# PHY 742 Quantum Mechanics II
# 12-12:50 PM MWF Olin 103

## Plan for Lecture 4
## Approximate solutions for stationary states
## Perturbation theory (Chap. 12 C & D, 13*) –
## Some additional tricks and famous results

1. Summary of basic formalism for non-degenerate problem
2. Polarizability of H atom
3. Summation tricks
4. More examples

* WKB method will be discussed after completing Chap. 13

# Course schedule for Spring 2022

(Preliminary schedule -- subject to frequent adjustment.)

| | Lecture date | Reading | Topic | HW | Due date |
|---|---|---|---|---|---|
| 1 | Mon: 01/10/2022 | Chap. 12 | Approximate solutions for stationary states -- The variational approach | #1 | 01/14/2022 |
| 2 | Wed: 01/12/2022 | Chap. 12 C | Approximate solutions for stationary states -- Perturbation theory | #2 | 01/19/2022 |
| 3 | Fri: 01/14/2022 | Chap. 12 D | Approximate solutions for stationary states -- Degenerate perturbation theory | #3 | 01/21/2022 |
| | Mon: 01/17/2022 | | MLK Holiday -- no class | | |
| 4 | Wed: 01/19/2022 | Chap. 12 C & D | Approximate solutions for stationary states -- Additional tricks | #4 | 01/24/2022 |
| 5 | Fri: 01/21/2022 | Chap. 13 | Examples of of the use of perturbation theory | | |

**Note that we will come back to the WKB method after completing the perturbation theory examples presented in Chap. 13**

# PHY 742 -- Assignment #4

January 19, 2022

Read Chapter 12, parts C & D in **Carlson's** textbook.

1. Verify the solution and energy of the quadratic Stark effect for ground state H atom in a uniform electric field discussed in Lecture 4.

## Review of non-degenerate perturbation formalism --

**Problem to solve –** $$H|n\rangle = E_n|n\rangle$$

**For a Hamiltonian of the form** $$H = H^0 + \epsilon H^1$$

Here $H^0$ denotes a Hamiltonian whose eigenstates we know

$$H^0|n^0\rangle = E_n^0|n^0\rangle$$

$H^1$ denotes another contribution to the Hamiltonian scaled by a small number $\epsilon$

**Corresponding notation in your textbook:** $$H = H_0 + \lambda W$$

$$H\left|n\right\rangle = E_n\left|n\right\rangle$$

$$H = H^0 + \epsilon H^1$$

Assume: $\left|n\right\rangle = \left|n^0\right\rangle + \epsilon\left|n^1\right\rangle + \epsilon^2\left|n^2\right\rangle + \ldots$

$$E_n = E_n^0 + \epsilon E_n^1 + \epsilon^2 E_n^2 + \ldots$$

**First order formula --**

$$E_n^1 = \left\langle n^0 \middle| H^1 \middle| n^0 \right\rangle$$

$$\left| n^1 \right\rangle = \sum_{m \neq n} \left( \frac{\left\langle m^0 \middle| H^1 \middle| n^0 \right\rangle}{E_n^0 - E_m^0} \right) \left| m^0 \right\rangle$$

**Second order formula --**

$$E_n^2 = \left\langle n^0 \middle| H^1 \middle| n^1 \right\rangle = \sum_{m \neq n} \frac{\left\langle n^0 \middle| H^1 \middle| m^0 \right\rangle \left\langle m^0 \middle| H^1 \middle| n^0 \right\rangle}{E_n^0 - E_m^0}$$

$$\left| n^2 \right\rangle = \sum_{m \neq n} \left| m^0 \right\rangle \sum_{l \neq n} \frac{\left\langle m^0 \middle| H^1 \middle| l^0 \right\rangle \left\langle l^0 \middle| H^1 \middle| n^0 \right\rangle}{\left(E_n^0 - E_m^0\right)\left(E_n^0 - E_l^0\right)} - \sum_{m \neq n} \left| m^0 \right\rangle \frac{\left\langle m^0 \middle| H^1 \middle| n^0 \right\rangle \left\langle n^0 \middle| H^1 \middle| n^0 \right\rangle}{\left(E_n^0 - E_m^0\right)^2} - \frac{1}{2} \left| n^0 \right\rangle \sum_{m \neq n} \frac{\left| \left\langle m^0 \middle| H^1 \middle| n^0 \right\rangle \right|^2}{\left(E_n^0 - E_m^0\right)^2}$$

