Quantum Mechanics and Atomic Physics Lecture 23: Approximation Methods I http://www.physics.rutgers.edu/ugrad/361 Prof. Sean Oh

Approximation Methods

- *Exact* solutions to Schrodinger's equation are possible only for mathematically simple potentials.
- However, many realistic potentials require **approximations**.
- This is true also for some remarkably simple ones
 - e.g. a linear potential $V(x) \propto x$
- Approximate solutions:
 - Analytic methods
 - Wentzel-Kramers-Brillouin (WKB) method (today)
 - Perturbation theory (today and next)
 - Variational methods (next)
 - Numerical methods
- Note: again the emphasis is to obtain *bound-state* solutions

The WKB Method

- This approximation is applicable when V rises sharply in the region V>E so that barrier penetration is very tiny.
- The WKB assumption is:
 - Take Ψ ~ 0 at the classical turning points E=V(x).
 - Then the oscillatory solutions for E>V must be such that an integral number of halfwavelengths must fit within the turning points.



Like a standing wave of vibrating string clamped on both ends:



FIGURE 9.1 Left: A string vibrating in the n = 3 mode. Right: A quantum wavefunction with n = 4.

Reed: Chapter 9

The WKB Method

 In general, however, V(x) will not be constant and the wavelength will be a function of position.
 So λ is not constant:

$$a = \frac{h}{P} = \frac{h}{\sqrt{2mk}} = \frac{h}{\sqrt{2m(E - V(x))}}$$

So as V(x) increases, $\lambda(x)$ increases.

The WKB Method

So a short distance dx (so between x and x+dx) over which the potential V(x) is effectively constant will contain a number of wavelengths given by:



And there must be an integral number of wavelengths, so:

$$\int \frac{dx}{\lambda(x)} = \frac{n}{2} \implies \int \sqrt{\frac{2m(E-V(x))}{h}} dx = \frac{n}{2}$$

$$= \frac{1}{2} \sqrt{2m} \int \sqrt{E_n - V(x)} dx \approx nh$$

The WKB Approximation

- This *is* the WKB approximation, for energy eigenvalues E_n.
- One can also obtain the approximate eigenstates, but that's beyond the scope of this course.

When is WKB approx. valid?

- The accuracy of the WKB approximation depends on the quantum wavelength λ not varying too rapidly over short distances.
- So we demand that any change dλ in λ over the distance dx be small:

From the deBroglie relation: $\gamma = W_P$

And classically:
$$p(x) = \sqrt{2m(E-v(x))}$$

So,

$$\frac{d\lambda}{dx} = -\frac{h}{p^{2}} \frac{dp}{dx}$$

$$= -\frac{h}{2m(E-V(x))} \frac{d}{dx} \left[\frac{2m(E-V(x))}{dx} \right]$$

$$= \frac{m}{(2m(E-V(x)))^{3/2}} \frac{dV(x)}{dx}$$

$$\frac{d\lambda}{dx} (c) = \sum \frac{m}{(2m(E-V(x)))^{3/2}} \left(\frac{dV(x)}{dx} \right) < c$$

- dV/dx is sometimes written as |dV/dx| since λ can either increase/decrease as V(x) decreases/increases.
- The above is referred to as the *classical approximation*.

Example

 Let's determine the approximate energy eigenvalues for a particle of mass m moving in this linear potential:





The turning points are:

$$\chi = 0, \chi = a$$

To do WKB problems

- Write E in terms of position where E cuts the V(x) line.
 - Here it's $\chi_1 = 0$, $\chi_2 = q$
- 2. Solve equation:

3. Solve for E_n .



For a linear potential like this, it turns out that the WKB approximation overestimates the ground state energy by about 20%.

Example (9.2)

- Let's use the WKB approximation to estimate the energy levels for the hydrogen atom.
- Let's treat it as a 1D system in the radial coordinate r.



