Quantum Mechanics and Atomic Physics

Lecture 24:

Approximation Methods II

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Last Time

- **<u>We introduced solvinging SE using approximations</u>**
  - Analytic methods
    - Wentzel-Kramers-Brillouin (WKB) method (last time)
    - Perturbation theory (last time and today)
    - Variational methods (today)

Time-independent Perturbation Theory

- Perturbation theory applies when the potential V(x) is a small deviation from another potential $V^0(x)$ for which we <u>can</u> solve S.E. exactly.

$$V(x) = V^0(x) + \Delta V(x)$$

- $V^0(x)$ is the **unperturbed potential**
- And we can solve:

$$H^0 \psi_n^0 = E_n^0 \psi_n^0$$

where $$H^0 = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V^0(x)$$

- V(x) is the **perturbed potential**
- $\Delta V(x)$ is the **perturbing potential**, or the **perturbation** (your book calls this V')

$$V(x) = V^{\circ}(x) + \Delta V(x)$$

- We want to solve: $H\psi_n = E_n\psi_n$

$$H\psi_n = E_n\psi_n$$

$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x) = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V^{\circ}(x) + \Delta V(x)$$

$$H = H^{\circ} + \Delta V(x)$$

- Let's define $f_n(x)$ so that $\psi_n(x) = \psi_n^{\circ}(x) + f_n(x)$
- Let's define ε_n so that $E_n = E_n^{\circ} + \varepsilon_n$
- Put into the equation above that we want to solve.

$$\Rightarrow \quad (H^\circ + \Delta V)(\psi_n^\circ + f_n) = (E_n^\circ + \varepsilon_n)(\psi_n^\circ + f_n)$$

$$\Rightarrow \quad H^\circ \psi_n^\circ + H^\circ f_n + \Delta V \psi_n^\circ + \Delta V f_n$$

$$= E_n^\circ \psi_n^\circ + E_n^\circ f_n + \varepsilon_n \psi_n^\circ + \varepsilon_n f_n$$

these are equal so they cancel.

$$\Rightarrow \quad (H^\circ - E_n^\circ) f_n + (\Delta V - \varepsilon_n)\psi_n^\circ = (\varepsilon_n - \Delta V) f_n$$

- So far, this is <u>exact</u>.
- Now let's introduce approximations:

$$\Delta V << V^\circ \quad , \quad \varepsilon_n << E_n^\circ \quad , \quad f_n << \psi_n^\circ$$

$$(H^0 - E_n^0) f_n + (\Delta V - \varepsilon_n)\Psi_n^0 = (\varepsilon_n - \Delta V) f_n$$

- The right hand side consist only of multiplication of two *tiny* quantities, whereas the left side has only one tiny quantity in each term
- The basic assumption of **first-order time-independed perturbation theory** is that the right hand side is set to zero:

$$\Rightarrow (H^0 - E_n^0) f_n + (\Delta V - \varepsilon_n)\Psi_n^0 \approx 0$$

$$\Rightarrow (H^0 - E_n^0) f_n \approx (\varepsilon_n - \Delta V)\Psi_n^0$$

- **Our goal is to solve for ε_n**
- So let's expand f_n in the complete set Ψ_n^0

$$f_n(x) = \sum_j a_{nj} \psi_j^0(x)$$

- So the left hand side of: $(H^0 - E_n^0) f_n \approx (\varepsilon_n - \Delta V)\psi_n^0$

becomes:

$$\begin{aligned}(H^0 - E_n^0) f_n &= (H^0 - E_n^0) \sum_j a_{nj} \psi_j^0 \\ &= \sum_j a_{nj} H^0 \psi_j^0 - E_n^0 \sum_j a_{nj} \psi_j^0 \\ &= \sum_j a_{nj} E_j^0 \psi_j^0 - \sum_j a_{nj} E_n^0 \psi_j^0 \\ &= \sum_j a_{nj} (E_j^0 - E_n^0) \psi_j^0\end{aligned}$$

$$\Rightarrow \quad \sum_j a_{nj}\left(E_j^0 - E_n^0\right)\Psi_j^0 \approx \left(\varepsilon_n - \Delta V\right)\Psi_n^0$$

- Now let's multiply by Ψ_n^{0*} and integrate:

$$\sum_j a_{nj}\left(E_j^0 - E_n^0\right)\underbrace{\int \Psi_n^{0*}\Psi_j^0\,dx}_{\substack{=0 \text{ if } n\neq j \\ =1 \text{ if } n=j}} \approx \int \Psi_n^{0*}\left(\varepsilon_n - \Delta V\right)\Psi_n^0\,dx$$

$\Downarrow$ But then

$\left(E_j^0 - E_n^0\right) = 0$!

