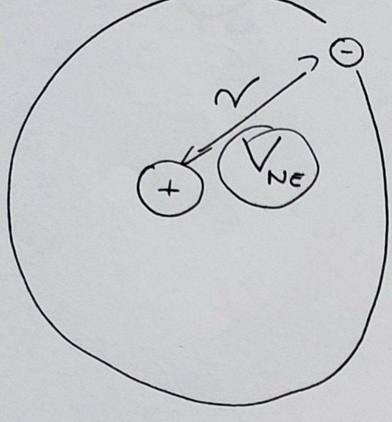
Approximation Methods

1. Variational Principle
   → Vary Ψ
2. Perturbation Theory
   → Vary $\hat{H}$

The problem:

H:



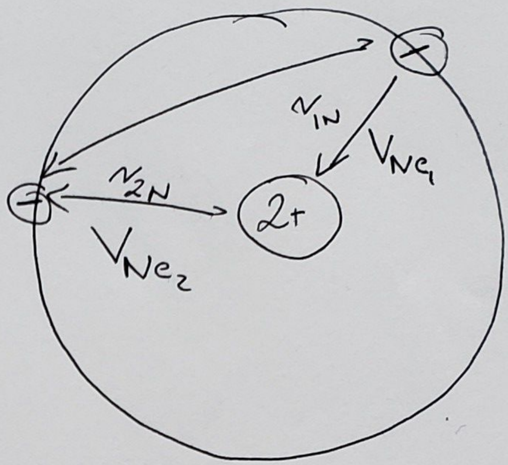
$$\hat{H} = \underbrace{-\frac{\hbar^2}{2m_e}\nabla^2}_{K.E.} \underbrace{- \frac{e^2}{4\pi\varepsilon_0 r}}_{P.E.}$$

- 1-electron system (1-body problem)

→ We can solve analytically $\left(\frac{1}{r}\right)$

$$\hat{H}\Psi_{nlm}(r) = E_n \Psi_{nlm}(r)$$

He:



$$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{e^2}{4\pi\varepsilon_0 r_{1N}}$$
$$-\frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{e^2}{4\pi\varepsilon_0 r_{2N}}$$
$$+\frac{e^2}{4\pi\varepsilon_0 r_{12}}$$

$$\hat{H}\Psi(r_1, r_2) = E\Psi(r_1, r_2)$$

Because of e-e:

→ $\Psi(r_1, r_2)$ →

→ E →

Problem:
S.E.:

1. Variational Principle

Let's ASSUME:

$$\Psi_0$$

Let's introduce new well-behaved function φ

$$E_\varphi =$$

$$E_\varphi \geqslant E_0$$

$$(\text{if } \varphi = \Psi_0 \Rightarrow E_\varphi = E_0)$$

- The φ could have any form.
- We can postulate:

$$E\varphi \underbrace{(\alpha, \beta, \gamma \dots)}_{\text{Variational parameter}} \geq E_0$$

H-atom

① $\varphi = e^{-\alpha r}$

② $\varphi = e^{-\alpha r^2}$

| trial functions

① ~~Normalization~~

Denominator (not normalized)

$$\int_0^{+\infty} \varphi^* \varphi\, r^2 dr \int_0^{\pi} \sin\Theta\, d\Theta \int_0^{2\pi} d\varphi =$$

Nominator

$$\hat{H} = -\frac{\hbar^2}{2m_e r^2}\left(\frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\right)\right) - \frac{e^2}{4\pi\varepsilon_0 r}$$

$$4\pi \int_0^{+\infty} \varphi^* \hat{H} \varphi\, r^2 dr = 4\pi \int_0^{+\infty} e^{-\alpha r} \hat{H} e^{-\alpha r} r^2 dr =$$

$$\boxed{\int_0^{+\infty} r^n e^{-\alpha r} dr = \frac{n!}{\alpha^{n+1}}}$$

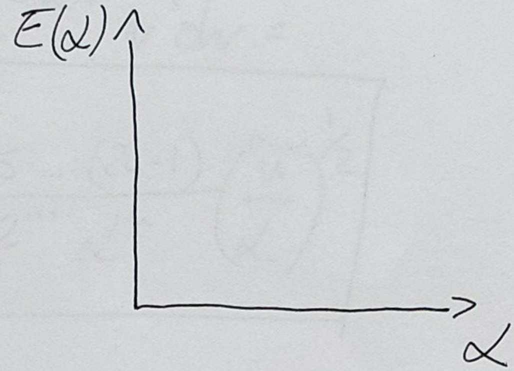
$$= -\frac{4\pi\hbar^2}{2m_e} \int_0^{+\infty} e^{-\alpha r}\left(-2\alpha r e^{-\alpha r} + \alpha^2 r^2 e^{-\alpha r}\right) dr$$

$$-\frac{e^2}{\varepsilon_0} \int_0^{+\infty} r e^{-2\alpha r} dr =$$

$$= \frac{4\pi\hbar^2\alpha}{m_e} \int_0^{+\infty} r e^{-2\alpha r} dr - \frac{2\pi\hbar^2\alpha^2}{m_e} \int_0^{+\infty} r^2 e^{-2\alpha r} dr - \frac{e^2}{\varepsilon_0} \int_0^{+\infty} r e^{-2\alpha r} dr =$$