The upper limit of integration is:

$$E = -\frac{e^2}{\sqrt{\pi\epsilon_s}a} = a E = -\frac{e^2}{\sqrt{\pi\epsilon_s}}$$

Integral becomes:
$$2\sqrt{2}m \int_{0}^{\infty} \sqrt{E-aE} dr \approx nh$$

• We are looking for bound-states: E < 0. So:

E = -|E|

• To simplify integral, we can make a change of variables:

$$\begin{aligned} \nabla = a \sin^{2} \beta \\ 4a \sqrt{2m} |e| \int_{0}^{\pi/2} \cos^{2} \beta \\ \pi/4 \\ \sqrt{2m} |e| \int_{0}^{\pi/2} \cos^{2} \beta \\ \sqrt{2m} |e| \int_{0}^{\pi/2} \cos^{2} \beta \\ \sqrt{2m} |e| \\ \sqrt{2m} \frac{h^{2}h^{2}}{2m\pi^{2}a^{2}} \\ \approx \frac{h^{2}h^{2}}{2m\pi^{2}} \\ \frac{h^{2}h^{2}}{2m\pi^{2}} \\ \frac{h^{2}h^{2}}{86^{2}h^{2}n^{2}} \end{aligned}$$

Remarkably, the WKB approximation gives us the <u>exact</u> levels given by Bohr and the S.E.!

Perturbation theory

- Pertrubation theory:
 - A general, yet powerful, method for expressing approximate wavefunctions and energies for potentials
 - Expressed as variants of potentials for which the SE can be solved exactly

• First let's revisit the superposition theorem ...

Superposition Theorem Revisited

- Any linear combination of solutions to the Timedependent S.E. is also a solution of the T.D.S.E.
- An essential ingredient was the orthogonality/orthonormality theorems:

$$\int_{-\infty}^{\infty} \Psi_{i} * \Psi_{i} dx = i \quad and \quad \int_{-\infty}^{\infty} \Psi_{j} * \Psi_{i} dx = 0 \quad i \neq j \neq i$$

$$\int_{-\infty}^{\infty} \Psi_{i} * \Psi_{i} dx = \int_{0}^{1} = \int_{0}^{1} = \int_{0}^{\infty} (\Psi_{i} * \Psi_{i}) dx = \int_{0}^{1} = \int_{0}^{1} (\Psi_{i} * \Psi_{i}) dx = \int_{0}^{1} (\Psi_{i}) dx =$$

Superposition Theorem Revisited

- Such a set of eigenfunctions forms a so-called complete set
 - Which means that any (well-behaved) function can be expanded in the set:

$$\varphi(x) = \sum_{n} a_n \Psi_n(x)$$

Vocabulary:

- A complete set of Ψ_n are called basis vectors or base vectors
- The a_n are called expansion coefficients or projections of φ(x) onto Ψ_n(x)

Superposition Theorem Revisited

Question:

- Suppose that φ(x) is a continuous, but arbitrary function valid over the same domain as Ψ_n(x).
- What values must the expansion coefficients take if we we want:

$$\varphi(x) = \leq_n a_n \Psi_n(x)$$

Let's figure out the a_n



The sum runs over all possible values of n. But since:

the only surviving term is for n=j. So,

$$n=j = a_{j}$$

$$=) (\Psi_{j} | \Psi_{j} = \sum_{n=0}^{j} a_{n} \delta_{n}^{n} = a_{j}$$

$$=) [a_{j} = \langle \Psi_{j} | \Psi_{j} \rangle$$

$$=) replace j by n =) [a_{n} = \int_{-\infty}^{\infty} \Psi_{n}^{*} u_{j} \Psi_{i} x_{j} dx]$$

Normalization

- Note: \$\overline{\phi(x)}\$ need not (and in general is not) be a solution to the Time-Independent S.E.
- $\phi(x)$ will be valid only over the domain of $\Psi(x)$
- So if \$\oplus(x)\$ is normalized over this range, we get a constraint on \$a_n\$:

$$= \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} a_n \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} a_n \sum_{n=1}^{\infty} \sum_{n=1}^{\infty} a_n \sum_{n=1}^{\infty} \sum_$$

- For a particular value of n, the inner sum runs over all possible values of m
- This is repeated for all possible values of n
- And in each case, $\delta_n^m = 0$ unless m=n
- So,

$$= \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} a_m \delta_n^m = \sum_{n=1}^{\infty} \sum_{n=1}^{\infty} a_n \delta_n^m = \sum_{n=1}^{\infty} \sum_{n=1}^{\infty} a_n \delta_n^n = \sum_{n=1}^{\infty} \sum_$$

