PHY 742 Quantum Mechanics II
1-1:50 AM MWF Olin 103

Plan for Lecture 7

Approximation methods for analyzing quantum mechanical systems

1. **Start reading Chapter 12-13**
   a. **Variational methods**

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Topics for Quantum Mechanics II

Single particle analysis
- Single particle interacting with electromagnetic fields – EC Chap. 9
- Scattering of a particle from a spherical potential – EC Chap. 14
- More time independent perturbation methods – EC Chap. 12, 13
- Single electron states of a multi-well potential ➔ molecules and solids – EC Chap. 2,6
- Time dependent perturbation methods – EC Chap. 15
- Path integral formalism (Feynman) – EC Chap. 11.C
- 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 – EC Chap. 10
- Multi electron atoms and materials
  - Hartree-Fock approximation
  - Density functional approximation

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MWF 1-1:50 PM	OPL 103	http://www.wfu.edu/~natalie/s20phy742/

Instructor: Natalie Holzwarth	Phone:758-5510	Office:300 OPL	e-mail:natalie@wfu.edu

Course schedule for Spring 2020

(Preliminary schedule -- subject to frequent adjustment.)

	Lecture date	Reading	Topic	HW	Due date
1	Mon: 01/13/2020	Chap. 9	Quantum mechanics of electromagnetic forces	#1	01/22/2020
2	Wed: 01/15/2020	Chap. 9	Quantum mechanics of particle in electrostatic field	#2	01/24/2020
3	Fri: 01/17/2020	Chap. 9	Quantum mechanics of particle in magnetostatic field	#3	01/27/2020
	Mon: 01/20/2020	No class	Martin Luther King Holiday		
4	Wed: 01/22/2020	Chap. 14	Scattering theory	#4	01/29/2020
5	Fri: 01/24/2020	Chap. 14	Scattering theory	#5	01/31/2020
6	Mon: 01/27/2020	Chap. 14	Scattering theory	#6	02/03/2020
7	Wed: 01/29/2020	Chap. 12	Variational methods	#7	02/05/2020
8	Fri: 01/31/2020				
9	Mon: 02/03/2020				
10	Wed: 02/05/2020				
11	Fri: 02/07/2020				
12	Mon: 02/10/2020				

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

Time independent Schrödinger equation:

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

Hermitian operator representing the Hamiltonian of the system

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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: $|\psi\rangle = \sum_i C_i|\varphi_i\rangle$

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

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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.

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

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

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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.

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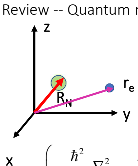
Review -- Quantum mechanics of the hydrogen atom



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

In center of mass system:

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

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

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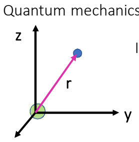
Quantum mechanics of the hydrogen atom



In center of mass coordinates

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

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

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

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

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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: $R(\rho)=e^{-\rho/2}F(\rho)$

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

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

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

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

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*.

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

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

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

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

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

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

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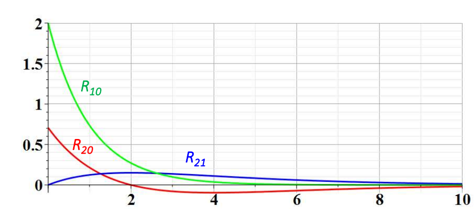
Hydrogen radial wavefunctions



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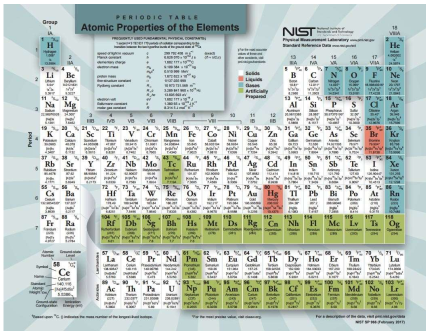

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Variational method for estimating ground state energy of a H atom:

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

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

$$\frac{df}{d\alpha} = 0 \qquad \Rightarrow \alpha = \frac{Ze^2\mu}{\hbar^2} = \frac{Z}{a_0} \qquad \Rightarrow \min_{\psi} f(\psi) = -\frac{Z^2e^2}{2a_0}$$

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

$$f(\psi) = \frac{\hbar^2}{2\mu}6\alpha - \frac{4Ze^2\sqrt{\alpha}}{\sqrt{\pi}}$$

$$\frac{df}{d\alpha} = 0 \qquad \Rightarrow \alpha = \frac{4Z^2}{9a_0^2\pi} \qquad \min_{\psi} f(\psi) = -\frac{Z^2e^2}{2a_0}\frac{8}{3\pi}$$

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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

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

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

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Variational methods for estimating ground state energy:

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

$$f(\psi) = \frac{e^2}{a_0}\left(Z^2 - \frac{27}{8}Z\right) \qquad \min_\psi f(\psi) = -\frac{e^2}{a_0}\left(\frac{27}{16}\right)^2$$

$$\frac{df}{dZ} = 0 \quad \Rightarrow Z_{opt} = \frac{27}{16} \qquad = -\frac{e^2}{2a_0}5.695$$

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

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