$$H = -\frac{\hbar^2}{2\mu}\sum_{i=1}^{N}\Delta_i - \sum_i \frac{Ze^2}{r_i} + \sum_{i<j}\frac{e^2}{r_{ij}}$$

COULOMB INTERACTION

$$H^0 = -\frac{\hbar^2}{2\mu}\sum_{i=1}^{N}\Delta_i - \sum_{i=1}^{N}\frac{Ze^2}{r_i} \equiv \sum_i^N h(i)$$

N. HYDROGEN ATOMS (INDEPENDENT, WITHOUT INTERACTION!)

EXAMPLE: $N=2$

$H^0 = h(1)+h(2) \Rightarrow$

$$\psi^0(1,2) = \psi_m(1)\psi_m(2)$$

PRODUCT OF ONE-ELECTRON FUNCTIONS

$$H^0\psi^0 = E^0\psi^0$$

$$(h(1)+h(2))\psi_m(1)\psi_m(2) = \psi_m(2)h(1)\psi_n(1) + \psi_n(1)h(2)\psi_m(2)$$

$$= E^0\psi_m(1)\psi_m(2) \;/\; \psi_n(1)\psi_m(2)$$

$$\frac{h(1)\psi_m(1)}{\psi_n(1)} = -\frac{h(2)\psi_m(2)}{\psi_m(2)} + E^0 = E_n$$

(SEPARATION OF VARIABLES)

INDEPENDENT

$$h(1)\psi_m(1) = E_n\psi_m(1)$$
$$h(2)\psi_m(2) = \underbrace{(E^0 - E_n)}_{E_m}\psi_m(2)$$

$$E^0 = E_n + E_m$$

$$\psi^0 = \psi_n(1)\psi_m(2)$$

ONE-ELECTRON SCHEME!

STILL EACH ELECTRON IS DESCRIBED BY OWN FUNCTION!

SINGLE ELECTRON APPROXIMATION

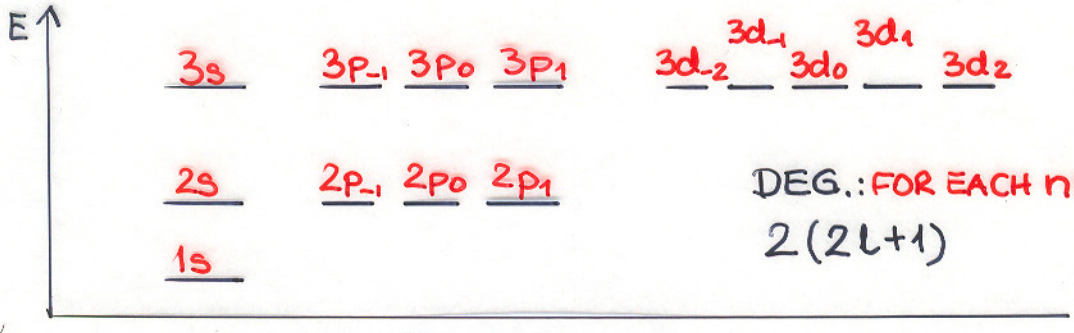
SINCE COULOMB INTERACTION IS TOO STRONG TO BE NEGLECTED!