**Note that this approach involves a lot of computation**

**The following approach is adapted from the textbook by Schiff --**

$$H|n\rangle = E_n|n\rangle$$

$$H = H^0 + \epsilon H^1$$

Assume: $|n\rangle = |n^0\rangle + \epsilon|n^1\rangle + \epsilon^2|n^2\rangle + ...$

$$E_n = E_n^0 + \epsilon E_n^1 + \epsilon^2 E_n^2 + ...$$

where $H^0|n^0\rangle = E_n^0|n^0\rangle$ is presumed to be known

First order solution:

$$\left(H^0 - E_n^0\right)|n^1\rangle = -\left(H^1 - E_n^1\right)|n^0\rangle \qquad \text{where } E_n^1 = \langle n^0|H^1|n^0\rangle$$

# First order solution:

$$\left(H^0 - E_n^0\right)\left|n^1\right\rangle = -\left(H^1 - E_n^1\right)\left|n^0\right\rangle \qquad \text{where } E_n^1 = \left\langle n^0\right|H^1\left|n^0\right\rangle$$

**➔In some cases, this inhomogeneous differential equation can be solved directly. Note that the equation has a singularity and it is essential to enforce the condition**

$$\left\langle n^0 \middle| n^1\right\rangle = 0$$

**Do you think that this is a good idea?**

1. **Yes**
2. **No**
3. **Yes, if someone else does the hard work….**

**Example – hydrogen atom in its ground state perturbed by a uniform electric field (note that this is the quadratic Stark effect we mentioned last time)**

$$H^0 = -\frac{\hbar^2}{2\mu}\nabla^2 - \frac{k_e e^2}{r} \qquad \left|n^0\right\rangle \equiv \left|(100)^0\right\rangle = \frac{e^{-r/a_0}}{\sqrt{\pi a_0^3}} \qquad E_n^0 = -\frac{k_e e^2}{2a_0 n^2}$$

**(*nlm*)**

*Bohr radius:*

$$a_0 \equiv \frac{\hbar^2}{\mu k_e e^2}$$

$H^1 = eFr\ \cos(\theta)$ assuming the field $F$ is oriented along the z-axis

Note that in this case, $E_n^1 = \left\langle n^0 \middle| H^1 \middle| n^0 \right\rangle = 0$

**Hydrogen atom in its ground state perturbed by a uniform electric field -- continued**

Differential equation for first order solution:

$$\left(H^0 - E_n^0\right)\left|n^1\right\rangle = -\left(H^1 - E_n^1\right)\left|n^0\right\rangle \qquad \text{where } E_n^1 = \left\langle n^0\middle|H^1\middle|n^0\right\rangle$$

$$\left(-\frac{\hbar^2}{2\mu}\nabla^2 - \frac{k_e e^2}{r} + \frac{k_e e^2}{2a_0}\right)\left|n^1\right\rangle = -eFr\ \cos\theta\ \frac{e^{-r/a_0}}{\sqrt{\pi a_0^3}}$$

Assume $\left|n^1\right\rangle = f(r)\cos\theta$

Differential equation for unknown radial function $f(r)$:

$$\left(\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr} - \frac{2}{r^2} + \frac{2}{a_0 r} - \frac{1}{a_0^2}\right)f(r) = \frac{2F}{ea_0\sqrt{\pi a_0^3}}re^{-r/a_0}$$

# Hydrogen atom in its ground state perturbed by a uniform electric field -- continued

Assume $\left|n^1\right\rangle = f(r)\cos\theta$

Differential equation

$$\left(\frac{d^2}{dr^2}+\frac{2}{r}\frac{d}{dr}-\frac{2}{r^2}+\frac{2}{a_0 r}-\frac{1}{a_0^2}\right)f(r)=\frac{2F}{ea_0\sqrt{\pi a_0^3}}re^{-r/a_0}$$

It can be shown that $\left|n^1\right\rangle = -\frac{Fa_0}{e\sqrt{\pi a_0^3}}re^{-r/a_0}\left(1+\frac{r}{2a_0}\right)\cos\theta$

Second order energy -- $E_n^2 = \left\langle n^0\right|H^1\left|n^1\right\rangle = -\frac{9}{4}a_0^3F^2$

**Examine (derive) these two results for HW #4.**

## Hydrogen atom in its ground state perturbed by a uniform electric field -- continued

Note that the general energy associated with the polarization of a neutral object in an electric field $F$ is given in terms of the polarizability $\alpha$ :  $E_{\text{polarization}} = -\frac{1}{2}\alpha F^2$

$\Rightarrow$ Second order perturbation theory result for $\alpha$ for H atom: $\alpha = \frac{9}{2}a_0^3$

## Additional "tricks" for evaluating second order energy (Ref. L. Schiff, Quantum Mechanics)

$$E_n^2 = \langle n^0 | H^1 | n^1 \rangle = \sum_{m \neq n} \frac{\langle n^0 | H^1 | m^0 \rangle \langle m^0 | H^1 | n^0 \rangle}{E_n^0 - E_m^0}$$

Note, typically we are interested in perturbations to the ground state, so that $|n^0\rangle$ represents the (non-degenerate) ground state and all $\{|m^0\rangle\}$ form a complete set of functions.

