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

Plan for Lecture 8

Approximation methods for analyzing quantum mechanical systems

1. **Continue reading Chapter 12**
   a. **Variational methods**
   b. **WKB or semi-classical approximation**

1

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	Chap. 12	Variational and other approximation methods	#8	02/07/2020
9	Mon: 02/03/2020				
10	Wed: 02/05/2020				
11	Fri: 02/07/2020				

2

Inequality behind variational approximation method for finding ground state energy E_0

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

Summary of variational method:

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

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

3

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

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

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

4

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

5

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

Normalization integral:

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

6

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

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

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

1/31/2020 PHY 742 -- Lecture 8 7

7

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

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

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

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

1/31/2020 PHY 742 -- Lecture 8 8

8

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

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 $\Psi(r_1,r_2)=f(r_1)f(r_2)$

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

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

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

1/31/2020 PHY 742 -- Lecture 8 9

9

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 --

10

Quasi classical or WKB (Wentzl, Kramers, and Brillouin) method

Consider the stationary state Schrödinger equation for a one-dimensional system --

$$-\frac{\hbar^2}{2m}\frac{d^2\Psi(x)}{dx^2}+V(x)\Psi(x)=E\Psi(x)$$

$$\hbar^2\frac{d^2\Psi(x)}{dx^2}+2m\left(E-V(x)\right)\Psi(x)=0$$

Define $p(x)=\sqrt{2m\left(E-V(x)\right)}$

$\pi(x)=\sqrt{2m\left(V(x)-E\right)}$

Seek solutions of the form: $\Psi(x)=e^{iu(x)/\hbar}$

$$i\hbar\frac{d^2u(x)}{dx^2}-\left(\frac{du}{dx}\right)^2+\left(p(x)\right)^2=0$$

11

Quasi classical or WKB (Wentzl, Kramers, and Brillouin) method -- continued

For: $\Psi(x)=e^{iu(x)/\hbar}$

$$i\hbar\frac{d^2u(x)}{dx^2}-\left(\frac{du(x)}{dx}\right)^2+\left(p(x)\right)^2=0$$

Suppose that $u(x)=u_0(x)+\frac{\hbar}{i}u_1(x)+\ldots$

Solution for order $\hbar^0$: $u_0(x)=\pm\int^x dx'\,p(x')$

Solution for order $\hbar^1$: $u_1(x)=-\ln\left(\sqrt{p(x)}\right)$

Wave function up to first order; defining $k(x)=p(x)/\hbar$:

$$\Psi(x)=\frac{C}{\sqrt{k(x)}}e^{\pm i\int^x k(x')dx'}$$

12

Quasi classical or WKB (Wentzl, Kramers, and Brillouin) method -- continued

Summary of first order WKB wavefunctions

For $k(x)=\sqrt{\frac{2m(E-V(x))}{\hbar^2}}=i\kappa(x)$

$$\Psi(x)=\frac{C}{\sqrt{k(x)}}e^{\pm i\int^x k(x')dx'} \quad \text{if } E>V(x)$$

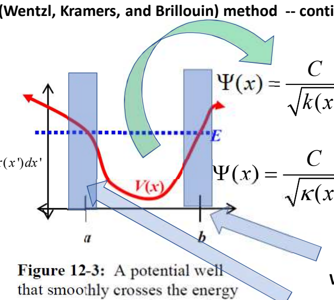
$$\Psi(x)=\frac{C}{\sqrt{\kappa(x)}}e^{\pm \int^x \kappa(x')dx'} \quad \text{if } E<V(x)$$

Note that for $E\approx V(x)$ the approximation is not valid

13

Quasi classical or WKB (Wentzl, Kramers, and Brillouin) method -- continued

$$\Psi(x)=\frac{C}{\sqrt{\kappa(x)}}e^{\pm \int^x \kappa(x')dx'}$$



$$\Psi(x)=\frac{C}{\sqrt{k(x)}}e^{\pm i\int^x k(x')dx'}$$

$$\Psi(x)=\frac{C}{\sqrt{\kappa(x)}}e^{\pm \int^x \kappa(x')dx'}$$

Figure 12-3: A potential well that smoothly crosses the energy line at the two classical turning points *a* and *b*.

WKB invalid

14

Analysis of exact solution for linear potential
Results will be used in their asymptotic limit to infer WKB connection formula

Suppose $\left(k(x)\right)^2=-\left(\kappa(x)\right)^2=A(x-a)$

15

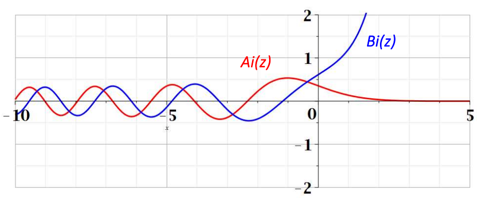
Differential equation:

$$\left(\frac{d^2}{dx^2} + A(x-a)\right)\psi(x) = 0$$

$$\left(\frac{d^2}{du^2} + Au\right)\psi(u) = 0 \qquad \text{where } u \equiv x-a$$

16

$$\frac{d^2w}{dz^2} = zw$$



17

Differential equation:

$$\left(\frac{d^2}{dx^2} + A(x-a)\right)\psi(x) = 0$$

$$\left(\frac{d^2}{du^2} + Au\right)\psi(u) = 0 \qquad \text{where } u \equiv x-a$$