if $n=j$

So, this is always zero

$$\Rightarrow \quad 0 = \int \psi_n^{0*} (\varepsilon_n - \Delta V) \psi_n^0 \, dx$$

$$= \varepsilon_n \underbrace{\int \psi_n^{0*} \psi_n^0 \, dx}_{\substack{=1 \\ \text{(normalization)}}} - \int \psi_n^{0*} \Delta V \psi_n^0 \, dx$$

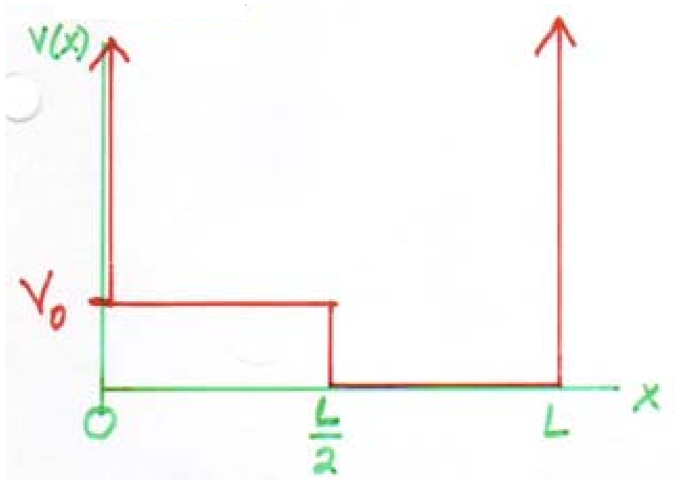
$$\Rightarrow \quad \varepsilon_n = \int \psi_n^{0*} \Delta V \psi_n^0 \, dx$$

$$\varepsilon_n = \underline{\langle \psi_n^0 | \Delta V | \psi_n^0 \rangle}$$

- Given a perturbation $\Delta V(x)$, this gives the first-order correction ε_n to the unperturbed energy E_n^0, and $E_n = E_n^0 + \varepsilon_n$

Example

- Perturbed infinite square well:



$V(x) = V_0 \qquad 0 < x \leq L/2$

$V(x) = 0 \qquad L/2 < x < L$

$V(x) = \infty \qquad \text{elsewhere}$

V_0 is "small".

- The unperturbed eigenfunctions: $\psi_n^0 = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L}$

- The unperturbed energies: $E_n^0 = \frac{n^2 \pi^2 \hbar^2}{2mL^2}$

- The perturbing potential: $\Delta V = V_0 \qquad 0 < x \leq L/2$

- The perturbed energies: $E_n = E_n^0 + \varepsilon_n$

- We want to find ε_n

$$\varepsilon_n = \int \psi_n^{0*} \, \Delta V \, \psi_n^{0} \, dx$$

$$= \frac{2}{L} \int_0^{L/2} V_0 \sin^2 \frac{n\pi x}{L} \, dx = \frac{2V_0}{L} \int_0^{L/2} \left(\frac{1}{2} - \frac{1}{2} \cos \frac{2n\pi x}{L} \right) dx$$

$$= \frac{V_0}{L} \left[x - \frac{L}{2n\pi} \sin \frac{2n\pi x}{L} \right]_0^{L/2} = \frac{V_0}{L} \frac{L}{2}$$

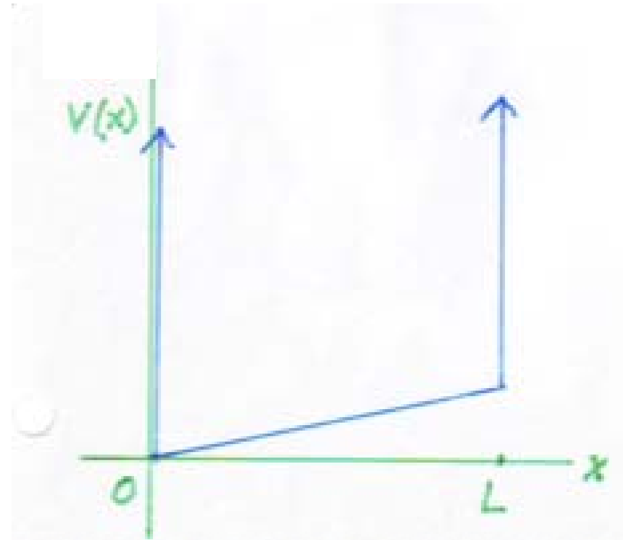
$$\Rightarrow \varepsilon_n = \frac{V_0}{2}$$

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2mL^2} + \frac{V_0}{2}$$

Example

- Assume an infinite square well has a tilted floor.

$$V(x) = \alpha x \qquad 0 < x < L$$



- Also assume αL is small compared to the ground state unperturbed energy
- Find the first order correction to energy eigenvalues.

