

Molecular Systems in a Strong Magnetic Field

Alexander V. Turbiner
ICN-UNAM, Mexico

London, April 2006

The goal:

How

ATOMIC - MOLECULAR PHYSICS

IN a strong MAGNETIC FIELD

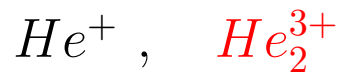
looks like

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

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

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

1e:



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

2e:



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

Why the problem is so difficult ?

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

$$E_{binding} \ll E_{total}$$

(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 Ψ_{trial} a trial Potential

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

hence, we know the Hamiltonian for which the normalized Ψ_{trial} is eigenfunction

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

then

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

- ❖ 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)

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

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

α, β variational parameters

with

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

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.

$$H : E_b(10000 \text{ a.u.}) = 27.95 \text{ Ry}$$

$$He^+ : E_b(10000 \text{ a.u.}) = 78.43 \text{ Ry}$$

- Hydrogen atom in a magnetic field (ground state)

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

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

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

$$E_{binding} = \log^2 B + \dots \quad , \quad B \rightarrow \infty$$

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

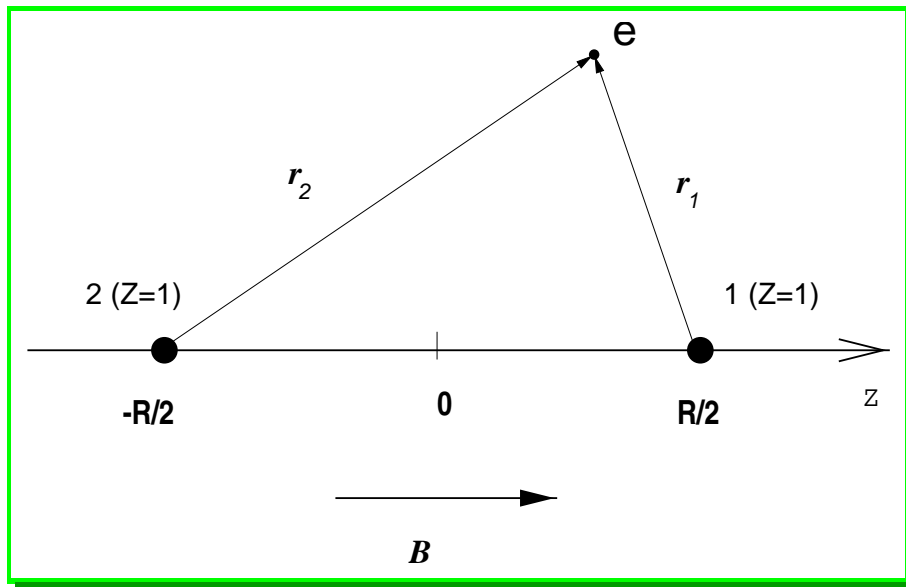
$$\frac{E_{binding}^{exact}}{\log^2 B} \approx 1/3$$

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

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

α_1, β_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

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

- ❖ α_2, β_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 $\psi_{3_1} \rightarrow \psi_1$
- ❖ If $\alpha_4 = 0$ then $\psi_{3_1} \rightarrow \psi_2$
- ❖ Ionic \leftrightarrow covalent coupling interpolation (verified *a posteriori*).
- ❖ $\alpha_3, \alpha_4, \beta_3, R$ are variational parameters

III-2 Linear Interpolation

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

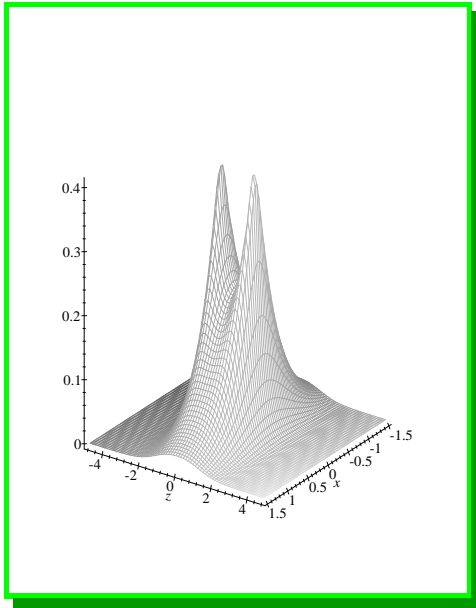
IV Superposition of the two kinds of interpolation

