PHY 742 Quantum Mechanics II
12-12:50 AM 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

Home

Physics 113

Physics 114

Research

Links

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

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.

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

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

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

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

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

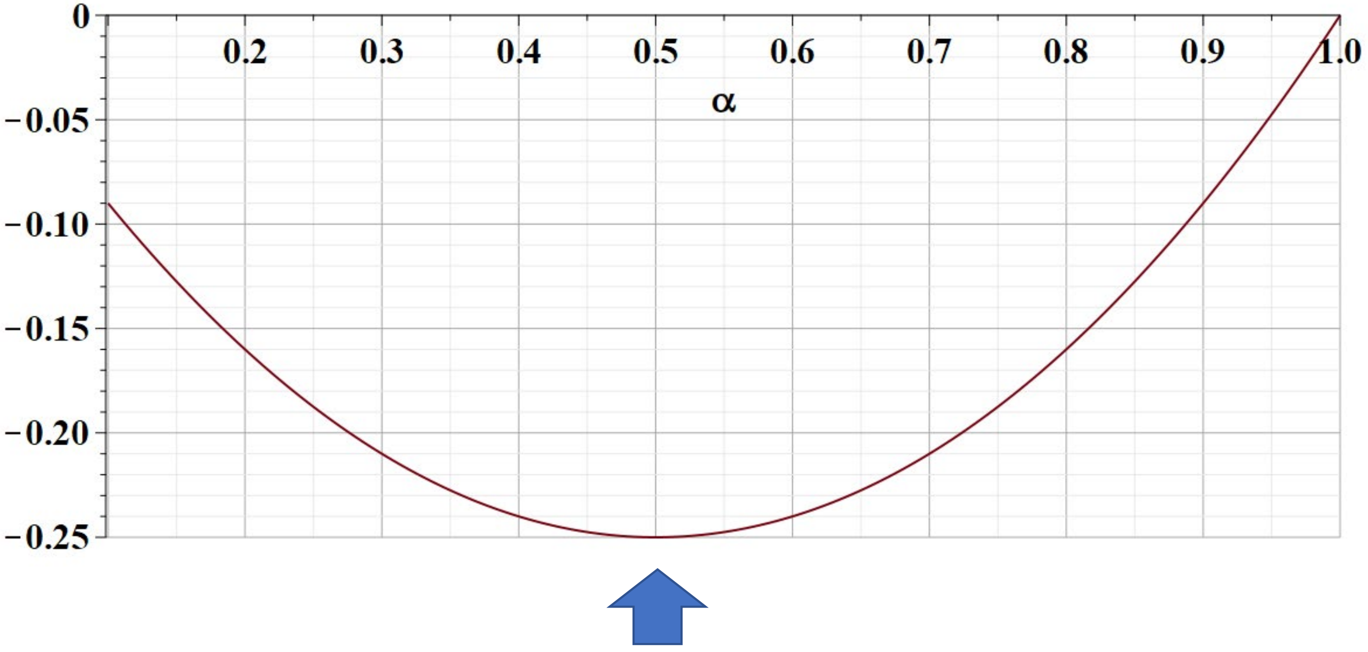
$$\Rightarrow \min_\psi f(\psi) = -\frac{Z^2e^2}{2a_0}$$

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

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

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

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

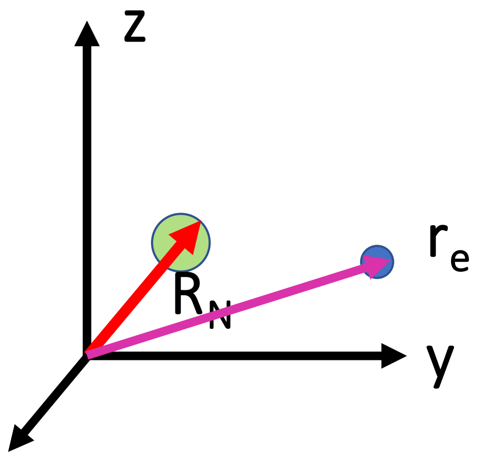


α_{opt}

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

What is the significance of this result?