HOW TO IMPROVE THE RESULTS? INCLUDE AT LEAST PART OF COULOMB INTERACTION

CENTRAL FIELD APPROXIMATION

ENERGY SCHEME

ONE-ELECTRON SYSTEM



$$H_H = -\frac{\hbar^2}{2\mu}\nabla^2 + V(r)$$

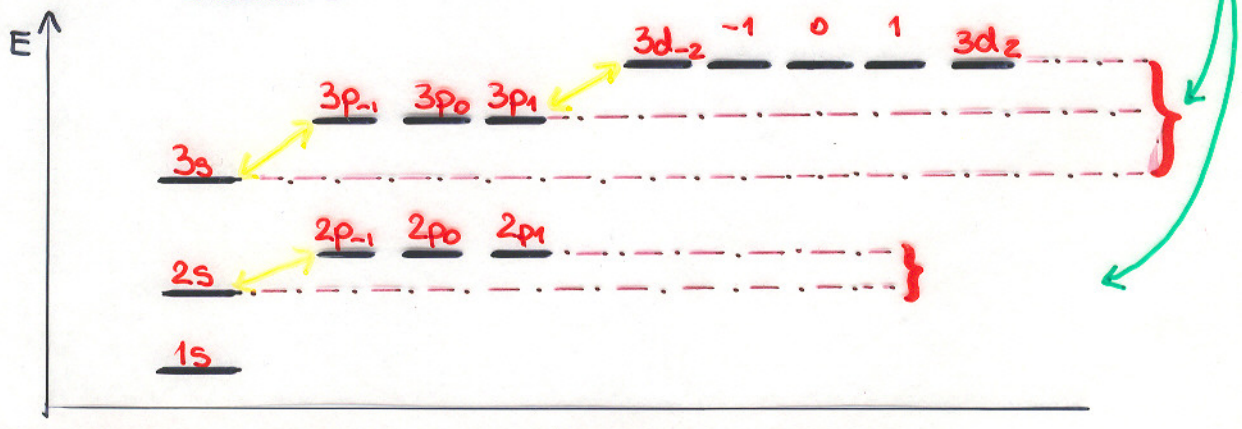
⇓

MANY-ELECTRON SYSTEM

$$H = \sum H_H + \sum_{i<j} \frac{e^2}{r_{ij}}$$

COULOMB INTERACTION

SUM OF ONE-ELECTRON OPERATORS



CENTRAL-FIELD APPROXIMATION

$$H = \sum_i^N \left(-\frac{\hbar^2}{2\mu}\nabla_i^2 + U(r_i)\right) + \sum_{i<j}^N \frac{e^2}{r_{ij}} - \sum_i^N U(r_i)$$

$\hat{\mathcal{H}}(i)$ — NEW POTENTIAL

$\mathcal{H}(i) = H_H$ WITH $V(r)$ REPLACED BY $U(r)$

THEORY OF ATOMS ⇒ FUTURE

HOW TO CONSTRUCT N-ELECTRON WAVE FUNCTION OF GOOD SYMMETRY ?

DIFFERENT LEVELS OF QUANTIZATION
FUNCTIONS OF GOOD SYMMETRY

PHYSICAL REALITY

$$H = \underbrace{-\frac{\hbar^2}{2\mu}\sum_{i=1}^{N}\nabla_i^2 - \sum_{i=1}^{N}\frac{Ze}{r_i}}_{\sum_i h(i)} + \sum_{i<j}^{N}\frac{e^2}{r_{ij}} \qquad H_1$$

2 : IMPOSSIBLE TO SEPARATE COORDINATES

CENTRAL FIELD APPROXIMATION

$$H = -\frac{\hbar^2}{2\mu}\sum_{i=1}^{N}\nabla_i^2 + \sum_i U'(r_i)$$

$$U'(r_i) = U(r_i) - \frac{Ze}{r_i}$$

$n\ell$ FOR EACH ELECTRON

$\hat{s}_1, \hat{s}_2, \hat{\ell}_1, \hat{\ell}_2$ SPIN-ORBITALS $\Rightarrow$

$(n_1\ell_1)(n_2\ell_2)\ldots(n_N\ell_N)$ ELECTRONIC CONFIGURATION (*)

SLATER DETERMINANT $|n_i s m_s \ell m_\ell\rangle$

LINEAR COMB.

$$+\sum_{i<j}^{N}\frac{e^2}{r_{ij}} - \sum_i^N U(r_i)$$

"ELECTRON CORRELATION"

$\hat{S}^2\ \hat{S}_z\ \hat{L}^2\ \hat{L}_z$

SPECTROSCOPIC TERMS $|\gamma S M_S L M_L\rangle$: ^{2S+1}L

$(2L+1)(2S+1)$ DEG.

MATRIX ELEM.

LINEAR COMB.

LEVELS FOR S AND L: $|\gamma J M_J\rangle \equiv |\gamma S L J M_J\rangle$

$(2J+1)$ DEG.

MATRIX ELEM.

H_2

$$+\sum_i \xi_i(r)\,\vec{s}_i\cdot\vec{\ell}_i$$

$\hat{J}^2, \hat{J}_z$

SPIN-ORBIT INTERACTION (WEAK)

$$\det\{s m_s \ell m_\ell\} \xrightarrow{\text{LINEAR COMBIN.}} |\gamma S M_S L M_L\rangle \xrightarrow{\text{LINEAR COMBIN}} |\gamma S L J M_J\rangle$$

"DEEPEST QUANT."