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

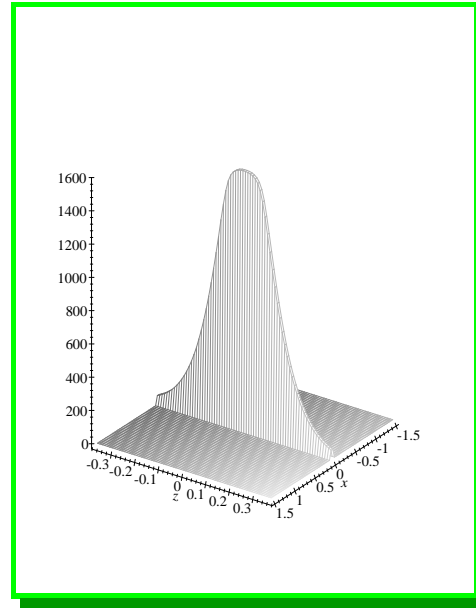
- ❖ 10 variational parameters
- ❖ ψ_4 gives the **lowest** total energies for the ground state compared with previous calculations (~ 50 calculations) for $B > 10^{10} G$ up to $B = 4.414 \times 10^{13} G$,
- ❖ For $B \lesssim 10^{10} G$: Relative accuracy $\sim 10^{-5}$ in binding energy (comparing 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



$B = 10^9 G$

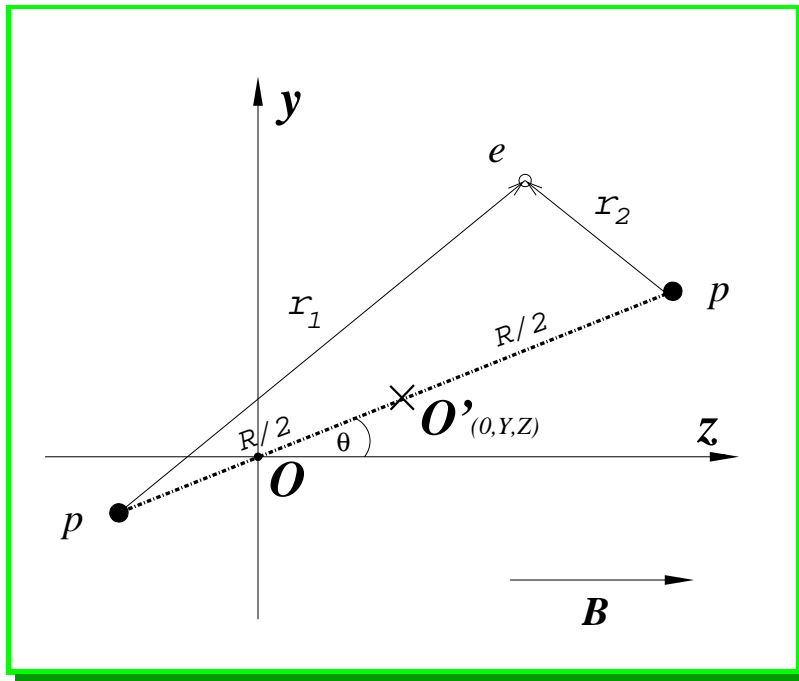


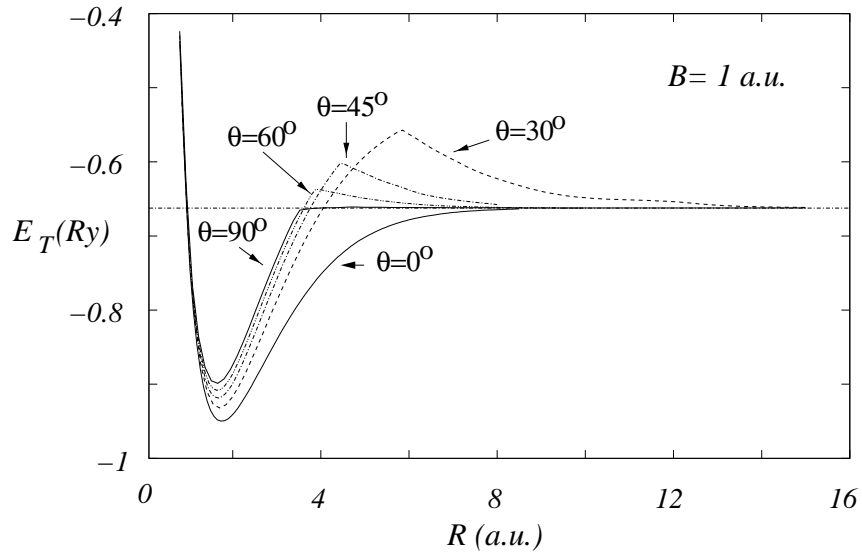
$B = 10^{13} G$

(ppe) system

H_2^+ : inclined configuration

(The molecular axis and magnetic line form angle θ)