Review -- Quantum mechanics of the hydrogen atom



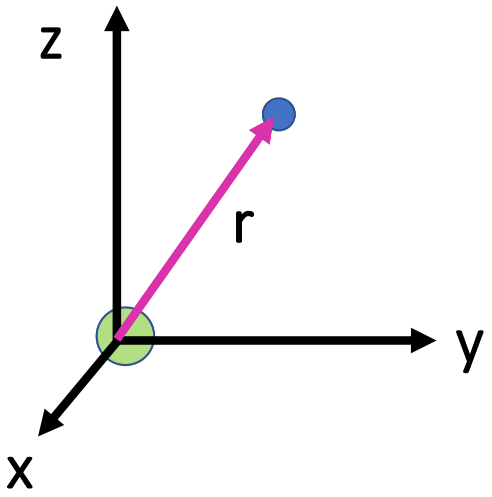
$$\left(-\frac{\hbar^2}{2M}\nabla^2_{R_N}-\frac{\hbar^2}{2m}\nabla^2_{r_e}-\frac{Ze^2}{|\mathbf{r}_e-\mathbf{R}_N|}\right)\Psi(\mathbf{R}_N,\mathbf{r}_e)=E_T\Psi(\mathbf{R}_N,\mathbf{r}_e)$$

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

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

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

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

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

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

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

For non-negative integers q and p.

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

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

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

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

Bohr radius:

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

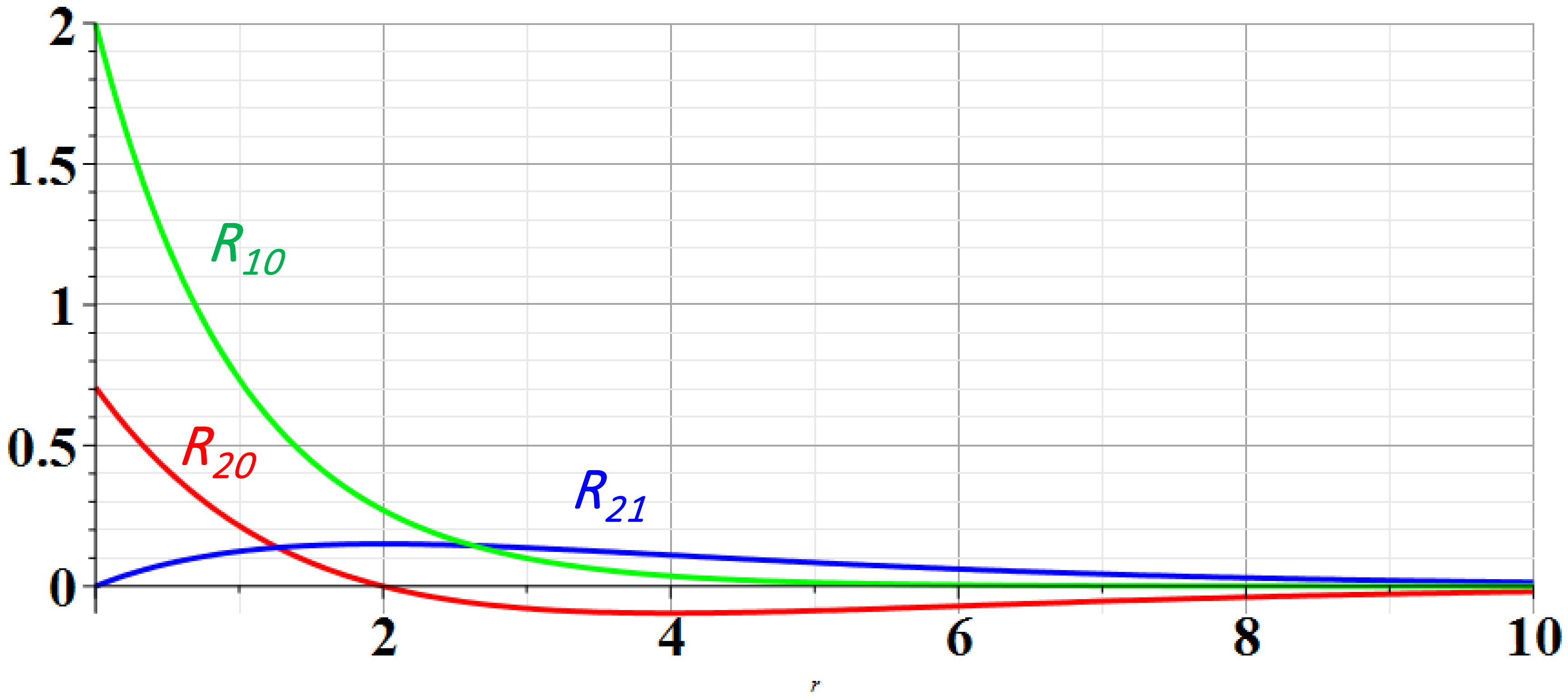
Example of normalized radial functions $R_{nl}(r)$:

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

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

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

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

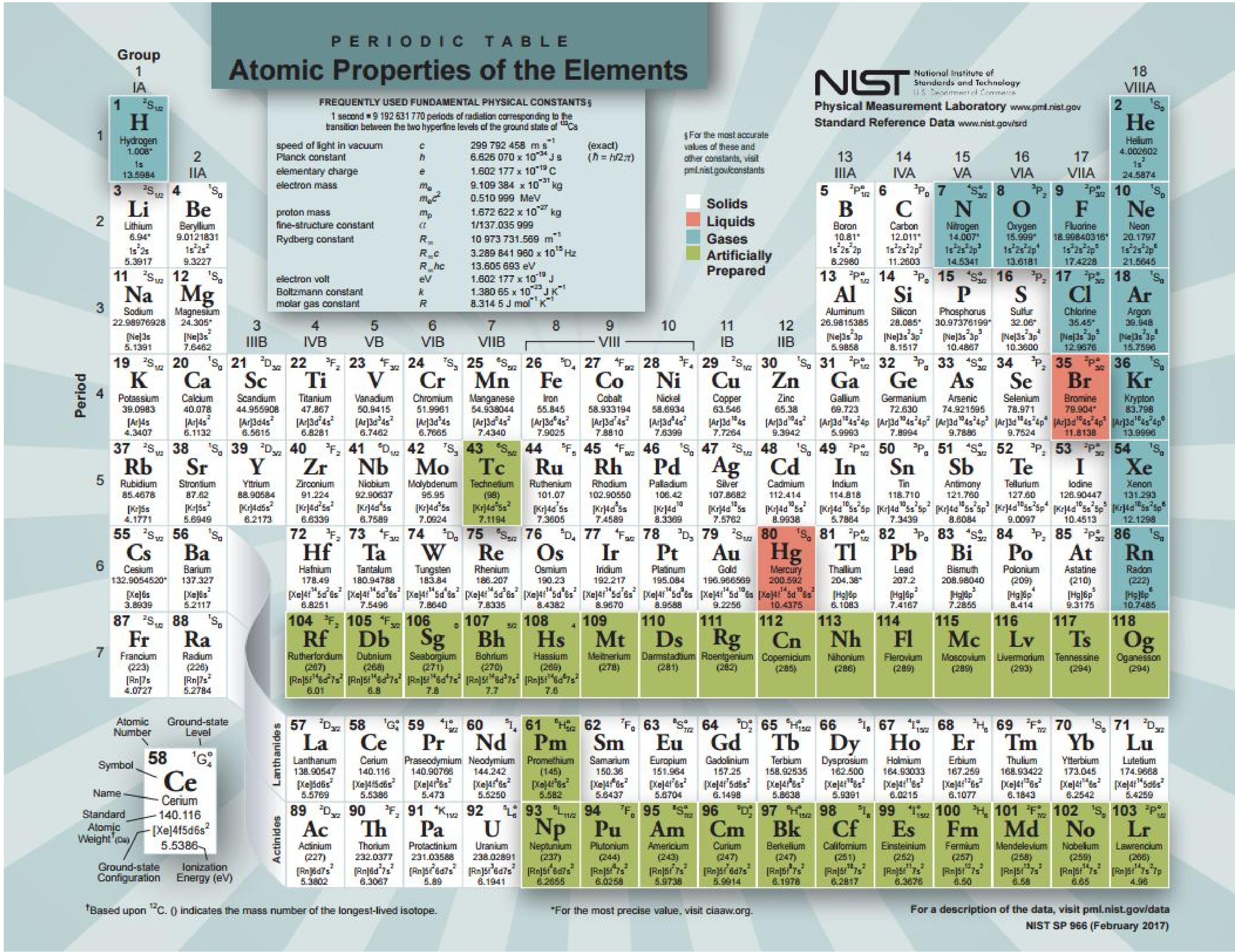
Note that this is your homework problem.

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.


PERIODIC TABLE
Atomic Properties of the Elements
FREQUENTLY USED FUNDAMENTAL PHYSICAL CONSTANTS
NIST National Institute of Standards and Technology
Physical Measurement Laboratory www.pml.nist.gov
Standard Reference Data www.nist.gov/srd
Solids
Liquids
Gases
Artificially Prepared
Lanthanides
Actinides
†Based upon ¹²C. () 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)

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

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

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

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

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

Normalization integral:

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

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

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

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

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

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

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

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

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

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

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

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

Experimental

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