# Molecular Systems in a Strong Magnetic Field

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**London, April 2006**

The goal:

How

ATOMIC - MOLECULAR PHYSICS

IN a strong MAGNETIC FIELD

looks like

*A particular overview of one-two electron molecular systems made out of protons and/or $\alpha$-particles which do exist in a strong magnetic field*

$$B \leq 4.414 \times 10^{13}\ G$$

(in collaboration with J.C. Lopez Vieyra & N. Guevara)

$1e$**:**

$H,\ H_2^+\ ,\quad H_3^{2+},\ H_4^{3+}$

$(HeH)^{2+}\ ,\ (H-He-H)^{3+}\ ,\ (He-H-He)^{4+}$

$He^+\ ,\quad He_2^{3+}$

(the list is complete for $B \leq 4.414 \times 10^{13}$ G)

$2e$**:**

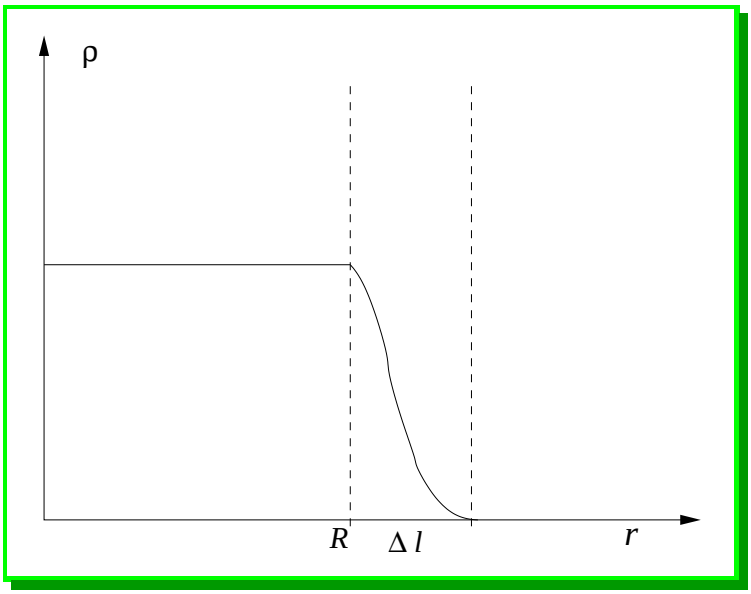
$H^-\ ,\ H_2\ ,\ H_3^+\ ,\quad H_4^{2+},\ H_5^{3+}\ etc$

$(HeH)^+\ etc$

$He\ ,\quad He_2^{2+}\ etc$

**$H$-atom is stable but has a highest total energy among $1e$ systems**

# NEUTRON STARS




core vacuum

$\sim 10^8 - 10^9$ (out of $10^{11}$) in our Galaxy

($\sim 1500$ in catalogue )

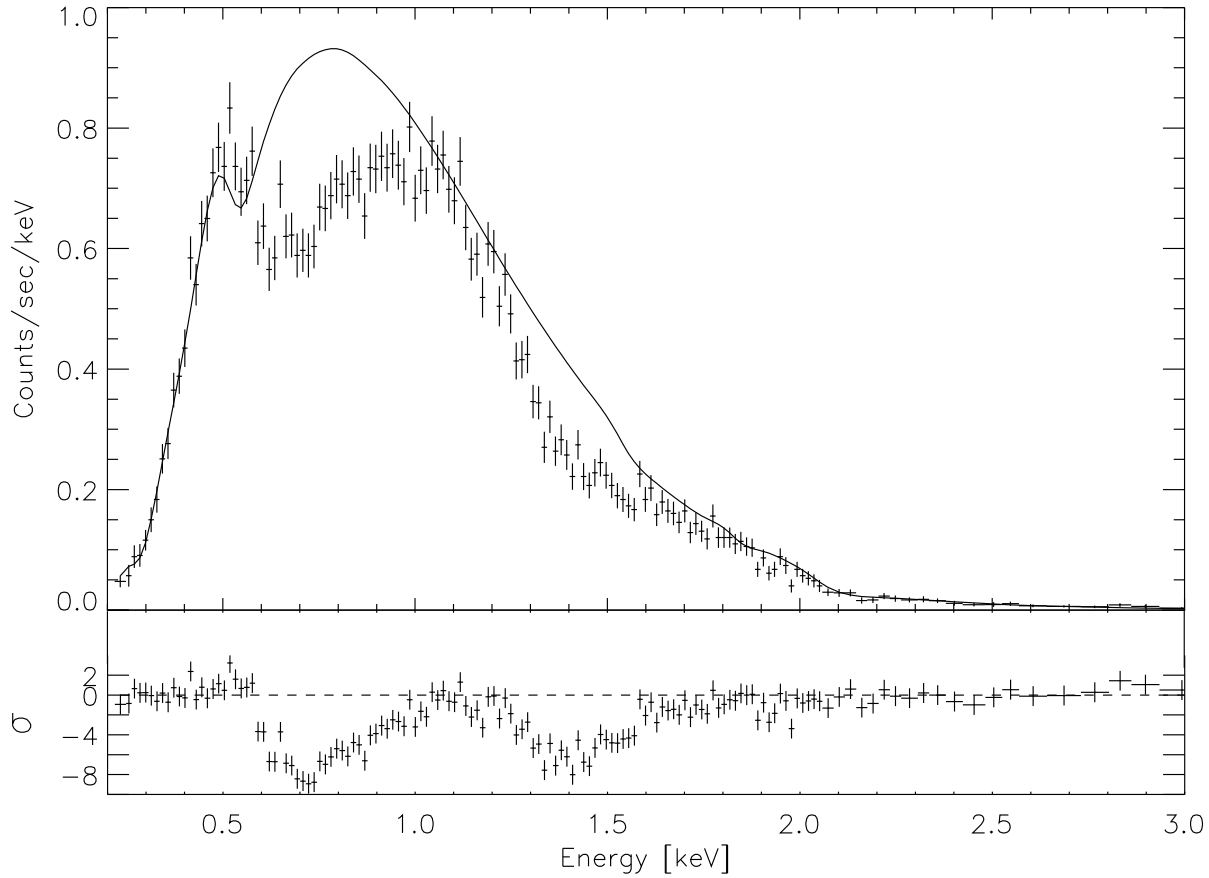
$M \sim 1.5\ M_\odot$

$r \sim 5 - 15\ Km$

$\Delta\ell \sim 1 - 10\ cm$

$T \sim 10 - 100 eV \quad (10^5 - 10^6\, K)$

$B \sim 10^{12} - 10^{13}\ G$




*Chandra + XMM-Newton data*
(Hailey & Mori, 2003)

Two absorption lines:

$$E_1 \;=\; 730 \pm 100 \text{ eV}$$

$$E_2 \;=\; 1400 \pm 130 \text{ eV}$$

## Why the problem is so difficult ?

- Highly-non-uniform asymptotics of potential at large distances
- Weakly-bound states

$$E_{binding} << E_{total}$$

(e.g. for $H_2^+$ at $B = 10^{13}$ G the ratio is $\lesssim 10^{-2}$)

## Method

- Variational Calculation
- *Simple* and unique trial functions applicable for the whole range of accessible magnetic fields $(0 - 4.414 \times 10^{13} G)$ which can lead to a sufficiently high accuracy in total energy

How to choose trial functions?