So the condition that \$\phi(x)\$ is normalized requires the above or

$$\leq a_n * a_n = 1$$

Example

Find the normalization constant here, where $\Psi_{n}(x)$ are energy eigenfunctions: $\phi(x) = A(2\Psi_{n}(x) + \Psi_{n}(x) + 3\Psi_{n}(x))$ Also, if φ(x) is chosen such that it is normalized over the domain of Ψ(x), it will happen automatically when we compute a_n

$$a_n = \langle \Psi_n | \varphi \rangle$$

since

$$\varphi(x) = \sum_{n} a_n \Psi_n(x)$$

represents an exact expression for $\phi(x)$

The probability that a measurement of energy will yield
 E_n is

Example: Approximate a straight line as a sum of rectangular well wavefunctions

Let's express a straight line, \$\oplus(x)=x\$, as a linear sum of infinite rectangular well eigenfunctions:

$$\Psi_{L}(\mathbf{x}) = \int_{L}^{2} \sin\left(\frac{n\pi \mathbf{x}}{L}\right)$$

$$a_n = L \Psi_n | \psi \rangle$$

= $\int_{L}^{2} \int_{1}^{L} \sin n \frac{\pi x}{L} \cdot x \cdot dx$

• Define
$$c = n\pi/L$$

$$\begin{aligned}
\Omega_n &= \int_{-L}^{2} \left[\frac{\sin(cx)}{c^2} - \frac{\chi}{c} \cos(cx) \right]_{0}^{L} \\
&= \left(\frac{2}{L} \left[-\frac{L}{c} \cos(cL) \right] = \left(\frac{2}{L} \left(-\frac{L^2}{n\pi} \cos n\pi \right) \right] \\
\end{aligned}$$
• Use
$$\begin{aligned}
\cos n\pi &= (-1)^n \int_{-L}^{2} \left[-\frac{L^2}{n\pi} \right] \\
&= (-1)^{n_{11}} \int_{-L}^{2} \left[\frac{C^2}{n\pi} - (-1)^{n_{11}} \frac{\pi}{n\pi} \right]^{3/L}
\end{aligned}$$

Note that the expansion coefficients a_n are functions of n - this occurs often.

$$= \sum_{n=1}^{\infty} \varphi(x) = x = \sum_{n=1}^{\infty} a_n \Psi_n(x) = \sum_{n=1}^{\infty} \left\{ -\frac{1}{n} \sum_{n=1}^{\infty} \sqrt{\frac{2}{n}} \sum_{n=1}^{\infty} \sqrt{\frac{2}{n}} \sum_{n=1}^{\infty} \sum_{n$$

Any function can be reproduced by adding together an infinite number of sinusoidal functions
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■ Terms up to n=20 -

I FIGURE 9.4 Approximating a Straight Line as a Sum of Rectangular-well Wavefunctions.

- An infinite number of terms needed to reproduce a straight line up to x=1
- \$\overline{\phi(x)}\$ goes to zero at x=1 because infinite well wavefunctions go to zero there

Example cont'd



Find a_n again for this normalized wavefunction. For A = 1 $\Rightarrow a_n = (-1)^n \left(\frac{1}{2} \left(-\frac{1}{n\pi}\right)\right)$ $= (-1)^{n\pi} \left(\frac{1}{2} \left(-\frac{1}{n\pi}\right)\right)$ $= (-1)^{n\pi} \left(\frac{1}{2} \left(-\frac{1}{n\pi}\right)\right)$ $= (-1)^{n\pi} \left(\frac{1}{2} \left(-\frac{1}{n\pi}\right)\right)$ $= (-1)^{n\pi} \left(\frac{1}{2} \left(-\frac{1}{n\pi}\right)\right)$

Example cont'd

This implies that $\begin{aligned} &|= \sum_{\substack{n=1\\n=1}}^{\infty} (a_n)^2 = \sum_{\substack{n=1\\n=1}}^{\infty} \left(\frac{\sqrt{2}}{n\pi}\right)^2 = \left[\sum_{\substack{n=1\\n=1}}^{\infty} \frac{1}{n^2}\right], \frac{6}{\pi^2} \end{aligned}$

• What is the probability of finding the system in the ground state of the infinite potential well?

Summary/Announcements

- Next time: Approximation Methods continued
- HW 12 due on Wed Dec 7th in class: no late HW accepted
- HW 13 due on Mon Dec 12th in class: no late HW accepted: HW 13 will be posted later today.