Molecular Systems in a Strong Magnetic Field

Alexander V. Turbiner
ICN-UNAM, Mexico

A particular overview of two electron Coloumb systems made out of several protons and/or α-particles which might 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^+ , $\underline{H_3^{2+}}$, H_4^{3+}

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

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

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

$2e$:

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

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

He , He_2^{2+}, $He_3^{4+}, \ldots$

H-atom is stable but has a highest total energy among $1e - 2e$ systems

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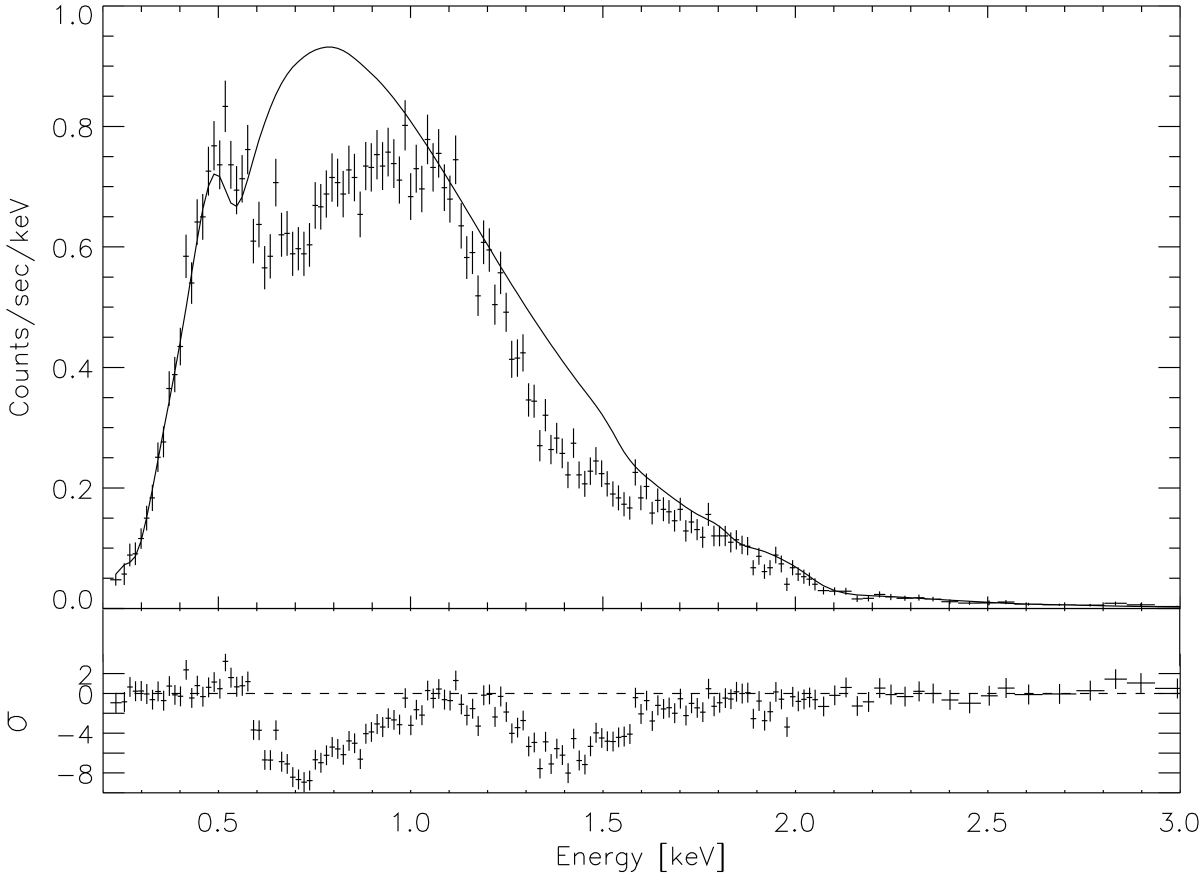
D. Sanwal, G.G. Pavlov, V.E. Zavlin and M.A. Teter (2002)
(First observation of absorption features)



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

Two absorption features:

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

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

Why the problem is so difficult ?

- Highly-non-uniform asymptotics of potential at large distances
- A problem of several centers
- 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

How to choose trial functions?