$$\varepsilon_n = \int \psi_n^{0*} (\Delta V) \psi_n^0 \, dx$$

$$\psi_n^0 = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L}$$

$$\varepsilon_n = \int_0^L \frac{2}{L} \alpha x \sin^2 \frac{n\pi x}{L} \, dx$$

$$= \frac{2\alpha}{L} \int_0^L \frac{1}{2}\left(x - x \cos \frac{2n\pi x}{L}\right) dx$$

$$= \frac{\alpha}{L} \left[\frac{x^2}{2} \Big|_0^L - \int_0^L x \cos \frac{2n\pi x}{L} \, dx \right]$$

$$= \frac{\alpha}{L} \left[\frac{L^2}{2} - \frac{L^2}{4n^2\pi^2} \cos \frac{2n\pi x}{L} \Big|_0^L \right]$$

$$\Rightarrow \varepsilon_n = \frac{\alpha L}{2}$$

- Also note that as $\alpha \to 0$ we get $\varepsilon_n \to 0$ as expected!

The Variational Method

- Method to estimate ground-state energies of potentials
- Make an educated guess at the mathematical form of the ground-state wavefunction
- Requirement:
  - Normalized trial wavefunction needs to satisfy the boundary conditions of the problem
- Need not satisfy the SE!

The Variational Method

- If $\phi(x)$ is trial ground-state wavefunction, the predicted ground-state energy is:

$$E = \langle \varphi | H | \varphi \rangle \qquad H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)$$

- If we know $\Psi_n(x)$, the exact energy eigenfunctions, we can expand $\phi(x)$ like we did last time:

$$\varphi(x) = \sum_n a_n \Psi_n(x) \qquad a_n = \langle \Psi_n | \varphi \rangle$$

- But, we do not know $\Psi_n(x)$.

Trial wavefunction

- $\phi(x)$, the trial ground-state wavefunction, needs to satisfy:
  - Boundary conditions - we'll discuss this in a moment
  - Normalization
    - This is ensured by:

$$\sum_n |a_n|^2 = 1$$

- Let's substitute $\varphi(x) = \sum_n a_n \psi_n(x)$

  into $E = \langle \varphi | H | \varphi \rangle$

$$\langle \varphi | H | \varphi \rangle = \int \left[\sum_n a_n^* \psi_n^* \right] H \left[\sum_m a_m \psi_m \right] dx$$

$$= \sum_n \sum_m a_n^* a_m \underbrace{\int \psi_n^* H \psi_m \, dx}_{\int \psi_n^* E_m \psi_m \, dx}$$

$$\Rightarrow \; = \sum_n \sum_m a_n^* a_m E_m \underbrace{\int \psi_n^* \psi_m \, dx}_{\delta_n^m}$$

$$\Rightarrow \; \langle \varphi | H | \varphi \rangle = \sum_n \sum_m a_n^* a_m E_m \delta_n^m$$

$$\Rightarrow \; = \sum_n a_n^* a_n E_n = \sum_n |a_n|^2 E_n$$

- So

$$E = \sum_n |a_n|^2 E_n$$

- Now, if the true ground state energy is E_0
- And all of the other states must have $E_n \geq E_0$
- So:

$$\sum_n |a_n|^2 E_n \geq \sum_n |a_n|^2 E_0$$

$$\geq E_0 \underbrace{\sum_n |a_n|^2}_{1}$$

$$\sum_n |a_n|^2 E_n \geq E_0$$

$$\Rightarrow \quad E \geq E_0$$

Trial wavefuction

- What does this mean?
  - If $\phi(x)$ is a normalized trial wavefunction for the ground state, then $\langle\phi|\mathbf{H}|\phi\rangle$ sets an upper limit to the ground state energy.
- How do we choose $\phi(x)$?

1. It should be normalizable (It should go to zero at infinitiy)
2. The better your trial wavefunction is, the closer you are to the true ground state energy.

Example

- Let's use the variational method to set an upper limit on the ground state energy of the linear potential:

$$V(x) = \begin{cases} \infty & x < 0 \\ \alpha x & x \geq 0 \end{cases}$$

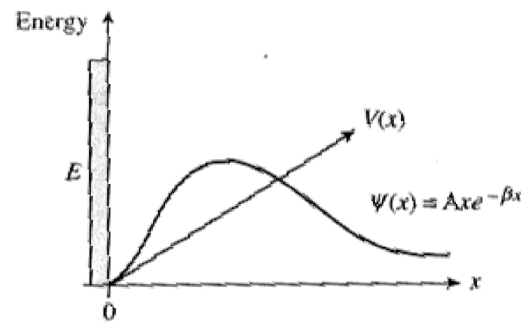


FIGURE 9.9 Hypothetical Linear Potential Ground State.

