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 $\underbrace{\text{analytically}}$ (解析解)

  idealized context ; mathematically involved

- Know the equation (TISE), but can't solve analytically!
  [e.g. all atoms except hydrogen! all molecules, ...!]

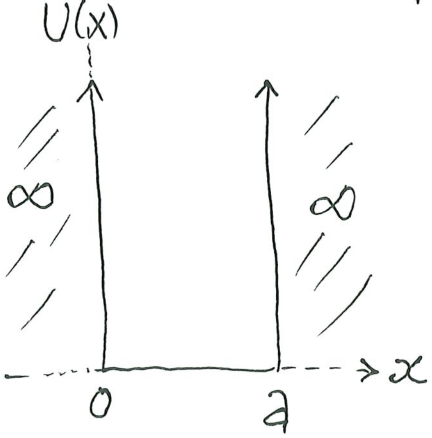
- Ways Out ?

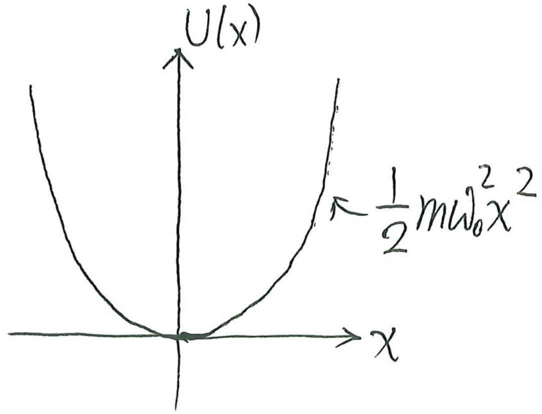
~~Give up!~~

Numerical Methods
(approaching exact solutions)
(精確)

Approximation Methods
(good physical sense, not exact)

A few problems with exact solutions (and not so difficult)





$$\psi_n(x) = \sqrt{\frac{2}{a}}\,\sin\left(\frac{n\pi}{a}x\right)$$

$$E_n = n^2\frac{\pi^2\hbar^2}{2ma^2}$$

and 2D, 3D versions of Particle-in-a-box problem

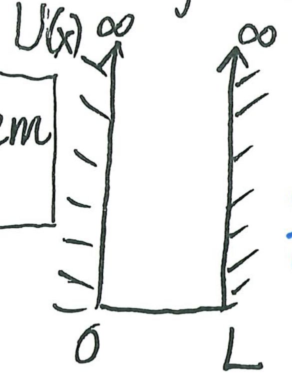
$$\psi_n(x) = \underset{\text{normalization}}{A_n}\ \underset{\text{a Gaussian}}{e^{-\frac{m\omega_0}{2\hbar}x^2}}\ \underbrace{H_n\left(\sqrt{\frac{m\omega_0}{\hbar}}\,x\right)}_{\text{Hermite Polynomial}}$$

