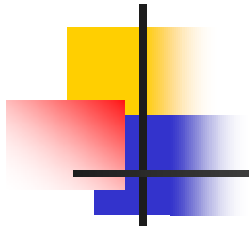


Liaison Chimique ‘07

Chap. II: The Helium Atom

Some remarks about units

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

1) SI units : $$H = -\frac{\mathbf{h}^2}{2m_e}\nabla^2 - \frac{e^2}{4pe_0 r}$$ (Hamiltonian for H)

Unit of mass : kg; charge : C and angular momentum : kg m^2/s

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

Unit of mass : g; charge : statcoulomb and g cm2

→ Important remark : **e'=e/4**pe_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 :ħ

Therefore : me = e' = ħ = 1

Atomic unit of length : 1 bohr ≡ $a_0 = \hbar/(m_e * e'^2)$ = 0.529177 Å

Atomic unit of energy : 1 Hartree ≡ $E_h = e'^2/a_0 = e^2/4\pi\varepsilon_0 a_0$ = 27.2114 eV

Alternative (obsolete but still used in spectroscopy) :

$H = -\nabla^2 - \frac{2}{r}$ (Hamiltonian for H) ⟶ **Atomic unit of energy : 1 Rydberg = 0.5 Ha**

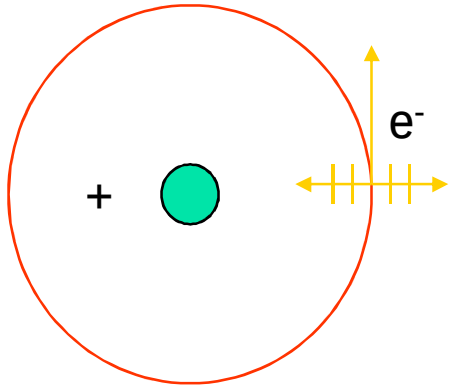
Hydrogen Atom

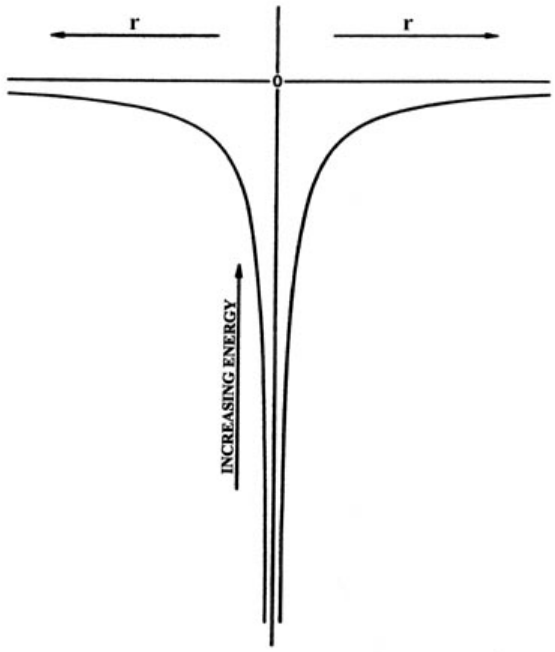
H

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

A central force problem

$V=-e^2/r$

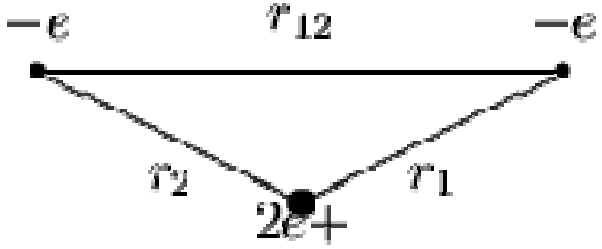




Helium Atom

He

Two electrons and Z= +2



$$H = T + V(r) = -\frac{\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r}$$ **SI units**

$$\hat{H} = \underbrace{-\frac{\hbar^2}{2\mu}\nabla^2_{r_1} - \frac{2e^2}{r_1}}_{\text{electron 1}} \underbrace{-\frac{\hbar^2}{2\mu}\nabla^2_{r_2} - \frac{2e^2}{r_2}}_{\text{electron 2}} + \underbrace{\frac{e^2}{r_{12}}}_{\text{electron 1 + electron 2}}.$$ **cgs Gaussian units**

