



# Liaison Chimique '07

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## Chap. II: The Helium Atom



# Some remarks about units

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First approximation :  $m_e \approx m$  (reduced mass)

1 ) SI units : 
$$H = -\frac{\hbar^2}{2m_e} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r}$$
 (Hamiltonian for H)

Unit of mass : kg; charge : C and angular momentum : kg m<sup>2</sup>/s

2 ) Cgs Gaussian units : 
$$H = -\frac{\hbar^2}{2m_e} \nabla^2 - \frac{e'^2}{r}$$
 (Hamiltonian for H)

Unit of mass : g; charge : statcoulomb and g cm<sup>2</sup>

→ Important remark :  $e' = e/4\pi\epsilon_0$  is the most rigorous notation. However, we often use  $e$  instead of  $e'$



# Some remarks about units (II)

3 ) Atomic units : 
$$H = -\frac{1}{2} \nabla^2 - \frac{1}{r}$$
 (Hamiltonian for H)

Unit of mass :  $m_e$ ; charge :  $e'$  and angular momentum :  $\hbar$   
Therefore :  $m_e = e' = \hbar = 1$

Atomic unit of length : 1 bohr  $\equiv a_0 = \hbar / (m_e * e'^2) = 0.529177 \text{ \AA}$

Atomic unit of energy : 1 Hartree  $\equiv E_h = e'^2 / a_0 = e^2 / 4\pi\epsilon_0 a_0 = 27.2114 \text{ eV}$

Alternative (obsolete but still used in spectroscopy) :

$$H = -\nabla^2 - \frac{2}{r} \longrightarrow \text{Atomic unit of energy : 1 Rydberg} = 0.5 \text{ Ha}$$

(Hamiltonian for H)

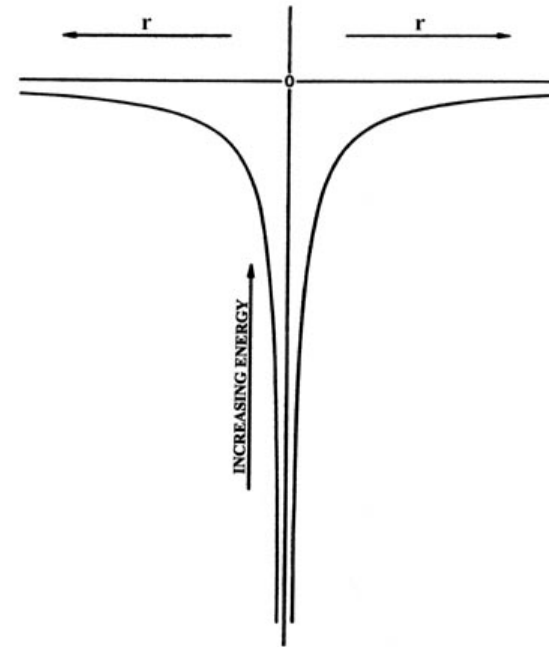
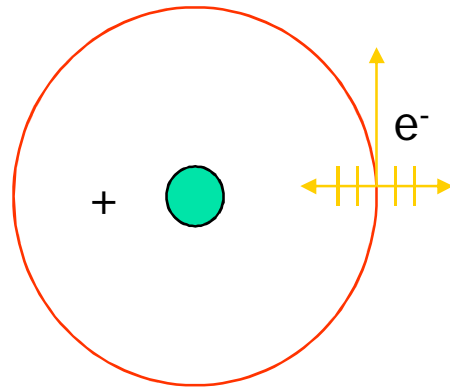
# Hydrogen Atom

H

- A simple « two body » problem, with an EXACT solution
- **Prototype** orbitals

A central force problem

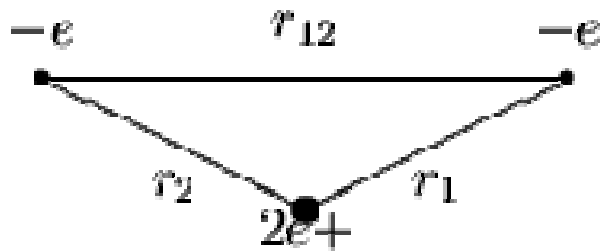
$$V = -e^2/r$$



# Helium Atom

He

Two electrons and  $Z = +2$



$$H = T + V(r) = -\frac{\hbar^2}{2m_e} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r} \quad \text{SI units}$$

$$\hat{H} = \underbrace{-\frac{\hbar^2}{2\mu} \nabla_{r_1}^2 - \frac{2e^2}{r_1}}_{\text{electron 1}} - \underbrace{\frac{\hbar^2}{2\mu} \nabla_{r_2}^2 - \frac{2e^2}{r_2}}_{\text{electron 2}} + \underbrace{\frac{e^2}{r_{12}}}_{\text{electron 1 + electron 2}}$$

cgs  
Gaussian  
units

For atoms with more than one electron, the **Schrödinger Equation cannot be solved exactly** (can't get **formulas!**)