$=$

$$E(\alpha) = \frac{N}{D} = \frac{\hbar^2 \alpha^2}{2m_e} - \frac{e^2 \alpha}{4\pi\varepsilon_0}$$



$$\frac{dE}{d\alpha} =$$

$$\alpha =$$

$$E(\alpha) =$$

$$\Psi_{(r)} =$$

// Ground state H-atom

② Trial function $\varphi = e^{-\alpha r^2}$

II): $4\pi \int e^{-\alpha r^2} e^{-\alpha r^2} r^2 \, dr =$

$$\boxed{\int_0^{+\infty} r^{2n} e^{-\alpha r^2} \, dr = \frac{1\cdot 3\cdot 5 \cdot \ldots \cdot (2n-1)}{2^{n+1}\alpha^{n}} \left(\frac{\pi}{\alpha}\right)^{1/2}}$$

N: $4\pi \int_0^{+\infty} \varphi^* \hat{H} \varphi \, r^2 dr = 4\pi \int_0^{+\infty} e^{-\alpha r^2} \left(-\frac{\hbar^2}{2m_e r^2} \frac{d}{dr}\left(r^2 \frac{\partial}{\partial r} \right) - \frac{e^2}{4\pi\varepsilon_0 r} \right) e^{-\alpha r^2} r^2 dr =$

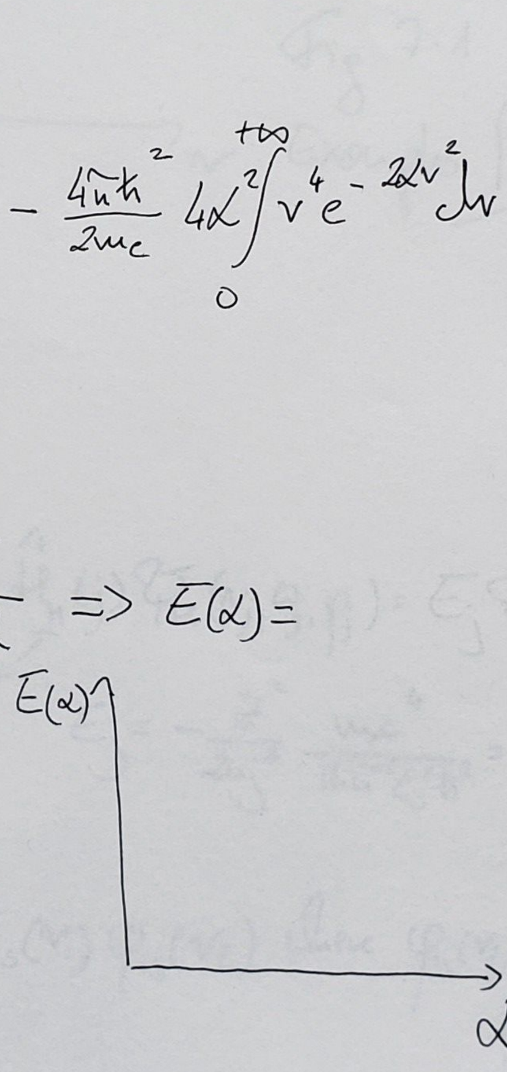
$=$

$$= + \frac{4\pi\hbar^2}{2m_e} \cdot 6\alpha \int_0^{+\infty} r^2 e^{-2\alpha r^2} dr - \frac{4\pi\hbar^2}{2m_e} 4\alpha^2 \int_0^{+\infty} r^4 e^{-2\alpha r^2} dr - \frac{e^2}{\varepsilon_0} \int_0^{+\infty} r e^{-2\alpha r^2} dr \overset{*}{=}$$

$$\boxed{\int_0^{+\infty} r^{2n+1} e^{-\alpha r^2} \, dr = \frac{n!}{2\alpha^{n+1}}} \qquad \overset{*}{=}$$

$$= \frac{3\hbar^2 \pi^{3/2}}{4 m_e (2\alpha)^{1/2}} - \frac{e^2}{4\varepsilon_0 \alpha} \Rightarrow E(\alpha) =$$