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

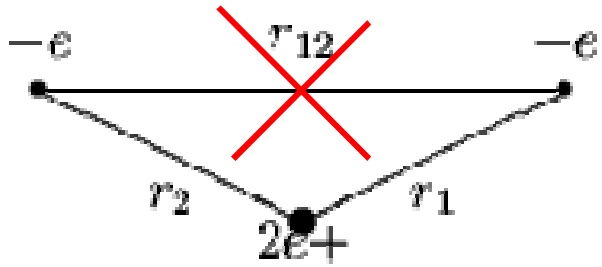
The simplest He

$$\hat{H} = -\frac{\hbar^2}{2\mu}\nabla^2_{r_1} - \frac{2e^2}{r_1} - \frac{\hbar^2}{2\mu}\nabla^2_{r_2} - \frac{2e^2}{r_2} + \frac{e^2}{r_{12}}.$$

The simplest approach: neglect the coupling = two independent e$^-$

$H = T_e + V_{eN}$

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



The simplest He (II)

$$\hat{H}^0 y^0 = E^0 y^0$$

$$\hat{H} = -\frac{\hbar^2}{2\mu}\nabla^2_{r_1} - \frac{2e^2}{r_1} - \frac{\hbar^2}{2\mu}\nabla^2_{r_2} - \frac{2e^2}{r_2}$$

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

$$y^0(x_1, y_1, z_1, x_2, y_2, z_2) = g_1(x_1, y_1, z_1) g_2(x_2, y_2, z_2)$$

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

$$\left[-\frac{h^2}{8p^2 m_e}\nabla^2_1 g_1 - \frac{2e^2}{r_1}\right] + \left[-\frac{h^2}{8p^2 m_e}\nabla^2_2 g_2 - \frac{2e^2}{r_2}\right] = E^0$$

The simplest He (III)

Or

$$-\frac{h^2}{8p^2 m_e}\nabla_1^2 g_1 - \frac{2e^2 g_1}{r_1} = E_1 g_1 \qquad -\frac{h^2}{8p^2 m_e}\nabla_1^2 g_2 - \frac{2e^2}{r_2} g_2 = E_2 g_2$$

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

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

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

calculated $E_{He} = -54.4\text{eV}$ experimental $E_{He} = -79.0\text{eV}$

Approximations

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

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

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:

Ψ = 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)

In practice

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

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

b) In the chosen function, we have parameters (e.g. λ) to vary in order to minimize the variational integral

if $\psi = \psi(\lambda)$ $\qquad \frac{\partial E}{\partial l} = 0$

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^+ wavefunctions but one electron "screens" the nuclear charge from the other

Z' = effective nuclear charge

The three ingredients:

The trial w.f. $\tilde{\psi} = A^2 e^{-\frac{z'}{a}(r_1+r_2)}$.

The variational integral $\tilde{E}(z') = < \tilde{\psi} | \hat{H} | \tilde{\psi} >,$

The Hamiltonian

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

He: a variational approach (II)