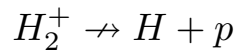




Parallel configuration is optimal for all magnetic fields

- 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



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

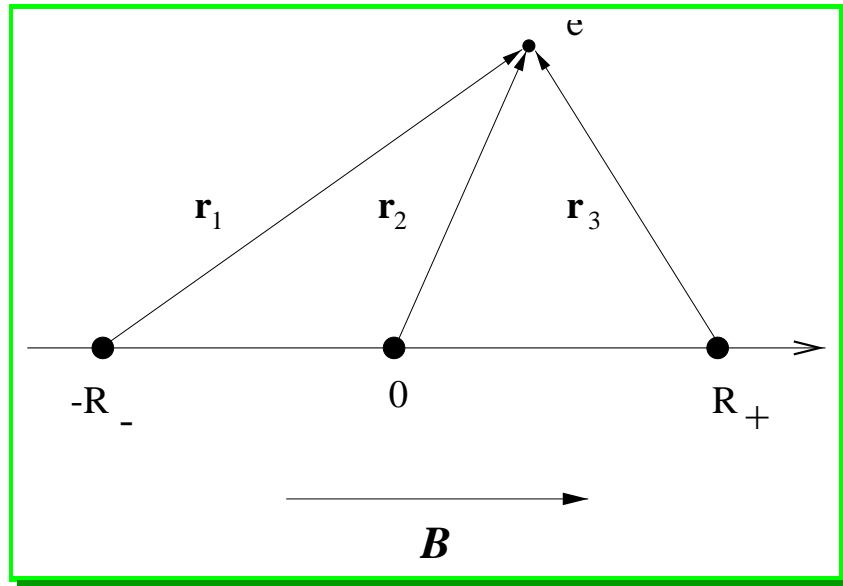
comparison with H : $E_b(10000 \text{ a.u.}) = 27.95 \text{ Ry}$

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

(*pppe*) system

H_3^{2+} : linear parallel configuration

(The molecular axis and magnetic line coincide)



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

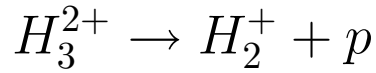
For $B \gtrsim 10^{11} G$ the system (*pppe*) has a bound state, which manifests existence of the exotic molecular ion H_3^{2+}

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

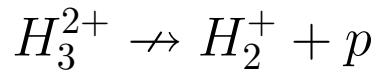
(Without magnetic field H_3^{2+} does **NOT** exist!)