- Recall, we used the WKB approximation on this same potential (see last lecture or example 9.1)
- Use the trial wavefunction $\varphi(x) = A\,x\,e^{-\beta x}$

  and find β that minimizes $\langle \varphi(x) | H | \varphi(x) \rangle$

- Variation method:

① Normalize

$$\varphi(x) = A x e^{-\beta x}$$

$$A^2 \underbrace{\int_0^\infty x^2 e^{-2\beta x}\, dx}_{\frac{2}{(2\beta)^3}} = 1$$

$$\frac{A^2}{4\beta^3} = 1 \Rightarrow A^2 = 4\beta^3$$

$$E \leq \langle \varphi | H | \varphi \rangle = \int \varphi^*(x) \left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x) \right] \varphi(x)\, dx$$

$$= \int \varphi^*(x)\, H \varphi(x)\, dx$$

② Evaluate $\langle \varphi | H | \varphi \rangle$

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

$$\frac{d^2\varphi}{dx^2} = \frac{d^2}{dx^2}\left[Axe^{-\beta x}\right] = A(\beta^2 x - 2\beta)e^{-\beta x}$$

$$H\varphi(x) = -\frac{\hbar^2}{2m}\left(A(\beta^2 x - 2\beta)e^{-\beta x}\right) + \alpha x \cdot Ax\, e^{-\beta x}$$

$$= Ae^{-\beta x}\left(2\varepsilon\beta - \varepsilon\beta^2 x + \alpha x^2\right)$$

$$\varepsilon = \frac{\hbar^2}{2m}$$

$$E \leq \langle \varphi | H | \varphi \rangle = \int_0^\infty A x e^{-\beta x} \cdot A e^{-\beta x} (2\varepsilon\beta - \varepsilon\beta^2 x + \alpha x^2)\, dx$$

$$= A^2 \Big[2\varepsilon\beta \underbrace{\int_0^\infty x e^{-2\beta x} dx}_{\frac{1}{4\beta^2}} - \varepsilon\beta^2 \underbrace{\int_0^\infty x^2 e^{-2\beta x} dx}_{\frac{2}{(2\beta)^3}} + \alpha \underbrace{\int_0^\infty x^3 e^{-2\beta x} d}_{\frac{6}{(2\beta)^4}}$$

$$E \leq 4\beta^3 \Big[\underbrace{\frac{\varepsilon}{2\beta} - \frac{\varepsilon}{4\beta}}_{\frac{\varepsilon}{4\beta}} + \alpha \cdot \frac{3}{8\beta^4} \Big] = \varepsilon\beta^2 + \frac{3\alpha}{2\beta}$$

③ Minimize $\langle g|H|g\rangle$

- We want to find the minimum Energy, thus dE/dβ =0 and solve for β:

$$\frac{dE}{d\beta} = 0$$

$$\frac{dE}{d\beta} = 2\varepsilon\beta - \frac{3\alpha}{2\beta^2} = 0$$

$$\Rightarrow \quad 2\varepsilon\beta = \frac{3\alpha}{2\beta^2} \quad \Rightarrow \quad \beta^3 = \left(\frac{3\alpha}{4\varepsilon}\right)$$

$$\Rightarrow \quad \beta_{min} = \left(\frac{3\alpha}{4\varepsilon}\right)^{1/3}$$

$$E_{min} = \varepsilon\left(\frac{3\alpha}{4\varepsilon}\right)^{2/3} + \frac{3\alpha}{2}\left(\frac{3\alpha}{4\varepsilon}\right)^{-1/3} = 2.476\,\alpha^{2/3}\varepsilon^{1/3}$$

$$E_0 \leq 2.476\,\alpha^{2/3}\varepsilon^{1/3}$$

Let's compare to WKB Approximation result

- Variational method: $E_0 \leq 2.476\, \alpha^{2/3}\, \varepsilon^{1/3}$

  ~6% higher than exact result

- WKB: $E_0 \sim 2.811 \left(\frac{\alpha \hbar}{\sqrt{2m}} \right)^{2/3} = 2.811\, \alpha^{2/3}\, \varepsilon^{1/3}$

- Exact: $2.338\, \alpha^{2/3}\, \varepsilon^{1/3}$

- Variational method:
  - The closer is the trial wavefunction to the true ground state wavefunction, the closer the evaluated energy will be to the ground state energy.

Summary/Announcements

- Next time: GRE problems/Final review
- HW13 is due on Monday Dec 12: no late HW accepted.

- Final Exam: Wed, December 21, 8:00 am-11:00 am, SEC-209:
  - Closed book with a Letter size formula sheet on both sides
  - Those who achieve more than 20% improvement in percentile score in the Final exam compared to the Midterm will get extra credit: details will be finalized next class.