- Physical relevance (as many as possible physics properties should be encoded)
- Mathematical (computational) simplicity should **not** be a guiding principle
- Resulting perturbation theory should be convergent (see below)

## *Variational calculation*

For chosen $\Psi_{trial}$ a trial Potential

$$V_{trial} \;=\; \frac{\nabla^2 \Psi_{trial}}{\Psi_{trial}} \;,\; E_{trial} = \; 0$$

hence, we know the Hamiltonian for which the normalized $\Psi_{trial}$ is eigenfunction

$$H_{trial}\; \Psi_{trial} = [p^2 + V_{trial}]\; \Psi_{trial} = 0$$

then

$$\begin{aligned} E_{var} &= \int \Psi^*_{trial}\; H\; \Psi_{trial} \\ &= \int \psi^*_{trial}\; \underbrace{H_{trial}\; \Psi_{trial}}_{=0} + \int \Psi^*_{trial}\, (H - H_{trial})\, \Psi_{trial} \\ &= 0 + \int \Psi^*_{trial}\, (V - V_{trial})\, \Psi_{trial}\; \text{“} + \ldots \text{”} \equiv E_0 + E_1 \text{“} + \ldots \text{”} \end{aligned}$$

- The variational energy is a sum of the first two terms of a certain perturbative series with perturbation $(V - V_{trial})$ ,
- How to calculate $E_2$ *in practice*? - in general, unsolved yet

## INSTRUCTIVE EXAMPLE

**Hydrogen in a magnetic field (ground state)**

$$V = -\frac{2}{r} + \frac{B^2}{4}\rho^2, \qquad \rho^2 = x^2 + y^2.$$

$$\psi_0 = \exp\left(-\alpha r - \beta B \rho^2/4\right)$$

$\alpha, \beta$ variational parameters

with

$$V_0 = \frac{\Delta\psi_0}{\psi_0} = -\frac{2\alpha}{r} + \frac{\beta^2 B^2}{4}\rho^2 + \underbrace{\frac{\alpha\beta B}{2}\frac{\rho^2}{r}}_{V - V_0}, \quad E_0 = -\alpha^2 + \beta B$$

Relative accuracy $\sim 10^{-4}$ *in total energy comparing to an accurate calculation.*

*REMARK (A.Potekhin & AT '01)*:

$$\psi_0 = \exp\left(-\sqrt{\alpha^2 r^2 + (\gamma_1 r^3 + \gamma_2 r^2\rho + \gamma_3 r\rho^2 + \gamma_4\rho^3) + \beta^2 B^2 \rho^4/16}\right)$$

gives relative accuracy $\sim 10^{-7}$ in total energy for magnetic fields $0 < B < 4.414 \times 10^{13}$ G.

$$H: \quad E_b(10000\, a.u.) \;=\; 27.95\, Ry$$

$$He^+: \quad E_b(10000\, a.u.) \;=\; 78.43\, Ry$$

- Hydrogen atom in a magnetic field (ground state)

$$V = -\frac{2}{r} + \frac{B^2}{4}(x^2 + y^2) \quad , \quad 0 \le B \le B_{Schwinger}$$

*several hundred articles since 1926, but quadrupole moment is calculated in 2001 only*

Howard-Hasegawa ('61) found leading term in asymptotics

$$E_{binding} \;=\; log^2 B + \ldots \quad , \quad B \to \infty$$

but at 2003 only (!) Karnakov-Popov paid attention (and tried to fix) that *even* at the Schwinger limit $B = B_{Schwinger} (\approx 2 \times 10^4\, a.u.)$ the ratio

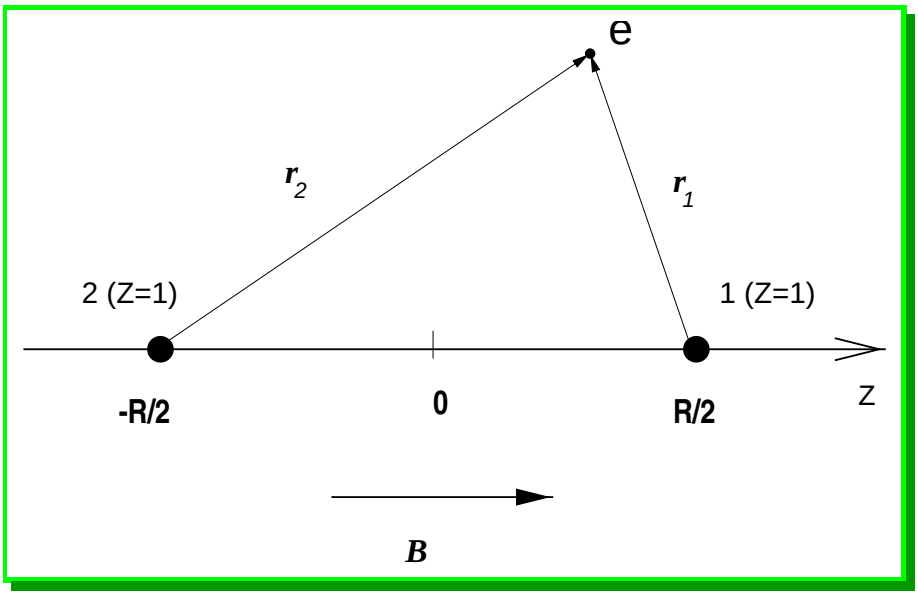
$$\frac{E^{exact}_{binding}}{log^2 B} \approx 1/3$$

asymptotics is delayed and ...

**NO DOMAIN OF APPLICABILITY OF ASYMPTOTIC METHODS in non-relativistic domain of $B$**

# $(ppe)$ system

## $H_2^+$ molecular ion ( Parallel Configuration)




$$V = -\frac{2}{r_1} - \frac{2}{r_2} + \frac{2}{R} + Bm_l + \frac{B^2\rho^2}{4}$$

$$\rho^2 = x^2 + y^2$$

# Trial Functions for $H_2^+$

I

$$\psi_1 = \underbrace{e^{-\alpha_1(r_1+r_2)}}_{\text{Heitler-London}} \quad \underbrace{e^{-\beta_1 B\rho^2/4}}_{\text{Landau}}$$

$\alpha_1, \beta_1, R$ variational parameters

$$V_1^{trial} = -2\alpha_1\left(\frac{1}{r_1}+\frac{1}{r_2}\right) + {\beta_1}^2\frac{B^2\rho^2}{4} + 2{\alpha_1}^2 - \beta_1 B + \underbrace{2{\alpha_1}^2\vec{n_1}\cdot\vec{n_2} + \alpha_1\beta_1 B\rho^2\left(\frac{1}{r_1}+\frac{1}{r_2}\right)}_{V-V_{trial}}$$

- $\alpha_1, \beta_1 \neq 1$

  (anti) screening of the nuclear charges and of the magnetic field, respectively

- We assume that the modified Heitler-London approximation can give a significant contribution for internuclear distances near equilibrium.

  'Covalent' coupling of the system to be verified *a posteriori*

II

$$\psi_2 = \underbrace{\left(e^{-\alpha_2 r_1} + \sigma e^{-\alpha_2 r_1}\right)}_{\text{Hund-Mulliken}} \; e^{-\beta_2 B\rho^2/4}$$

- $\alpha_2, \beta_2, R$ are variational parameters.
- We assume that this function can give a significant contribution for large internuclear distances
- 'Ionic' coupling, $H + p$ (to be verified *a posteriori*).