❖ Physical relevance (as many as possible physics properties should be encoded)

❖ Mathematical (computational) simplicity must **NOT** be a guiding principle

❖ Resulting perturbation theory should be convergent (see below)

Variational calculation

For chosen Ψ_{trial} a trial Potential

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

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

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

- The variational energy is a sum of the first two terms of a certain perturbative series with perturbation $(V - V_{trial})$, smaller E_{var} does not guarantee faster convergence

- How to calculate E_2 *in practice*? - in general, unsolved yet

HOW TO MEASURE DISTANCE $E_{var} - E_{exact}$?
open question....

INSTRUCTIVE EXAMPLE

Hydrogen in a magnetic field (ground state)

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

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

α, β variational parameters

with

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

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)

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

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 $B \le B_{Schwinger}$

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 our recent *Physics Reports*)

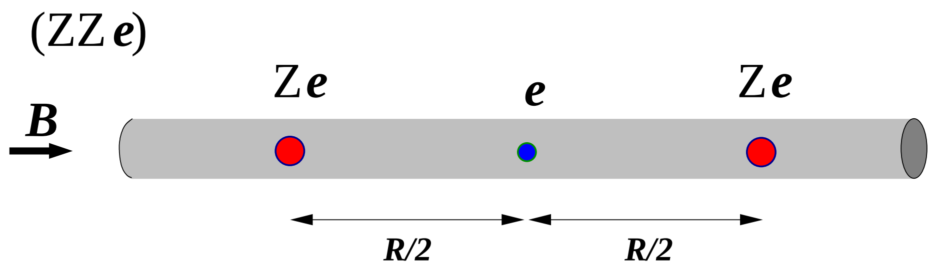
Optimal configuration of linear H_2^+, H_3^{2+}, $H_4^{(3+)}$, $(HeH)^{2+}$ *and* $He_2^{(3+)}$ *is parallel, along magnetic field (when exist)*

when magnetic field grows:

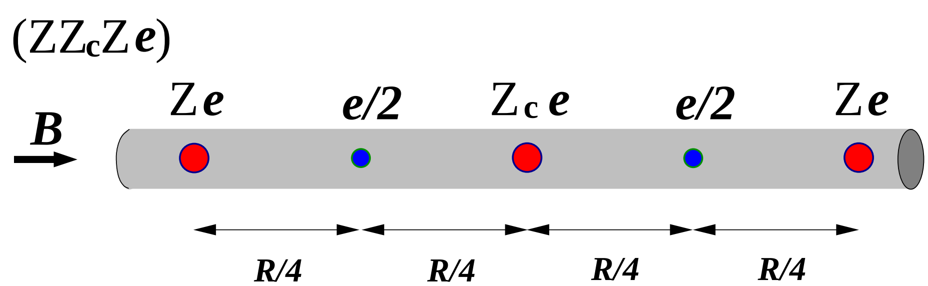
- Binding energy of H, H_2^+, H_3^{2+}, H_4^{3+}, $(HeH)^{2+}$ and He_2^{3+} grows (when exist)
- Natural size of the systems $H_2^+, H_3^{2+}, (HeH)^{2+}$ and He_2^{3+} decreases
- H_2^+ has the *lowest* E_{total} for $0 < B \lesssim 10^{13}\,G$ (made from protons)
- H_3^{2+} has the *lowest* E_{total} 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 ~ 700 eV, while for He_2^{3+} it is ~ 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.*



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



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

TWO ELECTRON SYSTEMS

Our Goal:

To study the Ground State $\Rrightarrow$ Existence

Phenomenon:

With a magnetic field change the quantum numbers of the ground state should change (true level crossing)

the ground state sequence:

$$\begin{array}{ccccc} {}^1\Sigma_g & \rightarrow & {}^3\Sigma_u & \rightarrow & {}^3\Pi_u \\ m_l = 0 & & m_l = 0 & & m_l = -1 \\ m_s = 0 & & m_s = -1 & & m_s = -1 \end{array}$$

$$B = 0$$

Born-Oppenheimer ground state energies

H_2

$E_{BO} = -2.3469$ Ry (James and Coolidge, 15 parameters)

$E_{BO} = -2.3478$ Ry (Heidelberg group, $>$ 200 Gaussian orbitals)

$E_{BO} = -2.3484$ Ry *(A.T., N.Guevara, 14 parameters)* *

$E_{BO} = -2.3489$ Ry (**record calculations**, $\gtrsim$ 7000 J-C type functions)

H_3^+

(Lowest Linear Spin-Triplet State)