TRANSFORMATION

TRANSFORMATION

SMALLEST DIMENSION OF SECULAR DETERM. IT BREAKS UP

(*) Eu^{3+}: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 4f^6$

CLOSED SHELLS; OCCUPATION OF ALL QUANTUM NUMBERS OF SPATIAL AND SPIN ORIENTATION

EQUIVALENT OUTSIDE C.S.

det: $|3^+ 3^- 2^+ 2^- 1^+ 1^-|$, $|3^+ 2^+ 1^+ 0^+ -1^+ -2^+|\ldots$ $n=4$ $\ell=3$

$m_\ell = -3, -2, \ldots 3$

PERTURBATION THEORY

ALWAYS DEFINED FOR GIVEN HAMILTONIAN

$$H = H_0 + \lambda V$$

VALID ONLY IF SUCH PARTITIONING IS POSSIBLE

H_0: ZEROTH ORDER HAMILTONIAN, UNPERTURBED

V: PERTURBATION

λ: PARAMETER, ASSUMED TO BE SMALL, MEASURE OF THE SIZE OF PERTURBATION

MEASURE OF THE SMALLNESS OF THE PERTURBATION

CONDITIONS:

1. IT IS POSSIBLE TO SOLVE IN AN EXACT WAY

$$H_0 \psi_n^0 = E_n^0 \psi_n^0$$

2. PERTURBATION IS „SMALL"

THE WAVEFUNCTIONS AND THE ENERGY ARE EXPANDED IN POWERS OF λ:

$$\psi_k = \psi_k^0 + \lambda \psi_k^{(1)} + \lambda^2 \psi_k^{(2)} + \dots$$

CORRECTIONS TO THE WAVEFUNCTION

$$E_k = E_k^0 + \lambda E_k^{(1)} + \lambda^2 E_k^{(2)} + \dots$$

CORRECTIONS TO THE ENERGY

$$H\psi_k = E_k \psi_k$$

HOW TO FIND (EVALUATE) CORRECTIONS OF CERTAIN ORDER?

$$(H_0 + \lambda V)(\psi_k^0 + \lambda \psi_k^{(1)} + \lambda^2 \psi_k^{(2)} + \dots) =$$

$$(E_k^0 + \lambda E_k^{(1)} + \lambda^2 E_k^{(2)} + \dots)(\psi_k^0 + \lambda \psi_k^{(1)} + \lambda^2 \psi_k^{(2)} + \dots)$$

THE TERMS AT EACH POWER OF λ MUST BE SEPARATELY EQUAL

$$\sum_i \lambda^i (H_0 + \lambda V) \psi_k^{(i)} = \sum_{ij} \lambda^{i+j} E_k^{(j)} \psi_k^{(i)}$$

λ^0: $H_0 \psi_k^0 = E_k^0 \psi_k^0$ ZEROTH ORDER IN λ

λ^1: $H_0 \psi_k^{(1)} + V \psi_k^0 = E_k^0 \psi_k^{(1)} + E_k^{(1)} \psi_k^0$ FIRST ORDER IN λ

λ^2: $H_0 \psi_k^{(2)} + V \psi_k^{(1)} = E_k^0 \psi_k^{(2)} + E_k^{(1)} \psi_k^{(1)} + E_k^{(2)} \psi_k^0$ SECOND ORDER IN λ

⋮

IN GENERAL:

$$H_0 \psi_k^{(n)} + V \psi_k^{(n-1)} = \sum_{l=0}^{n} E_k^{(l)} \psi_k^{(n-l)}$$

ALL THE OTHER CORRECTIONS!

HOW TO EVALUATE $E_k^{(1)}$?

$\psi_k^{(1)*}$ | $H_0 \psi_k^0 = E_k^0 \psi_k^0$

ψ_k^{0*} | $H_0 \psi_k^{(1)} + V \psi_k^0 = E_k^0 \psi_k^{(1)} + E_k^{(1)} \psi_k^0$

$$\langle \psi_k^{(1)} | H_0 | \psi_k^0 \rangle = E_k^0 \langle \psi_k^{(1)} | \psi_k^0 \rangle$$

$$\langle \psi_k^0 | H_0 | \psi_k^{(1)} \rangle + \langle \psi_k^0 | V | \psi_k^0 \rangle = E_k^0 \langle \psi_k^0 | \psi_k^{(1)} \rangle + E_k^{(1)} \underbrace{\langle \psi_k^0 | \psi_k^0 \rangle}_{=1}$$

MINUS

$$\langle \psi_k^{(1)} | H_0 | \psi_k^0 \rangle^* = E_k^0 \langle \psi_k^{(1)} | \psi_k^0 \rangle^*$$

$$\langle \psi_k^0 | H_0^+ | \psi_k^{(1)} \rangle = E_k^0 \langle \psi_k^0 | \psi_k^{(1)} \rangle$$

$H_0 = H_0^+$

$$\boxed{E_k^{(1)} = \langle \psi_k^0 | V | \psi_k^0 \rangle}$$

ZEROTH ORDER WAVEFUNCTION

HOW TO FIND $\psi_k^{(1)}$?