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

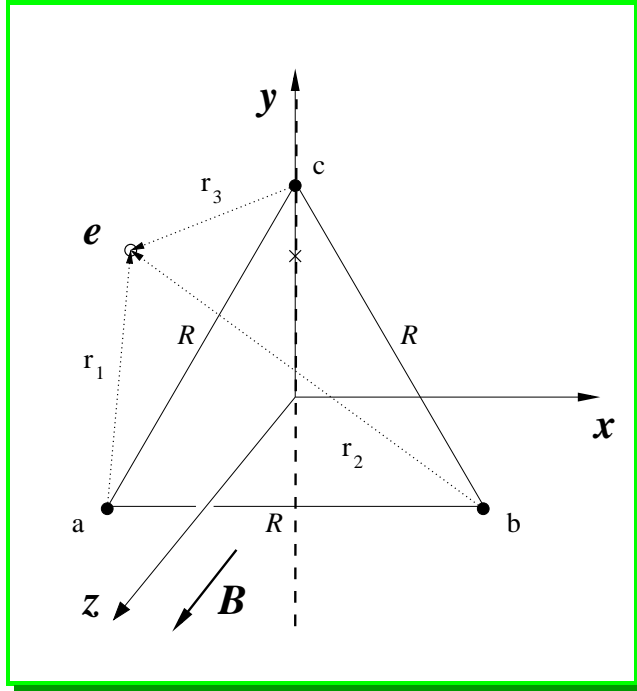


* * *

$$E_b(10000 \text{ a.u.}) = 45.41 \text{ Ry}$$

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

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

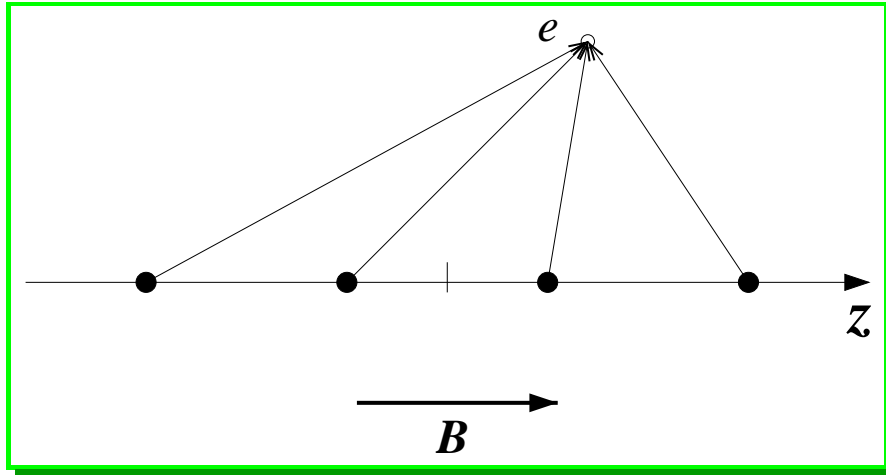
No more spatial configurations found!

(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

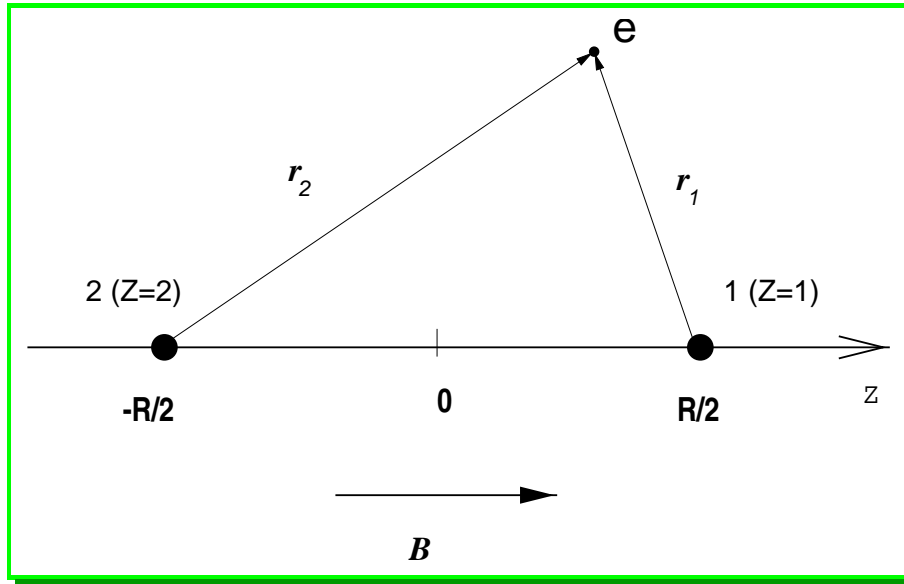
→ the existence of the molecular ion $H_4^{(3+)}$ as metastable state as well as its excited state $1\pi_u$

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

(αpe) system

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

(A.T. and J.C. López V. '04)



- For $B \gtrsim 10^{12}$ G the system (αpe) 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 $B \gtrsim 10^{13}$ G it becomes stable:
 $(HeH)^{(2+)} \rightarrow He^+ + p$
- **Parallel Configuration is always optimal**

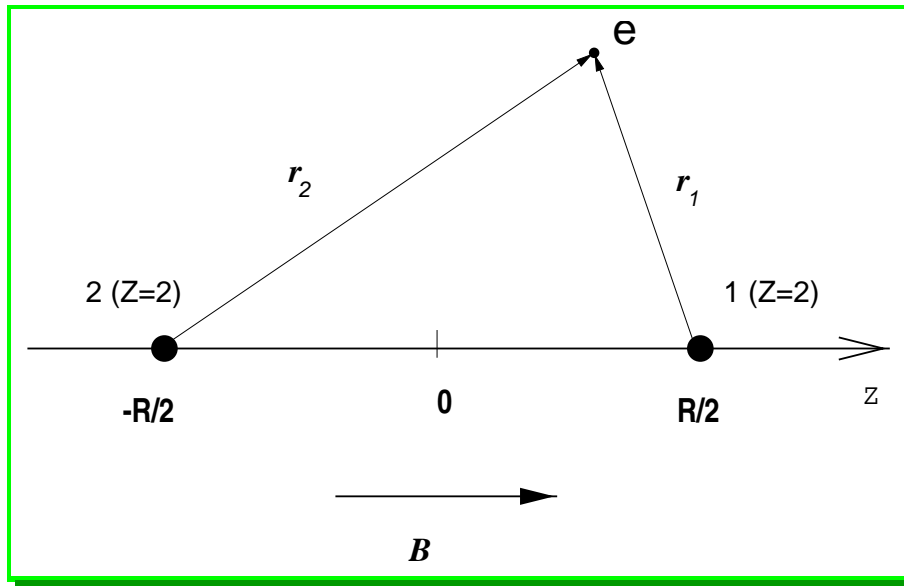
$$E_b(10000 \text{ a.u.}) = 77.30 \text{ Ry}$$

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

$(\alpha\alpha e)$ 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**:
 $He_2^{(3+)} \rightarrow He^+ + \alpha$
- **Parallel Configuration is always optimal**

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

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

The striking relation between the binding energies of the most bound one-electron systems made from α -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*)

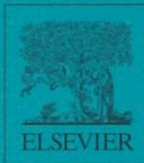
*Optimal configuration of linear H_2^+ , H_3^{2+} , $H_4^{(3+)}$, $(HeH)^{2+}$ and $He_2^{(3+)}$ is **parallel**, along magnetic field (when exist)*

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 α -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-trivial 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.



