lowering $|0\rangle \rightarrow 0$ and $a_1^\dagger$ by orthogonality. The same will be true for x_2

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4F

At second order

$$E_0^{(2)} = \sum_{n_1=1}^{\infty} \sum_{n_2=1}^{\infty} \frac{|\langle 00 | H' | n_1 n_2 \rangle|^2}{E_{00} - E_{n_1 n_2}}$$

$$= \left(\frac{e^2}{2\pi\epsilon_0 R^3} \right)^2 \sum_{n_1=1}^{\infty} \sum_{n_2=1}^{\infty} \frac{1}{E_{00} - E_{n_1 n_2}} |\langle 00 | x_1 x_2 | n_1 n_2 \rangle|^2$$

Again, recalling $x_i = \sqrt{\frac{\hbar}{2m\omega}} (a_i + a_i^\dagger)$

the only non-zero term is $|11\rangle$ as all others go to zero by orthogonality.

$$E_{11} = \hbar\omega_0(1+1+1) = 3\hbar\omega_0$$

$$E_{00} = \hbar\omega_0(0+0+1) = \hbar\omega_0$$

$$E_{00} - E_{11} = -2\hbar\omega_0$$

$$|\langle 00 | x_1 x_2 | 11 \rangle|^2 = \left| \sqrt{\frac{\hbar}{2m\omega}} \sqrt{\frac{\hbar}{2m\omega}} \sqrt{1} \sqrt{1} \right|^2$$

$$= \left(\frac{\hbar}{2m\omega} \right)^2$$

$$\therefore E_0^{(2)} = \left(\frac{e^2}{2\pi\epsilon_0} \right)^2 \left(\frac{-1}{2\hbar\omega_0} \right) \left(\frac{\hbar}{2m\omega} \right)^2 \frac{1}{R^6}$$

$$E_0^{(2)} = -\frac{\hbar}{8m^2\omega_0^3} \left(\frac{e^2}{2\pi\epsilon_0} \right)^2 \frac{1}{R^6} \quad \text{o.e.d.}$$