RAYLEIGH-SCHRÖDINGER PERTURBATION THEORY

THE SIMPLEST REALIZATION

$$H_0 \psi_k^0 = E_k^0 \psi_k^0$$

ASSUMPTION: $\{\psi_k^0\}_k^{ALL}$: COMPLETE SET!
KNOWN FUNCTIONS!

$$\psi_k^{(1)} = \sum_m^{ALL} C_{nk} \psi_n^{(0)}$$

EXPANDED IN A SERIES IN THE $\psi_n^{(0)}$

$$\psi_k^{(1)} = \sum_n c_{nk}\,\psi_n^0$$

$$V\psi_k^0 = \sum_n b_{nk}\,\psi_n^0$$

ψ_m^{0*} /

$$\langle\psi_m^0|V|\psi_k^0\rangle = \sum_n b_{nk}\underbrace{\langle\psi_m^0|\psi_n^0\rangle}_{\delta_{mn}} = b_{mk}$$

$$b_{mk} = \langle\psi_m^0|V|\psi_k^0\rangle \Rightarrow b_{mm} = E_m^{(1)}$$

$$V\psi_k^0 = E_k^{(1)}\psi_k^0 + \sum_{n\neq k}\langle\psi_n^0|V|\psi_k^0\rangle\,\psi_n^0$$

BUT FIRST ORDER EQUATION HAS THE FORM:

$$H_0\psi_k^{(1)} + V\psi_k^0 = E_k^0\psi_k^{(1)} + E_k^{(1)}\psi_k^0$$

$$H_0\sum_n c_{nk}\psi_n^0 + \cancel{E_k^{(1)}\psi_k^0} + \sum_{n\neq k}\langle\psi_n^0|V|\psi_k^0\rangle\,\psi_n^0$$

$$= E_k^0\psi_k^{(1)} + \cancel{E_k^{(1)}\psi_k^0}$$

$$H_0\psi_n^0 = E_n^0\psi_n^0$$

$$\sum_n c_{nk}E_n^0\psi_n^0 + \sum_{n\neq k}\langle\psi_n^0|V|\psi_k^0\rangle\,\psi_n^0 =$$

$$= E_k^0\sum_n c_{nk}\psi_n^0$$

$$\sum_n (E_k^0 - E_n^0)c_{nk}\psi_n^0 = \sum_{n\neq k}\langle\psi_n^0|V|\psi_k^0\rangle\psi_n^0$$

$$c_{nk} = \frac{\langle\psi_n^0|V|\psi_k^0\rangle}{(E_k^0 - E_n^0)} \qquad n\neq k$$

$$\boxed{\psi_k^{(1)} = \sum_{n\neq k}\frac{\langle\psi_n^0|V|\psi_k^0\rangle}{(E_k^0 - E_n^0)}\psi_n^0}$$

$$\psi_k^{(1)} = \sum_n{}' \frac{\langle\psi_n^0|V|\psi_k^0\rangle}{(E_k^0 - E_n^0)}\psi_n^0$$

WHAT ABOUT C_{nn}?

IF

$$\langle \psi_n^0 | \psi_n^{(1)} \rangle = 0 \qquad \text{(ASSUMPTION)}$$

$$\langle \psi_m^0 | \psi_m^{(1)} \rangle = \sum_k C_{kn} \underbrace{\langle \psi_m^0 | \psi_k^0 \rangle}_{\delta_{mk}} = C_{nm} = 0$$

HIGHER ORDER CORRECTIONS:

$$E_k^{(2)} = \sum_n{}' \frac{\langle \psi_k^0 | V | \psi_m^0 \rangle \times \langle \psi_m^0 | V | \psi_k^0 \rangle}{(E_k^0 - E_m^0)} = \langle \psi_k^0 | V | \psi_k^{(1)} \rangle$$