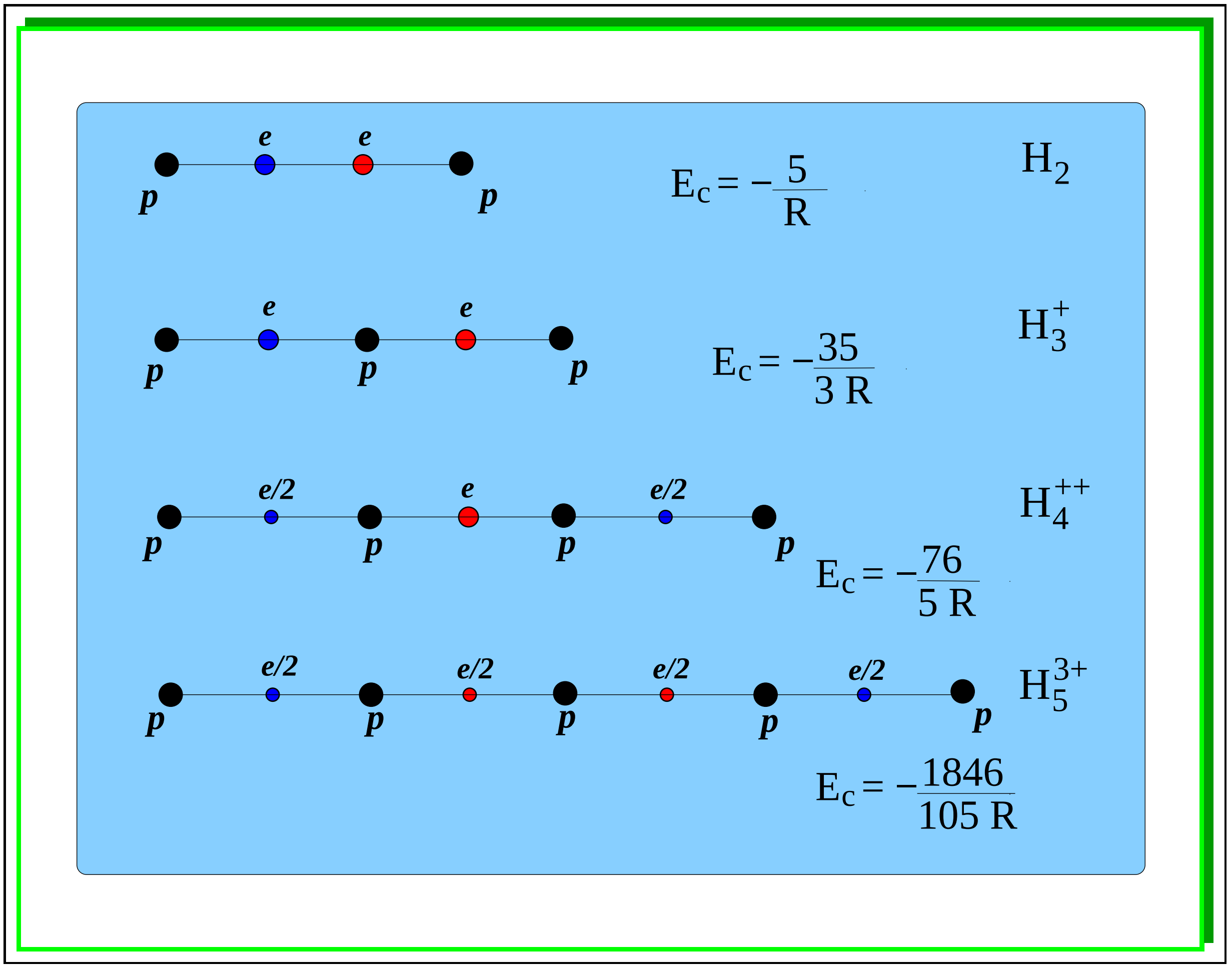
$E_{BO} = -2.2284$ Ry (Schaad et al, '74, CI)

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

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

* Leading to the most accurate energy based on few-parametric trial functions.