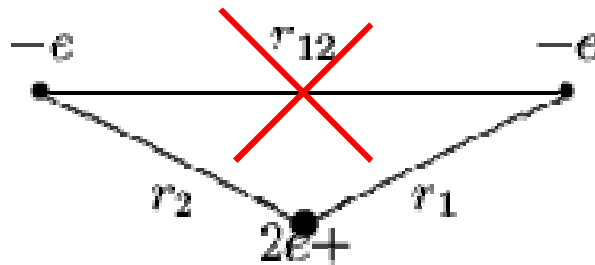
# The simplest He

$$\hat{H} = -\frac{\hbar^2}{2\mu} \nabla_{r_1}^2 - \frac{2e^2}{r_1} - \frac{\hbar^2}{2\mu} \nabla_{r_2}^2 - \frac{2e^2}{r_2} + \cancel{\frac{e^2}{r_{12}}}$$

The simplest approach: neglect the coupling =  
two independent e<sup>-</sup>

$$H = T_e + V_{eN}$$

$$V_{eN} = -\frac{2e^2}{r_1} - \frac{2e^2}{r_2}$$





## The simplest He (II)

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$$\hat{H}^0 y^0 = E^0 y^0 \qquad \hat{H} = -\frac{\hbar^2}{2\mu} \nabla_{r_1}^2 - \frac{2e^2}{r_1} - \frac{\hbar^2}{2\mu} \nabla_{r_2}^2 - \frac{2e^2}{r_2}$$

So the w.f. is factorized in two independent (hydrogen-like) parts

$$y^0(\mathbf{x}_1, \mathbf{y}_1, \mathbf{z}_1, \mathbf{x}_2, \mathbf{y}_2, \mathbf{z}_2) = g_1(\mathbf{x}_1, \mathbf{y}_1, \mathbf{z}_1) g_2(\mathbf{x}_2, \mathbf{y}_2, \mathbf{z}_2)$$

The Hamiltonian is the sum of two mono-electronic  $H_e^+$

$$\left[ -\frac{\hbar^2}{8p^2 m_e} \nabla_1^2 g_1 - \frac{2e^2}{r_1} \right] + \left[ -\frac{\hbar^2}{8p^2 m_e} \nabla_2^2 g_2 - \frac{2e^2}{r_2} \right] = E^0$$



# The simplest He (III)

Or

$$-\frac{\hbar^2}{8m_e} \nabla_1^2 g_1 - \frac{2e^2}{r_1} g_1 = E_1 g_1 \quad -\frac{\hbar^2}{8m_e} \nabla_2^2 g_2 - \frac{2e^2}{r_2} g_2 = E_2 g_2$$

The Energy is the sum of H-like contributions  $E_0 = E_1 + E_2$

$$E_1 = \frac{4E_H}{n_1^2} \text{ and } E_2 = \frac{4E_H}{n_2^2} \quad \text{Two He}^+ \text{ energies « corrected » } E_H = \frac{-2m_e e^4}{\hbar^2}$$

vs. experiments  $\text{He (ground state)} \rightarrow \text{He}^+ + e^-$

calculated  $E_{\text{He}} = -54.4 \text{ eV}$

experimental  $E_{\text{He}} = -79.0 \text{ eV}$



# Approximations

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$$\frac{e^2}{r_{12}}$$

The difference comes from the interaction between electrons

To deal with this term we have to introduce **approximation methods**

These approximate methods are **very good** e.g., the energy of the He atom can be found accurately to **eight significant figures!**

One fruitful approximation method is called the **orbital approximation**. **It describes each electron individually** with one wavefunction (orbital). For each electron, we say that each electron is “in an orbital”. These **orbitals resemble to H-atom orbitals with** three quantum numbers similar shapes, number of nodes, etc.



# The variation principle

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AIM: Obtain an approximate ground state energy for a system of several interacting particles

*We need a criterion of what makes a good approximation.*

$$\langle H \rangle = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} \geq E_0$$

# The variation principle (II)

$$\langle H \rangle = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} \geq E_0$$

*Theorem:* The expectation value of a Hamiltonian calculated using a **trial** wavefunction is never lower in value than the true **ground state energy** which is the **expectation** value of  $H$  calculated using the true ground state wavefunction.

## Glossary:

$\Psi$  = well behaved **trial** w.f.