Using the above ingredients we can compute the variational integral

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

or

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

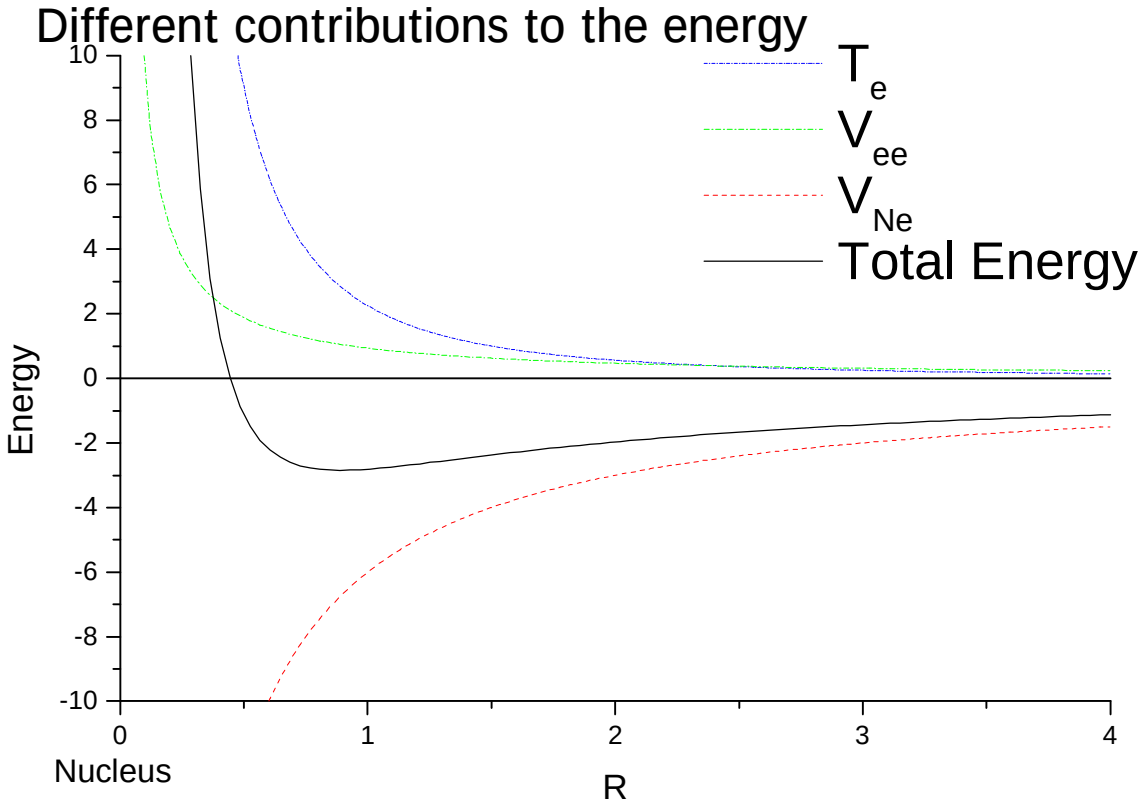
the optimum parameter Z' is then obtained

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

Z'=1.875 < 2

We find : $\mathbf{E_0 = -77.5\ eV}$, 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

- First step : decompose the hamiltonian

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

Hamiltonian of the perturbed system (real system)

Hamiltonian for which The solution is known (unperturbed system)

Perturbation

Example : anharmonic oscillator :

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

harmonic

perturbation

Perturbational approach (II)

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

$$H = H^0 + l\,H'$$

Pertubation parameter : 0 <= λ <=1

λ =0 (unperturbed) -> λ =1 (fully perturbed)

Perturbational approach (III)

Our framework :
the non degenerate perturbation theory (NDPT)

$$H = H^0 + lH'$$

For the unperturbed Hamiltonian H^0 : $H^0 y_n^{(0)} = E_n^{(0)} y_n^{(0)}$ (λ=0)

So : $Hy_n = (H^0 + lH')y_n = E_n y_n \longrightarrow \begin{cases} E_n = E_n(l) \\ y_n = y_n(l, q) \end{cases}$

Perturbational approach (IV)

Taylor expansion of ψ_n and E_n in powers of λ :

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

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

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

and by introducing the abbreviations :

$$y_n^{(k)} = \frac{1}{k!}\frac{\partial^k y_n}{\partial l^k}\Big|_{l=0} \quad \text{and} \quad E_n^{(k)} = \frac{1}{k!}\frac{d^k y_n}{dl^k}\Big|_{l=0} \qquad \mathrm{k} = 1,2,\ldots$$