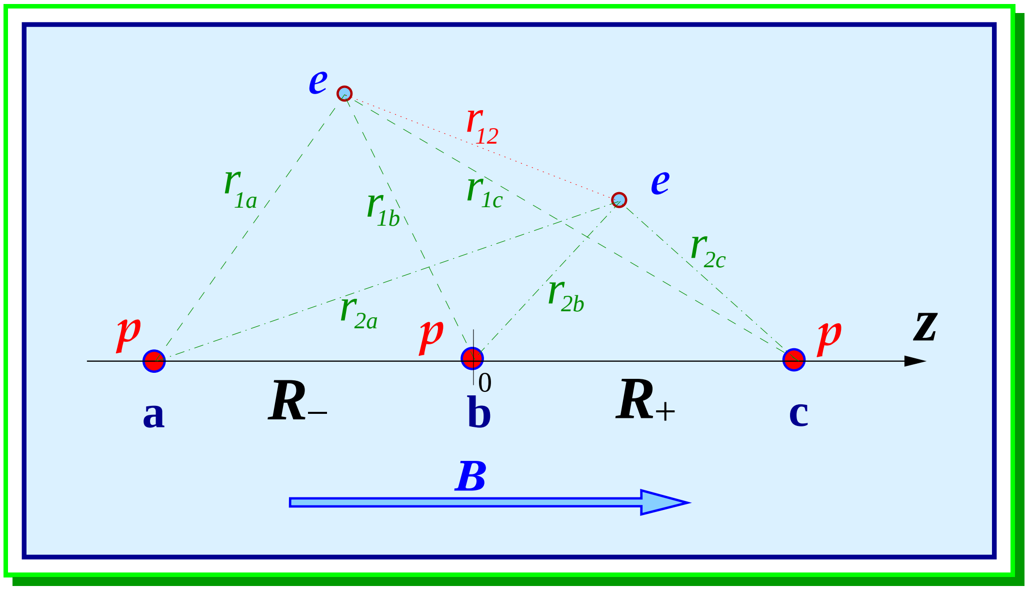
Electronic correlation appears in exponential form $exp(ar_{12})$ in our trial functions



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

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

(linear, parallel configuration, the lowest states)



Basic trial function:

$$\psi^{(trial)} = (1+\sigma_e P_{12}) (1+\sigma_{_N} P_{ac})(1+\sigma_{N_a} P_{ab}+\sigma_{N_a} P_{bc})$$
$$\rho_1^{|m|} e^{im\phi_1}\ e^{\gamma r_{12}}\ \ e^{-\alpha_1 r_{1a}-\alpha_2 r_{1b}-\alpha_3 r_{1c}-\alpha_4 r_{2a}-\alpha_5 r_{2b}-\alpha_6 r_{2c}-B\beta_1\frac{\rho_1^2}{4}-B\beta_2\frac{\rho_2^2}{4}}$$

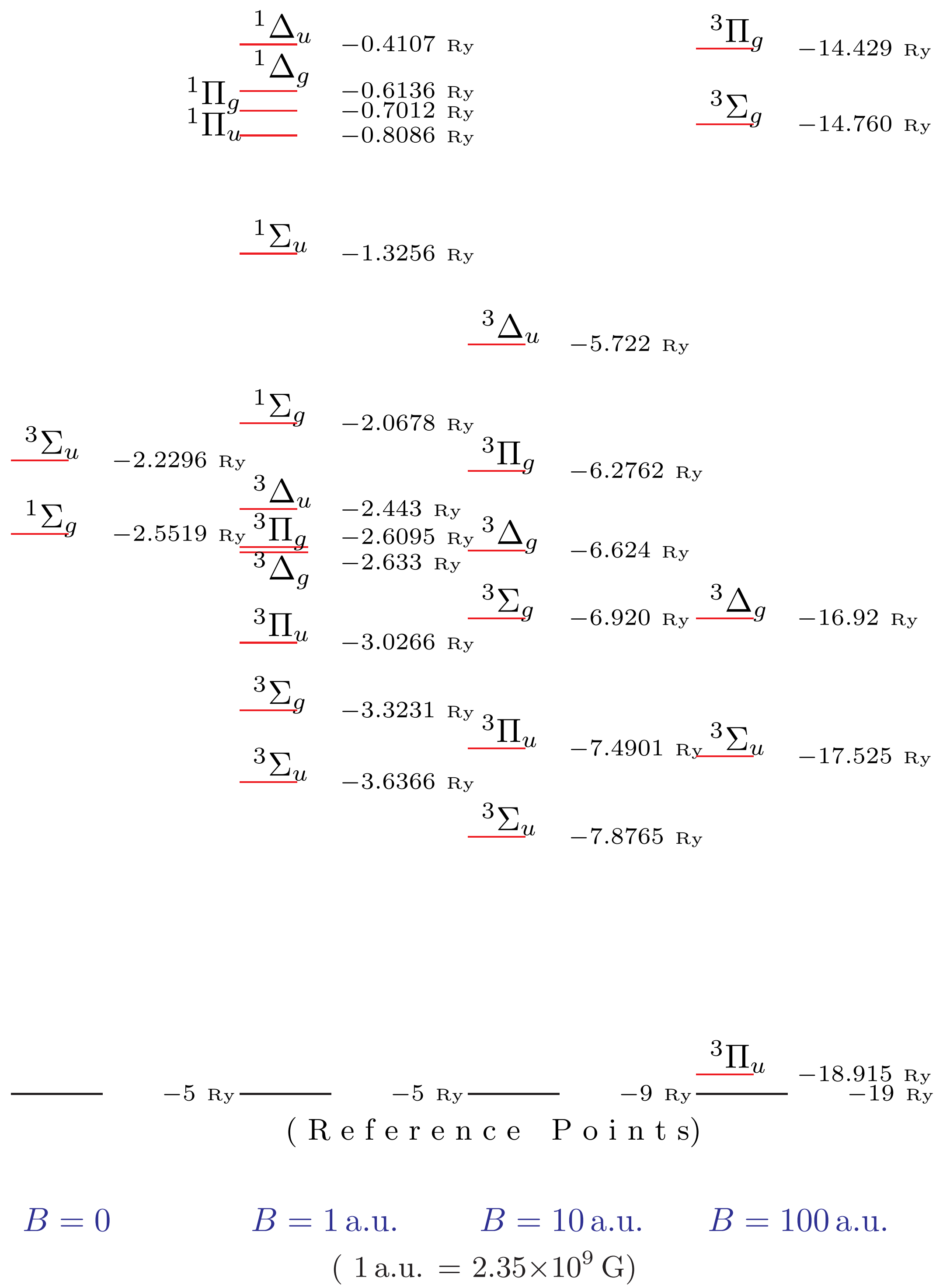
and its possible degenerations.