$H$  = **Hamiltonian** of the system

$E_0$  = **ground state** energy

$\langle \Psi | H | \Psi \rangle = E$  = **expectation value** of the system energy

$\langle \Psi | H | \Psi \rangle$  = **variational integral**



# The variation principle (III)

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In practice

- a) We try **different trial functions** and look for the one that gives the lowest values of the variational integral

$$\Rightarrow \frac{\partial E}{\partial \psi} = 0$$

- b) In the chosen function, we have **parameters (e.g.  $\lambda$ )** to vary in order to minimize the variational integral

$$\text{if } \psi = \psi(\lambda) \quad \frac{\partial E}{\partial \lambda} = 0$$

**It's important to start from a good trial function**



# He: a variational approach

**Strategy:** add **one parameter** and **optimize** that parameter to minimize the energy

**Starting point:** He<sup>+</sup> wavefunctions but one electron “screens” the nuclear charge from the other

**Z'** = effective nuclear charge

The three ingredients:

The trial w.f.

$$\tilde{\psi} = A^2 e^{-\frac{z'}{a_0}(r_1+r_2)}$$

The variational integral

$$\tilde{E}(z') = \langle \tilde{\psi} | \hat{H} | \tilde{\psi} \rangle,$$

The Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2\mu} \nabla_{r_1}^2 - \frac{z'e^2}{r_1} - \frac{\hbar^2}{2\mu} \nabla_{r_2}^2 - \frac{z'e^2}{r_2} - \frac{(2-z')e^2}{r_1} - \frac{(2-z')e^2}{r_2} + \frac{e^2}{r_{12}}.$$



# He: a variational approach (II)

Using the above ingredients we can compute the variational integral

$$\tilde{E}(z') = -\frac{z'^2 e^2}{a} - 2A^2 \int dr e^{-\frac{z'2r}{a}} r^2 \frac{(2-z')}{r} e^2 + A^2 \int dr_1 \int dr_2 \frac{e^{-\frac{2z'}{a}(r_1+r_2)} r_1^2 e^2 r_2^2}{r_1 - r_2},$$

or

$$\tilde{E}(z') = -\frac{z'^2 e^2}{a} - 2z' \frac{(2-z')}{a} e^2 + \frac{5}{8} z' \frac{e^2}{a}.$$

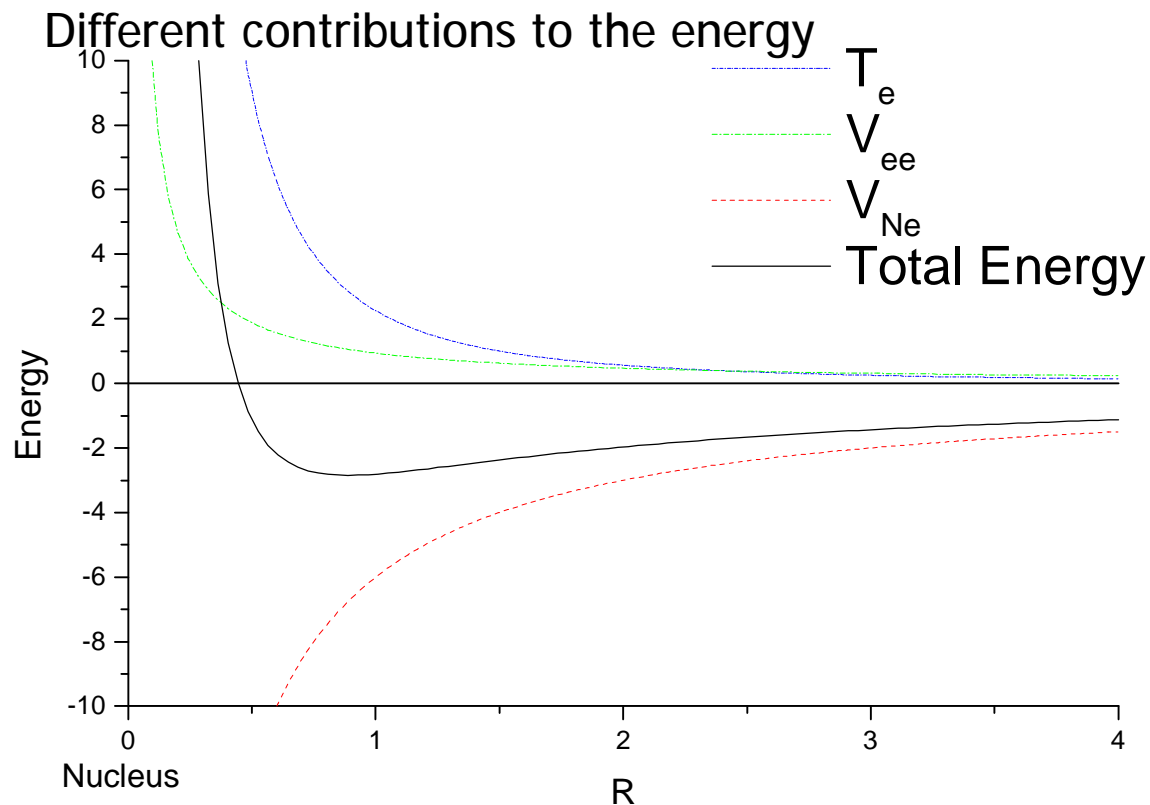
the optimum parameter  $Z'$  is then obtained

$$\frac{\partial \tilde{E}(z')}{\partial z'} = 0, \rightarrow z'_{\text{opt}} = 2 - \frac{5}{16}, \rightarrow \tilde{E}(z'_{\text{opt}}) = \left(2 - \frac{5}{16}\right)^2 \frac{e^2}{a} - 2 \left(2 - \frac{5}{16}\right) 2 \frac{e^2}{a} + \frac{5}{8} \left(2 - \frac{5}{16}\right) \frac{e^2}{a}.$$

