Online Teaching starts here...

Approximation Methods in QM

(Formulation & Physical Sence)

Module on Approximation Methods

- A formal and exact method
  - Turn TISE into a huge matrix problem
    - convenient for numerical approaches
    - help understand approximation methods better
- Several approximations for allowed energies and eigenstates of time-independent problems
  - Handling TISE that can't be solved analytically

Motivation : Why do we need approximation methods?

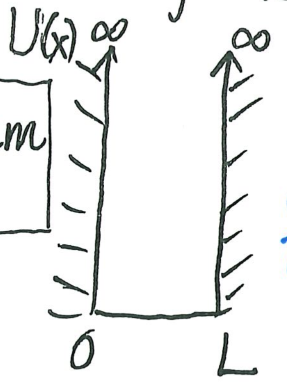
- Very few QM problems can be solved analytically (解析解)

  idealized context ; mathematically involved

- Know the equation (TISE), but can't solve analytically!
  [e.g. all atoms except hydrogen! all molecules, ...!]
- Ways Out ?
  - ~~Give up!~~
  - Numerical Methods
    (approaching exact solutions)
    (精確)
  - Approximation Methods
    (good physical sense, not exact)

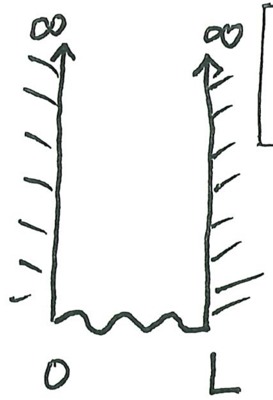
- 1D infinite well

Problem A



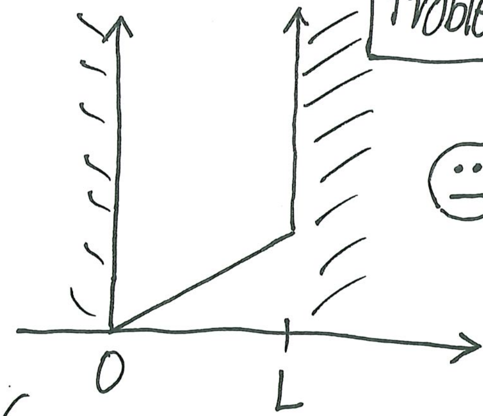
Exactly Solvable

$\{\psi_n^{(A)} \leftrightarrow E_n^{(A)}\}$ KNOWN



Problem B

Can't solve TISE



Problem C

→ Constant $\vec{\mathcal{E}}$-field on a charged particle in a well

Think like a physicist!

- May be... $E_n^{(B)}$ <u>not too far</u> from $\overbrace{E_n^{(A)}}^{\text{known}}$
- Perhaps... $E_n^{(B)} = \underset{\boxed{\text{known}}}{E_n^{(A)}} + \underbrace{\text{Corrections due to bumps in } U(x) \text{ inside the well}}_{\text{"perturbation" (微擾)}}$

and $\psi_n^{(B)} \approx \underset{\boxed{\text{known}}}{\psi_n^{(A)}} + \underbrace{\text{Corrections}}_{\text{"perturbation"}}$

any approximation method for these corrections?

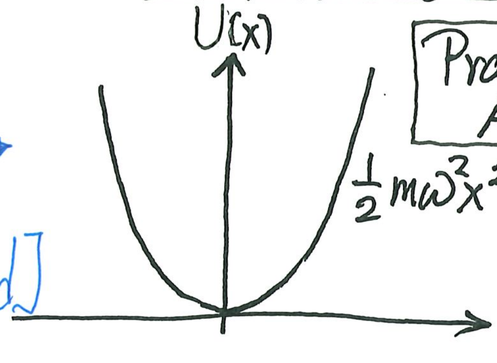
$E_n^{(C)} = E_n^{(A)} + \underbrace{\text{Corrections due to } U_c(x)}$

How to find them?