$\psi_k^{(1)}$

$$E_k^{(3)} = \langle \psi_k^{(1)} | V | \psi_k^{(1)} \rangle - E_k^{(1)}$$

PROPERTY: WITH THE FUNCTIONS UP TO THE m-th ORDER IT IS POSSIBLE TO EVALUATE THE ENERGY UP TO $(2m+1)$-th ORDER

IN GENERAL:

$$E_k = E_k^0 + \lambda \langle \psi_k^0 | V | \psi_k^0 \rangle + \lambda^2 \sum_n{}' \frac{\langle \psi_k^0 | V | \psi_m^0 \rangle \times \langle \psi_m^0 | V | \psi_k^0 \rangle}{(E_k^0 - E_m^0)} + \dots$$

$$= E_k^0 + \lambda V_{kk} + \lambda^2 \sum_n{}' \frac{V_{kn} V_{nk}}{(E_k^0 - E_m^0)} + \dots$$

ENERGY SEPARATION

$$\psi_k = \psi_k^0 + \lambda \sum_n{}' \frac{V_{nk}}{E_k^0 - E_n^0} \psi_m^0 + \dots$$

WHAT TO DO WITH λ ?

WHEN THE ENERGY IS EVALUATED → $\lambda = 1$

$$H = H_0 + \lambda V$$

$$\langle \psi_k^0 | H | \psi_k^0 \rangle = \langle \psi_k^0 | H_0 | \psi_k^0 \rangle + \langle \psi_k^0 | V | \psi_k^0 \rangle = E_k^0 + E_k^{(1)}$$

EXPECTATION VALUE OF THE WHOLE HAMILTONIAN

ZEROTH ORDER

λ $E_k^{(1)}$ $\lambda = 1$

VARIATIONAL PRINCIPLE

- THERE ARE NO LIMITATIONS
  NO CONDITIONS TO BE SATISFIED...

$$H\Psi_m = E_m \Psi_m$$

E_0 - ENERGY OF THE GROUND STATE (THE LOWEST ENERGY)

$$E_0 < E_m \quad m > 0$$

$$E_0 < E_1 < E_2 < \dots$$

Ψ_m, E_m - UNKNOWN

Φ - TRIAL FUNCTION, DEFINED IN THE SAME SPACE AS EXACT FUNCTION Ψ_m
APPROXIMATION TO THE CORRECT WAVEFUNCTION

ESTIMATE OF THE TRUE ENERGY

$$\varepsilon = \frac{\langle \Phi | H | \Phi \rangle}{\langle \Phi | \Phi \rangle}$$ ENERGY FUNCTIONAL

- IF Φ DESCRIBES AN ENERGY STATE OF A SYSTEM $\Rightarrow$
  ε IS AN AVERAGE ENERGY IN THAT STATE

- IF Φ IS ARBITRARY, IS ε CONNECTED WITH ENERGY?

EXACT EIGENFUNCTIONS Ψ_m FORM COMPLETE SET
Φ IS EXPANDED INTO SERIES

$$\Phi = \sum_m c_m \Psi_m$$

IF $\langle \Phi | \Phi \rangle = 1 \Rightarrow \quad \langle \sum_n c_n \Psi_n | \sum_m c_m \Psi_m \rangle =$

$$= \sum_n \sum_m c_n^* c_m \underbrace{\langle \Psi_n | \Psi_m \rangle}_{\delta_{nm}} = \sum_n |c_n|^2 = 1$$

$$\varepsilon = \frac{\langle \phi | H | \phi \rangle}{\langle \phi | \phi \rangle}$$

$\phi = \sum_n c_n \psi_n$ $\qquad \langle \phi | \phi \rangle = 1$

$$\varepsilon = \langle \sum_n c_n \psi_n | H | \sum_m c_m \psi_m \rangle =$$

$$= \sum_n \sum_m c_n^* c_m \langle \psi_n | H | \psi_m \rangle = \qquad H\psi_m = E_m \psi_m$$

$$= \sum_n \sum_m c_n^* c_m E_m \langle \psi_n | \psi_m \rangle \qquad \langle \psi_n | \psi_m \rangle = \delta_{nm}$$

$$= \sum_n |c_n|^2 E_m$$

$$\varepsilon = \sum_n |c_n|^2 E_n \qquad / -E_0$$

↑ PROBABILITY THAT ψ_n WITH ENERGY E_n IS PART OF ϕ

$$\varepsilon - E_0 = \sum_n (E_n - E_0) |c_n|^2 \qquad E_0 \cdot 1 = E_0 \sum_n |c_n|^2$$