We have…

Perturbational approach (V)

Taylor expansion of ψ_n and E_n in powers of λ :

$$y_n = y_n^{(0)} + l\, y_n^{(1)} + l^2 y_n^{(2)} + \ldots + l^k y_n^{(k)} + \ldots$$
$$E_n = E_n^{(0)} + l\, E_n^{(1)} + l^2 E_n^{(2)} + \ldots + l^k E_n^{(k)} + \ldots$$

<u>Hypothesis</u> : we assume that these series converge for $l=1$ 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 : $\left\langle y_n^{(0)} \middle| y_n^{(0)} \right\rangle = 1$ and $\left\langle y_n^{(0)} \middle| y_n \right\rangle = 1$ → ***Intermediate normalization*** simplifies the derivation and does not affect the results

So : $\left\langle y_n^{(0)} \middle| y_n \right\rangle = \left\langle y_n^{(0)} \middle| y_n^{(0)} \right\rangle + l \left\langle y_n^{(0)} \middle| y_n^{(1)} \right\rangle + l^2 \left\langle y_n^{(0)} \middle| y_n^{(2)} \right\rangle + \ldots = 1$

True for all values of l !

Perturbational approach (VI)

From the previous equation, we can prove :

$$\left\langle y_n^{(0)} \middle| y_n^{(1)} \right\rangle = \left\langle y_n^{(0)} \middle| y_n^{(2)} \right\rangle = \ldots = 0$$

⟶ *In other words, the corrections to the wavefunction are orthogonal to* $y_n^{(0)}$ *when intermediate normalization is used.*

We can now rewrite the Schrödinger equation using the two series we have developped. If we collect the terms like powers of λ, we have :

$$H^0 y_n^{(0)} + l\,(H' y_n^{(0)} + H^0 y_n^{(1)}) + l^2 (H' y_n^{(1)} + H^0 y_n^{(2)}) + \ldots =$$
$$E_n^{(0)} y_n^{(0)} + l\,(E_n^{(1)} y_n^{(0)} + E_n^{(0)} y_n^{(1)}) + l^2 (E_n^{(2)} y_n^{(0)} + E_n^{(1)} y_n^{(1)} + E_n^{(0)} y_n^{(2)}) + \ldots$$

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

Perturbational approach (VII)

$$H^0 y_n^{(0)} + l\,(H' y_n^{(0)} + H^0 y_n^{(1)}) + l^2 (H' y_n^{(1)} + H^0 y_n^{(2)}) + \ldots =$$
$$E_n^{(0)} y_n^{(0)} + l\,(E_n^{(1)} y_n^{(0)} + E_n^{(0)} y_n^{(1)}) + l^2 (E_n^{(2)} y_n^{(0)} + E_n^{(1)} y_n^{(1)} + E_n^{(0)} y_n^{(2)}) + \ldots$$

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

We deduce :

$$H^0 y_n^{(0)} = E_n^{(0)} y_n^{(0)} \quad \text{for } l^0 \text{ terms}$$
$$H' y_n^{(0)} + H_0 y_n^{(1)} = E_n^{(1)} y_n^{(0)} + E_n^{(0)} y_n^{(1)} \quad \text{for } l^1 \text{ terms}$$

Perturbational approach (VIII)

First-order energy correction (1)

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

or

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

$$\boxed{\langle y_m^{(0)}|}\, H^0 \,|y_n^{(1)}\rangle - E_n^{(0)} \boxed{\langle y_m^{(0)}|}\, y_n^{(1)}\rangle = E_n^{(1)} \boxed{\langle y_m^{(0)}|}\, y_n^{(0)}\rangle - \boxed{\langle y_m^{(0)}|}\, H' |y_n^{(0)}\rangle$$

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

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

Perturbational approach (IX)

