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 –

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

For a Hamiltonian of the form

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

Here H^0 denotes a Hamiltonian whose eigenstates we know

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

H^1 denotes another contribution to the Hamiltonian scaled by a small number ϵ

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

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

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 --

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

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

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

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

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

First order solution:

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

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)

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

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

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

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 α: $E_{\text{polarization}} = -\frac{1}{2}\alpha F^2$

$\Rightarrow$ Approximate value of α 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:

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

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

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

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

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

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

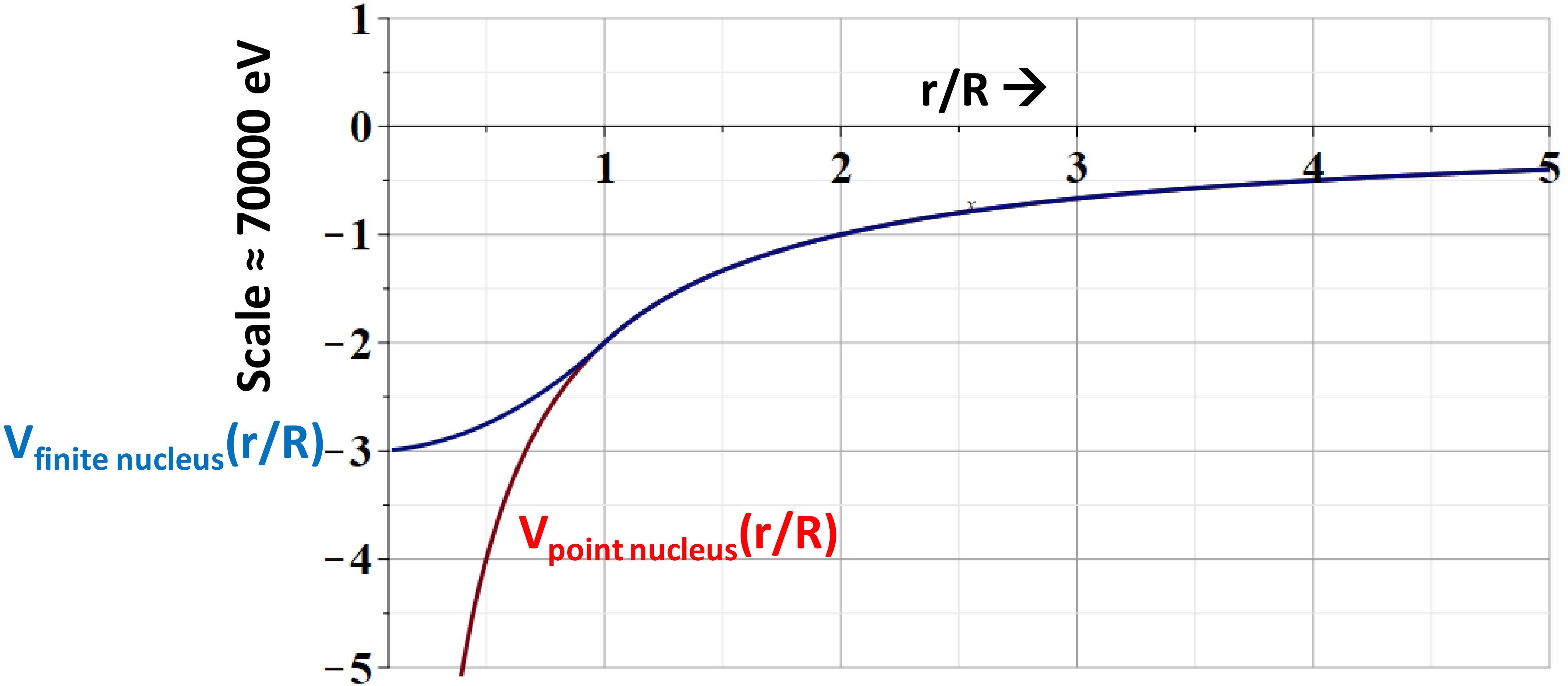
Generalization of second order Stark effect calculation discussed previously.

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:

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

More convenient notation –

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

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

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

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 -- $\left|n^0\right\rangle \equiv \left|(100)^0\right\rangle = \frac{e^{-r/a_0}}{\sqrt{\pi a_0^3}}$ $\quad E_1^0 = -\frac{k_e e^2}{2a_0}$

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.