In order to describe both domains $R \simeq R_{eq}$ and $R \gg R_{eq}$:
we use *interpolations*

III-1 Non-linear Interpolation (simplest)

$$\psi_{3_1} = \underbrace{\left(e^{-\alpha_3 r_1 - \alpha_4 r_2} + \sigma e^{-\alpha_3 r_2 - \alpha_4 r_1}\right)}_{\text{Guillemin-Zener}} \; e^{-\beta_3 B\rho^2/4}$$

- If $\alpha_3 = \alpha_4$ then $\psi_{3_1} \to \psi_1$
- If $\alpha_4 = 0$ then $\psi_{3_1} \to \psi_2$
- Ionic $\leftrightarrow$ covalent coupling interpolation (verified *a posteriori*).
- $\alpha_3, \alpha_4, \beta_3, R$ are variational parameters

III-2 Linear Interpolation

$$\psi_{3_2} = A_1\psi_1 + A_2\psi_2$$

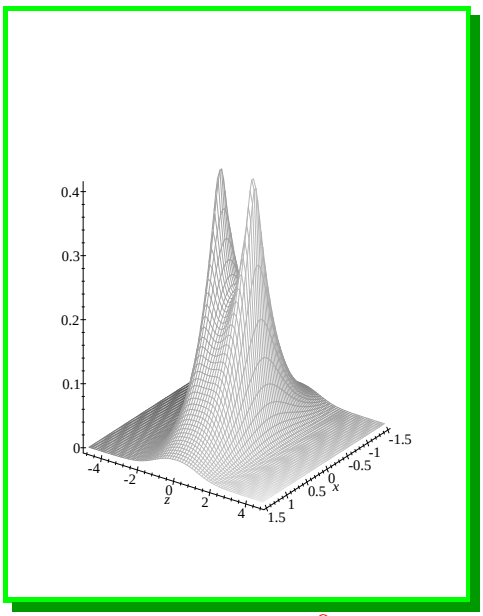
## IV Superposition of the two kinds of interpolation

$$\psi_4 = A_{3_1}\psi_{3_1} + A_{3_2}\psi_{3_2}$$

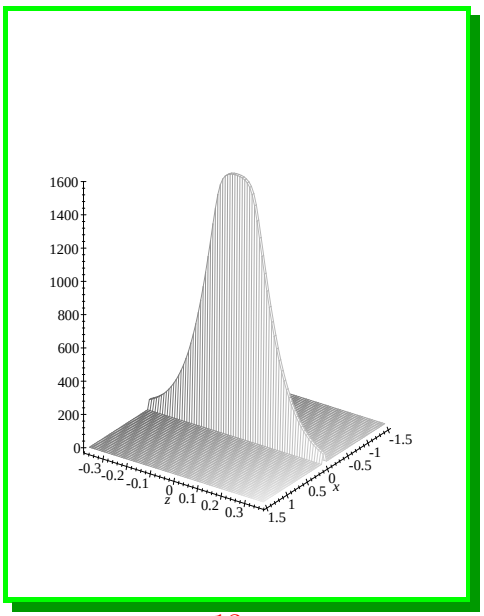
- *10 variational parameters*
- $\psi_4$ *gives the* **lowest** *total energies for the ground state compared with previous calculations* ($\sim 50$ *calculations*) *for* $B > 10^{10}\,G$ *up to* $B = 4.414 \times 10^{13}\,G$,
- *For* $B \lesssim 10^{10}\,G$*: Relative accuracy* $\sim 10^{-5}$ *in binding energy (comparing to the most accurate calculation by Guan et al '03)*
- *Excited states* $1\sigma_u, 1\pi_{g,u}, 1\delta_{g,u}$ *were studied in details*

Physical Phenomenon:

**For $B \sim 5 \times 10^{11} G$ the coupling changes from 'ionic' type to 'covalent' type**




$B = 10^9$ G

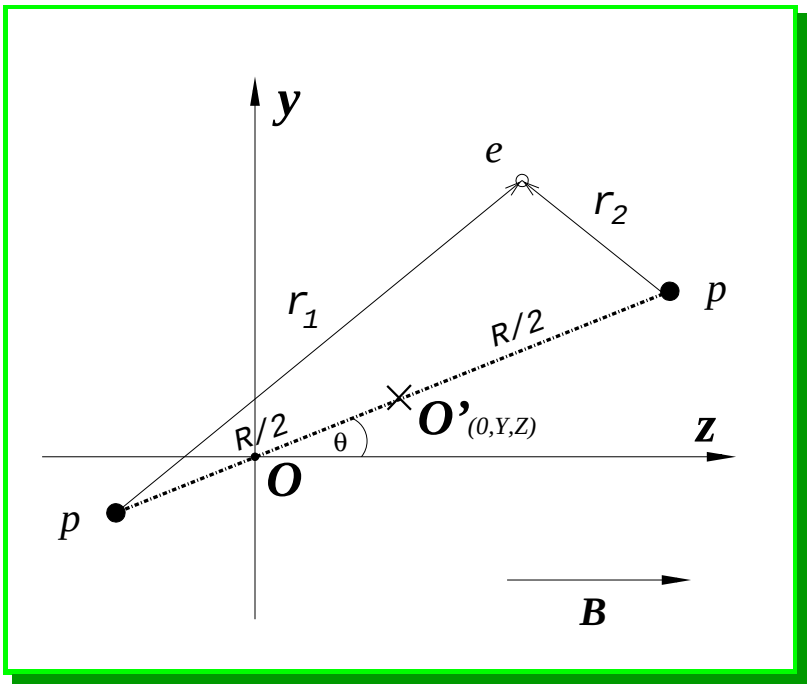


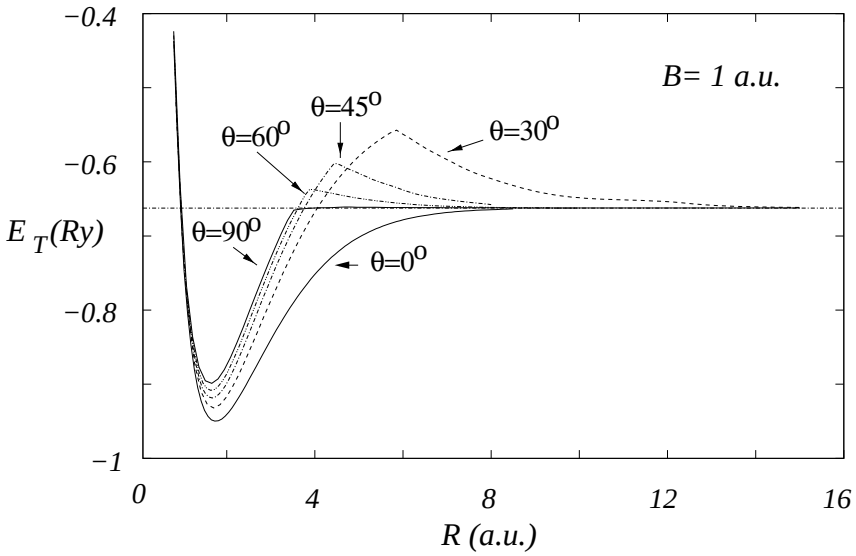

$B = 10^{13}$ G

# $(ppe)$ system

## $H_2^+$: inclined configuration

(The molecular axis and magnetic line form angle $\theta$)






**Parallel configuration is optimal for all magnetic fields**

- $H_2^+$ does not exist for large inclinations at $B > 10^{11}$ G

*$H_2^+$ is stable for all $B$ and the most bound $1e$-system made from protons for $B \lesssim 10^{13}$ G*