First-order energy correction (2)

$$\boxed{\langle y_m^{(0)} | H^0 | y_n^{(1)} \rangle} - E_n^{(0)} \langle y_m^{(0)} | y_n^{(1)} \rangle = E_n^{(1)} \langle y_m^{(0)} | y_n^{(0)} \rangle - \langle y_m^{(0)} | H' | y_n^{(0)} \rangle$$

$$\boxed{E_m^{(0)} \langle y_m^{(0)} | y_n^{(1)} \rangle} - E_n^{(0)} \langle y_m^{(0)} | y_n^{(1)} \rangle = E_n^{(1)} \langle y_m^{(0)} | y_n^{(0)} \rangle - \langle y_m^{(0)} | H' | y_n^{(0)} \rangle$$

$$\longrightarrow \quad (E_m^{(0)} - E_n^{(0)}) \langle y_m^{(0)} | y_n^{(1)} \rangle = E_n^{(1)} d_{mn} - \langle y_m^{(0)} | H' | y_n^{(0)} \rangle$$

If m=n : $$\boxed{E_n^{(1)} = \langle y_n^{(0)} | H' | y_n^{(0)} \rangle = H'_{nn}}$$ **First-order correction**

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

Perturbational approach (X)

First-order wavefunction correction (1)

$$\text{if } \; m \neq n: \;\; (E_m^{(0)} - E_n^{(0)}) \left\langle y_m^{(0)} \middle| y_n^{(1)} \right\rangle = -\left\langle y_m^{(0)} \middle| H' \middle| y_n^{(0)} \right\rangle \longrightarrow y_n^{(1)} \;\; ???$$

Expansion in terms of the complete orthonormal set of unperturbed eigenfunctions $y_m^{(0)}$ of the Hermitian operator *H*

$$y_n^{(1)} = \sum_k a_k y_k^{(0)} \quad \text{where} \quad \boxed{a_m = \left\langle y_m^{(0)} \middle| y_n^{(1)} \right\rangle}$$

So : $$(E_m^{(0)} - E_n^{(0)}) a_m = -\left\langle y_m^{(0)} \middle| H' \middle| y_n^{(0)} \right\rangle \quad \text{if} \quad m \neq n$$

$$a_m = \frac{\left\langle y_m^{(0)} \middle| H' \middle| y_n^{(0)} \right\rangle}{(E_n^{(0)} - E_m^{(0)})}$$

Ok for non-degenerate case !!

Perturbational approach (XI)

First-order wavefunction correction (2)

if $m \neq n$

$$a_m = \frac{\langle y_m^{(0)} | H' | y_n^{(0)} \rangle}{(E_n^{(0)} - E_m^{(0)})}$$

else

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

(intermediate normalization)

First-order correction

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

Setting $\mathrm{l} = \mathbf{1}$:

$$y_n \approx y_n^{(0)} + \sum_{m \neq n} \frac{\langle y_m^{(0)} | H' | y_n^{(0)} \rangle}{(E_n^{(0)} - E_m^{(0)})} y_m^{(0)}$$

Perturbational approach (XII)

Second-order energy correction (1)

We start again from :

$$H^0 y_n^{(0)} + l\,(H' y_n^{(0)} + H^0 y_n^{(1)}) + l^2 (H' y_n^{(1)} + H^0 y_n^{(2)}) + \ldots =$$
$$E_n^{(0)} y_n^{(0)} + l\,(E_n^{(1)} y_n^{(0)} + E_n^{(0)} y_n^{(1)}) + l^2 (E_n^{(2)} y_n^{(0)} + E_n^{(1)} y_n^{(1)} + E_n^{(0)} y_n^{(2)}) + \ldots$$

$$\downarrow$$

$$H' y_n^{(1)} + H^0 y_n^{(2)} = E_n^{(2)} y_n^{(0)} + E_n^{(1)} y_n^{(1)} + E_n^{(0)} y_n^{(2)} \text{ for } l^2 \text{ terms}$$

$$H^0 y_n^{(2)} - E_n^{(0)} y_n^{(2)} = E_n^{(2)} y_n^{(0)} + E_n^{(1)} y_n^{(1)} - H' y_n^{(1)}$$