Optimal configuration:

linear, parallel, symmetric $R_+ = R_-(= R_{eq})$,

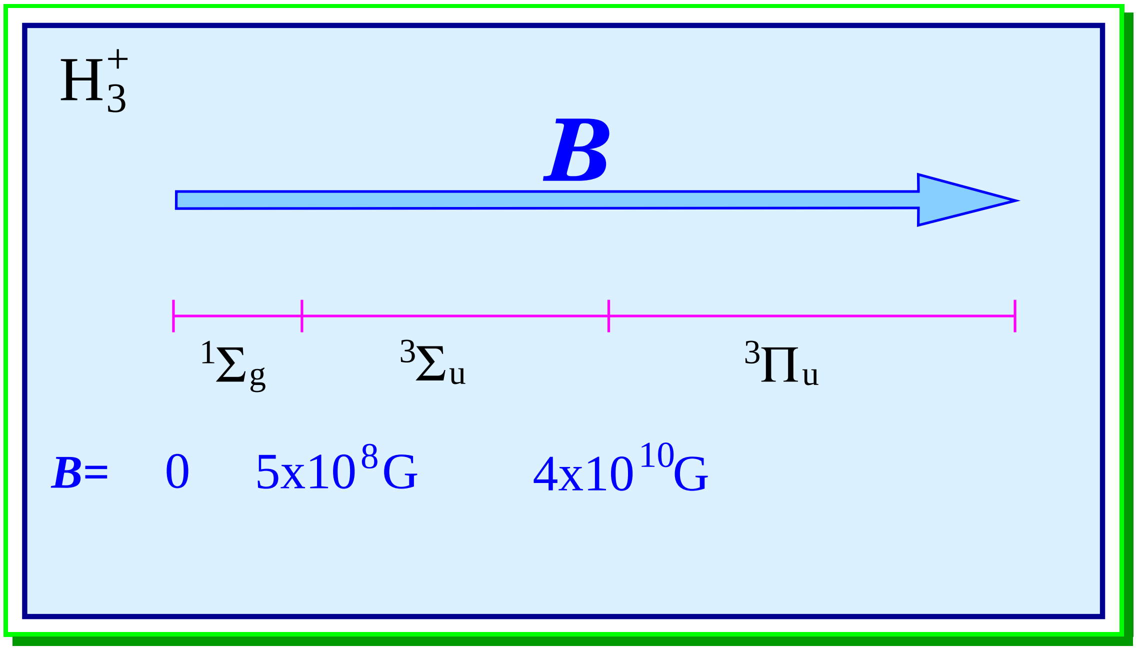
At $B \geq 0.1$ a.u. *it is stable towards all small deviations*