$$Z' = 1.875 < 2$$

We find :  $E_0 = -77.5$  eV, but the experimental energy is  $-79.0$  eV

# He: a variational approach (III)



$V_{Ne}$  goes as  $-R^{-1}$

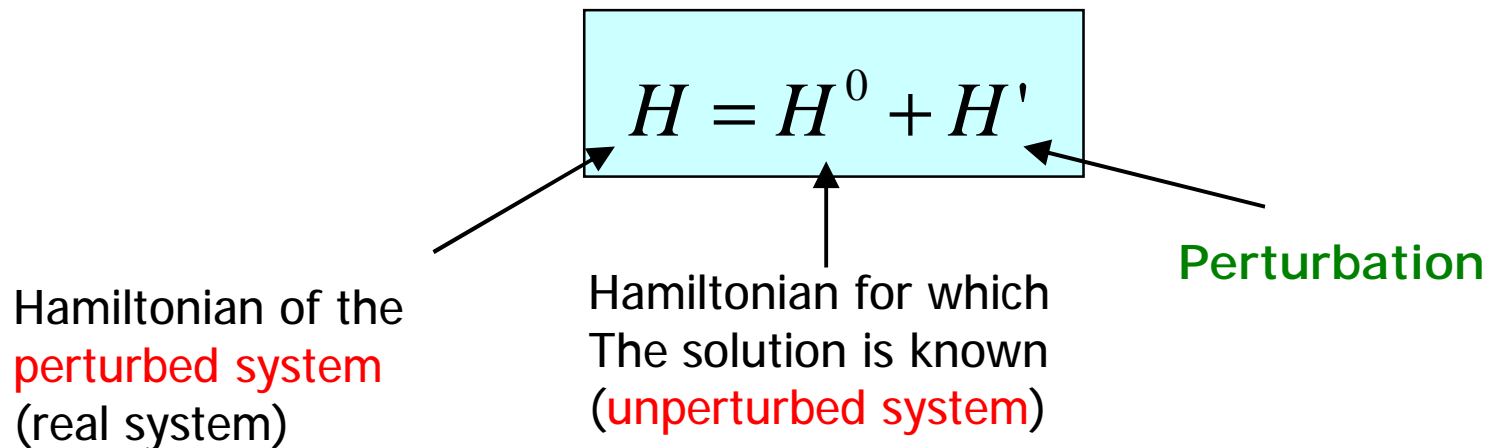
$T_{ee}$  goes as  $R^{-2}$

Equilibrium at  $R=1$

The electron does not collapse into the nucleus under the influence of the **attractive coulombic** interaction because of the **repulsive effect** of the kinetic energy

# Perturbational approach

- n First step : decompose the hamiltonian



Example : anharmonic oscillator :

$$H = \underbrace{-\frac{\hbar^2}{2m} \frac{d}{dx^2} + \frac{1}{2} kx^2}_{H^0 \text{ harmonic}} + \underbrace{cx^3 + dx^4}_{H' \text{ perturbation}}$$



# Perturbational approach (II)

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- n Second step : insert (switch on) the perturbation gradually

$$H = H^0 + \lambda H'$$

Perturbation parameter :  $0 \leq \lambda \leq 1$

$\lambda = 0$  (unperturbed)  $\rightarrow \lambda = 1$  (fully perturbed)



# Perturbational approach (III)

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Our framework :  
the non degenerate perturbation theory (NDPT)

$$H = H^0 + IH'$$

For the unperturbed Hamiltonian  $H^0$  :  $H^0 \mathbf{y}_n^{(0)} = E_n^{(0)} \mathbf{y}_n^{(0)}$  ( $\lambda=0$ )

$$\text{So : } H \mathbf{y}_n = (H^0 + IH') \mathbf{y}_n = E_n \mathbf{y}_n \longrightarrow \begin{cases} E_n = E_n(I) \\ \mathbf{y}_n = \mathbf{y}_n(I, q) \end{cases}$$



# Perturbational approach (IV)

Taylor expansion of  $\psi_n$  and  $E_n$  in powers of  $\lambda$  :

$$y_n = y_n \Big|_{l=0} + \frac{\partial y_n}{\partial l} \Big|_{l=0} l + \frac{\partial^2 y_n}{\partial l^2} \Big|_{l=0} \frac{l^2}{2!} + \dots$$

$$E_n = E_n \Big|_{l=0} + \frac{dE_n}{dl} \Big|_{l=0} l + \frac{d^2 E_n}{dl^2} \Big|_{l=0} \frac{l^2}{2!} + \dots$$