Perturbational approach (XIII)

Second-order energy correction (2)

$$\boxed{\langle y_m^{(0)}|}H^0|y_n^{(2)}\rangle - E_n^{(0)}\boxed{\langle y_m^{(0)}|}y_n^{(2)}\rangle$$
$$= E_n^{(2)}\boxed{\langle y_m^{(0)}|}y_n^{(0)}\rangle + E_n^{(1)}\boxed{\langle y_m^{(0)}|}y_n^{(1)}\rangle - \boxed{\langle y_m^{(0)}|}H'|y_n^{(1)}\rangle$$

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

Similarly, we can show that : $\langle y_m^{(0)}|H^0|y_n^{(2)}\rangle = E_m^0\langle y_m^{(0)}|y_n^{(2)}\rangle$

Perturbational approach (XIV)

Second-order energy correction (3)

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

$$(E_m^{(0)} - E_n^{(0)})\langle y_m^{(0)} | y_n^{(2)} \rangle = E_n^{(2)} d_{mn} + E_n^{(1)} \langle y_m^{(0)} | y_n^{(1)} \rangle - \langle y_m^{(0)} | H' | y_n^{(1)} \rangle$$

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

$$\longrightarrow \boxed{E_n^{(2)} = \langle y_m^{(0)} | H' | y_n^{(1)} \rangle}$$

Second-order correction

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

Perturbational approach (XV)

Second-order energy correction (4)

We know that : $$y_n^{(1)} = \sum_m a_m y_m^{(0)} = \sum_{m \neq n} \frac{\langle y_m^{(0)} | H' | y_n^{(0)} \rangle}{(E_n^{(0)} - E_m^{(0)})} y_m^{(0)}$$

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

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

And finally : $$E_n^{(2)} = \sum_{m \neq n} \frac{\left| \langle y_m^{(0)} | H' | y_n^{(0)} \rangle \right|^2}{(E_n^{(0)} - E_m^{(0)})}$$

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

Perturbational approach (XVI)

Second-order energy correction (5)

$$E_n^{(2)} = \sum_{m \neq n} \frac{\left| \left\langle y_m^{(0)} \middle| H' \middle| y_n^{(0)} \right\rangle \right|^2}{(E_n^{(0)} - E_m^{(0)})} = \sum_{m \neq n} \frac{\left| H'_{mn} \right|^2}{(E_n^{(0)} - E_m^{(0)})}$$

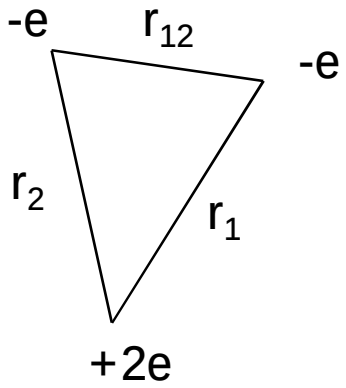
Setting $\lambda = 1$:

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

*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)

$$E_0 = \langle y_0^{(0)} | H | y_0^{(0)} \rangle = \langle y_0^{(0)} | H_1^0 | y_0^{(0)} \rangle + \langle y_0^{(0)} | H_2^0 | y_0^{(0)} \rangle + \langle y_0^{(0)} | H' | y_0^{(0)} \rangle$$

E_1=-2 u.a. E_2=-2 u.a. $\langle y_0 | \frac{1}{r_{12}} | y_0 \rangle$

$E_0^{(0)}$ = - 4 u.a.

$E_0^{(1)}$ = + 5/4 u.a.

⟶ See details in **TD1**

We find : **E_0 = -11/4 u.a. = -74.8 eV**, including first-order energy correction

This result has to be compared to **-77.5 eV** (variationnal approach with 1 parameter) and **-79.0 eV** (experimental)