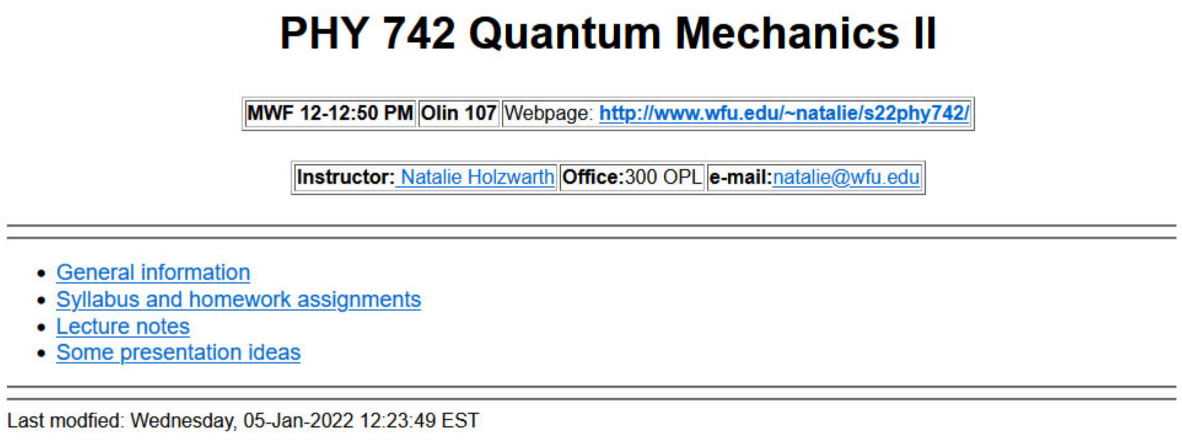
PHY 742 Quantum Mechanics II
12-12:50 PM MWF Olin 107

Plan for Lecture 1

1. Structure of the course
2. Review of main concepts from Quantum Mechanics I
3. Preview of topics for Quantum Mechanics II
4. Topic for today – Approximations for stationary quantum systems

   Reading: Chapter 12 in Carlson's textbook

https://users.wfu.edu/natalie/s22phy742/



PHY 742 Quantum Mechanics II

MWF 12-12:50 PM	**Olin 107**	Webpage: **http://www.wfu.edu/~natalie/s22phy742/**

Instructor: Natalie Holzwarth	**Office:**300 OPL	**e-mail:**natalie@wfu.edu

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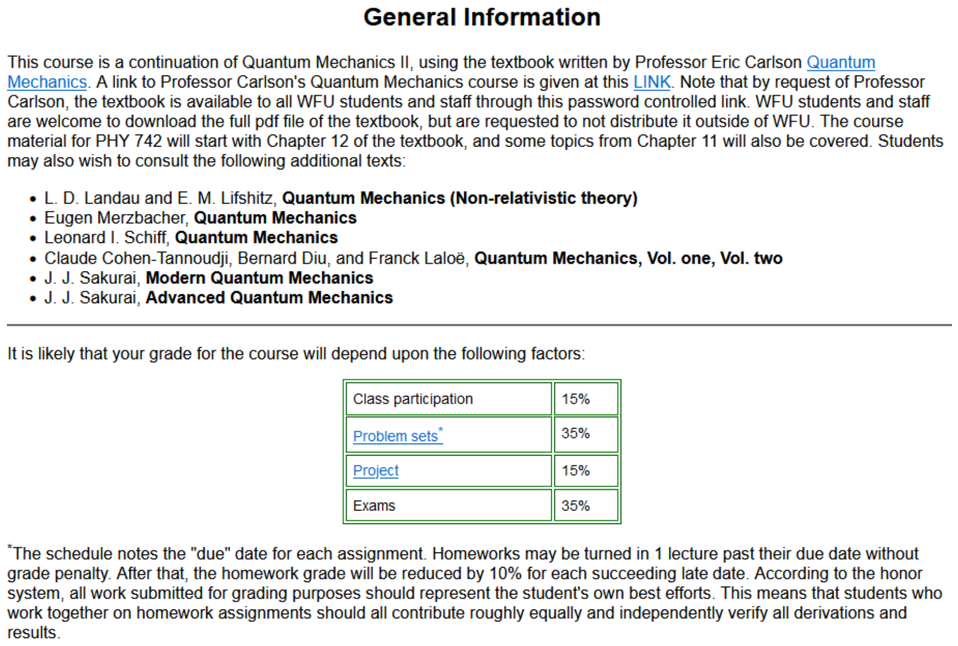
- General information
- Syllabus and homework assignments
- Lecture notes
- Some presentation ideas

Last modfied: Wednesday, 05-Jan-2022 12:23:49 EST



General Information

This course is a continuation of Quantum Mechanics II, using the textbook written by Professor Eric Carlson Quantum Mechanics. A link to Professor Carlson's Quantum Mechanics course is given at this LINK. Note that by request of Professor Carlson, the textbook is available to all WFU students and staff through this password controlled link. WFU students and staff are welcome to download the full pdf file of the textbook, but are requested to not distribute it outside of WFU. The course material for PHY 742 will start with Chapter 12 of the textbook, and some topics from Chapter 11 will also be covered. Students may also wish to consult the following additional texts:

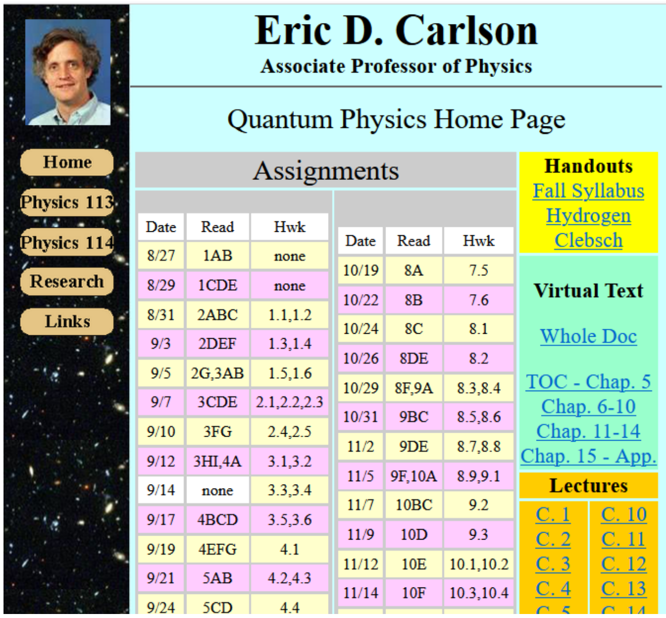
- L. D. Landau and E. M. Lifshitz, **Quantum Mechanics (Non-relativistic theory)**
- Eugen Merzbacher, **Quantum Mechanics**
- Leonard I. Schiff, **Quantum Mechanics**
- Claude Cohen-Tannoudji, Bernard Diu, and Franck Laloë, **Quantum Mechanics, Vol. one, Vol. two**
- J. J. Sakurai, **Modern Quantum Mechanics**
- J. J. Sakurai, **Advanced Quantum Mechanics**

It is likely that your grade for the course will depend upon the following factors:

Class participation	15%
Problem sets*	35%
Project	15%
Exams	35%

*The schedule notes the "due" date for each assignment. Homeworks may be turned in 1 lecture past their due date without grade penalty. After that, the homework grade will be reduced by 10% for each succeeding late date. According to the honor system, all work submitted for grading purposes should represent the student's own best efforts. This means that students who work together on homework assignments should all contribute roughly equally and independently verify all derivations and results.

https://users.wfu.edu/ecarlson/quantum/index1.html



Eric D. Carlson

Associate Professor of Physics

Quantum Physics Home Page

Assignments

Date	Read	Hwk
8/27	1AB	none
8/29	1CDE	none
8/31	2ABC	1.1,1.2
9/3	2DEF	1.3,1.4
9/5	2G,3AB	1.5,1.6
9/7	3CDE	2.1,2.2,2.3
9/10	3FG	2.4,2.5
9/12	3HI,4A	3.1,3.2
9/14	none	3.3,3.4
9/17	4BCD	3.5,3.6
9/19	4EFG	4.1
9/21	5AB	4.2,4.3
9/24	5CD	4.4

Date	Read	Hwk
10/19	8A	7.5
10/22	8B	7.6
10/24	8C	8.1
10/26	8DE	8.2
10/29	8F,9A	8.3,8.4
10/31	9BC	8.5,8.6
11/2	9DE	8.7,8.8
11/5	9F,10A	8.9,9.1
11/7	10BC	9.2
11/9	10D	9.3
11/12	10E	10.1,10.2
11/14	10F	10.3,10.4

Handouts

Fall Syllabus
Hydrogen
Clebsch

Virtual Text

Whole Doc

TOC - Chap. 5
Chap. 6-10
Chap. 11-14
Chap. 15 - App.

Lectures

C. 1	C. 10
C. 2	C. 11
C. 3	C. 12
C. 4	C. 13

Today, we will start with XII A, followed with C and D and then B.

Tentative additional information –

Mon Jan 17 – MLK Holiday
Spring break March 5-13
Mid term grades due March 7
APS March meeting March 14-18 (no class)
Fri April 15 – Good Friday Holiday
Thurs Apr 21 – Student wellness day (no class)
Wed Apr 27 – Last day of class
Apr 29-May 6 – Final exams

Particular for QM II:

1. **Where/how to share supplemental texts?**
2. **Presentations -- how to interface with PHY 712?**

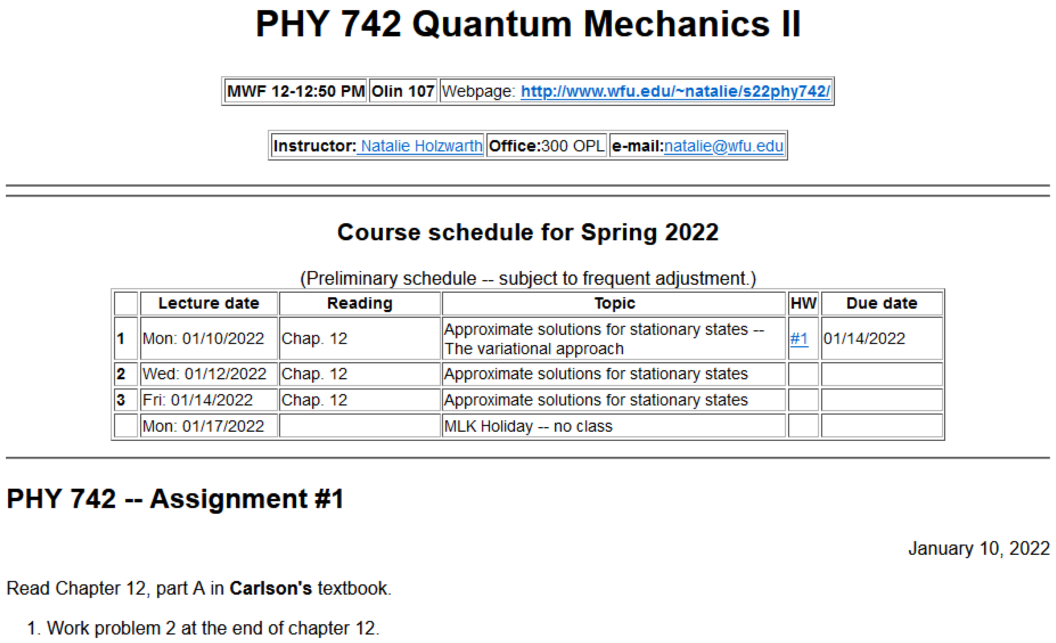
Summary of topics covered in Quantum Mechanics I