Volume 424, No. 6, March 2006
Last issue of this volume

ISSN 0370-1573

PHYSICS REPORTS

A Review Section of Physics Letters

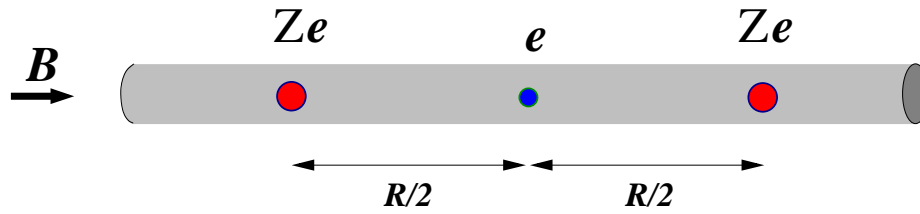
ONE-ELECTRON MOLECULAR SYSTEMS IN A STRONG MAGNETIC FIELD

Alexander V. TURBINER, Juan Carlos LÓPEZ VIEYRA

Also available on
SCIENCE @ DIRECT®
www.sciencedirect.com

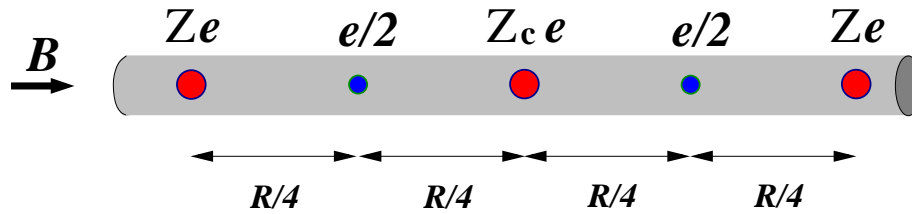
<http://www.elsevier.com/locate/physrep>

(ZZe)



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

(ZZ_cZe)



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

TWO ELECTRON SYSTEMS

(preliminary results)

Ground State \Rightarrow Existence

$$B = 0$$



$E_{BO} = -2.3469$ 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)



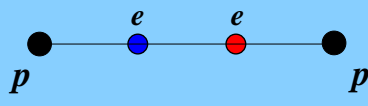
(Lowest Linear Spin-Triplet State)

$E_{BO} = -2.2284$ Ry (Schaad et al, '74, CI)

$E_{BO} = -2.2298$ Ry (*A.T., J.C.Lopez V., N.Guevara, 22 parameters*)

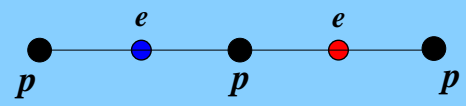
$E_{BO} = -2.2322$ (Clementi et al '91, CI + J-C type)