At $B \leq 0.1$ a.u. the ground state is of triangular geometry, linear configuration is unstable



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

H_3^+: ground state



At $B = 10000$ a.u.

$$E_T = -95.21\,Ry \qquad (R_{\pm}^{eq} = 0.093\,a.u.)$$

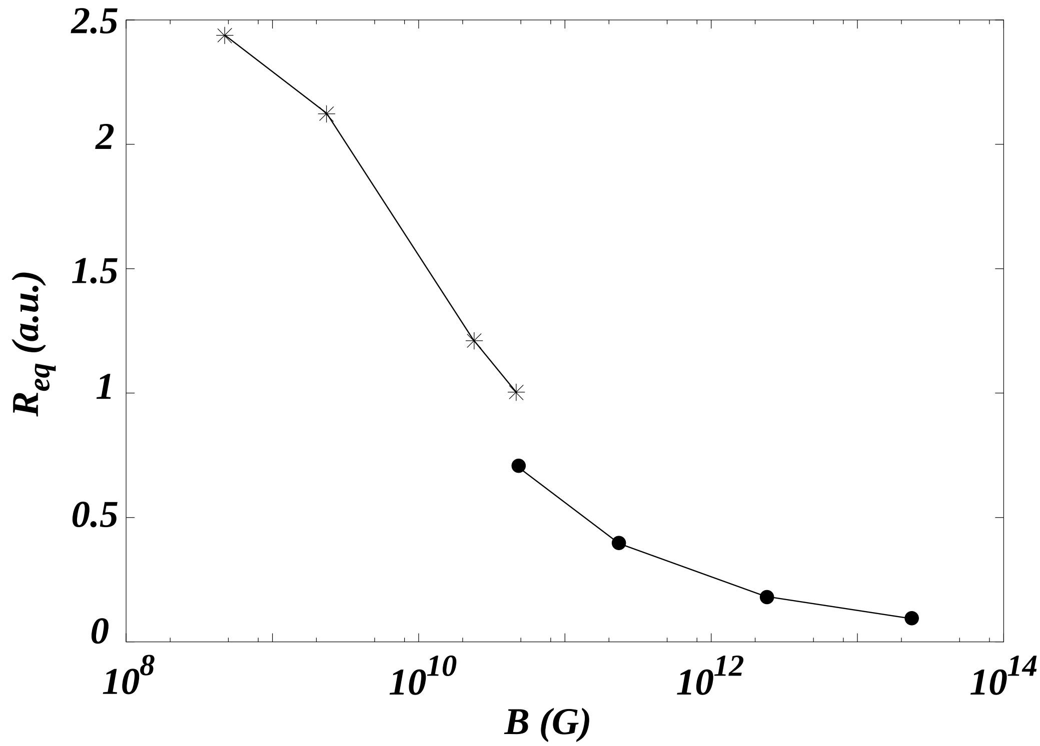
$$E_0^{vib} \;=\; 3.15\,Ry$$

$$E_T(H_2(^3\Pi_u)) = -71.39\,Ry\;\;,\;E_T(H_2^+(1\pi_u){+}H(1s)) = -62.02\,Ry$$

Dissociation energy: $H_3^+ \to H_2 + p$ is large, 23.82 Ry

Transition energy (from ground state to lowest excited state):