≥ 0 $\quad$ > 0

$\varepsilon - E_0 \geq 0$

$$\boxed{\varepsilon \geq E_0}$$

ε IS THE UPPER BOUND (LIMIT) OF EXACT ENERGY

(= REACHED ONLY IN THE CASE OF EXACT FUNCTION, IT MEANS – ONLY FOR HYDROGEN ATOM)

TRIAL FUNCTIONS: $\phi_1, \phi_2, \phi_3, \ldots$

THE BEST IS SUCH, FOR WHICH

$$\boxed{\varepsilon[\phi] = \min}$$

FOR GIVEN CLASS OF FUNCTIONS: OPTIMAL SOLUTION

TRIAL FUNCTION DEPENDS ON PARAMETERS (VARIATIONAL PARAMETERS) α_i, $i = 1, \ldots s$

$$\varepsilon[\phi] \equiv \varepsilon[\alpha_i] \Rightarrow \frac{\partial \varepsilon}{\partial \alpha_i} = 0 \qquad \frac{\partial^2 \varepsilon}{\partial \alpha_i^2} > 0 \text{ (minimum)}$$

$i = 1, \ldots s$

NON-LINEAR PARAMETERS $\longrightarrow \{\alpha_1^{OP}\ \alpha_2^{OP} \ldots \alpha_s^{OP}\}$ THE BEST PARAMETERS

$\varepsilon[\alpha_1^{OP}\ \alpha_2^{OP} \ldots \alpha_s^{OP}]$ THE BEST APPROXIMATION OF ENERGY

RITZ METHOD (APPROXIMATION)

- BASED ON VARIATIONAL PRINCIPLE
- WITH LINEAR VARIATIONAL PARAMETERS

THE TRIAL FUNCTION IS EXPRESSED AS A LINEAR COMBINATION OF KNOWN FUNCTIONS

$$\Phi = \sum_{p=1}^{n} c_p \chi_p$$

↑ UNKNOWN COEFFICIENTS
LINEAR VARIATIONA PARAMETERS

$\varepsilon \Rightarrow \varepsilon[c_1, c_2, \dots c_n]$

$\min \varepsilon[c_1, c_2, \dots c_n] \Rightarrow$ EQUATIONS FOR c_i $(1, \dots n)$

$$\varepsilon = \frac{\langle \Phi | H | \Phi \rangle}{\langle \Phi | \Phi \rangle}$$

$\{\chi_p\}_i^{all}$ DO NOT NEED TO BE ORTHONORMAL

$$\langle \Phi | H | \Phi \rangle = \left\langle \sum_p c_p \chi_p \middle| H \middle| \sum_r c_r \chi_r \right\rangle =$$

$$= \sum_p \sum_r c_p^* c_r \langle \chi_p | H | \chi_r \rangle = \sum_p \sum_r c_p^* c_r H_{pr}$$

MATRIX ELEMENT

$$\varepsilon \langle \Phi | \Phi \rangle = \varepsilon \left\langle \sum_p c_p \chi_p \middle| \sum_r c_r \chi_r \right\rangle =$$

$$= \varepsilon \sum_p \sum_r c_p^* c_r \langle \chi_p | \chi_r \rangle = \varepsilon \sum_p \sum_r c_p^* c_r S_{pr}$$

OVERLAP INTEGRAL

DEF.:

$\langle \chi_p | H | \chi_r \rangle = H_{pr}$

$\langle \chi_p | \chi_r \rangle = S_{pr}$ $(= \delta_{pr}$ FOR ORTHONORMAL SET)

$$\varepsilon \sum_p \sum_r c_p^* c_r S_{pr} = \sum_p \sum_r c_p^* c_r H_{pr}$$

UNKNOWN:

$$\varepsilon, c_1, \dots c_n, c_1^* \dots c_n^*$$

$\min \varepsilon[c_1, \dots c_n, c_1^*, \dots c_m^*] \Rightarrow$ EQUATIONS

$$\frac{\partial}{\partial c_q^*}\left(\varepsilon \sum_p \sum_r c_p^* c_r S_{pr} = \sum_p \sum_r c_p^* c_r H_{pr}\right)$$

$$\frac{\partial \varepsilon}{\partial c_q^*} \sum_p \sum_r c_p^* c_r S_{pr} + \varepsilon \sum_r c_r S_{qr} = \sum_r c_r H_{qr}$$