Topic	Chapters in EC Text
Fundamentals and formalism of QM	**1,3,4,11**
Solution of S. E. for simple 1-dim potentials	**2**
Quantum mechanics of harmonic oscillator	**5**
Various symmetries	**6**
Angular momentum	**7**
Addition and rotation of angular momentum including spin	**8**
Hydrogen atom	**7**
Electromagnetic forces	**9**
Multiple independent particles	**10**

Topics for Quantum Mechanics II

Single particle analysis
- Time independent perturbation methods – EC Chap. 12, 13
- Scattering of a particle from a spherical potential – EC Chap. 14
- Single electron states of a multi-well potential ➔ molecules and solids – EC Chap. 2,6
- Feynman path integral formalism – EC Chap. 11 C
- Time dependent perturbation methods – EC Chap. 15
- Relativistic effects and the Dirac Equation – EC Chap. 16

Multiple particle analysis
- Quantization of the electromagnetic fields – EC Chap. 17
- Photons and atoms – EC Chap. 18
- Multi particle systems; Bose and Fermi particles – review EC Chap. 10
- Multi electron atoms and materials
  - Hartree-Fock approximation
  - Density functional approximation



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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	Approximate solutions for stationary states		
3	Fri: 01/14/2022	Chap. 12	Approximate solutions for stationary states		
	Mon: 01/17/2022		MLK Holiday -- no class		

PHY 742 -- Assignment #1

January 10, 2022

Read Chapter 12, part A in **Carlson's** textbook.

1. Work problem 2 at the end of chapter 12.

Your questions –
From Owen -- What are the benefits and disadvantages of the various approximation methods?

Comment – This is a very important question to ask. In general –

- Variational methods – Very powerful for finding the lowest eigenstate of a system
- Perturbation theory – Works well when you write the Hamiltonian as $H = H_{large} + H_{small}$ and you can find a full set of solutions for H_{large}
- WKB – Historically important and also useful for tunneling situations for example

Variational methods for estimating the lowest energy eigenstate of a quantum mechanical system

Time independent Schrödinger equation:

$$H(\mathbf{r})\Psi(\mathbf{r}) = E\Psi(\mathbf{r})$$

Energy eigenvalue

Hermitian operator representing the Hamiltonian of the system

Consider a Hamiltonian H having lowest eigenvalue E_0 :

It can be shown that for any function ψ

$$\frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle} \geq E_0$$

Proof: The Hamiltonian has a complete set of eigenvalues and eigenvectors: $H|\varphi_i\rangle = E_i|\varphi_i\rangle$

Expanding $|\psi\rangle$ in eigenvector basis: $|\psi\rangle = \sum_i C_i|\varphi_i\rangle$

$$\frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle} = \frac{\sum_i |C_i|^2 E_i}{\sum_i |C_i|^2} \geq E_0$$

Significance of this inequality --

$$\frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle} \geq E_0$$

The inequality motivates a class of estimation methods known as variational methods to converge to the ground state energy E_0 and the corresponding ground state probability amplitude.

$$\text{Define} \quad E_{trial}(\Psi_{trial}) \equiv \frac{\langle\psi_{trial}|H|\psi_{trial}\rangle}{\langle\psi_{trial}|\psi_{trial}\rangle}$$

$$\text{Minimize} \; E_{trial}(\Psi_{trial}) \text{ with respect to } \Psi_{trial}$$

Variational method for estimating ground state energy of a H atom:

Define $f(\psi) \equiv \frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle}$ $\quad\quad$ $\min_\psi f(\psi) \geq E_0$

Example: $H(\mathbf{r}) = -\frac{\hbar^2}{2\mu}\nabla_r^2 - \frac{Ze^2}{r}$

Try: $|\psi\rangle = e^{-\alpha r}$

$$f(\psi) = \frac{\hbar^2}{2\mu}\alpha^2 - Ze^2\alpha$$

$$\frac{df}{d\alpha} = 0 \quad\quad \Rightarrow \alpha = \frac{Ze^2\mu}{\hbar^2} = \frac{Z}{a_0}$$

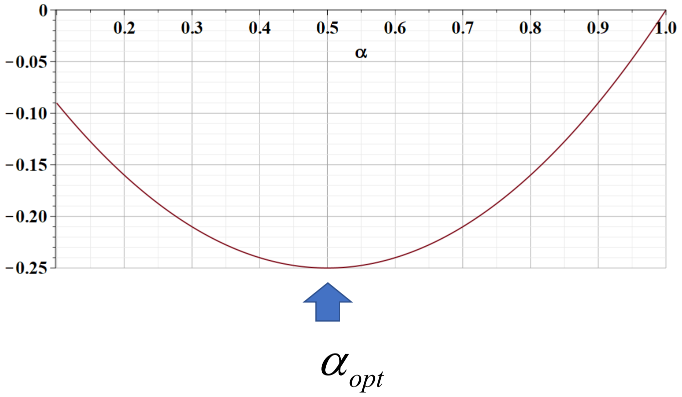
$$\Rightarrow \min_\psi f(\psi) = -\frac{Z^2e^2}{2a_0}$$

Example: $H(\mathbf{r}) = -\frac{\hbar^2}{2\mu}\nabla_r^2 - \frac{Ze^2}{r}$

Try: $|\psi\rangle = e^{-\alpha r}$

$$f(\psi) = \frac{\hbar^2}{2\mu}\alpha^2 - Ze^2\alpha$$

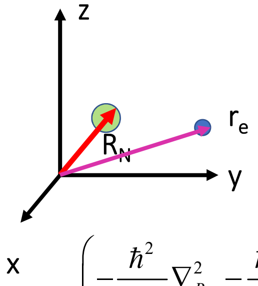
$$\left.\frac{df}{d\alpha}\right|_{\alpha_{opt}} = 0 \qquad \Rightarrow \alpha_{opt} = \frac{Ze^2\mu}{\hbar^2} = \frac{Z}{a_0}$$



$$\Rightarrow \min_\psi f(\psi) = -\frac{Z^2e^2}{2a_0}$$

What is the significance of this result?