By hypothesis :  $\psi_n \Big|_{\lambda=0} = \psi_n^{(0)}$  and  $E_n \Big|_{l=0} = E_n^{(0)}$  when  $l \rightarrow 0$

and by introducing the abbreviations :

$$y_n^{(k)} = \frac{1}{k!} \frac{\partial^k y_n}{\partial l^k} \Big|_{l=0} \quad \text{and} \quad E_n^{(k)} = \frac{1}{k!} \frac{d^k y_n}{dl^k} \Big|_{l=0} \quad k = 1, 2, \dots \quad \textit{We have...}$$

# Perturbational approach (V)

Taylor expansion of  $\psi_n$  and  $E_n$  in powers of  $\lambda$  :

$$\begin{aligned} \mathbf{y}_n &= \mathbf{y}_n^{(0)} + I \mathbf{y}_n^{(1)} + I^2 \mathbf{y}_n^{(2)} + \dots + I^k \mathbf{y}_n^{(k)} + \dots \\ E_n &= E_n^{(0)} + I E_n^{(1)} + I^2 E_n^{(2)} + \dots + I^k E_n^{(k)} + \dots \end{aligned}$$

*Hypothesis* : we assume that these series converge for  $I=1$  and we hope that, for a small perturbation, taking the first few terms of the series will give a good approximation of the true energy and wavefunction

We take  $\langle \mathbf{y}_n^{(0)} | \mathbf{y}_n^{(0)} \rangle = 1$  and  $\langle \mathbf{y}_n^{(0)} | \mathbf{y}_n \rangle = 1$   $\rightarrow$  *Intermediate normalization* simplifies the derivation and does not affect the results

So :  $\langle \mathbf{y}_n^{(0)} | \mathbf{y}_n \rangle = \langle \mathbf{y}_n^{(0)} | \mathbf{y}_n^{(0)} \rangle + I \langle \mathbf{y}_n^{(0)} | \mathbf{y}_n^{(1)} \rangle + I^2 \langle \mathbf{y}_n^{(0)} | \mathbf{y}_n^{(2)} \rangle + \dots = 1$

*True for all values of I!*



# Perturbational approach (VI)

From the previous equation, we can prove :

$$\langle \mathbf{y}_n^{(0)} | \mathbf{y}_n^{(1)} \rangle = \langle \mathbf{y}_n^{(0)} | \mathbf{y}_n^{(2)} \rangle = \dots = 0$$

→ *In other words, the corrections to the wavefunction are orthogonal to  $\mathbf{y}_n^{(0)}$  when intermediate normalization is used.*

We can now rewrite the Schrödinger equation using the two series we have developed. If we collect the terms like powers of  $\lambda$ , we have :

$$\begin{aligned} H^0 \mathbf{y}_n^{(0)} + \lambda (H' \mathbf{y}_n^{(0)} + H^0 \mathbf{y}_n^{(1)}) + \lambda^2 (H' \mathbf{y}_n^{(1)} + H^0 \mathbf{y}_n^{(2)}) + \dots = \\ E_n^{(0)} \mathbf{y}_n^{(0)} + \lambda (E_n^{(1)} \mathbf{y}_n^{(0)} + E_n^{(0)} \mathbf{y}_n^{(1)}) + \lambda^2 (E_n^{(2)} \mathbf{y}_n^{(0)} + E_n^{(1)} \mathbf{y}_n^{(1)} + E_n^{(0)} \mathbf{y}_n^{(2)}) + \dots \end{aligned}$$

*Note that we must assume a suitable convergence for both series.*



# Perturbational approach (VII)

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$$H^0 \mathbf{y}_n^{(0)} + I (H' \mathbf{y}_n^{(0)} + H^0 \mathbf{y}_n^{(1)}) + I^2 (H' \mathbf{y}_n^{(1)} + H^0 \mathbf{y}_n^{(2)}) + \dots =$$
$$E_n^{(0)} \mathbf{y}_n^{(0)} + I (E_n^{(1)} \mathbf{y}_n^{(0)} + E_n^{(0)} \mathbf{y}_n^{(1)}) + I^2 (E_n^{(2)} \mathbf{y}_n^{(0)} + E_n^{(1)} \mathbf{y}_n^{(1)} + E_n^{(0)} \mathbf{y}_n^{(2)}) + \dots$$

We note that the coefficients of like powers must be equal on both sides.

We deduce :

$$H^0 \mathbf{y}_n^{(0)} = E_n^{(0)} \mathbf{y}_n^{(0)} \quad \text{for } I^0 \text{ terms}$$

$$H' \mathbf{y}_n^{(0)} + H^0 \mathbf{y}_n^{(1)} = E_n^{(1)} \mathbf{y}_n^{(0)} + E_n^{(0)} \mathbf{y}_n^{(1)} \quad \text{for } I^1 \text{ terms}$$

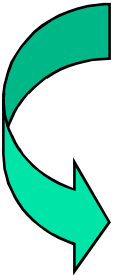
# Perturbational approach (VIII)