$$E_n = \left(n+\frac{1}{2}\right)\hbar\omega_0$$

and 2D, 3D versions of harmonic Oscillator problems

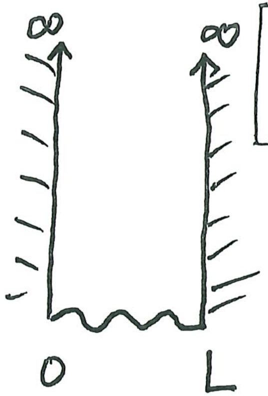
- 1D infinite well

Problem A



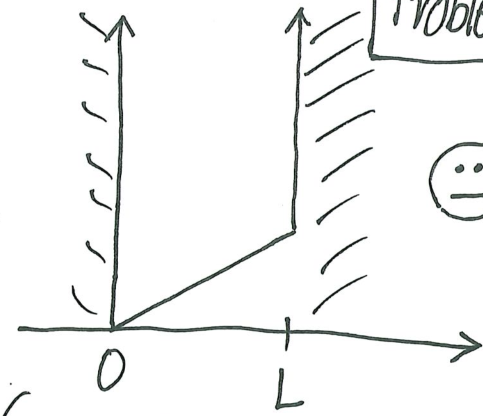
Exactly Solvable

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

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

$\boxed{\text{any approximation method for these corrections?}}$

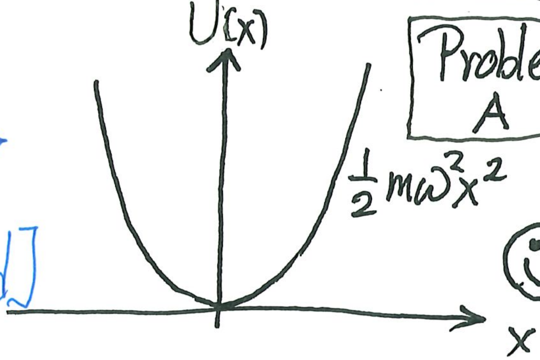
$E_n^{(c)} = E_n^{(A)} + \underbrace{\text{Corrections due to } U_c(x)}$

How to find them?

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

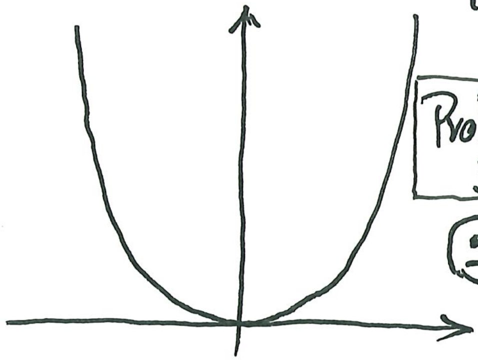
▪ Harmonic Oscillator

Analytic Solutions [exactly solved] →



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

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

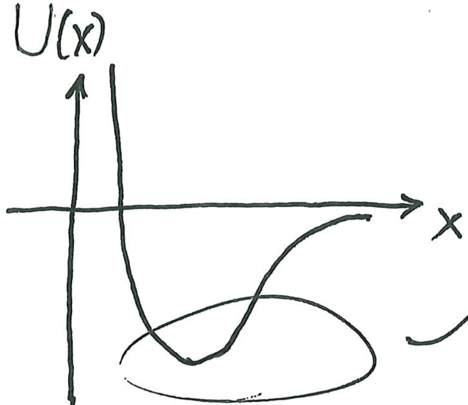


$\boxed{\text{Problem B}}$

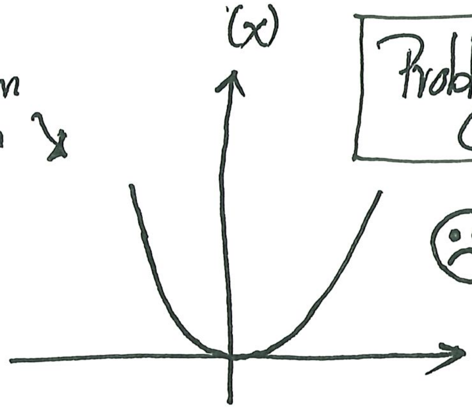
Actual U(x) for real physical problems ! →

[2 atoms] (molecules)

[2 nucleons] (nuclei)



Zoom in



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

Potential energy of two atoms separated by a distance x

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

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

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

Hydrogen Atom (almost correct version)

$$U(r) = \frac{-e^2}{4\pi\varepsilon_0}\frac{1}{r} \qquad \left(\text{3D problem, } \underset{\text{general}}{U(\vec{r})} = \underbrace{U(r,\theta,\phi) = \underset{\text{special case}}{U(r)}}_{\text{spherically symmetric}}\right)$$

$$\left[\frac{-\hbar^2}{2m}\nabla^2 + U(r)\right]\psi(\vec{r}) = E\,\psi(\vec{r})$$

$$\psi_{n\ell m_\ell}(r,\theta,\phi) = R_{n\ell}(r)\,\underbrace{Y_{\ell m_\ell}(\theta,\phi)}_{\text{Spherical Harmonics}}$$

[not including spin]