Review -- Quantum mechanics of the hydrogen atom



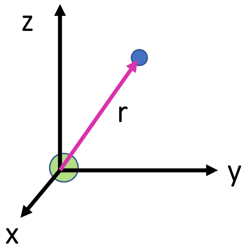
$$\left(-\frac{\hbar^2}{2M}\nabla^2_{R_N} - \frac{\hbar^2}{2m}\nabla^2_{r_e} - \frac{Ze^2}{|\mathbf{r}_e - \mathbf{R}_N|}\right)\Psi(\mathbf{R}_N,\mathbf{r}_e) = E_T\Psi(\mathbf{R}_N,\mathbf{r}_e)$$

In center of mass system:

$$\mathbf{R} = \frac{M\mathbf{R}_N + m\mathbf{r}_e}{M+m} \qquad \mathbf{r} = \mathbf{r}_e - \mathbf{R}_N \qquad \mu = \frac{mM}{m+M}$$

$$\left(-\frac{\hbar^2}{2(M+m)}\nabla^2_{R} - \frac{\hbar^2}{2\mu}\nabla^2_{r} - \frac{Ze^2}{r}\right)\Psi(\mathbf{R},\mathbf{r}) = E_T\Psi(\mathbf{R},\mathbf{r})$$

Quantum mechanics of the hydrogen atom



In center of mass coordinates

Reduced mass: $\mu = \frac{mM}{m+M}$

typically $\frac{m}{M} < \frac{1}{2000}$

$$\left(-\frac{\hbar^2}{2\mu}\nabla_r^2 - \frac{Ze^2}{r}\right)\psi(\mathbf{r}) = E\psi(\mathbf{r})$$

$$\psi(\mathbf{r}) = R_{El}(r)Y_{lm}\left(\hat{\mathbf{r}}\right)$$

Differential equation for radial wavefunction:

$$\left(-\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{d}{dr}r^2\frac{d}{dr}-\frac{l(l+1)}{r^2}\right]-\frac{Ze^2}{r}\right)R_{El}(r)=ER_{El}(r)$$

Convenient coordinate change

$$\rho\equiv\frac{\sqrt{8\mu|E|}}{\hbar}r \qquad \text{let } \lambda=\frac{Ze^2}{\hbar}\sqrt{\frac{\mu}{2|E|}}$$

$$\left(\frac{1}{\rho^2}\frac{d}{d\rho}\rho^2\frac{d}{d\rho}-\frac{l(l+1)}{\rho^2}+\frac{\lambda}{\rho}-\frac{1}{4}\right)R_{El}(\rho)=0$$

For bound states, $E=-\varepsilon$ where $\varepsilon>0$.

Try solution of the form: $R(\rho)=e^{-\rho/2}F(\rho)$

$$\left(\frac{1}{\rho^2}\frac{d}{d\rho}\rho^2\frac{d}{d\rho}-\frac{l(l+1)}{\rho^2}+\frac{\lambda}{\rho}-\frac{1}{4}\right)R_{El}(\rho)=0$$

For bound states, $E=-\varepsilon$ where $\varepsilon>0$.

Try solution of the form: $R(\rho)=e^{-\rho/2}F(\rho)$

$$\frac{d^2F}{d\rho^2}+\left(\frac{2}{\rho}-1\right)\frac{dF}{d\rho}+\left(\frac{\lambda-1}{\rho}-\frac{l(l+1)}{\rho^2}\right)F(\rho)=0$$

Let $F(\rho)=\rho^l L(\rho)$

$$\rho\frac{d^2L}{d\rho^2}+\left(2(l+1)-\rho\right)\frac{dL}{d\rho}+(\lambda-l-1)L=0$$

$$\rho\frac{d^2L}{d\rho^2}+\big(2(l+1)-\rho\big)\frac{dL}{d\rho}+(\lambda-l-1)L=0$$

Suppose $\lambda-l-1=n'$ where $n'\geq 0$

$$\rho\frac{d^2L}{d\rho^2}+\big(2(l+1)-\rho\big)\frac{dL}{d\rho}+n'L=0$$

Associated Laguerre polynomial $L_q^p(x)$:

$$x\frac{d^2L_q^p}{dx^2}+\big(p+1-x\big)\frac{dL_q^p}{dx}+\big(q-p\big)L_q^p=0$$

For non-negative integers q and p.

$$R(\rho) = \rho^l e^{-\rho/2} L^{2l+1}_{n'+2l+1}(\rho)$$

Let $n \equiv n' + l + 1 = \lambda$

$$R(\rho) = \rho^l e^{-\rho/2} L^{2l+1}_{n+l}(\rho)$$

Corresponding energy eigenvalue:

$$\lambda = \frac{Ze^2}{\hbar}\sqrt{\frac{\mu}{2|E|}} = n$$

$$\Rightarrow E = -\frac{Z^2 e^4 \mu}{2\hbar^2}\frac{1}{n^2} \equiv -\frac{Z^2 e^2}{2a_0}\frac{1}{n^2}$$

$$\rho = \frac{2Z}{na_0} r$$

Defining $a_0 \equiv \dfrac{\hbar^2}{\mu e^2}$

Bohr radius:

$a_0 \equiv \dfrac{\hbar^2}{me^2}$=0.529 177 210 67 x 10^{-10}m

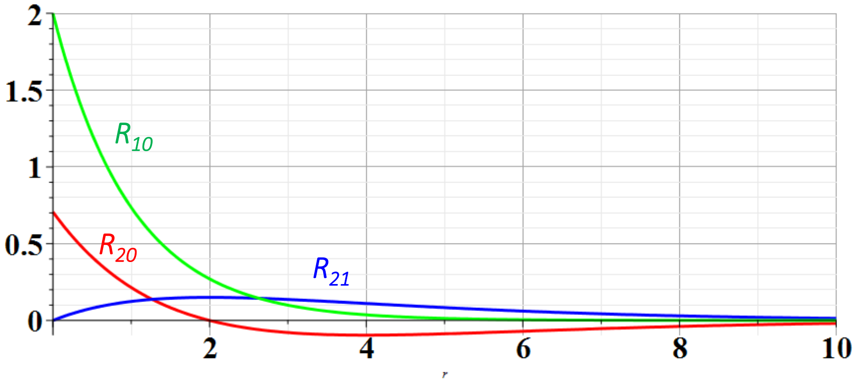
Example of normalized radial functions $R_{nl}(r)$:

$$R_{10}(r) = \left(\frac{Z}{a_0}\right)^{3/2} 2e^{-Zr/a_0}$$

$$R_{20}(r) = \left(\frac{Z}{2a_0}\right)^{3/2} \left(2 - \frac{Zr}{a_0}\right) e^{-Zr/(2a_0)}$$

$$R_{21}(r) = \left(\frac{Z}{2a_0}\right)^{3/2} \frac{Zr}{\sqrt{3}a_0} e^{-Zr/(2a_0)}$$

Hydrogen radial wavefunctions



Note that for the variational method, if we are so lucky as to use the correct shape function for our trial, we find the exact solution – in this case for the ground state of a hydrogen atom when we used an exponential form.

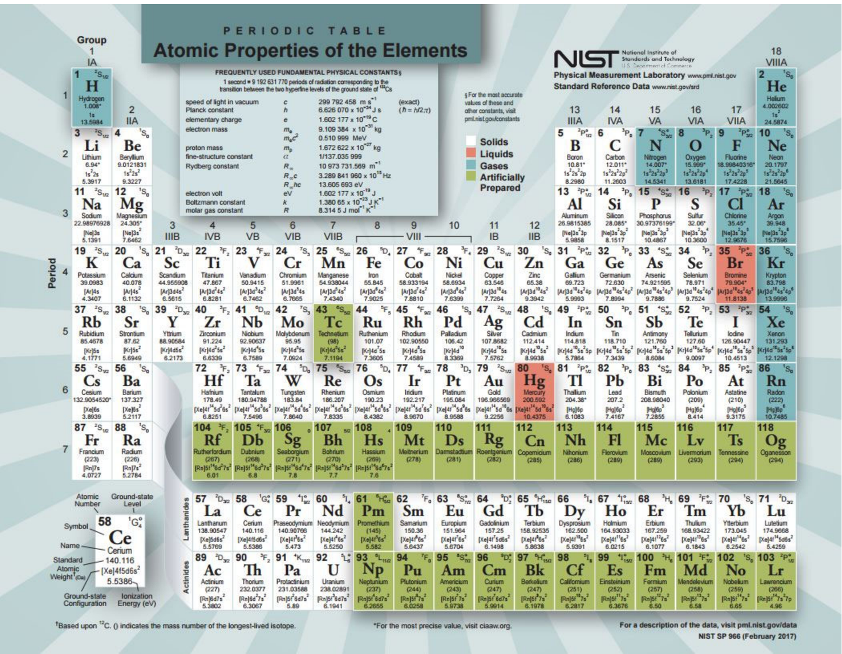
On the other hand, the variational method is still quite powerful even if we do not use the correct shape function for our trial. This is illustrated in the following example when we use a Gaussian shape function.

Variational methods for estimating ground state energy
-- continued

Example: $H(\mathbf{r}) = -\frac{\hbar^2}{2\mu}\nabla_r^2 - \frac{Ze^2}{r}$

Try: $|\psi\rangle = e^{-\alpha r^2}$

Note that this is your homework problem.



PERIODIC TABLE

Atomic Properties of the Elements

NIST National Institute of Standards and Technology U.S. Department of Commerce
Physical Measurement Laboratory www.pml.nist.gov
Standard Reference Data www.nist.gov/srd

FREQUENTLY USED FUNDAMENTAL PHYSICAL CONSTANTS§

1 second = 9 192 631 770 periods of radiation corresponding to the transition between the two hyperfine levels of the ground state of ^{133}Cs

speed of light in vacuum	c	299 792 458 m s^{-1}	(exact)
Planck constant	h	$6.626\,070 \times 10^{-34}$ J s	($\hbar = h/2\pi$)
elementary charge	e	$1.602\,177 \times 10^{-19}$ C	
electron mass	m_e	$9.109\,384 \times 10^{-31}$ kg	
	m_ec^2	0.510 999 MeV	
proton mass	m_p	$1.672\,622 \times 10^{-27}$ kg	
fine-structure constant	α	1/137.035 999	
Rydberg constant	R_∞	10 973 731.569 m^{-1}	
	$R_\infty c$	$3.289\,841\,960 \times 10^{15}$ Hz	
	$R_\infty hc$	13.605 693 eV	
electron volt	eV	$1.602\,177 \times 10^{-19}$ J	
Boltzmann constant	k	$1.380\,65 \times 10^{-23}$ J K^{-1}	
molar gas constant	R	8.314 5 J mol^{-1} K^{-1}	