$$H_2^+ \nrightarrow H + p$$

$$E_b(10^{12}\,G) \;=\; 17.14\,Ry\;,\;\; E_b(10000\,a.u.) \;=\; 45.80\,Ry$$

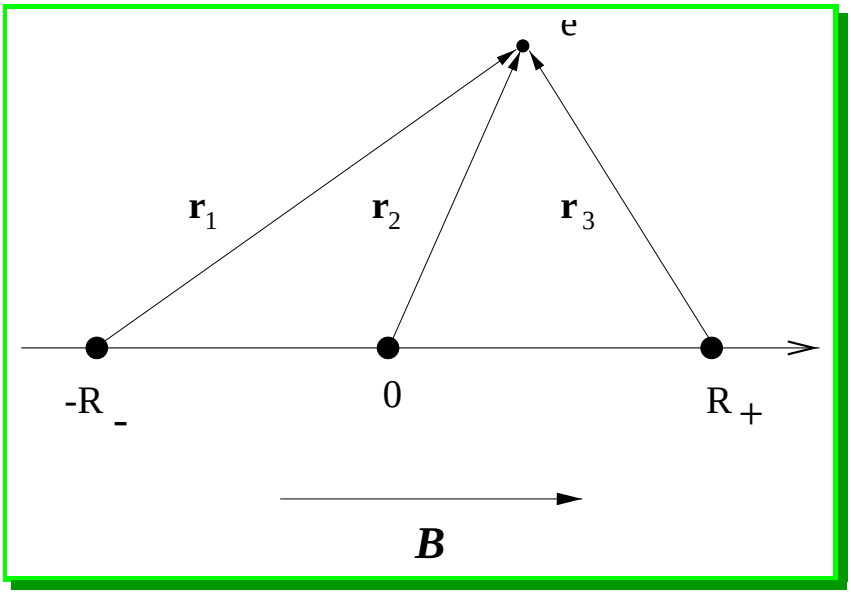
comparison with $H$ : $E_b(10000\,a.u.) \;=\; 27.95\,Ry$

$$\Delta E(1\sigma_g \rightarrow 1\pi_u) \;=\; 11.73\,Ry \text{ at } 10000\,a.u.$$

$(pppe)$ system

$H_3^{2+}$: linear parallel configuration

(The molecular axis and magnetic line coincide)




$$V = \frac{2}{R_-} + \frac{2}{R_+} + \frac{2}{R_- + R_+} - \frac{2}{r_1} - \frac{2}{r_2} - \frac{2}{r_3} + \frac{B^2(x^2+y^2)}{4},$$

For $B \gtrsim 10^{11}\,G$ the system $(pppe)$ has a bound state, which manifests existence of the exotic molecular ion $H_3^{2+}$

(A.T., J.C. López V. and U. Solis H. '99)

( *Without magnetic field* $H_3^{2+}$ *does NOT exist!* )

For $B \gtrsim 10^{11}\,G$ the total energy $E(R_+, R_-)$ has minimum for finite $R_+ = R_-$ which is stable towards small deviations from linearity

(parallel configuration is optimal)

$H_3^{2+}$ ion can exist for $B \gtrsim 10^{11}\,G$ as well as its excited states $1\pi_u, 1\delta_g$

$$H_3^{2+} \rightarrow H_2^+ + p$$

$$H_3^{2+} \nrightarrow H + p + p$$

$H_3^{2+}$ is stable and the most bound $1e$-system made from protons for $B \gtrsim 3 \times 10^{13}\,G$

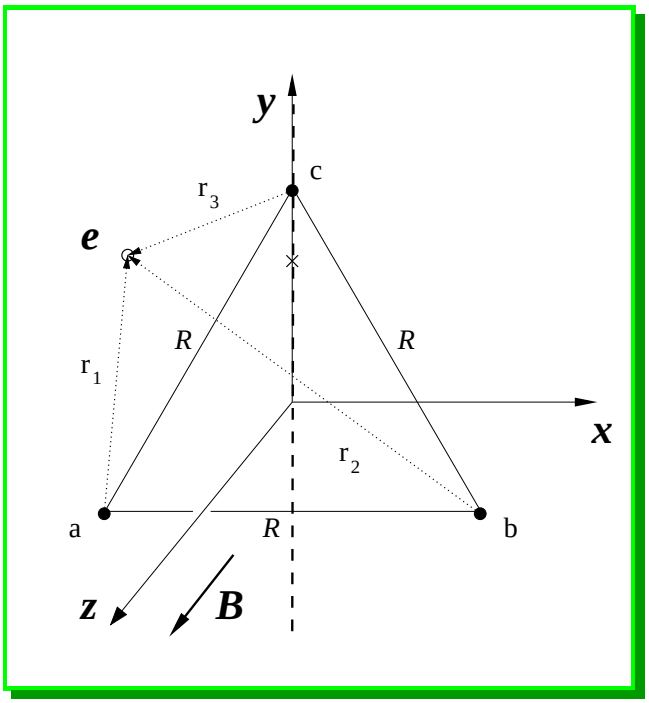
$$H_3^{2+} \nrightarrow H_2^+ + p$$

$$* \; * \; *$$

$$E_b(10000\,a.u.) \;=\; 45.41\,Ry$$

$$\Delta E(1\sigma_g \rightarrow 1\pi_u) \;=\; 12.78\,Ry \text{ at } 10000\,a.u.$$

# $H_3^{2+}$ ion (triangular configuration)




**Does the system $(pppe)$ in equilateral triangular configuration have a bound state in a magnetic field ?**

At $B < 10^8\,G$ or $B > 10^{11}\,G$ the total energy $E(R)$ has no minimum at finite $R$

At $10^8\,G \lesssim B \lesssim 10^{11}\,G$ the total energy $E(R)$ has a well-pronounced minimum at finite $R$ manifesting existence of $H_3^{2+}$ in triangular configuration as a metastable (or unstable) system

precursor to linear configuration

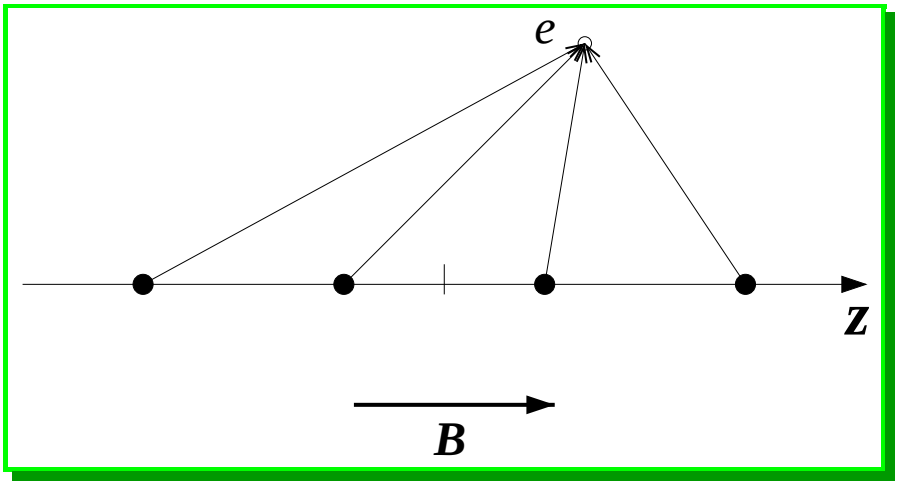
No more spatial configurations found!

(A.T. and J.C. López V. '02)

# $(ppppe)$ system

## $H_4^{3+}$ molecular ion ( Parallel Configuration)

(J.C. López V. and A.T. '00, H.Olivares P. '04)