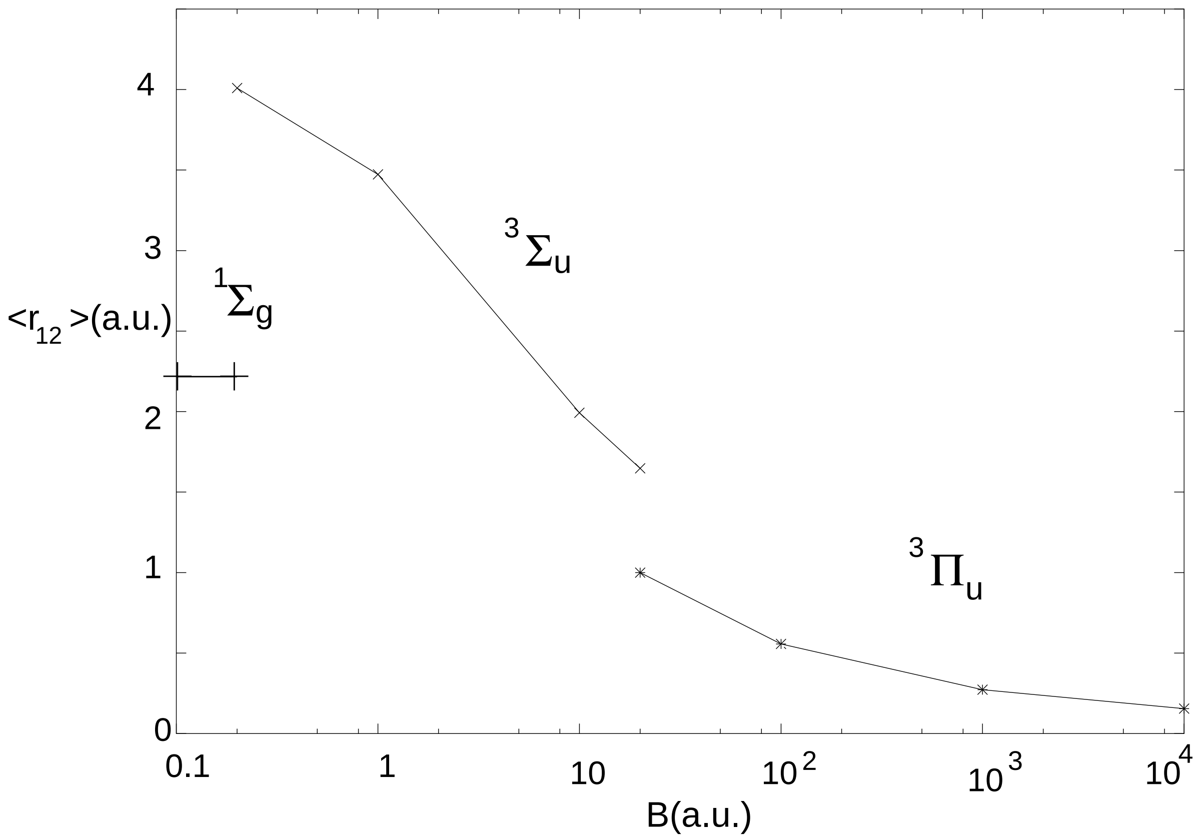
$$\Delta E(^3\Pi_u \to {}^3\Delta_g) = 7.76\,Ry$$



Equilibrium distance for the ground state: ${}^3\Sigma_u$ (stars) and ${}^3\Pi_u$ (bullets).

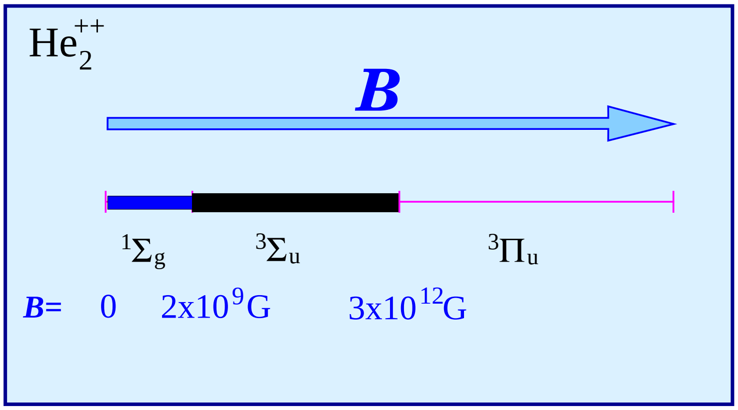
H_3^+ is the most stable system among those made from protons for $0 \leq B \lesssim 2000\,\mathrm{a.u.}$

Stable - the lowest total energy, the highest energy is needed to dissociate (ionize) comparing to any other system



Pauli repulsion effects

He_2^{2+}: ground state
(A.T., N. Guevara, *PRA* (Dec. 2006), the first study)



Parallel configuration is optimal

metastable at $B < 0.85$ a.u. $(He_2^{2+} \to He^+ + He^+)$

stable at $B > 1100$ a.u., otherwise does not exist!
At $B = 10000$ a.u.