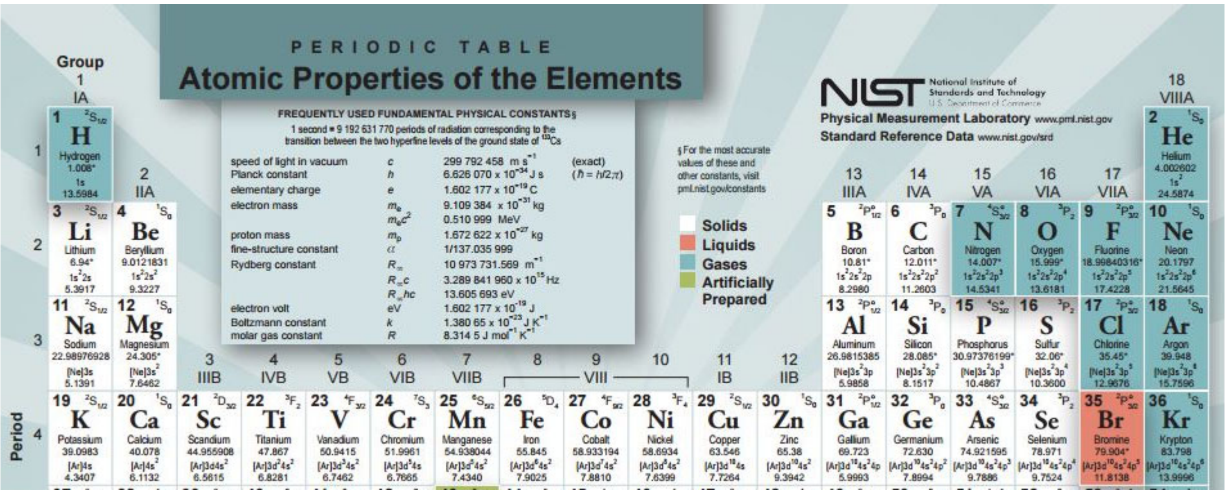
§ For the most accurate values of these and other constants, visit pml.nist.gov/constants

- ☐ Solids
- 🟥 Liquids
- 🟦 Gases
- 🟩 Artificially Prepared

†Based upon ^{12}C. () indicates the mass number of the longest-lived isotope.

*For the most precise value, visit ciaaw.org.

For a description of the data, visit pml.nist.gov/data
NIST SP 966 (February 2017)



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speed of light in vacuum	c	299 792 458 m s^{-1}	(exact)
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elementary charge	e	1.602 177 x 10^{-19} C	
electron mass	m_e	9.109 384 x 10^{-31} kg	
	m_ec^2	0.510 999 MeV	
proton mass	m_p	1.672 622 x 10^{-27} kg	
fine-structure constant	α	1/137.035 999	
Rydberg constant	R_∞	10 973 731.569 m^{-1}	
	$R_\infty c$	3.289 841 960 x 10^{15} Hz	
	$R_\infty hc$	13.605 693 eV	
electron volt	eV	1.602 177 x 10^{-19} J	
Boltzmann constant	k	1.380 65 x 10^{-23} J K^{-1}	
molar gas constant	R	8.314 5 J mol^{-1} K^{-1}	

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⬜ **Solids**
🟥 **Liquids**
🟦 **Gases**
🟩 **Artificially Prepared**

NIST National Institute of Standards and Technology U.S. Department of Commerce
Physical Measurement Laboratory www.pml.nist.gov
Standard Reference Data www.nist.gov/srd