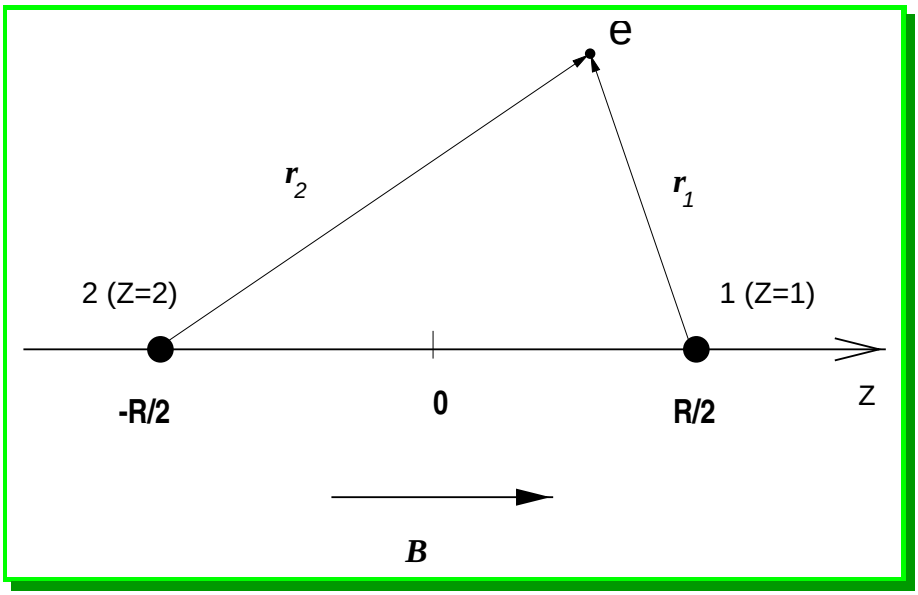

For $B \gtrsim 10^{13}\,G$ the system $(ppppe)$ has a minimum in total energy
$\rightarrow$ the existence of the molecular ion $H_4^{(3+)}$ as metastable state as well as its excited state $1\pi_u$

$$E_b(3 \times 10^{13}\,G) \;=\; 38.42\,Ry$$

# $(\alpha pe)$ system

## $(HeH)^{(2+)}$ molecular ion

(A.T. and J.C. López V. '04)




- For $B \gtrsim 10^{12}\,\mathrm{G}$ the system $(\alpha pe)$ has a bound state manifesting the possible existence of the molecular ion $(HeH)^{(2+)}$ as well as its excited states $1\pi, 1\delta$
- For $B \gtrsim 10^{13}\,\mathrm{G}$ it becomes stable: $(HeH)^{(2+)} \nrightarrow He^{+} + p$
- Parallel Configuration is always optimal

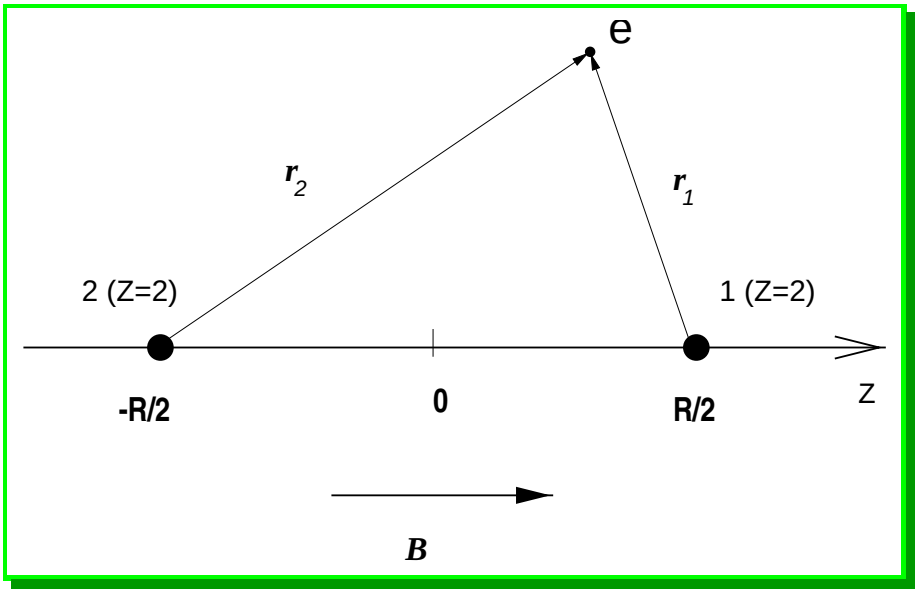
$$E_b(10000\,a.u.) \;=\; 77.30\,Ry$$

$$\Delta E(1\sigma \rightarrow 1\pi) \;=\; 20.80\,Ry \text{ at } 10000\,a.u.$$

# $(\alpha\alpha e)$ system

## $He_2^{(3+)}$ molecular ion

(A.T. and J.C. López V. '04)




- For $B \gtrsim 2 \times 10^{11}$ G the system $(\alpha\alpha e)$ has bound states manifesting the existence of the molecular ion $He_2^{(3+)}$ as well as its excited states of positive parity $1\pi_u, 1\delta_g$.
- For $B \gtrsim 10^{12}$ G it becomes stable:
$He_2^{(3+)} \nrightarrow He^+ + \alpha$
- Parallel Configuration is always optimal

$$E_b(10000\,a.u.) \;=\; 86.23\,Ry \quad [E_b^{He^+}(10000\,a.u.) \;=\; 78.43\,Ry]$$

$$\Delta E(1\sigma_g \rightarrow 1\pi_u) \;=\; 24.69\,Ry \text{ at } 10000\,a.u.$$

The striking relation between the binding energies of the most bound one-electron systems made from $\alpha-$particles and made from protons:

$$E_b^{He^+, He_2^{(3+)}} \approx 2\ E_b^{H_2^+, H_3^{2+}}$$

for $10^{11}\, G < B < 10^{14}\, G$

- For $B < 10^{12}\, G$ in l.h.s. $E_b$ of $He^+$, otherwise $E_b$ of the exotic $He_2^{3+}$
- For $B < 10^{13}\, G$ in r.h.s. $E_b$ of $H_2^+$, otherwise $E_b$ of the exotic $H_3^{2+}$

# Summary

## One-electron linear systems

(for details see recent *Physics Reports*)

*Optimal configuration of linear* $H_2^+$, $H_3^{2+}$, $H_4^{(3+)}$, $(HeH)^{2+}$ *and* $He_2^{(3+)}$ *is parallel, along magnetic field (when exist)*

when magnetic field grows:

- Binding energy of $H$, $H_2^+$, $H_3^{2+}$, $H_4^{3+}$, $(HeH)^{2+}$ and $He_2^{3+}$ grows (when exist)
- Natural size of the systems $H_2^+, H_3^{2+}, (HeH)^{2+}$ and $He_2^{3+}$ decreases
- $H_2^+$ has the *lowest* $E_{total}$ for $0 < B \lesssim 10^{13}\,G$ (made from protons)
- $H_3^{2+}$ has the *lowest* $E_{total}$ for $B \gtrsim 10^{13}\,G$ (made from protons)
- Possible existence of the system $H_5^{(4+)}$ for $B > 4.4 \times 10^{13}\,G$; but a reliable statement requires a consideration of relativistic corrections
- For $B \gtrsim 10^{12}\,G$ the exotic $He_2^{3+}$ has the **lowest total energy** among systems made from protons and/or $\alpha-$particles
- **$H_2^+$ and linear $H_3^{2+}$ binding energies $\equiv$ ionization energies at $B \sim 3 \times 10^{13}$ G coincide, both are $\sim 700$ eV, while for $He_2^{3+}$ it is $\sim 1400$ eV**
- Something non-trial may happen at the Schwinger limit $B \sim 4.414 \times 10^{13}$ G (see Table)

• Technical point:

*Many even quite sophisticated methods allow to find 1,2,3 significant digits in binding energy (e.g. E. Salpeter et al '92 for $H_2^+$ at $10^{11}\,G$ gives a single digit only), a problem comes when you want to go beyond, to higher accuracy.*

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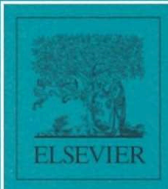


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A Review Section of Physics Letters