$\frac{\partial \varepsilon}{\partial c_q^*} = 0$ FOR EXTREMUM OF $\varepsilon[c_1, \dots c_n, c_1^*, \dots c_m^*]$

$\varepsilon_{min} \equiv E$

$$E \sum_r c_r S_{qr} = \sum_r c_r H_{qr}$$

$$\text{(*)} \quad \boxed{\sum_{r=1}^{n} c_r (H_{qr} - E S_{qr}) = 0} \qquad q = 1, \dots n$$

SET OF HOMOGENOUS LINEAR EQUATIONS

WHAT IS THE CONDITION FOR NON-TRIVIAL SOLUTIONS?

$$\boxed{|H_{qr} - E S_{qr}| = 0}$$

SECULAR EQUATION (MO LCAO)

$$\begin{vmatrix} H_{11}-E & H_{12} & \dots & H_{1n} \\ H_{21} & H_{22}-E & \dots & H_{2n} \\ \vdots & & \ddots & \\ H_{n1} & H_{n2} & \dots & H_{nn}-E \end{vmatrix} = 0$$

FOR $S_{qr} = \delta_{qr}$: ORTHONORMAL SET OF FUNCTIONS χ

COMMON PRACTICE IN THE CASE OF ATOMS

n SOLUTIONS, THE LOWEST VALUE OF E IS THE BEST APPROXIMATION OF THE ENERGY OF THE GROUND STATE; THE OPTIMAL VALUE OBTAINED FOR GIVEN CLASS OF FUNCTIONS

E_1^{op} (GROUND), $E_2^{op}, \dots E_n^{op}$

BACK TO (*)

$$\sum_{r=1}^{n} c_r (H_{qr} - E_i^{op} S_{qr}) = 0 \Rightarrow \Phi_i^{op} = \sum_p^n c_{pi}^{op} \chi_p \qquad q = 1, \dots n$$

$i = 1$ GROUND STATE

EXAMPLE.: PARTICLE IN A BOX (1. DIMENSION)

POTENTIAL ENERGY INSIDE THE BOX $V = 0$

OUTSIDE THE BOX $V \longrightarrow \infty$

WAVEFUNCTION

$$\psi_n(x) = \begin{cases} k \sin \frac{n\pi x}{a} & 0 \leq x \leq a \\ 0 & \text{OTHERWISE} \end{cases}$$

SIZE OF A BOX

HOMEWORK: EVALUATE THE ENERGY OF THIS PARTICLE

$$E_n = \frac{n^2 \hbar^2 \pi^2}{2ma^2} = \frac{n^2 h^2}{8ma^2}$$

VERIFY THAT $\psi_n(x)$ DEFINED ABOVE IS THE SOLUTION OF THE SCHRÖDINGER EQUATION

$$H\psi_n(x) = E_n \psi_n(x)$$

USING THE VARIATIONAL PRINCIPLE EVALUATE THE ENERGY OF A PARTICLE IN A BOX USING THE TRIAL (APPROXIMATE) FUNCTION OF THE FORM

$$\varphi(x) = N x (x-a)$$

$$\left.\begin{aligned} &\varphi(0) = \varphi(a) = 0 \\ &H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} \end{aligned}\right\} \quad \varepsilon[\varphi] = \frac{\langle \varphi | H | \varphi \rangle}{\langle \varphi | \varphi \rangle}$$

1°. NORMALIZATION

$$N^2 \int_0^a x^2 (x-a)^2 dx = N^2 \int_0^a x^2 (x^2 - 2ax + a^2) dx = 1$$

$$N = \sqrt{\frac{30}{a^5}}$$

2° ENERGY FUNCTIONAL

$$\varepsilon = \langle \varphi | H | \varphi \rangle = -\frac{\hbar^2}{2m} \cdot \frac{30}{a^5} \left\langle x(x-a) \left| \frac{d^2}{dx^2} \right| x(x-a) \right\rangle$$

$$\frac{d^2}{dx^2}(x^2 - xa) = \frac{d}{dx}(2x - a) = 2$$

$$\varepsilon = -\frac{\hbar^2 30}{ma^5}\int_0^a x(x-a)\,dx = -\frac{\hbar^2 30}{ma^5}\int_0^a (x^2-ax)\,dx =$$

$$= -\frac{\hbar^2 30}{ma^5}\left(\frac{a^3}{3}-\frac{a^3}{2}\right) = \frac{5\hbar^2}{ma^2} = \frac{5h^2}{4\pi^2 ma^2}$$