Suppose that we can find an operator $G$ such that:

$$\langle m^0 | G | n^0 \rangle = \frac{\langle m^0 | H^1 | n^0 \rangle}{E_n^0 - E_m^0}$$

Then: $$E_n^2 = \sum_m \langle n^0 | H^1 | m^0 \rangle \langle m^0 | G | n^0 \rangle - \langle n^0 | H^1 | n^0 \rangle \langle n^0 | G | n^0 \rangle$$

Because of completeness of the functions, $\sum_m | m^0 \rangle \langle m^0 | = \mathbf{1}$

$$\Rightarrow E_n^2 = \langle n^0 | H^1 G | n^0 \rangle - \langle n^0 | H^1 | n^0 \rangle \langle n^0 | G | n^0 \rangle$$

How can we find $G$? Note that $\langle m^0 | [G, H^0] | n^0 \rangle = \left( E_n^0 - E_m^0 \right) \langle m^0 | G | n^0 \rangle = \langle m^0 | H^1 | n^0 \rangle$

It follows that $[G, H^0] = H^1 + (\text{constant})$ and $(\text{constant}) = -\langle n^0 | H^1 | n^0 \rangle$

Further, we can find the first order wavefunction

$| \tilde{n}^1 \rangle = \left( G - \langle n^0 | G | n^0 \rangle \right) | n^0 \rangle$ can be obtained by solving

$$\left( E_n^0 - H^0 \right) | \tilde{n}^1 \rangle = \left( H^1 - \langle n^0 | H^1 | n^0 \rangle \right) | n^0 \rangle \qquad \Rightarrow \qquad E_n^2 = \langle n^0 | H^1 | \tilde{n}^1 \rangle$$

**Generalization of second order Stark effect calculation discussed previously.**

## A few more details --

How can we find $G$? Note that $\left\langle m^0 \middle| [G, H^0] \middle| n^0 \right\rangle = \left(E_n^0 - E_m^0\right)\left\langle m^0 \middle| G \middle| n^0 \right\rangle = \left\langle m^0 \middle| H^1 \middle| n^0 \right\rangle$

It follows that $[G, H^0] = H^1 + (\text{constant})$ and $(\text{constant}) = -\left\langle n^0 \middle| H^1 \middle| n^0 \right\rangle$

Further, we can find the first order wavefunction

$\left|\tilde{n}^1\right\rangle = \left(G - \left\langle n^0 \middle| G \middle| n^0 \right\rangle\right)\left|n^0\right\rangle$ can be obtained by solving

$$\left(E_n^0 - H^0\right)\left|\tilde{n}^1\right\rangle = \left(H^1 - \left\langle n^0 \middle| H^1 \middle| n^0 \right\rangle\right)\left|n^0\right\rangle \quad \Rightarrow \quad E_n^2 = \left\langle n^0 \middle| H^1 \middle| \tilde{n}^1 \right\rangle$$