# ONE-ELECTRON MOLECULAR SYSTEMS IN A STRONG MAGNETIC FIELD

Alexander V. TURBINER, Juan Carlos LÓPEZ VIEYRA



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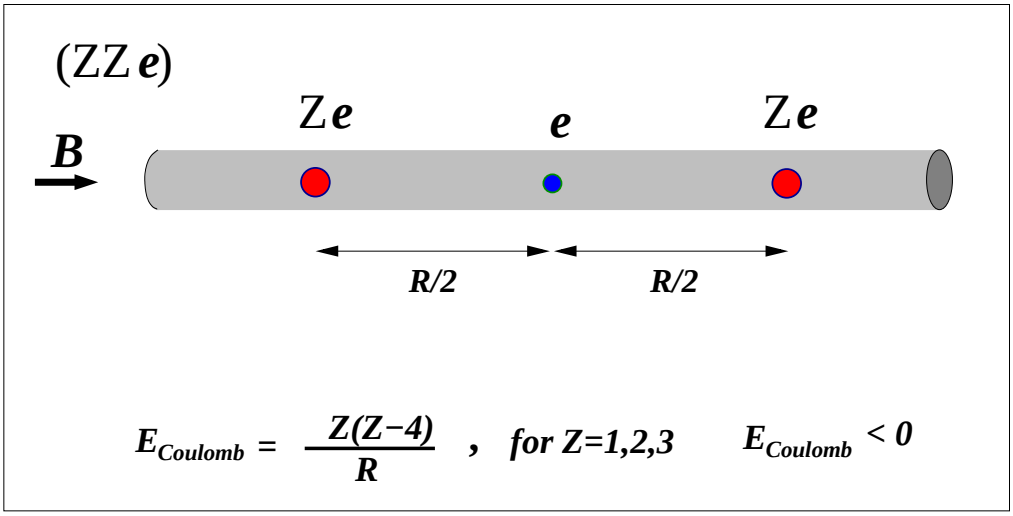
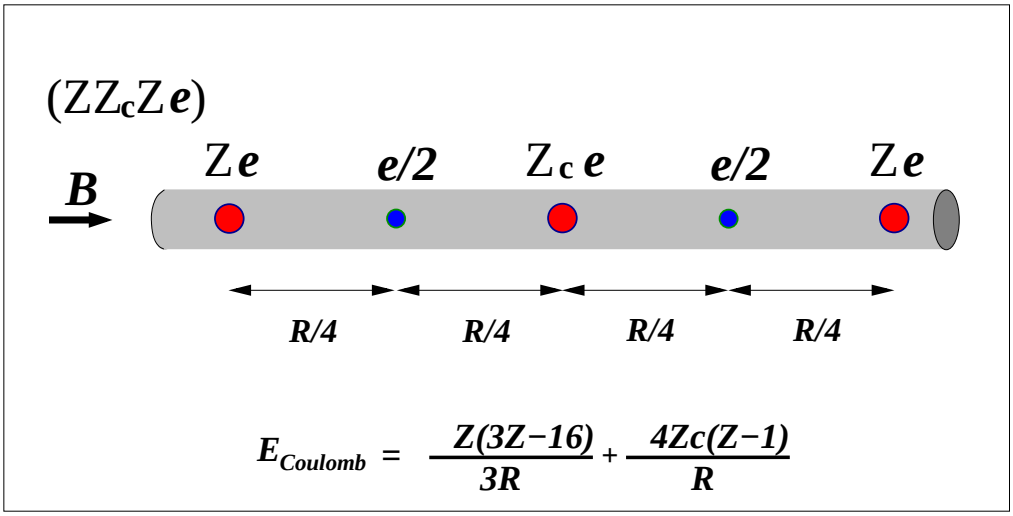



$$E_{Coulomb} = \frac{Z(Z-4)}{R} \quad , \quad for\ Z=1,2,3 \qquad E_{Coulomb} < 0$$




$$E_{Coulomb} = \frac{Z(3Z-16)}{3R} + \frac{4Zc(Z-1)}{R}$$

# TWO ELECTRON SYSTEMS

(preliminary results)

Ground State $\Rrightarrow$ Existence

$B = 0$

$H_2$

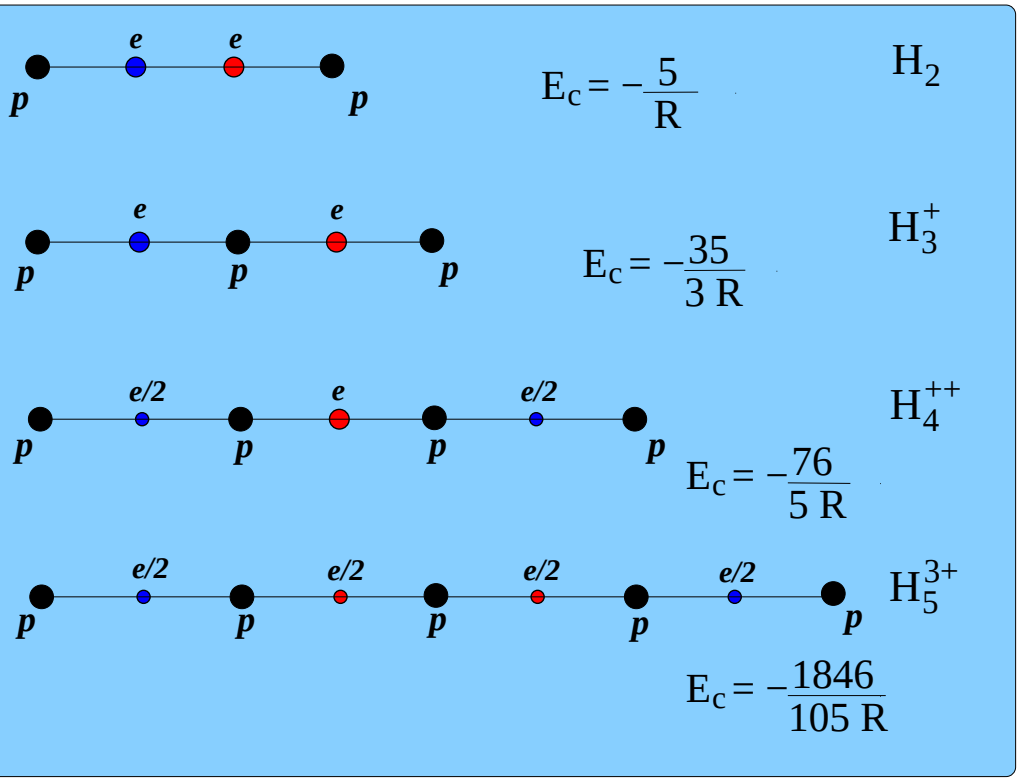
$E_{BO} = -2.3469$ Ry (James and Coolidge, 15 parameters)
$E_{BO} = -2.3478$ Ry (Heidelberg group, $> 2000$ gaussian orbitals)
$E_{BO} = -2.3484$ Ry *(A.T., N.Guevara, 14 parameters)*
$E_{BO} = -2.3489$ Ry (**record calculations**, $\gtrsim 1000$ J-C type functions)

$H_3^+$

(Lowest Linear Spin-Triplet State)