$\frac{dE(\alpha)}{d\alpha} =$



$\alpha =$

$$E(\alpha_0) = \frac{3\hbar^2}{2m_e}\cdot\frac{m_e^2 e^4}{18\pi^3\varepsilon_0^2\hbar^4} - \frac{e^2}{(\pi)^{3/2}\sqrt{2}\varepsilon_0}\cdot\frac{m_e e^2}{3\sqrt{2}(\pi)^{3/2}\varepsilon_0\hbar^2} =$$

$$= -\frac{4}{3\pi}\left(\frac{m_e e^4}{16\pi^2\varepsilon_0^2\hbar^2}\right) = -0.424\ [He]$$

$$\varphi = \frac{8}{3\sqrt{2}\pi}\frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2} e^{-\left(\frac{8}{9\pi}\right)\frac{r^2}{a_0^2}}$$

$$E_0 = -\frac{1}{2}[He] < -0.424\,[He] = E_\varphi$$

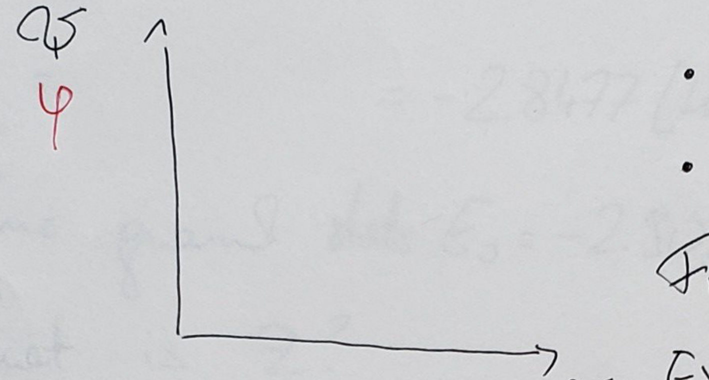


Fig 7-1

Examples $\boxed{7.1 - 7.3}$

Helium Atom:

$\hat{H} =$

We know that: $\hat{H}_H(j)\Psi_H(r_j,\theta_j,\varphi_j) = E_j\Psi_H(r_j,\theta_j,\varphi_j)$ $j = 1 \text{ a } 2$

H-like

$$E_j = -\frac{Z^2}{2n_j^2}\frac{m_e e^4}{16\pi^2\varepsilon_0^2\hbar^2} = -\frac{Z^2}{2n_j^2}[He]$$

Let's assume:

$$\Psi_0(r_1,r_2) = \varphi_{1s}(r_1)\,\varphi_{1s}(r_2) \text{ where } \varphi_{1s}(r_j) = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-\frac{Zr_j}{a_0}}$$

$j = 1, 2$

W-f is normalized.

$$E = \int \varphi_{1s}^*(\vec{r}_1)\varphi_{1s}^*(\vec{r}_2)\,\hat{H}\,\varphi_{1s}(\vec{r}_1)\varphi_{1s}(\vec{r}_2)\,d\vec{r}_1\,d\vec{r}_2 =$$

Problems 7.30 - 7.32

($\hat{H}_H(j)$ is trivial)

$\left(\frac{e^2}{4\pi\varepsilon_0|r_1-r_2|}\right.$ is hard)

$$E(Z) = Z^2 - \frac{27}{8}Z\ [H_0]$$

$$\frac{dE}{dZ} =$$

$E_{Z_0} = \quad = -2.8477\ [H_e]$

True ground state $E_0 = -2.9037 H_e$

V.P. holds

What is Z?

$Z = \quad \longrightarrow$

In Practice:

Fig 7-2

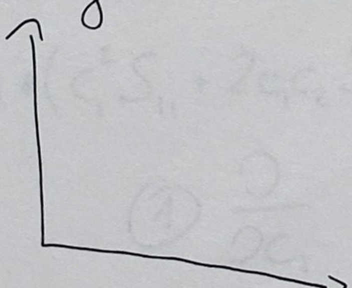
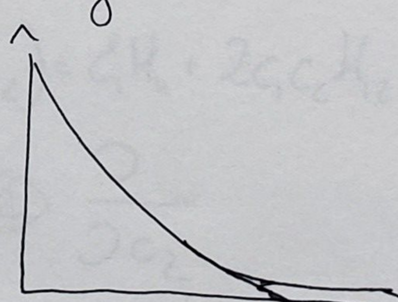


Fig 11-2



A true wavefunction is approximated by multiple basis functions!

$$\Phi = \sum_{i=1}^{N} c_i \varphi_i = \sum_{i=1}^{N} c_i e^{-\alpha_i r^2}$$

Secular Equation / Intro to Hückel Method

$N=2$ $\qquad \Phi =$

① $\mathbb{1}$: $\int (c_1\varphi_1^* + c_2\varphi_2^*)(c_1\varphi_1 + c_2\varphi_2)\, d\tau \overset{*}{=}$

