PHY 741 Quantum Mechanics
12-12:50 PM MWF Olin 103

Plan for Lecture 19:

Welcome back from fall break

1. **Comments on mid-term exam**
2. **Comments on "computational projects"**
3. **Quantum mechanics of atoms (Chapter 13)**

Three events this week --

Special Seminar: Oct. 16, 2017 at 3 PM
Special WFU Physics Seminar
TITLE: "Quantum Information Science"
SPEAKER: Jaewan Kim Korea Institute for Advanced Study TIME: Monday, October 16, 2017, at 3:00pm PLACE: Olin 101 There will be a reception ...

Career Event: Oct. 18 at 12:00 pm + pizza
WFU Physics Career Advising Event TITLE: "Opportunities for Undergraduate, Graduate, and Postdoctoral Research at Oak Ridge National Laboratory (ORNL)"
SPEAKER: Zachary D. Hood School of Chemistry and Biochemistry, Georgia Institute of ...

Colloquium: Oct. 18, 2017 at 4 PM
WFU Physics and Chemistry Colloquium
TITLE: "Solid Electrolytes and Their Interfaces: Bridging Mechanistic Understanding to Their Performance"
SPEAKER: Zachary D. Hood School of Chemistry and Biochemistry, Georgia Institute of Technology, ...

7	Mon, 9/11/2017	Chap. 5	Schrödinger equation in one-dimension		
8	Wed, 9/13/2017	Chap. 7	Schrödinger equation in one-dimension	#6	9/15/2017
9	Fri, 9/15/2017	Chap. 7	Schrödinger equation in one-dimension	#7	9/20/2017
10	Mon, 9/18/2017	Chap. 5 and 7	Schrödinger equation in one-dimension		
11	Wed, 9/20/2017	Chap. 9	Commutator formalism	#8	9/22/2017
12	Fri, 9/22/2017	Chap. 10	Quantum mechanics of multiparticle systems	#9	9/25/2017
13	Mon, 9/25/2017	Chap. 10-12	Multiparticle systems and angular momentum		
14	Wed, 9/27/2017	Chap. 12	Eigenstates of angular momentum		
15	Fri, 9/29/2017	Chap. 1,4,5,7,9,10,12	Review		
	Mon, 10/02/2017		*Take-home exam -- No class*		
	Wed, 10/04/2017		*Take-home exam -- No class*		
16	Fri, 10/06/2017	Chap. 12-13	Spherically symmetric systems		
17	Mon, 10/09/2017	Chap. 13	Quantum mechanics of a hydrogen atom	#10	10/16/2017
18	Wed, 10/11/2017	Chap. 13	Quantum mechanics of multi-electron atoms		
	Fri, 10/13/2017		*Fall break -- No class*		
19	Mon, 10/16/2017		Discuss exam questions and topics for presentations	Topic	10/18/2017
20	Wed, 10/18/2017				
21	Fri, 10/20/2017				
22	Mon, 10/23/2017				
23	Wed, 10/25/2017				

1. Consider a particle of mass m in a one-dimensional square well potential

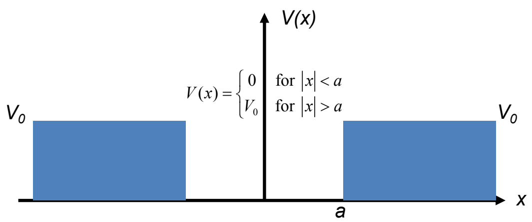
$$V(x) = \begin{cases} 0 & \text{for } |x| \leq a \\ V_0 & \text{for } |x| > a \end{cases}$$

(a) Find the forms of the bound eigenstates of the system both for even parity $\phi(x) = \phi(-x)$ and odd parity $\phi(x) = -\phi(-x)$ states.