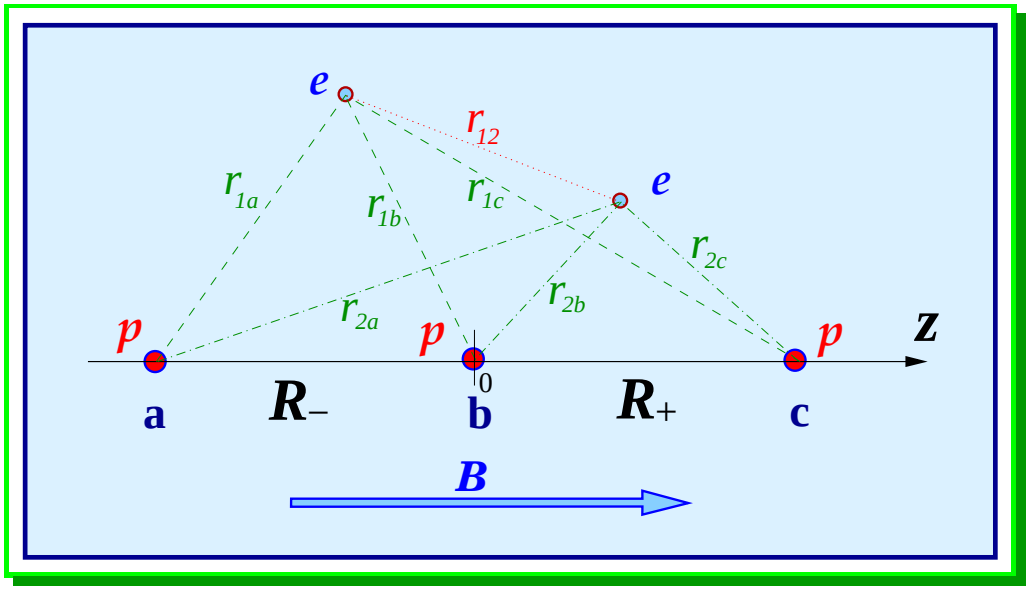
$E_{BO} = -2.2284$ Ry (Schaad et al, '74, CI)
$E_{BO} = -2.2298$ Ry *(A.T., J.C.Lopez V., N.Guevara, 22 parameters)*
$E_{BO} = -2.2322$ (Clementi et al '91, CI + J-C type )

Electronic correlation appears in explicit form $exp(ar_{12})$ in trial functions


e
e
p
p
$E_c = -\frac{5}{R}$
$H_2$
e
e
p
p
p
$E_c = -\frac{35}{3\,R}$
$H_3^+$
e/2
e
e/2
p
p
p
p
$E_c = -\frac{76}{5\,R}$
$H_4^{++}$
e/2
e/2
e/2
e/2
p
p
p
p
p
$E_c = -\frac{1846}{105\,R}$
$H_5^{3+}$

$H_3^+$ (first detailed study, A.T., N. Guevara, J.C. Lopez V. '06)

(linear, parallel configuration, the lowest states)




Basic trial function:

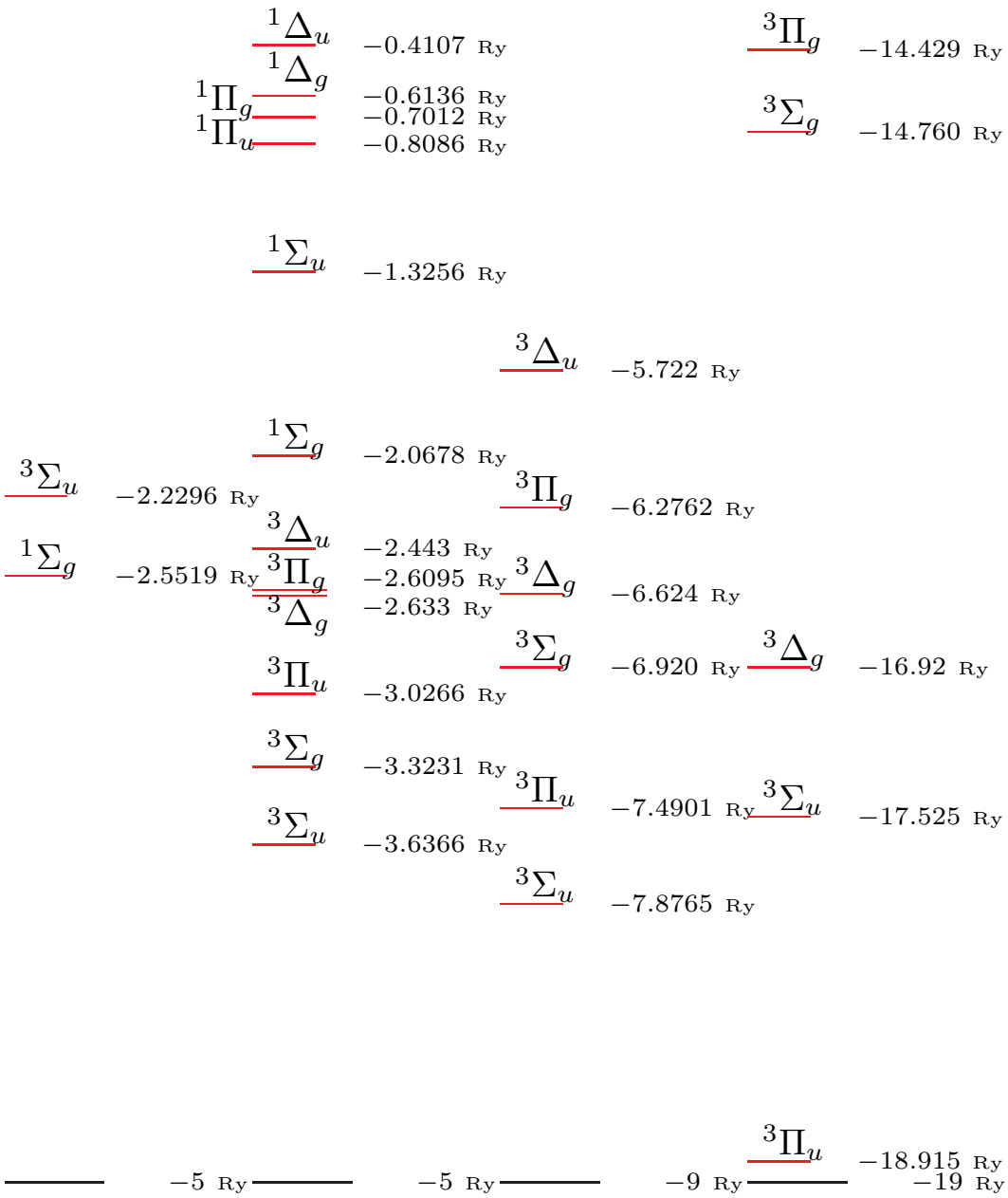
$$\psi^{(trial)} = (1+\sigma_e P_{12}) \\ (1+\sigma_N P_{ac})(1+\sigma_{N_a} P_{ab}+\sigma_{N_a} P_{bc})$$

$$\rho_1^{|m|} e^{im\phi_1}\ e^{\gamma r_{12}}\ e^{-\alpha_1 r_{1a}-\alpha_2 r_{1b}-\alpha_3 r_{1c}-\alpha_4 r_{2a}-\alpha_5 r_{2b}-\alpha_6 r_{2c}-B\beta_1\frac{\rho_1^2}{4}-B\beta_2\frac{\rho_2^2}{4}}$$

and its possible degenerations.

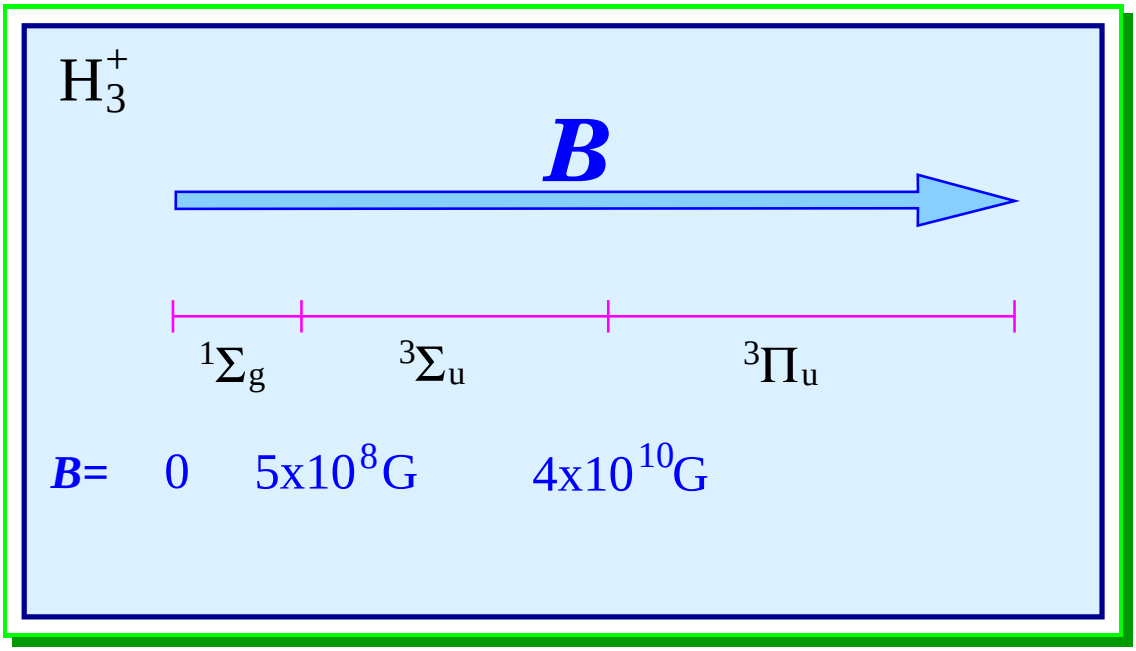
Optimal configuration:
linear, parallel, symmetric ($R_+ = R_-$),