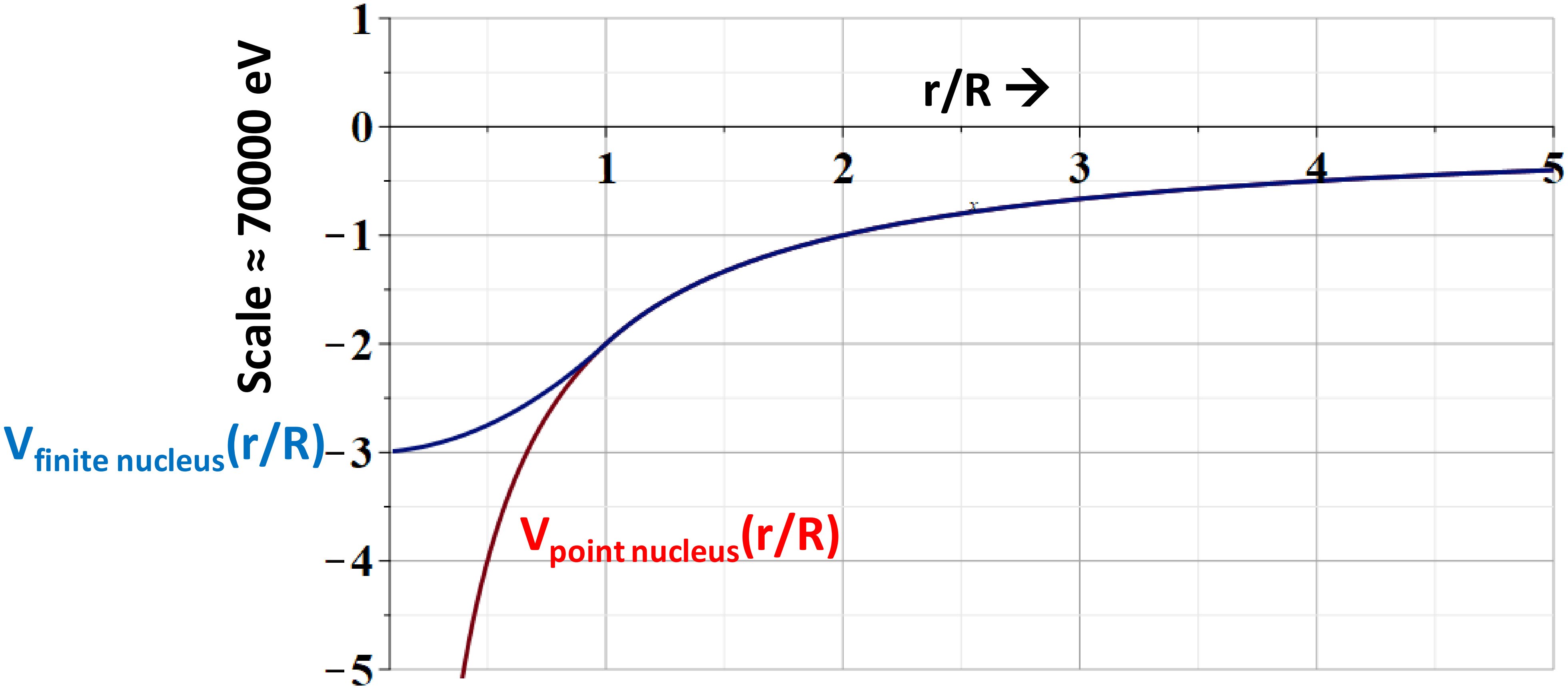
**Note that we need to solve for the unknown first order wavefunction** $\left|\tilde{n}^1\right\rangle$ **analytically or numerically.**

## More examples of perturbation theory estimates from Chap. 13 of your textbook

**Finite size of the nucleus**

Bohr radius $a_0 = 0.529 \times 10^{-10}$ m

Nuclear radius $R \approx 10^{-15}$ m



# Finite nucleus model used in textbook

A. Finite Nuclear Size

The nucleus is not in fact an infinitesimal object, but instead an object of finite radius $a$. We will treat the nucleus as a uniformly charged sphere of total charge $Ze$. The total charge inside a sphere of radius $r$ will therefore be

$$q(r) = \begin{cases} Ze & r > a, \\ Zer^3/a^3 & r < a. \end{cases}$$

Gauss's Law can then be used to find the electric field everywhere

$$\mathrm{E}(r) = \begin{cases} k_e Ze/r^2 & r > a, \\ k_e Zer/a^3 & r < a. \end{cases}$$

The potential energy is the negative of the integral of the force on the particle used to bring it in from infinity:

$$V(r) = -\int_\infty^r \left[-e\mathrm{E}(r')\right] dr' = \begin{cases} -k_e Ze^2/r & r > a\,, \\ k_e Ze^2\left(\dfrac{r^2}{2a^3} - \dfrac{3}{2a}\right) & r < a\,. \end{cases} \qquad (13.3)$$

**More convenient notation –**

**Bohr radius** $a_0 = 0.529 \times 10^{-10}$ m

**Nuclear radius** $R \approx 10^{-15}$ m

$$V_{\text{finite nucleus}}(r) = -\frac{k_e e^2}{2a_0}\frac{a_0}{R}\begin{cases}\left(3-\left(\frac{r}{R}\right)^2\right) & 0 \le r < R \\ \frac{2}{r/R} & r > R\end{cases}$$

Perturbation for $0 \le r \le R$:

$$H^1(r) = -\frac{k_e e^2}{2a_0}\frac{a_0}{R}\left(3-\left(\frac{r}{R}\right)^2 - \frac{2R}{r}\right)$$

**Correction for ground state of H atom --** $\left|n^0\right\rangle \equiv \left|(100)^0\right\rangle = \frac{e^{-r/a_0}}{\sqrt{\pi a_0^3}} \qquad E_1^0 = -\frac{k_e e^2}{2a_0}$

Perturbation for $0 \le r \le R$:

$$H^1(r) = -\frac{k_e e^2}{2a_0}\frac{a_0}{R}\left(3 - \left(\frac{r}{R}\right)^2 - \frac{2R}{r}\right)$$

First order: $E_1^1 = \left\langle (100)^0 \middle| H^1 \middle| (100)^0 \right\rangle$

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

$$\approx \frac{k_e e^2}{2a_0}\left(\frac{R}{a_0}\right)^2\frac{8}{10} \approx 13.6\ \text{eV} \times \left(3\times 10^{-10}\right)$$

**More significant corrections for larger Z.**