## First-order energy correction (1)

$$H'y_n^{(0)} + H^0 y_n^{(1)} = E_n^{(1)} y_n^{(0)} + E_n^{(0)} y_n^{(1)} \text{ for } l^1 \text{ terms}$$

or

$$H^0 y_n^{(1)} - E_n^{(0)} y_n^{(1)} = E_n^{(1)} y_n^{(0)} - H'y_n^{(0)} \longrightarrow E_n^{(1)} \quad ???$$



$$\underbrace{\langle y_m^{(0)} | H^0 | y_n^{(1)} \rangle - E_n^{(0)} \langle y_m^{(0)} | y_n^{(1)} \rangle}_{\text{left side}} = E_n^{(1)} \langle y_m^{(0)} | y_n^{(0)} \rangle - \langle y_m^{(0)} | H' | y_n^{(0)} \rangle$$

$$\begin{aligned} \langle y_m^{(0)} | H_0 | y_n^{(1)} \rangle &= \langle y_n^{(1)} | H^0 | y_m^{(0)} \rangle^* = \langle y_n^{(1)} | H_0 y_m^{(0)} \rangle^* = \langle y_n^{(1)} | E_m^{(0)} y_m^{(0)} \rangle^* \\ &= E_m^{(0)*} \langle y_n^{(1)} | y_m^{(0)} \rangle^* = E_m^{(0)} \langle y_n^{(1)} | y_m^{(0)} \rangle^* \end{aligned}$$

$$= E_m^{(0)} \langle y_m^{(0)} | y_n^{(1)} \rangle$$



# Perturbational approach (IX)

## First-order energy correction (2)

$$\langle \mathbf{y}_m^{(0)} | H^0 | \mathbf{y}_n^{(1)} \rangle - E_n^{(0)} \langle \mathbf{y}_m^{(0)} | \mathbf{y}_n^{(1)} \rangle = E_n^{(1)} \langle \mathbf{y}_m^{(0)} | \mathbf{y}_n^{(0)} \rangle - \langle \mathbf{y}_m^{(0)} | H' | \mathbf{y}_n^{(0)} \rangle$$

$$E_m^{(0)} \langle \mathbf{y}_m^{(0)} | \mathbf{y}_n^{(1)} \rangle - E_n^{(0)} \langle \mathbf{y}_m^{(0)} | \mathbf{y}_n^{(1)} \rangle = E_n^{(1)} \langle \mathbf{y}_m^{(0)} | \mathbf{y}_n^{(0)} \rangle - \langle \mathbf{y}_m^{(0)} | H' | \mathbf{y}_n^{(0)} \rangle$$

$$\longrightarrow (E_m^{(0)} - E_n^{(0)}) \langle \mathbf{y}_m^{(0)} | \mathbf{y}_n^{(1)} \rangle = E_n^{(1)} d_{mn} - \langle \mathbf{y}_m^{(0)} | H' | \mathbf{y}_n^{(0)} \rangle$$

If  $m=n$  :

$$E_n^{(1)} = \langle \mathbf{y}_n^{(0)} | H' | \mathbf{y}_n^{(0)} \rangle = H'_{nn} \quad \text{First-order correction}$$

Setting  $l=1$  :

$$E_n \approx E_n^{(0)} + E_n^{(1)} = E_n^{(0)} + H'_{nn}$$



# Perturbational approach (X)

## First-order wavefunction correction (1)

$$\text{if } m \neq n: (E_m^{(0)} - E_n^{(0)}) \langle \mathbf{y}_m^{(0)} | \mathbf{y}_n^{(1)} \rangle = - \langle \mathbf{y}_m^{(0)} | H | \mathbf{y}_n^{(0)} \rangle \longrightarrow \mathbf{y}_n^{(1)} \text{ ???}$$

Expansion in terms of the complete orthonormal set of unperturbed eigenfunctions  $\mathbf{y}_m^{(0)}$  of the Hermitian operator  $H$

$$\left. \begin{array}{l} \text{Expansion in terms of the} \\ \text{complete orthonormal set of} \\ \text{unperturbed eigenfunctions } \mathbf{y}_m^{(0)} \\ \text{of the Hermitian operator } H \end{array} \right\} \mathbf{y}_n^{(1)} = \sum_k a_k \mathbf{y}_k^{(0)} \text{ where } a_m = \langle \mathbf{y}_m^{(0)} | \mathbf{y}_n^{(1)} \rangle$$

$$\text{So : } (E_m^{(0)} - E_n^{(0)}) a_m = - \langle \mathbf{y}_m^{(0)} | H | \mathbf{y}_n^{(0)} \rangle \quad \text{if } m \neq n$$

$$a_m = \frac{\langle \mathbf{y}_m^{(0)} | H | \mathbf{y}_n^{(0)} \rangle}{(E_n^{(0)} - E_m^{(0)})}$$

**Ok for non-degenerate case !!**



# Perturbational approach (XI)

## First-order wavefunction correction (2)

if  $m \neq n$

$$a_m = \frac{\langle \mathbf{y}_m^{(0)} | H' | \mathbf{y}_n^{(0)} \rangle}{(E_n^{(0)} - E_m^{(0)})}$$

else

$$a_n = \langle \mathbf{y}_n^{(0)} | \mathbf{y}_n^{(1)} \rangle = 0$$

(intermediate normalization)