(b) Now consider the specific case of

$$V_0 = 9\frac{\hbar^2}{2ma^2}.$$

Example: Particle of mass *m* confined within an finite square well:



After some algebra, we found that the energy eigenvalues E were solutions of transcendental equations:

$$\tan\left(\frac{\sqrt{2mE}}{\hbar}a\right) = \sqrt{\frac{V_0 - E}{E}} \Rightarrow \tan\left(\frac{\sqrt{2mV_0}a}{\hbar}\sqrt{\frac{E}{V_0}}\right) = \sqrt{\frac{1 - E/V_0}{E/V_0}}$$ For even parity

$$\cot\left(\frac{\sqrt{2mE}}{\hbar}a\right) = -\sqrt{\frac{V_0 - E}{E}} \Rightarrow \cot\left(\frac{\sqrt{2mV_0}a}{\hbar}\sqrt{\frac{E}{V_0}}\right) = -\sqrt{\frac{1 - E/V_0}{E/V_0}}$$ For odd parity

Let $u \equiv \frac{\sqrt{2mV_0}a}{\hbar}$ $\quad \epsilon \equiv \sqrt{\frac{E}{V_0}}$

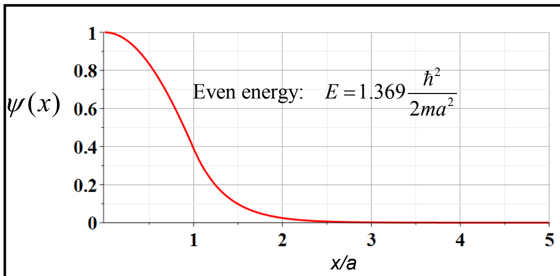
$$\tan(u\epsilon) = \sqrt{\frac{1-\epsilon^2}{\epsilon^2}}$$

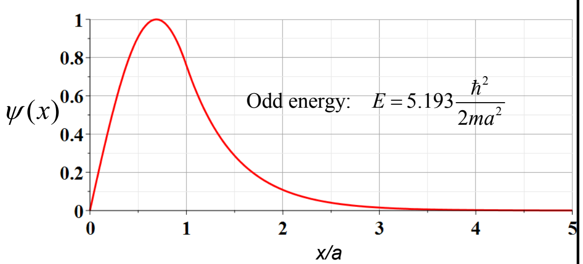
or $$\cot(u\epsilon) = -\sqrt{\frac{1-\epsilon^2}{\epsilon^2}}$$

For exam problem:

$$V_0 = 9\frac{\hbar^2}{2ma^2}$$

$$\Rightarrow u = 3$$





Calculation of the variance

$$\Delta x \equiv \left(\langle \psi | x^2 | \psi \rangle - \langle \psi | x | \psi \rangle^2 \right)^{1/2}$$

$$\Delta p \equiv \left(\langle \psi | p^2 | \psi \rangle - \langle \psi | p | \psi \rangle^2 \right)^{1/2}$$

Note that for this problem, $\langle \psi | x | \psi \rangle = 0$

$$\langle \psi | p | \psi \rangle = 0$$

$$\frac{\langle\psi|x^2|\psi\rangle}{\langle\psi|\psi\rangle} = 0.25898 \quad \text{for even solution}$$

$$\frac{\langle\psi|x^2|\psi\rangle}{\langle\psi|\psi\rangle} = 0.68114 \quad \text{for odd solution}$$

$\langle\psi|p^2|\psi\rangle$ is discontinuous

$$p^2|\psi\rangle = \begin{cases} 2mE|\psi\rangle & \text{for } |x| < a \\ 2m(E-V_0)|\psi\rangle & \text{for } |x| > a \end{cases}$$

Performing integrals:

For even solution: $\sqrt{\langle\psi|x^2|\psi\rangle\langle\psi|p^2|\psi\rangle} = 0.5102\hbar$

For odd solution: $\sqrt{\langle\psi|x^2|\psi\rangle\langle\psi|p^2|\psi\rangle} = 1.5293\hbar$

2. Consider the eigenstates of $\mathbf{J}^2$ and J_z, of the form $|jm\rangle$ for the case that $j = 3/2$. In this basis, evaluate the following operators in matrix form:

(a) $\mathbf{J}^2$

(b) J_z

(c) J_x

(d) J_y

$$\mathbf{J}^2 = \frac{15}{4}\hbar^2 \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

$$J_z = \hbar \begin{pmatrix} \frac{3}{2} & 0 & 0 & 0 \\ 0 & \frac{1}{2} & 0 & 0 \\ 0 & 0 & -\frac{1}{2} & 0 \\ 0 & 0 & 0 & -\frac{3}{2} \end{pmatrix}$$

$$J_x = \hbar \begin{pmatrix} 0 & \frac{\sqrt{3}}{2} & 0 & 0 \\ \frac{\sqrt{3}}{2} & 0 & 1 & 0 \\ 0 & 1 & 0 & \frac{\sqrt{3}}{2} \\ 0 & 0 & \frac{\sqrt{3}}{2} & 0 \end{pmatrix}$$

$$J_y = \hbar \begin{pmatrix} 0 & \frac{-i\sqrt{3}}{2} & 0 & 0 \\ \frac{i\sqrt{3}}{2} & 0 & -i & 0 \\ 0 & i & 0 & \frac{-i\sqrt{3}}{2} \\ 0 & 0 & \frac{i\sqrt{3}}{2} & 0 \end{pmatrix}$$

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3. Consider the following Hamiltonian describing the quantum mechanics of a particle of mass m in a potential $V(x)$.

$$H(x) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x).$$

Simplify the following commutation relations

(a) $[x, H(x)]$
(b) $[x^2, H(x)]$
(c) $[p, H(x)]$
(d) $[p^2, H(x)]$

$$H = \frac{p^2}{2m} + V(x)$$

Note that $[x, p] = i\hbar$

$[x, x] = 0$ and $[p, p] = 0$

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$$[x, H] = \left[x, \frac{p^2}{2m}\right] + \left[x, V(x)\right]$$

$$= \frac{1}{2m}[x, p^2] + 0 = \frac{1}{2m}\left([x, p]p + p[x, p]\right)$$

$$= \frac{i\hbar}{m} p$$

$$[p, H] = \left[p, \frac{p^2}{2m}\right] + \left[p, V(x)\right]$$

$$= 0 - i\hbar\frac{dV}{dx}$$

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4. Suppose that a given Hamiltonian system has two eigenstates $|\varepsilon_1\rangle$ and $|\varepsilon_2\rangle$ where ε_i denotes the eigenstate energy with $\varepsilon_2 - \varepsilon_1 > 0$. At time $t = 0$ the state vector for the system has the form

$$\psi(t=0) = (|\varepsilon_1\rangle + |\varepsilon_2\rangle).$$

(a) Write the form of the state vector at times $t > 0$.

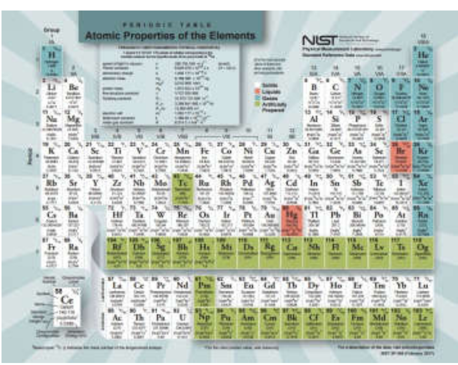
(b) What is the probability of finding the particle in state $|\varepsilon_2\rangle$ as a function of t?

$$\phi(t) = \left(\left|\varepsilon_1\right\rangle e^{-i\varepsilon_1 t/\hbar} + \left|\varepsilon_2\right\rangle e^{-i\varepsilon_2 t/\hbar}\right)$$

Picking topic for "project"

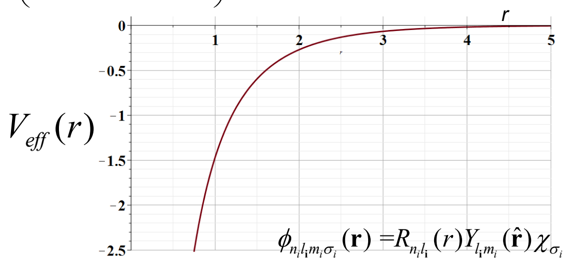
- Prepare ~ 10 minute presentation to teach us (and yourself) something related to quantum mechanics
- Similar effort to take-home exam
- Can combine with classical mechanics project