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



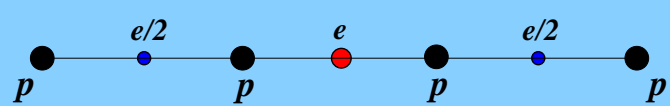
$$E_c = -\frac{5}{R}$$

H₂



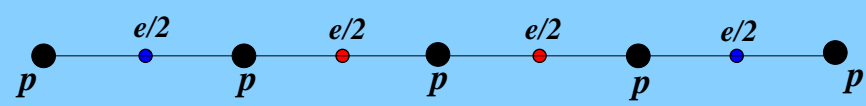
$$E_c = -\frac{35}{3R}$$

H₃⁺



$$E_c = -\frac{76}{5R}$$

H₄⁺⁺

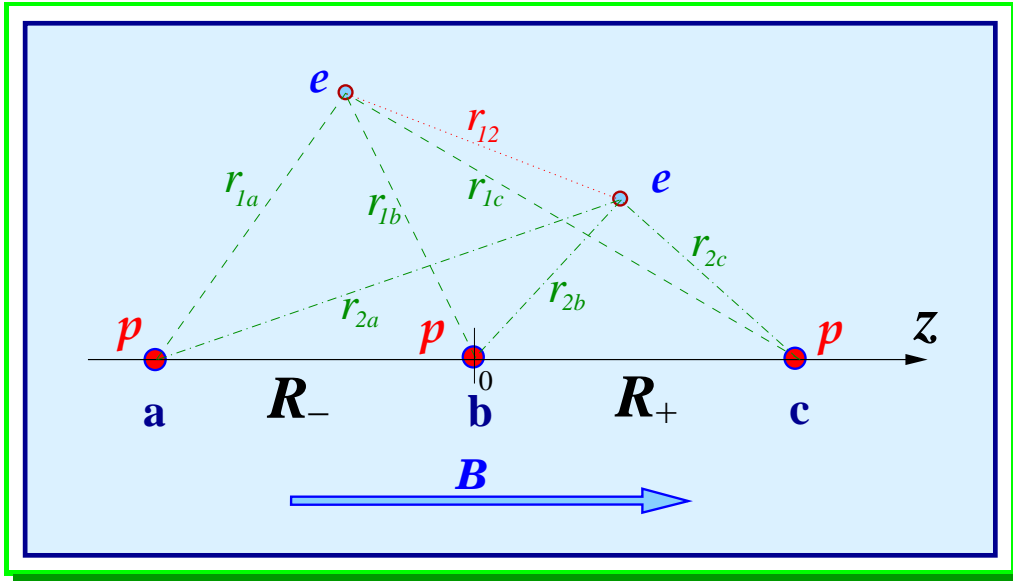


$$E_c = -\frac{1846}{105R}$$

H₅³⁺

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

(linear, parallel configuration, the lowest states)



Basic trial function:

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

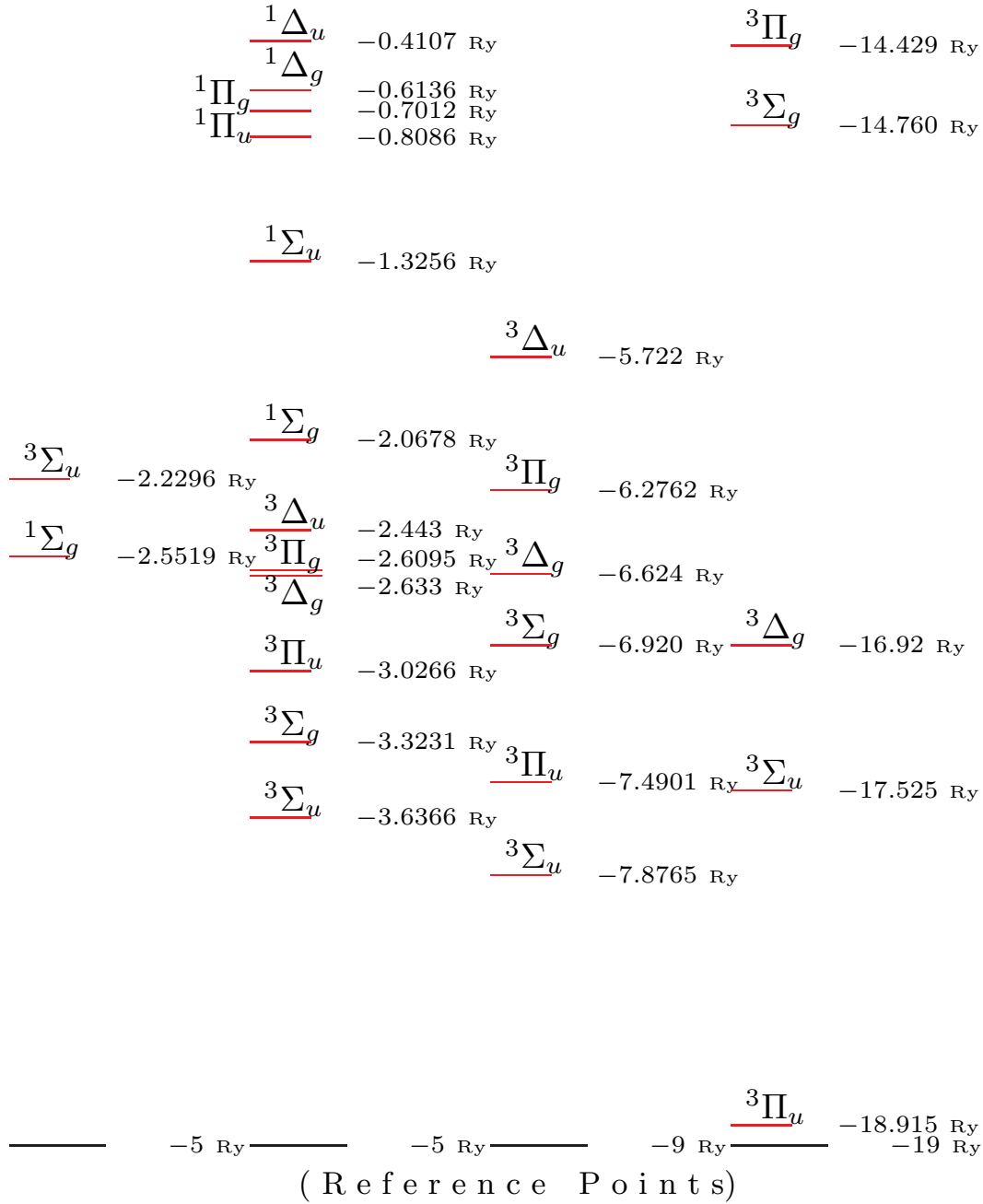
$$\rho_1^{|m|} e^{im\phi_1} e^{\gamma r_{12}} e^{-\alpha_1 r_{1a} - \alpha_2 r_{1b} - \alpha_3 r_{1c} - \alpha_4 r_{2a} - \alpha_5 r_{2b} - \alpha_6 r_{2c} - B\beta_1 \frac{\rho_1^2}{4} - B\beta_2 \frac{\rho_2^2}{4}}$$