### First-order correction

$$\mathbf{y}_n^{(1)} = \sum_m a_m \mathbf{y}_m^{(0)} = \sum_{m \neq n} \frac{\langle \mathbf{y}_m^{(0)} | H' | \mathbf{y}_n^{(0)} \rangle}{(E_n^{(0)} - E_m^{(0)})} \mathbf{y}_m^{(0)}$$



Setting  $l = 1$  :

$$\mathbf{y}_n \approx \mathbf{y}_n^{(0)} + \sum_{m \neq n} \frac{\langle \mathbf{y}_m^{(0)} | H' | \mathbf{y}_n^{(0)} \rangle}{(E_n^{(0)} - E_m^{(0)})} \mathbf{y}_m^{(0)}$$



# Perturbational approach (XII)


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## Second-order energy correction (1)

We start again from :

$$H^0 \mathbf{y}_n^{(0)} + I (H' \mathbf{y}_n^{(0)} + H^0 \mathbf{y}_n^{(1)}) + I^2 (H' \mathbf{y}_n^{(1)} + H^0 \mathbf{y}_n^{(2)}) + \dots =$$
$$E_n^{(0)} \mathbf{y}_n^{(0)} + I (E_n^{(1)} \mathbf{y}_n^{(0)} + E_n^{(0)} \mathbf{y}_n^{(1)}) + I^2 (E_n^{(2)} \mathbf{y}_n^{(0)} + E_n^{(1)} \mathbf{y}_n^{(1)} + E_n^{(0)} \mathbf{y}_n^{(2)}) + \dots$$




$$H' \mathbf{y}_n^{(1)} + H^0 \mathbf{y}_n^{(2)} = E_n^{(2)} \mathbf{y}_n^{(0)} + E_n^{(1)} \mathbf{y}_n^{(1)} + E_n^{(0)} \mathbf{y}_n^{(2)} \text{ for } I^2 \text{ terms}$$
$$H^0 \mathbf{y}_n^{(2)} - E_n^{(0)} \mathbf{y}_n^{(2)} = E_n^{(2)} \mathbf{y}_n^{(0)} + E_n^{(1)} \mathbf{y}_n^{(1)} - H' \mathbf{y}_n^{(1)}$$



# Perturbational approach (XIII)

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## Second-order energy correction (2)

$$\begin{aligned} & \langle \mathbf{y}_m^{(0)} | H^0 | \mathbf{y}_n^{(2)} \rangle - E_n^{(0)} \langle \mathbf{y}_m^{(0)} | \mathbf{y}_n^{(2)} \rangle \\ &= E_n^{(2)} \langle \mathbf{y}_m^{(0)} | \mathbf{y}_n^{(0)} \rangle + E_n^{(1)} \langle \mathbf{y}_m^{(0)} | \mathbf{y}_n^{(1)} \rangle - \langle \mathbf{y}_m^{(0)} | H' | \mathbf{y}_n^{(1)} \rangle \end{aligned}$$

For the first-order correction, we have proved that :  $\langle \mathbf{y}_m^{(0)} | H^0 | \mathbf{y}_n^{(1)} \rangle = E_m^0 \langle \mathbf{y}_m^{(0)} | \mathbf{y}_n^{(1)} \rangle$

Similarly, we can show that :  $\langle \mathbf{y}_m^{(0)} | H^0 | \mathbf{y}_n^{(2)} \rangle = E_m^0 \langle \mathbf{y}_m^{(0)} | \mathbf{y}_n^{(2)} \rangle$



# Perturbational approach (XIV)

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## Second-order energy correction (3)

We can then deduce (see again first-order correction to the energy) :

$$(E_m^{(0)} - E_n^{(0)}) \langle \mathbf{y}_m^{(0)} | \mathbf{y}_n^{(2)} \rangle = E_n^{(2)} d_{mn} + E_n^{(1)} \langle \mathbf{y}_m^{(0)} | \mathbf{y}_n^{(1)} \rangle - \langle \mathbf{y}_m^{(0)} | H' | \mathbf{y}_n^{(1)} \rangle$$

If  $m=n$  : 
$$E_n^{(2)} = -E_n^{(1)} \langle \mathbf{y}_n^{(0)} | \mathbf{y}_n^{(1)} \rangle + \langle \mathbf{y}_n^{(0)} | H' | \mathbf{y}_n^{(1)} \rangle$$

→ 
$$E_n^{(2)} = \langle \mathbf{y}_n^{(0)} | H' | \mathbf{y}_n^{(1)} \rangle$$
 **Second-order correction**

Important remark : corrections to the wavefunctions through the  $k$ th order allow to calculate the corrections to the energy through order  $2k+1$ .