$$E_T = -174.51\,Ry \qquad (R_{eq} = 0.106\,a.u.)$$

$$E_0^{vib} \;=\; 1.16\,a.u.$$

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

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

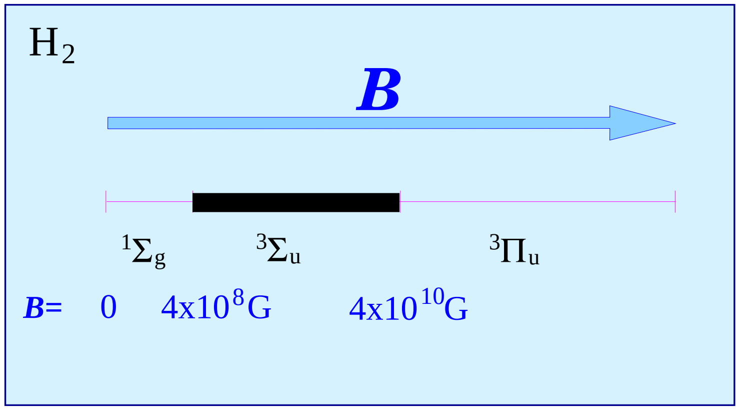
Transition energy from the ground state $^3\Pi_u$ to the lowest excited state $^3\Delta_g$

$$\Delta E(^3\Pi_u \to {}^3\Delta_g) = 13.87\,Ry$$

H_2:

ground state

(A.T. '83, ... Heidelberg group '90-'03, A.T., N.Guevara, J.C. Lopez Vieyra, '06-'07)



Parallel configuration is optimal,

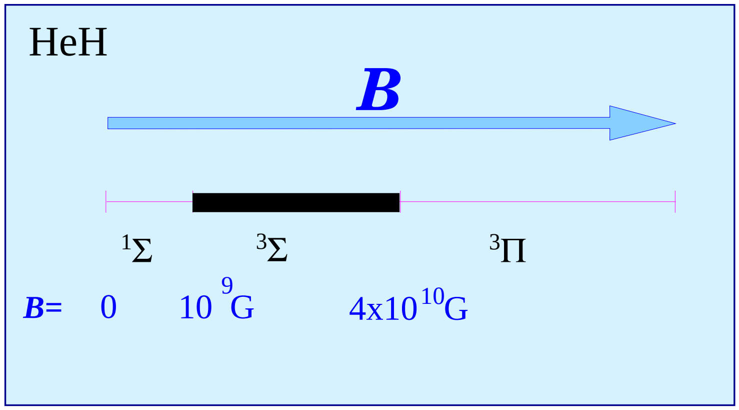
stable, when exists, but always

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

$(HeH)^+$:

ground state

(A.T., N.Guevara,'07 (in progress))



Parallel configuration is optimal,

stable, when exists, but always

At $B = 10000$ a.u.

$$E_T = -133.49\, Ry \qquad (R_{eq} = 0.104\, a.u.)$$

$E_T = -129.7$ Ry (Heyl & Hernquist, '98)

$$E_0^{vib} \;=\; 1.41\, a.u.$$

$$E_T(He^+ + H) = -86.79\, Ry\ (2p_{-1}1s)\ ,\ = -99.98\, Ry\ (1s2p_{-1})$$

$$E_T(He(1^3(-1)^+ + p) = -110.30\, Ry$$

Transition energy from the ground state $^3\Pi$ to the lowest excited state $^3\Delta$

$$\Delta E(^3\Pi \to {}^3\Delta) = 9.87\, Ry$$

CONCLUSION

- For all studied systems the optimal geometry is linear parallel
(all heavy particles are situated along magnetic line)

- For all studied systems a transition occurs at $B \sim 10^8$ Gauss:
the spin-singlet ground state becomes the spin-triplet state of the lowest energy (bound or unbound)

- For all studied $2e$ proton contained-systems at $B \sim 10^{11}$ Gauss the spin-triplet strongly bound ground state ${}^3\Pi_{(u)}$ appears $(m_l = m_s = -1)$

- The ion H_4^{2+} begins to exist at 10^{11} Gauss (linear parallel configuration) with ${}^3\Pi_u$ as ground state.
At first, H_4^{2+} decays to H_3^+ but for $B \gtrsim 5 \times 10^{12}$ Gauss the ion H_4^{2+} becomes stable(!): it is a short, charged, Ruderman chain

All transition and ionization energies

at $B \sim 10^{12} - 10^{13}$ Gauss of two-electron systems

found so far are in the region 100-1000 eV

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 radiation transitions
(bound-bound, bound-free)
of H_2^+ , H_3^{2+} etc

(iii)

The effects of magnetic line curvature??

(iv)

The finite-mass effects (beyond Born-Oppenheimer approximation)?

(iv)

(Sub)-atomic traps?