and its possible degenerations.

Optimal configuration:

linear, parallel, symmetric ($R_+ = R_-$),

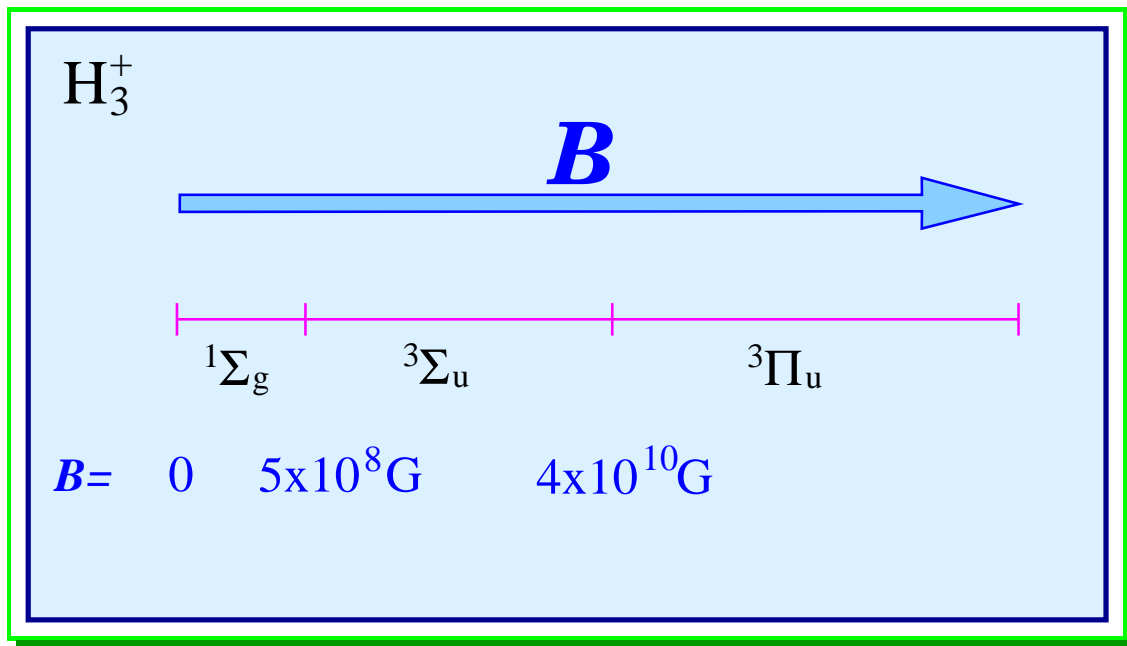
it is stable towards all small deviations



$B = 0$ $B = 1 \text{ a.u.}$ $B = 10 \text{ a.u.}$ $B = 100 \text{ a.u.}$
 (1 a.u. = $2.35 \times 10^9 \text{ G}$)