# Perturbational approach (XV)

## Second-order energy correction (4)

We know that :

$$\mathbf{y}_n^{(1)} = \sum_m a_m \mathbf{y}_m^{(0)} = \sum_{m \neq n} \frac{\langle \mathbf{y}_m^{(0)} | H' | \mathbf{y}_n^{(0)} \rangle}{(E_n^{(0)} - E_m^{(0)})} \mathbf{y}_m^{(0)}$$

$$E_n^{(2)} = \langle \mathbf{y}_m^{(0)} | H' | \mathbf{y}_n^{(1)} \rangle = \sum_{m \neq n} \frac{\langle \mathbf{y}_m^{(0)} | H' | \mathbf{y}_n^{(0)} \rangle}{(E_n^{(0)} - E_m^{(0)})} \langle \mathbf{y}_n^{(0)} | H' | \mathbf{y}_m^{(0)} \rangle$$

Moreover, it's easy to prove that :  $\langle \mathbf{y}_m^{(0)} | H' | \mathbf{y}_n^{(0)} \rangle \langle \mathbf{y}_n^{(0)} | H' | \mathbf{y}_m^{(0)} \rangle = \left| \langle \mathbf{y}_m^{(0)} | H' | \mathbf{y}_n^{(0)} \rangle \right|^2$

And finally :

$$E_n^{(2)} = \sum_{m \neq n} \frac{\left| \langle \mathbf{y}_m^{(0)} | H' | \mathbf{y}_n^{(0)} \rangle \right|^2}{(E_n^{(0)} - E_m^{(0)})}$$

**Second-order correction  
in terms of the unperturbed  
wavefunctions and energies**



# Perturbational approach (XVI)

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## Second-order energy correction (5)

$$E_n^{(2)} = \sum_{m \neq n} \frac{|\langle \mathbf{y}_m^{(0)} | H' | \mathbf{y}_n^{(0)} \rangle|^2}{(E_n^{(0)} - E_m^{(0)})} = \sum_{m \neq n} \frac{|H'_{mn}|^2}{(E_n^{(0)} - E_m^{(0)})}$$

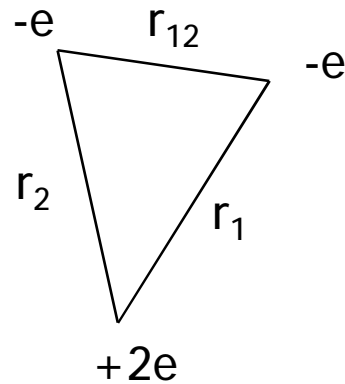
Setting  $l = 1$  :

$$E_n \approx E_n^{(0)} + H'_{nn} + \sum_{m \neq n} \frac{|H'_{mn}|^2}{(E_n^{(0)} - E_m^{(0)})}$$

*Comment: the largest contributions come from the states  $m$  near to  $n$  in terms of energy*

# Application of NDPT

Back to He :



$$y_0 = y_0(r_1, q_1, j_1; r_2, q_2, j_2)$$

$$H = -\frac{1}{2} \nabla_1^2 - \frac{2}{r_1} - \frac{1}{2} \nabla_2^2 - \frac{2}{r_2} + \frac{1}{r_{12}}$$

(in atomic units, energy in Hartree)

Perturbation approach :  $H = H^0 + H'$

$$H^0 = H_1^0 + H_2^0 = \left( -\frac{1}{2} \nabla_1^2 - \frac{2}{r_1} \right) + \left( -\frac{1}{2} \nabla_2^2 - \frac{2}{r_2} \right)$$

$$H' = \frac{1}{r_{12}}$$

# Application of NDPT (II)

$$\begin{aligned}
 E_0 &= \langle \mathbf{y}_0^{(0)} | H | \mathbf{y}_0^{(0)} \rangle = \langle \mathbf{y}_0^{(0)} | H_1^0 | \mathbf{y}_0^{(0)} \rangle + \langle \mathbf{y}_0^{(0)} | H_2^0 | \mathbf{y}_0^{(0)} \rangle + \langle \mathbf{y}_0^{(0)} | H' | \mathbf{y}_0^{(0)} \rangle \\
 &\quad \downarrow \qquad \qquad \qquad \downarrow \qquad \qquad \qquad \downarrow \\
 &\quad E_1 = -2 \text{ u.a.} \qquad E_2 = -2 \text{ u.a.} \qquad \langle \mathbf{y}_0 | \frac{1}{r_{12}} | \mathbf{y}_0 \rangle \\
 &\quad \underbrace{\hspace{10em}} \\
 &\quad E_0^{(0)} = -4 \text{ u.a.} \\
 &\quad \downarrow \\
 &\quad E_0^{(1)} = +5/4 \text{ u.a.}
 \end{aligned}$$

→ See details in TD1

We find :  $E_0 = -11/4 \text{ u.a.} = -74.8 \text{ eV}$ , including first-order energy correction

This result has to be compared to  $-77.5 \text{ eV}$  (variational approach with 1 parameter) and  $-79.0 \text{ eV}$  (experimental)