$R_{n\ell}$: related to Associated Laguerre Polynomials

Spherical Harmonics: $\ell = 0, 1, \cdots$ (up to $n-1$), $m_\ell = \ell, \ell-1, \cdots, -\ell$

$$E = E_n = \frac{-me^4}{2(4\pi\varepsilon_0)^2\hbar^2}\cdot\frac{1}{n^2}$$

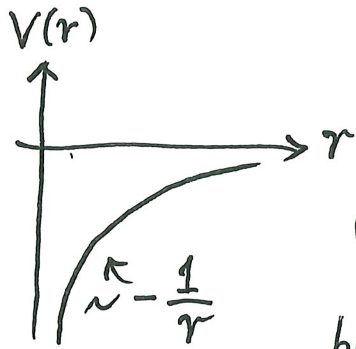
(independent of ℓ and m_ℓ)
high degeneracy

How about 2D "Hydrogen" atom?

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!)

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

[+] Much modern-time condensed matter physics relies on spin-orbit interaction, as a way to get a magnetic field without buying a magnet.

More variations on the Hydrogen Atom problem

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

- Zeeman Effect : $\underbrace{\text{Applied } \vec{B}_{ext}}_{\text{extra term(s): } \vec{B}_{ext} \text{ interacts with magnetic dipole moment(s)}}$ (magnetic field)

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

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

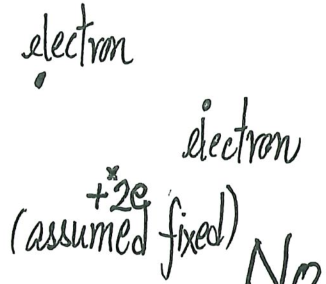
$$\hat{H} = \hat{H}_0^{(H\text{-atom})} + e z \underbrace{\mathcal{E}_0 \cos \omega t}_{\text{incident light of angular frequency } \omega}$$

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

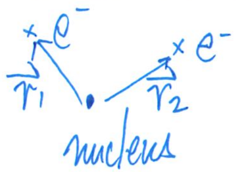
> Is it possible to approximate the 2-electron problem by a single-electron problem and how?

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

<u>Aside</u>: How to write down the Hamiltonian that goes into TISE?

$$\boxed{\text{Think Classical, then Go Quantum!}}$$

He atom



$H_{\text{(think classical)}}$ = k.e. of electron 1 + k.e. of electron 2
+ p.e. of electron 1 (seeing the nucleus)
+ p.e. of electron 2 (seeing the nucleus)
+ p.e. of el-el interaction

$$= \frac{p_1^2}{2m} + \frac{p_2^2}{2m} - \frac{2e^2}{4\pi\varepsilon_0 r_1} - \frac{2e^2}{4\pi\varepsilon_0 r_2} + \frac{e^2}{4\pi\varepsilon_0 |\vec{r}_1 - \vec{r}_2|}$$

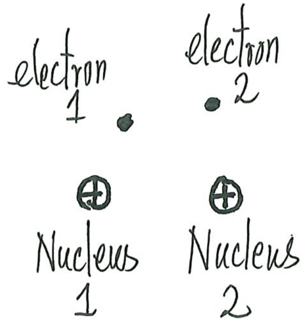
Go Quantum

$$\hat{H}_{He} = -\frac{\hbar^2}{2m}\nabla^2_{\vec{r}_1} - \frac{\hbar^2}{2m}\nabla^2_{\vec{r}_2} - \frac{2e^2}{4\pi\varepsilon_0 r_1} - \frac{2e^2}{4\pi\varepsilon_0 r_2} + \frac{e^2}{4\pi\varepsilon_0 |\vec{r}_1 - \vec{r}_2|}$$

$\hat{H}_{He}\,\psi(\vec{r}_1, \vec{r}_2) = E\,\psi(\vec{r}_1, \vec{r}_2)$ gives allowed energy of a $\underbrace{\text{Helium Atom}}_{\text{whole atom}}$.

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 $\psi_{n\ell m_\ell}$?

Summary

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

$$\hat{H} = \hat{H}_0 + \underbrace{\hat{H}'}$$

$\boxed{\text{real problem}}$

This is the actual physical problem

idealized but has the merit of solvable

- 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!