$\psi_n^{(C)} = \psi_n^{(A)} + \overbrace{\text{Corrections}}$

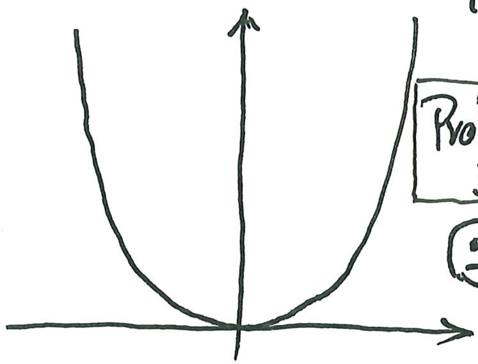
■ Harmonic Oscillator

Analytic Solutions [exactly solved] →



$\boxed{\text{Problem A}}$

$$U(x) = \frac{1}{2}m\omega^2x^2 + \beta x^4$$

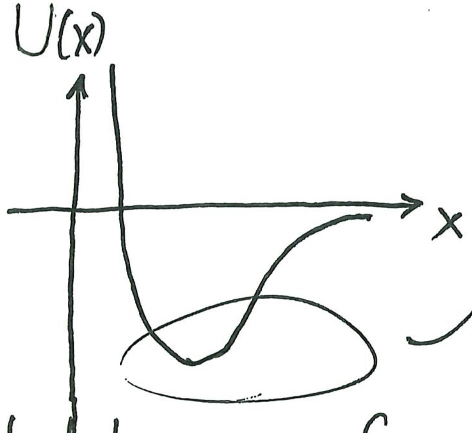


$\boxed{\text{Problem B}}$

Actual U(x) for real physical problems! →

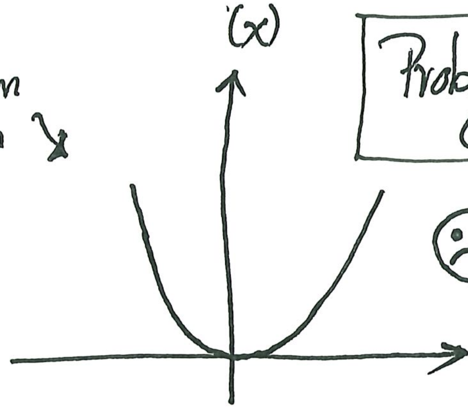
[2 atoms] (molecules)

[2 nucleons] (nuclei)



Potential energy of two atoms separated by a distance x

Zoom in



$\boxed{\text{Problem C}}$

$$E_n^{(B)(C)} \overset{?}{=} E_n^{(A)} + \text{Corrections}$$

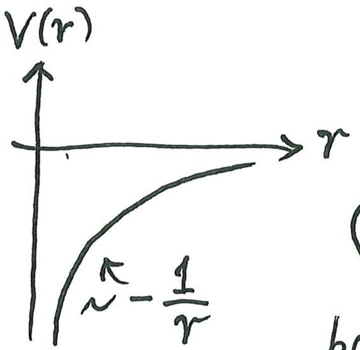
$$\psi_n^{(B)(C)} = \psi_n^{(A)} + \text{Corrections}$$

$\boxed{\text{Q: Systematic Way of getting the corrections?}}$

Analytic solutions

Hydrogen atom

$$\hat{H}_0 = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r}$$



but math is not easy!

Reality is more complicated/interesting

- But orbital angular momentum interacts with spin angular momentum

$$\hat{H} = \underbrace{-\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r}}_{\hat{H}_0} + \underbrace{f(\vec{r})\,\vec{L}\cdot\vec{S}}_{\text{spin-orbit coupling}}$$

an extra term to $\hat{H}_0$ (real stuff!)

$$\boxed{\text{Q: How to solve TISE for } \hat{H}\text{, given that we know } \psi_{n\ell m_\ell m_s} \text{ and } E_n \text{ for } \hat{H}_0\text{?}}$$

More variations on the Hydrogen Atom problem

- $$\hat{H} = \hat{H}_0^{(H\text{-atom})} + \text{extra term(s)}$$

- Zeeman Effect : $\underbrace{\text{Applied } \vec{B}_{ext}}$ (magnetic field)

  extra term(s): $\vec{B}_{ext}$ interacts with magnetic dipole moment(s)

- Absorption : Shine light (EM wave) on H-atom

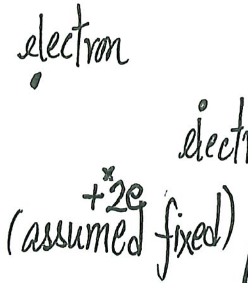
  $$\hat{H} = \hat{H}_0^{(H\text{-atom})} + ez\underbrace{\mathcal{E}_0 \cos\omega t}_{\text{incident light of angular frequency } \omega}$$

  - Time-dependent $\hat{H}$ (harder!)
  - Study effects of $ez\mathcal{E}_0\cos\omega t$ based on $\psi_{n\ell m_\ell}(r,\theta,\phi)$ of $\hat{H}_0$?