APPROXIMATE VALUE OF ENERGY

$$\varepsilon_{app} = \frac{5\hbar^2}{ma^2}$$

$$\varepsilon_{ex} = \frac{\hbar^2\pi^2}{2ma^2} = E_1$$

$$\Delta = \frac{\varepsilon_{app} - E_1}{E_1} = \left(\frac{5\hbar^2}{ma^2} - \frac{\hbar^2\pi^2}{2ma^2}\right)\frac{2ma^2}{\hbar^2\pi^2} \times 100\%$$

$$= \left(\frac{10}{\pi^2} - 1\right) \times 100\% = 1.3\%$$

(ERROR)

HOMEWORK: EVALUATE THE ENERGY OF THE GROUND STATE OF A PARTICLE IN A BOX USING THE RITZ METHOD FOR THE TRIAL FUNCTION

$\varphi = c_1 x(x-a)$

COMPARE THE RESULT WITH THE EXACT VALUE OF THE ENERGY

EXAMPLE:

THE TRIAL FUNCTION THAT DESCRIBES THE GROUND STATE OF HYDROGEN ATOM HAS THE FORM:

$$\psi = \sqrt{\frac{\alpha^3}{\pi a_0^3}}\, e^{-\alpha r/a_0}$$

α - VARIATIONAL PARAMETER

1° EVALUATE $\langle T \rangle_\psi$ AND $\langle V \rangle_\psi$

2° FIND THE OPTIMAL WAVEFUNCTION AND THE BEST APPROXIMATION OF ENERGY

3° COMPARE THE RESULT WITH THE EXACT SOLUTIONS

TO SIMPLIFY THE TASK USE THE FOLLOWING RESULT

$$\int_0^\infty x^n e^{-\alpha x}\, dx = \frac{n!}{\alpha^{n+1}}$$

ATTENTION: TO EVALUATE KINETIC ENERGY ($\langle T \rangle_\psi$) USE A PROPER FORM OF Δ_r

NOTE ALSO THAT

$$a_0 = \frac{\hbar^2}{me^2}$$

EXAMPLE: ACCURACY OF THE RITZ METHOD

1° FIND THE BEST APPROXIMATION TO THE GROUND STATE ENERGY OF HYDROGEN ATOM USING THE FOLLOWING TRIAL FUNCTIONS

$$\chi_1 = e^{-r/2} \qquad \chi_2 = r e^{-r/2}$$

2° FOR THE ENERGY EVALUATED FIND THE OPTIMAL FUNCTION

3° COMPARE THE RESULTS WITH THE EXACT SOLUTIONS

4° EVALUATE $\langle r \rangle$ WITH EXACT AND APPROXIMATE FUNCTIONS

ATTENTION: χ_1 AND χ_2 ARE NOT ORTHOGONAL!

EXAMPLE: FOR ϕ_{EXACT} OF THE GROUND STATE OF HYDROGEN ATOM AND

$\Phi_{app} = c_1\chi_1 + c_2\chi_2$ WITH χ_1 AND χ_2 FROM THE PREVIOUS PROBLEM

1º EVALUATE (USE ATOMIC UNITS ≡ a.u.)

H	ε	$\langle T \rangle$	$\langle V \rangle$	$\langle r \rangle$	$P(r_0)$	r_0
ϕ_{ex}						
ϕ_{app}						
δ						

$$\delta = \frac{a_{ex} - a_{app}}{a_{ex}} \times 100\%$$

RADIAL DISTRIBUTION FUNCTION max value

↑ POINT OF MAXIMUM RADIAL PROBABILITY

2º ANALYZE THE PLOTS OF RADIAL DISTRIBUTION FUNCTIONS OF BOTH CASES

EXAMPLE: FIND THE COEFFICIENTS OF LINEAR COMBINATION

$$\Psi = c_1\varphi_1 + c_2\varphi_2$$

ASSUMING THAT:

$$\langle \varphi_i | \varphi_j \rangle = \delta_{ij}$$

$$H_{11} = H_{22} = \alpha$$

$$H_{12} = H_{21} = \beta$$

THE ENERGY IN THE STATE Ψ IS THE BEST (OPTIMAL) FOR THIS CLASS OF FUNCTION