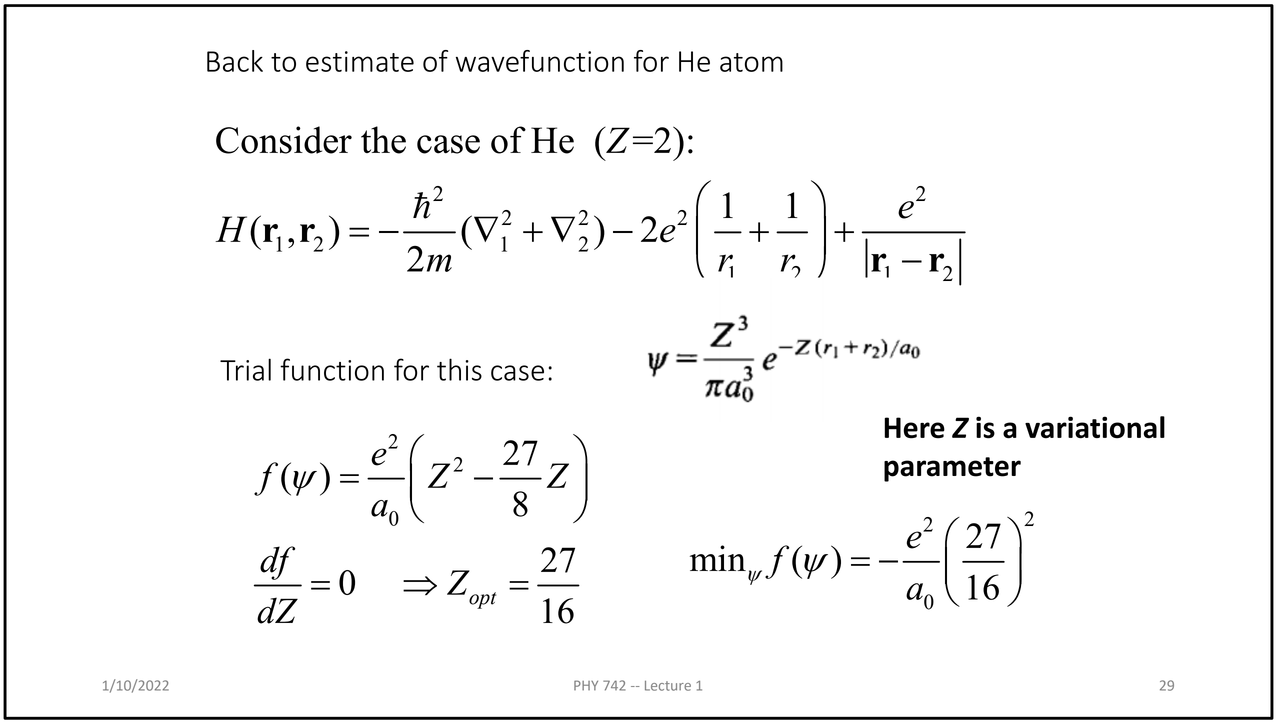
Period	Group 1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8 VIII	9 VIII	10 VIII	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1	1 $^2S_{1/2}$ **H** Hydrogen 1.008* 1s 13.5984																	2 $^1S_0$ **He** Helium 4.002602 $1s^2$ 24.5874
2	3 $^2S_{1/2}$ **Li** Lithium 6.94* $1s^22s$ 5.3917	4 $^1S_0$ **Be** Beryllium 9.0121831 $1s^22s^2$ 9.3227											5 $^2P^\circ_{1/2}$ **B** Boron 10.81* $1s^22s^22p$ 8.2980	6 $^3P_0$ **C** Carbon 12.011* $1s^22s^22p^2$ 11.2603	7 $^4S^\circ_{3/2}$ **N** Nitrogen 14.007* $1s^22s^22p^3$ 14.5341	8 $^3P_2$ **O** Oxygen 15.999* $1s^22s^22p^4$ 13.6181	9 $^2P^\circ_{3/2}$ **F** Fluorine 18.99840316* $1s^22s^22p^5$ 17.4228	10 $^1S_0$ **Ne** Neon 20.1797 $1s^22s^22p^6$ 21.5645
3	11 $^2S_{1/2}$ **Na** Sodium 22.98976928 [Ne]3s 5.1391	12 $^1S_0$ **Mg** Magnesium 24.305* [Ne]$3s^2$ 7.6462											13 $^2P^\circ_{1/2}$ **Al** Aluminum 26.9815385 [Ne]$3s^23p$ 5.9858	14 $^3P_0$ **Si** Silicon 28.085* [Ne]$3s^23p^2$ 8.1517	15 $^4S^\circ_{3/2}$ **P** Phosphorus 30.97376199* [Ne]$3s^23p^3$ 10.4867	16 $^3P_2$ **S** Sulfur 32.06* [Ne]$3s^23p^4$ 10.3600	17 $^2P^\circ_{3/2}$ **Cl** Chlorine 35.45* [Ne]$3s^23p^5$ 12.9676	18 $^1S_0$ **Ar** Argon 39.948 [Ne]$3s^23p^6$ 15.7596
4	19 $^2S_{1/2}$ **K** Potassium 39.0983 [Ar]4s 4.3407	20 $^1S_0$ **Ca** Calcium 40.078 [Ar]$4s^2$ 6.1132	21 $^2D_{3/2}$ **Sc** Scandium 44.955908 [Ar]$3d4s^2$ 6.5615	22 $^3F_2$ **Ti** Titanium 47.867 [Ar]$3d^24s^2$ 6.8281	23 $^4F_{3/2}$ **V** Vanadium 50.9415 [Ar]$3d^34s^2$ 6.7462	24 $^7S_3$ **Cr** Chromium 51.9961 [Ar]$3d^54s$ 6.7665	25 $^6S_{5/2}$ **Mn** Manganese 54.938044 [Ar]$3d^54s^2$ 7.4340	26 $^5D_4$ **Fe** Iron 55.845 [Ar]$3d^64s^2$ 7.9025	27 $^4F_{9/2}$ **Co** Cobalt 58.933194 [Ar]$3d^74s^2$ 7.8810	28 $^3F_4$ **Ni** Nickel 58.6934 [Ar]$3d^84s^2$ 7.6399	29 $^2S_{1/2}$ **Cu** Copper 63.546 [Ar]$3d^{10}4s$ 7.7264	30 $^1S_0$ **Zn** Zinc 65.38 [Ar]$3d^{10}4s^2$ 9.3942	31 $^2P^\circ_{1/2}$ **Ga** Gallium 69.723 [Ar]$3d^{10}4s^24p$ 5.9993	32 $^3P_0$ **Ge** Germanium 72.630 [Ar]$3d^{10}4s^24p^2$ 7.8994	33 $^4S^\circ_{3/2}$ **As** Arsenic 74.921595 [Ar]$3d^{10}4s^24p^3$ 9.7886	34 $^3P_2$ **Se** Selenium 78.971 [Ar]$3d^{10}4s^24p^4$ 9.7524	35 $^2P^\circ_{3/2}$ **Br** Bromine 79.904* [Ar]$3d^{10}4s^24p^5$ 11.8138	36 $^1S_0$ **Kr** Krypton 83.798 [Ar]$3d^{10}4s^24p^6$ 13.9996

Example --

Consider the case of a He (Z=2) atom:

$$H(\mathbf{r}_1,\mathbf{r}_2)=-\frac{\hbar^2}{2m}(\nabla_1^2+\nabla_2^2)-Ze^2\left(\frac{1}{r_1}+\frac{1}{r_2}\right)+\frac{e^2}{|\mathbf{r}_1-\mathbf{r}_2|}$$

Unlike the case of a H atom, this Hamiltonian cannot be solved analytically.