Airy's equation

$$\left(\frac{d^2}{dz^2} - z\right)Ai(z) = 0$$

Note that the Schrödinger equation can be multiplied by a constant:

$$C\left(\frac{d^2}{du^2} + Au\right)\psi(u) = 0$$

Changing variables: $z = CAu$

$$C\frac{d^2}{du^2} = C^3A^2\frac{d^2}{dz^2} \quad \Rightarrow C = A^{-2/3} \qquad \Rightarrow z = -A^{1/3}u$$

$$\Rightarrow \psi(u) = \mathcal{N} Ai(-A^{1/3}u)$$

18

Some properties of Airy functions –
Integral form:

$$\mathrm{Ai}(x) = \frac{1}{\pi}\int_0^\infty \cos\left(\tfrac{1}{3}t^3 + xt\right)\,\mathrm{d}t.$$

Behavior as $z \to \infty$

$$Ai(z) \approx \frac{1}{2\sqrt{\pi}z^{1/4}} e^{-\frac{2}{3}z^{3/2}}$$

Behavior as $-z \to \infty$

$$Ai(-z) \approx \frac{1}{\sqrt{\pi}z^{1/4}} \sin\left(\frac{2}{3}z^{3/2} + \frac{\pi}{4}\right)$$

19

Relating asymptotic forms to WKB solutions (from Carlson's textbook)

$$\psi(x) \to \begin{cases} \dfrac{N_a}{2\sqrt{\pi}A^{1/4}(a-x)^{1/4}} \exp\left[-\tfrac{2}{3}\sqrt{A}(a-x)^{3/2}\right] & \text{as } x-a \to -\infty, \\ \dfrac{N_a}{\sqrt{\pi}A^{1/4}(x-a)^{1/4}} \sin\left[\tfrac{2}{3}\sqrt{A}(x-a)^{3/2} + \tfrac{1}{4}\pi\right] & \text{as } x-a \to \infty. \end{cases}$$

A similar analysis must be considered for a turning point on the other side.

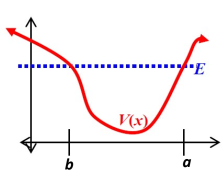
Summary of turning point relationships

$$\frac{2}{\sqrt{k}}\cos\left(\int_x^a k(x')dx' - \frac{\pi}{4}\right) \leftrightarrow \frac{1}{\sqrt{\kappa}}\exp\left(-\int_a^x \kappa(x')dx'\right) \qquad \frac{1}{\sqrt{k}}\sin\left(\int_x^a k(x')dx' - \frac{\pi}{4}\right) \leftrightarrow -\frac{1}{\sqrt{\kappa}}\exp\left(\int_a^x \kappa(x')dx'\right)$$

$$\frac{1}{\sqrt{\kappa}}\exp\left(-\int_x^b \kappa(x')dx'\right) \leftrightarrow \frac{2}{\sqrt{k}}\cos\left(\int_b^x k(x')dx' - \frac{\pi}{4}\right) \qquad -\frac{1}{\sqrt{\kappa}}\exp\left(\int_x^b \kappa(x')dx'\right) \leftrightarrow \frac{1}{\sqrt{k}}\sin\left(\int_b^x k(x')dx' - \frac{\pi}{4}\right)$$

20

WKB estimate of bound state energies



Summary of turning point relationships

$$\frac{2}{\sqrt{k}}\cos\left(\int_x^a k(x')dx' - \frac{\pi}{4}\right) \leftrightarrow \frac{1}{\sqrt{\kappa}}\exp\left(-\int_a^x \kappa(x')dx'\right)$$

$$\frac{1}{\sqrt{\kappa}}\exp\left(-\int_x^b \kappa(x')dx'\right) \leftrightarrow \frac{2}{\sqrt{k}}\cos\left(\int_b^x k(x')dx' - \frac{\pi}{4}\right)$$

Form within potential well:

$$\frac{2}{\sqrt{k}}\cos\left(\int_x^a k(x')dx' - \frac{\pi}{4}\right) = \frac{2}{\sqrt{k}}\cos\left(\int_b^a k(x')dx' - \int_b^x k(x')dx' - \frac{\pi}{4}\right)$$

$$= \frac{2}{\sqrt{k}}\cos\left(\int_b^a k(x')dx'\right)\sin\left(\int_x^a k(x')dx' - \frac{\pi}{4}\right) + \frac{2}{\sqrt{k}}\sin\left(\int_b^a k(x')dx'\right)\cos\left(\int_x^a k(x')dx' - \frac{\pi}{4}\right)$$

must vanish

21

$$\frac{2}{\sqrt{k}}\cos\left(\int_b^a k(x')dx'\right)=0$$

$$\Rightarrow \int_b^a k(x')dx' = \frac{(2n+1)\pi}{2} = \left(n+\frac{1}{2}\right)\pi$$

➔**WKB estimate of bound state energy**

Let's apply our quantization rule Eq. (12.29a) to a particle of mass m contained in the harmonic oscillator potential, $V(x)=\frac{1}{2}m\omega^2x^2$. The first step is to find the turning points, defined as the points where $V(x)=E$. Solving this equation is straightforward:

$$a,b=\pm\frac{1}{\omega}\sqrt{\frac{2E}{m}}.$$

We then substitute these limits in the quantization rule Eq. (12.29a), and to the integral with the help of Eq. (A.12g)

$$\left(n+\tfrac{1}{2}\right)\pi\hbar=\int_{-\sqrt{2E/m}/\omega}^{\sqrt{2E/m}/\omega} dx\sqrt{2mE-m^2\omega^2x^2}=\cdots=\frac{\pi E}{\omega}. \qquad E_n=\hbar\omega\left(n+\frac{1}{2}\right)$$

1/31/2020 PHY 742 -- Lecture 8 22

22