$\boxed{S_{ij} = \int \varphi_i^* \varphi_j \, d\tau}$ $\qquad \overset{*}{=}$

overlap integral

② N: $\int (c_1\varphi_1^* + c_2\varphi_2^*)\hat{H}(c_1\varphi_1 + c_2\varphi_2)\, d\tau \overset{*}{=}$

$\boxed{H_{ij} = \int \varphi_i^* \hat{H} \varphi_j \, d\tau}$ $\qquad \overset{*}{=}$

$E(c_1, c_2) =$

$$E(c_1c_2) * (c_1^2 S_{11} + 2c_1c_2 S_{12} + c_2^2 S_{22}) = c_1^2 H_{11} + 2c_1c_2 H_{12} + c_2^2 H_{22}$$

① $\frac{\partial}{\partial c_1}$ $\qquad$ ② $\frac{\partial}{\partial c_2}$

① $\frac{\partial E}{\partial c_1}(c_1^2 S_{11} + 2c_1c_2 S_{12} + c_2^2 S_{22}) + E(2c_1 S_{11} + 2c_2 S_{12}) = 2c_1 H_{11} + 2c_2 H_{12}$

② .

$c_1(H_{11} - ES_{11}) + c_2(H_{12} - ES_{12})$

$c_1(H_{12} - ES_{12}) + c_2(H_{22} - ES_{22}) = 0$

in matrix notation:

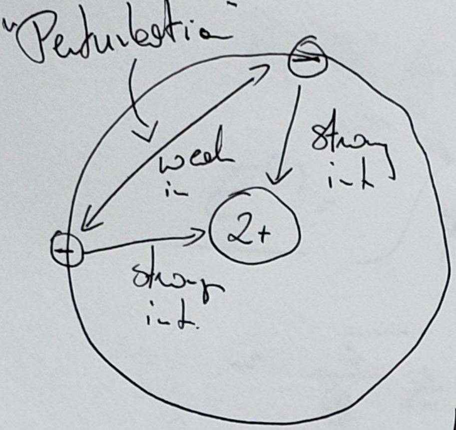
The non-trivial solution exist only for:

Secular Determinant -> Secular Equation for E in degree of the determinant's order.
(Here -> 2^{nd} degree)

- if we know (S_{ij}, H_{ij}) -> easy to solve for
- From E -> you can determine c_i's.

Read the example (particle in a box)

Perturbation Theory:



$$\hat{H} = \underset{\swarrow}{\hat{H}_0} + \underset{\searrow}{\hat{H}_1}$$

Also

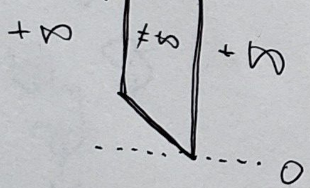
$$\Psi = \boxed{\Psi^{(0)}} + \overline{\Psi^{(1)} + \Psi^{(2)} + \dots}$$

$$E = \boxed{E^{(0)}} + \underline{E^{(1)} + E^{(2)} + \dots}$$

Unperturbed solution — Corrections

Anharm Osc:

Box with slanted potential



First Order P.T. for Helium Atom:

$$E = E^{(0)} + E^{(1)}$$

$$\Psi = \Psi^{(0)} + \Psi^{(1)}$$

$$\psi^{(0)} = \cancel{\frac{1}{\pi}\left(\frac{2}{a_0}\right)^{3/2} e^{-2r/a_0}}$$

$$\hat{H} = \hat{H}_H(1) + \hat{H}_H(2) + \hat{H}_{12}$$

$\Phi_0(r_1, r_2) = \varphi_{0,1s}(r_1) \cdot \varphi_{0,1s}(r_2)$ / What is missing?

$\hat{H}_0 \Rightarrow E_0^{(0)}(1) + E_0^{(0)}(2) = -2 \cdot \frac{Z^2}{2} [He] = -4 [He]$

$\underline{E^{(1)}} = \int \varphi_{1s}^*(\vec{r}_1) \varphi_{1s}^*(\vec{r}_2) \frac{e^2}{4\pi\varepsilon_0 |\vec{r}_{12}|} \varphi_{1s}(\vec{r}_1) \varphi_{1s}(\vec{r}_2) \, d\vec{r}_1 \, d\vec{r}_2 =$

$= \frac{5}{8} Z = \frac{5}{4} [He]$ (positive:)

$E = E^{(0)} + E^{(1)} = -2.75 [He]$

(we don't correct ~~doing~~ the $\Phi^{(1)}$ in 1st order)

V.P. and P.T. are two very different things applicable to different problems

V.P. → vary Φ → Φ → E change is continuous

P.T. → vary $\hat{H}$ ⇒ E change is discrete

Because of that, P.T. does not obey V.P.

$E^{(0)} + E^{(1)} + E^{(2)} = -2.910 < -2.9033$ (Exact)