*it is stable towards all small deviations*




*Low-lying states of the $H_3^+$ in a magnetic field in parallel configuration*

$H_3^+$: ground state




Parallel configuration is optimal,

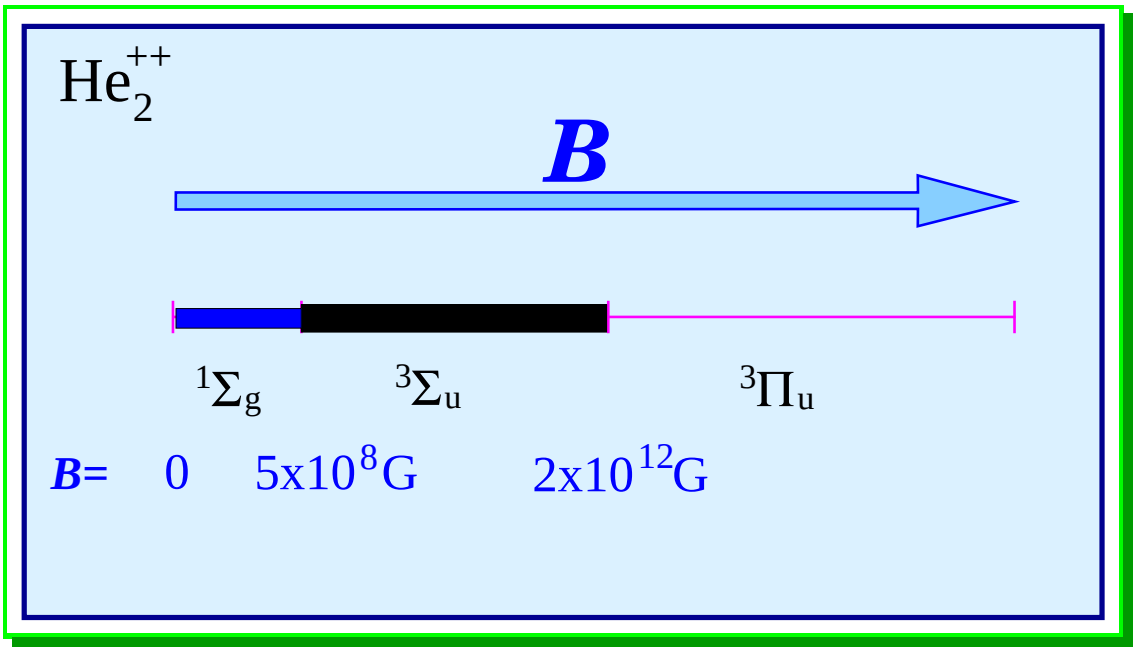
always stable

At $B = 10000$ a.u.

$$E_T = -95.21\, Ry$$

$E_T(H_2(^3\Pi_u)) = -71.34\, Ry$ , $E_T(H_2^+(1\pi_u)+H(1s)) = -62.02\, Ry$

$He_2^{2+}$: ground state (the first study)




Parallel configuration is optimal,

metastable at $B < 0.2$ a.u. $(He_2^{2+} \rightarrow He^+ + He^+)$

stable at $B > 1000$ a.u., otherwise does not exist!

At $B = 10000$ a.u.

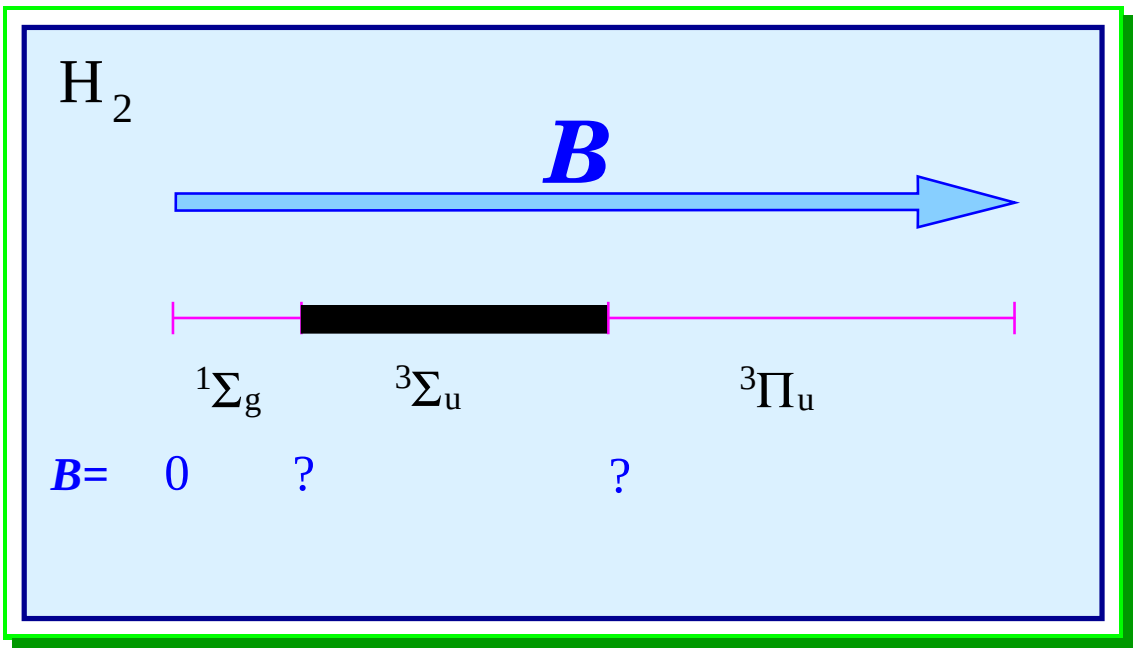
$$E_T = -174.506\, Ry$$

$$E_T(He^+ + He^+) = -156.85\, Ry\ (1s1s)\ , = -137.26\, Ry\ (1s2p_{-1})$$

$$E_T(He_2^{3+}(1\sigma_g) + e) = -86.233$$

$H_2$:

ground state (A.T. '83, ... Heidelberg group '90-'01)




Parallel configuration is optimal,

stable, when exists, but always

$$E_T(H_3^+) \; < \; E_T(H_2)$$

A lot of controversy...

*Further studies:*

(i)

$H_4^{2+}$ , $H_5^{3+}$ ... (hydrogenic linear chains?)

$(H-He-H)^{++}$ , $(He-H-He)^{3+}$ ...

$He_3^{4+}$ ...

Do they exist?

(ii)

A study of radiative transitions
(bound-bound, bound-free)
of $H_2^+$ , $H_3^{2+}$ etc

(iii)

The effects of magnetic line curvature

(iv)

(Sub)-atomic traps?