Back to estimate of wavefunction for He atom

Consider the case of He (Z=2):

$$H(\mathbf{r}_1,\mathbf{r}_2) = -\frac{\hbar^2}{2m}(\nabla_1^2+\nabla_2^2) - 2e^2\left(\frac{1}{r_1}+\frac{1}{r_2}\right) + \frac{e^2}{|\mathbf{r}_1-\mathbf{r}_2|}$$

Trial function for this case: $\psi = \frac{Z^3}{\pi a_0^3} e^{-Z(r_1+r_2)/a_0}$

Here *Z* is a variational parameter

$$f(\psi) = \frac{e^2}{a_0}\left(Z^2 - \frac{27}{8}Z\right)$$

$$\frac{df}{dZ} = 0 \quad \Rightarrow Z_{opt} = \frac{27}{16} \qquad \min_\psi f(\psi) = -\frac{e^2}{a_0}\left(\frac{27}{16}\right)^2$$

Some details

Example of He (Z=2) atom:

$$H(\mathbf{r}_1,\mathbf{r}_2) = -\frac{\hbar^2}{2m}(\nabla_1^2+\nabla_2^2) - 2e^2\left(\frac{1}{r_1}+\frac{1}{r_2}\right) + \frac{e^2}{|\mathbf{r}_1-\mathbf{r}_2|}$$

$\Psi(r_1,r_2) = e^{-Z(r_1+r_2)/a_0}$, where Z is a variational parameter

and $a_0 = \dfrac{\hbar^2}{me^2}$

Normalization integral:

$$\langle\Psi|\Psi\rangle = \left(4\pi\int_0^\infty dr_1\ r_1^2 e^{-2Zr_1/a_0}\right)^2 = \left(\frac{\pi a_0{}^3}{Z^3}\right)^2$$

More details $\frac{\langle\Psi|K|\Psi\rangle}{\langle\Psi|\Psi\rangle}$ for $K \equiv -\frac{\hbar^2}{2m}(\nabla_1^2+\nabla_2^2)$

Kinetic energy operator in spherical polar coordinates:

$$\int d^3r\, f(r)\nabla^2 f(r) = \int d^3r\, \nabla\cdot\left(f(r)\nabla f(r)\right) - \int d^3r\, \left|\nabla f(r)\right|^2$$

=0

For $f(r) = e^{-Zr/a_0}$:

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

$$\Rightarrow \frac{\langle\Psi|K|\Psi\rangle}{\langle\Psi|\Psi\rangle} = 2\frac{\hbar^2}{2m}\left(\frac{Z}{a_0}\right)^2 = \frac{e^2}{a_0}\left(Z^2\right)$$

More details $$\frac{\langle\Psi|N|\Psi\rangle}{\langle\Psi|\Psi\rangle} \quad \text{for} \quad N \equiv -2e^2\left(\frac{1}{r_1}+\frac{1}{r_2}\right)$$

$$\text{For } f(r) = e^{-Zr/a_0} \ :$$

$$\int d^3r \ \frac{|f(r)|^2}{r} = 4\pi\int_0^\infty dr \ r\left(f(r)\right)^2 = \pi\left(\frac{a_0^2}{Z^2}\right)$$

$$\Rightarrow \frac{\langle\Psi|N|\Psi\rangle}{\langle\Psi|\Psi\rangle} = -4e^2\frac{Z}{a_0} = -\frac{e^2}{a_0}(4Z)$$

More details $$\frac{\langle\Psi|C|\Psi\rangle}{\langle\Psi|\Psi\rangle} \quad \text{for} \quad C \equiv \frac{e^2}{|\mathbf{r}_1-\mathbf{r}_2|}$$

Useful identity:

$$\frac{1}{|\mathbf{r}-\mathbf{r}'|} = \sum_{lm} \frac{4\pi}{2l+1} \frac{r_<^{\,l}}{r_>^{\,l+1}} Y_{lm}(\theta,\varphi) Y_{lm}^{\,*}(\theta',\varphi')$$

For $f(r) = e^{-Zr/a_0}$ and $\Psi(r_1,r_2) = f(r_1)f(r_2)$

$$\langle\Psi|C|\Psi\rangle = e^2(4\pi)^2 \int_0^\infty dr_1\, r_1^2 \left(f(r_1)\right)^2 \left(\frac{1}{r_1}\int_0^{r_1} dr_2\, r_2^2 \left(f(r_2)\right)^2 + \int_{r_1}^\infty dr_2\, r_2 \left(f(r_2)\right)^2 \right)$$

$$= e^2\, 2(4\pi)^2 \int_0^\infty dr_1\, r_1 \left(f(r_1)\right)^2 \int_0^{r_1} dr_2\, r_2^2 \left(f(r_2)\right)^2 = e^2\pi^2 \frac{5}{8}\left(\frac{a_0}{Z}\right)^5$$

$$\Rightarrow \frac{\langle\Psi|C|\Psi\rangle}{\langle\Psi|\Psi\rangle} = \frac{e^2}{a_0}\left(\frac{5Z}{8}\right)$$

More details

$$\frac{\langle\Psi|K+N+C|\Psi\rangle}{\langle\Psi|\Psi\rangle}=\frac{e^2}{a_0}\left(Z^2-4Z+\frac{5}{8}Z\right)=\frac{e^2}{a_0}\left(Z^2-\frac{27}{8}Z\right)$$

Consistent with earlier slides --

Variational methods for estimating ground state energy of He atom:

Define $f(\psi) \equiv \frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle}$ $\quad\quad \min_\psi f(\psi) \geq E_0$

$$f(\psi) = \frac{e^2}{a_0}\left(Z^2 - \frac{27}{8}Z\right)$$

$$\frac{df}{dZ} = 0 \quad \Rightarrow Z_{opt} = \frac{27}{16}$$

$$\min_\psi f(\psi) = -\frac{e^2}{a_0}\left(\frac{27}{16}\right)^2$$

$$= -\frac{e^2}{2a_0}5.695$$

Experimental

value $\approx -\frac{e^2}{2a_0}5.807$