Back to the quantum mechanics of atoms



Shell structure of atoms based on Hartree and Hartree-Fock treatments

$$\left(-\frac{\hbar^2}{2m}\nabla^2+V_{eff}(\mathbf{r})\right)\phi_{n_i l_i m_i \sigma_i}(\mathbf{r})=\epsilon_{n_i l_i}\phi_{n_i l_i m_i \sigma_i}(\mathbf{r})$$



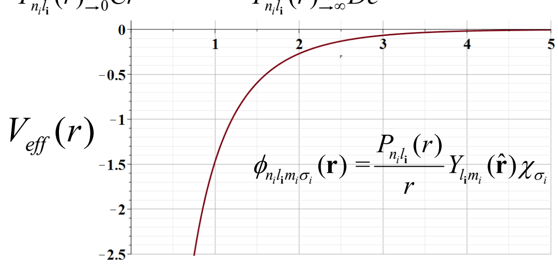
$$\phi_{n_i l_i m_i \sigma_i}(\mathbf{r})=R_{n_i l_i}(r)Y_{l_i m_i}(\hat{\mathbf{r}})\chi_{\sigma_i}$$

Shell structure of atoms

Principal Quantum Number	Angular momentum Quantum Number	Number of States
n=1	*l=0 (s)*	*2*
n=2	*l=0 (s)*	*2*
	l=1 (p)	*6*
n=3	*l=0 (s)*	*2*
	l=1 (p)	*6*
	l=2 (d)	*10*
n=4	*l=0 (s)*	*2*
	l=1 (p)	*6*
	l=2 (d)	*10*
	l=3 (f)	*14*

$$\left(-\frac{\hbar^2}{2m}\left(\frac{d^2}{dr^2}-\frac{l(l+1)}{r^2}\right)+V_{eff}(\mathbf{r})\right)P_{n_i l_i}(r)=\epsilon_{n_i l_i}P_{n_i l_i}(r)$$

$$P_{n_i l_i}(r)\underset{r\to 0}{\simeq} Cr^{l_i+1} \qquad P_{n_i l_i}(r)\underset{r\to\infty}{\simeq} De^{-\sqrt{\epsilon_{n_i l_i}}\,r}$$



$$\phi_{n_i l_i m_i \sigma_i}(\mathbf{r})=\frac{P_{n_i l_i}(r)}{r}Y_{l_i m_i}(\hat{\mathbf{r}})\chi_{\sigma_i}$$

Self-consistent treatment of the $V_{eff}(r)$

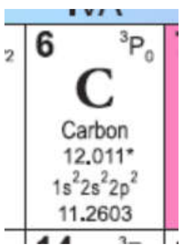
$$V_{eff}(r) = -\frac{Ze^2}{r} + e^2 \int d^3r' \frac{n(r')}{|\mathbf{r}-\mathbf{r'}|} + V_{xc}(n(r))$$

$$n(r) = \sum_{n_i l_i} w_{n_i l_i} \frac{|P_{n_i l_i}(r)|^2}{4\pi r^2}$$

For spherically symmetric atom:

$$\phi_{n_i l_i m_i}(\mathbf{r}) = \frac{P_{n_i l_i}(r)}{r} Y_{l_i m_i}(\hat{\mathbf{r}})$$

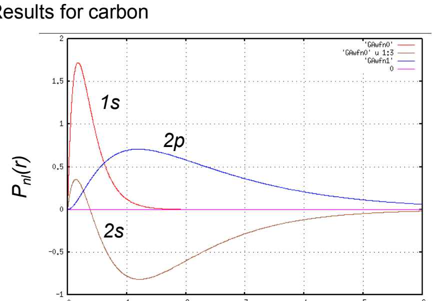
Example for carbon



$$n(r) = \sum_i w_{n_i l_i} \frac{|P_{n_i l_i}(r)|^2}{4\pi r^2}$$

$$= \frac{1}{4\pi r^2}\left(2|P_{1s}(r)|^2 + 2|P_{2s}(r)|^2 + 2|P_{2p}(r)|^2\right)$$

Results for carbon



E_{1s}=-19.9 Ry
E_{2s}=-1.0 Ry
E_{2p}=-0.4 Ry

r (Bohr)