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

H_3^+ : ground state



Parallel configuration is optimal,

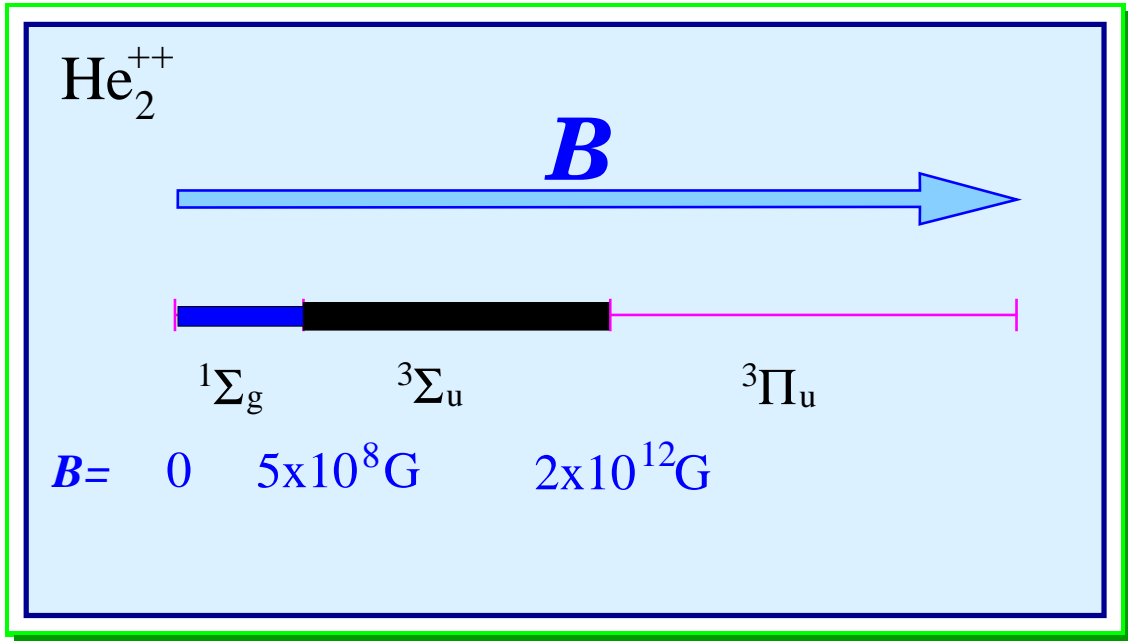
always stable

At $B = 10000 \text{ a.u.}$

$$E_T = -95.21 \text{ Ry}$$

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

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



Parallel configuration is optimal,

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

stable at $B > 1000 \text{ a.u.}$, otherwise does not exist!

At $B = 10000 \text{ a.u.}$

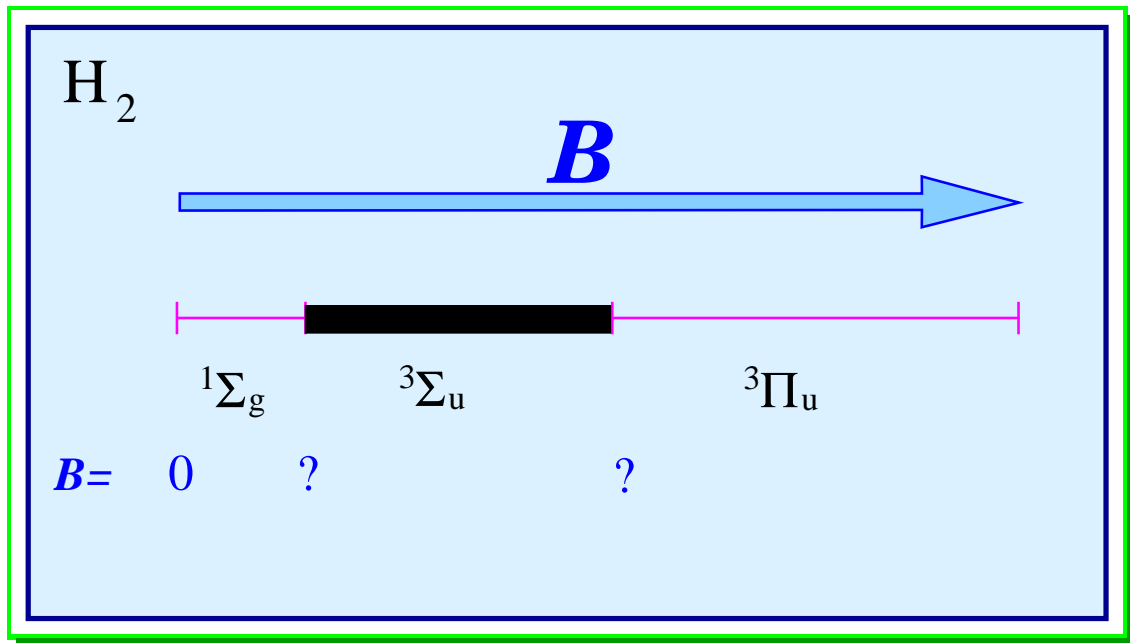
$$E_T = -174.506 \text{ Ry}$$

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

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

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?