Helium atom (next "simplest") [2-electron problem]

$$\hat{H}_{He} = \underbrace{\frac{-\hbar^2}{2m}\nabla_1^2 - \frac{2e^2}{4\pi\varepsilon_0 r_1}}_{\text{electron "1"}} \underbrace{-\frac{\hbar^2}{2m}\nabla_2^2 - \frac{2e^2}{4\pi\varepsilon_0 r_2}}_{\text{electron "2"}} + \underbrace{\frac{e^2}{4\pi\varepsilon_0 |\vec{r}_1 - \vec{r}_2|}}_{\text{Coulomb repulsion between electrons}}$$

Make the problem insolvable (∵ separation of variables won't work)



No exact solutions! ☹

Don't feel bad! No one can solve it analytically!

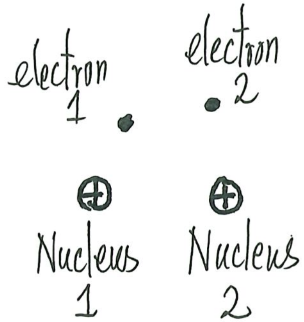
Q: Can we understand helium and other atoms, based on what we learned from the hydrogen atom problem? Periodic Table?

Is it possible to approximate the 2-electron problem by a single-electron problem and how?

- How about other atoms?
- Getting into Quantum Chemistry!

How about molecules?

Simplest molecule H_2 (2 nuclei + 2 electrons)



$$\hat{H} = \underbrace{-\frac{\hbar^2}{2M}\nabla^2_{\vec{R}_1} - \frac{\hbar^2}{2M}\nabla^2_{\vec{R}_2}}_{\text{k.e. of nuclei}} \underbrace{-\frac{\hbar^2}{2m}\nabla^2_{\vec{r}_1} - \frac{\hbar^2}{2m}\nabla^2_{\vec{r}_2}}_{\text{k.e. of electrons}}$$

$$\underbrace{-\frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{|\vec{r}_1-\vec{R}_1|} + \frac{1}{|\vec{r}_1-\vec{R}_2|} + \frac{1}{|\vec{r}_2-\vec{R}_1|} + \frac{1}{|\vec{r}_2-\vec{R}_2|}\right)}_{\text{p.e. of electrons with nuclei}}$$

$$+\frac{e^2}{4\pi\varepsilon_0}\left(\underbrace{\frac{1}{|\vec{r}_1-\vec{r}_2|}}_{\text{el-el repulsion}} + \underbrace{\frac{1}{|\vec{R}_1-\vec{R}_2|}}_{\text{nucleus-nucleus repulsion}}\right)$$

- No problem writing down TISE
- But TISE cannot be solved analytically

Question:

Can we understand approximately the formation of chemical bond in H_2 based on what we know about the hydrogen atom $\psi_{n l m_\ell}$?

Summary

- Many important real-life QM problems can't be solved analytically
- They often have the form

$$\underset{\boxed{\text{real problem}}}{\hat{H}} = \underset{\substack{\text{idealized}\\ \text{but has the}\\ \text{merit of solvable}}}{\hat{H}_0} + \underbrace{\hat{H}'}$$

This is the actual physical problem

- extra term that makes $\hat{H}$ not analytically solvable
- methods needed to treat $\hat{H}'$ either exactly OR, more often, approximately

- We will discuss a few approximation methods

The art is to explore...

How far can we understand atoms, molecules, nuclei, solids, which are intrinsically many-particle QM problems, by avoiding the complexity of solving many-particle problems?

This is Street-Fighting QM with elegance!

It will be fun!