Hydrogen Molecule in a Weak Magnetic Field

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MAGNETIC FIELDS and NEUTRON STAR SURFACE
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✦ In quantum systems, the quantum numbers of the ground state can depend on values of an external parameter in the Hamiltonian.

- Particular case: behavior of the quantum numbers of the ground state of two-electron atomic and molecular systems in a magnetic field.

$$\boxed{B = 0}$$

Standard situation ⇒
Spin singlet ground state (total spin is zero)

$$\boxed{B > B_c}$$

⇒ Spin triplet ground state (total spin is one)
(spins are oriented against the magnetic field)

Chemistry in magnetic field

(overview)

✦ Possible formation of exotic linear systems in strong magnetic field (polymers)
(Kadomtsev-Kudryavtsev '71, Ruderman '71)

- $H_2,\ H_3,\ H_4, \ldots$ can exist in strong magnetic field (Salpeter et al '92)

- $H_3^{(2+)}$, $He_2^{(3+)}$,... can exist in magnetic field $B \gtrsim 10^{11}\,G$.

  A. Turbiner, J.C. Lopez Vieyra. Phys. Report. 424, 309(2006)

Where ?

Neutron star atmospheres (possible candidate)

Magnetic Field

Earth	Lab (stable)	Lab (impulses)	White dwarf	Neutron stars
$0.5\ G$	$10^5\ G$	$10^7\ G$	$10^6 - 10^9\ G$	$10^{12} - 10^{13}\ G$

Scales

Magnetic field of the order of atomic magnetic field: (cycloton radius ∼ Bohr radius)

$$B \sim B_0 = \frac{m_e^2 e^3 c}{\hbar^3} = 2.35 \times 10^9 G \equiv 1 a.u. \tag{1}$$

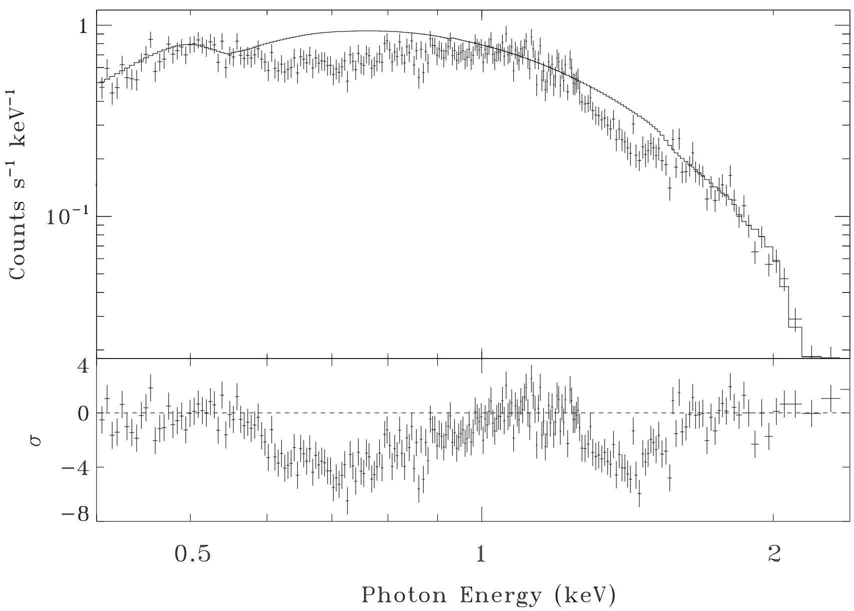
(Measure unit of magnetic field)

Magnetic field in which the cycloton energy is comparable with the electron rest mass

$$B \leq B_{rel} = \frac{m_e^2 c^3}{\hbar e} = 4.414 \times 10^{13} G \tag{2}$$

(no contributions from relativistic effect)

Neutron star (1E1207.4-5209)



Chandra X-ray Observatory (D. Sanwal, G. G. Pavlov, V. E. Zavlin and M. E. Teter, Apj, 574, L61(2002))

Two absorption features:

$$E_1 \;=\; 730 \pm 100 \text{ eV} \qquad E_2 \;=\; 1400 \pm 130 \text{ eV}$$

$$T \sim 10 - 100 eV \quad (10^5 - 10^6\, K)$$
$$B \sim 10^{12} - 10^{13}\; G$$

Objective

- ✦ Study of the ground state of the hydrogen molecule in a magnetic field:

$$(ppee) \quad \Rightarrow H_2,$$

Method

- ✦ Variational method

- ✦ A simple and unique trial function for all the range of magnetic fields

How to choose the trial function ψ_{trial}?

Trial Function ψ_{trial}

Potential

$$V_{trial} \equiv \frac{\nabla^2 \psi_{trial}}{\psi_{trial}}$$

It should reproduce:

- ✦ Coulomb singularity$(1/r, 1/r_{12})$
- ✦ Asymptotic behavior at large distance — Harmonic oscillator $|x|, |y| \to \infty$

Symmetries

Identical charge centers:

ψ_{trial} is symmetric (antisymmetric) under charge permutations

Technical Aspects

✦ Variational calculations imply two steps

- Multidimensional Numerical Integration
- Minimization

- Integration subroutine
  - *Adaptive multidimensional integration NAG-LIB*
  - Manual partition of the integration domain in subdomain to reproduce the integrand profile in an optimal way

- Minimization subroutine
  - *MINUIT CERN-LIB*

✦ Computational resources:

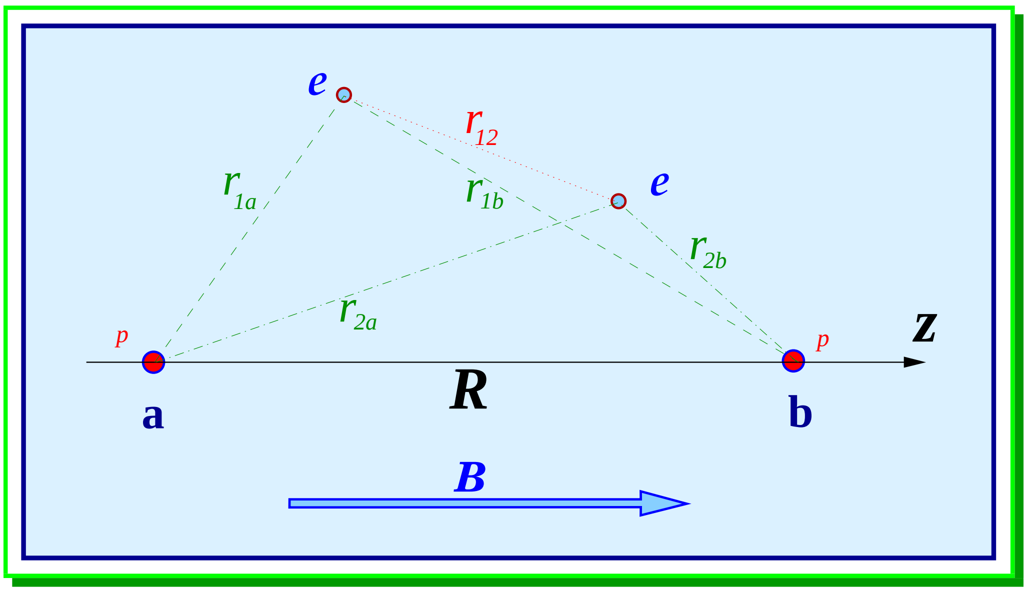
estándar PC and Cluster

⇒ (Parallelization)

H_2

(Parallel configuration)

$(ppee)$



Hamiltonian

$$\mathcal{H} = \sum_{\ell=1}^{2} \left(-\nabla_\ell^2 + \frac{B^2}{4}\rho_\ell^2 \right) - \sum_{\ell,\kappa} \frac{2}{r_{\ell\kappa}} + \frac{2}{r_{12}} + \frac{2}{R}$$

$$+B(\hat{L}_z + 2\hat{S}_z),$$

H_2: Classification of states

$$^{2S+1}M_p$$

$$m = 0$$

$$^1\Sigma_g \;,\; ^1\Sigma_u \;,\; ^3\Sigma_g \;,\; ^3\Sigma_u$$

$$m = -1$$

$$^1\Pi_g \;,\; ^1\Pi_u \;,\; ^3\Pi_g \;,\; ^3\Pi_u$$

$$m = -2$$

$$^1\Delta_g \;,\; ^1\Delta_u \;,\; ^3\Delta_g \;,\; ^3\Delta_u$$

Trial function for the ground state $({}^1\Sigma_g)$:$(B=0)$

$$\psi^{(trial)} = A_1\psi_1 + A_2\psi_2 + A_3\psi_3$$

$$\begin{aligned}
\psi_1 &= (1+P_{12})(1+P_{ab})e^{-\alpha_1 r_{1a}-\alpha_2 r_{1b}-\alpha_3 r_{2a}-\alpha_4 r_{2b}+\gamma_1 r_{12}}\,,\\
\psi_2 &= (1+P_{12})e^{-\alpha_5(r_{1a}+r_{2b})-\alpha_6(r_{1b}+r_{2a})+\gamma_2 r_{12}}\,,\\
\psi_3 &= (1+P_{12})e^{-\alpha_7(r_{1a}+r_{1b})-\alpha_8(r_{2a}+r_{2b})+\gamma_3 r_{12}}
\end{aligned}$$

ψ_2 is a degeneration of ψ_1 when $\alpha_1=\alpha_4, \alpha_2=\alpha_3$ $(\rightarrow 'H+H')$

ψ_3 is a degeneration of ψ_1 when $\alpha_1=\alpha_2, \alpha_3=\alpha_4$ $(\rightarrow 'H_2^+ + e')$

$\psi_1 \rightarrow$ non-linear interpolation between ψ_2 and ψ_3

P_{12} electron interchange$(1 \leftrightarrow 2)$

P_{ab} proton interchange a and b

$$\begin{aligned}
f_1(r_{12}) &= 1+r_{12} \rightarrow V^1_{trial}(r_{12}) \approx \frac{1}{r_{12}(1+r_{12})}\,,\\
f_2(r_{12}) &= \exp(\gamma r_{12}^2) \rightarrow V^2_{trial}(r_{12}) \approx r_{12}^2\,,\\
f_3(r_{12}) &= \exp(-\alpha r_{12}) \rightarrow V^3_{trial}(r_{12}) \approx \frac{1}{r_{12}}
\end{aligned}$$

only factor $f_3(r_{12})$ fulfills the above requirement.

H_2: **Ground state($^1\Sigma_g$)(B=0)**

E_T (Ry)	$< r_{12}^{-1} >$	$< r_1^2 >$
-2.34697 [a]		
-2.34778 [b]		
-2.348382 [c]		2.5347
-2.348393 [d]	0.5874	2.5487
-2.34888 [e]	0.5874	
-2.34895 [f]		

[a] James and Coolidge, 14 parameters

[b] Heidelberg group, > 200 non spherical gaussian orbitals

[c] W. Kolos and C.C.J. Roothan using James- Coolidge type functions, 14 parameters

[d] Present work, *(A. Turbiner, N.Guevara, 14 parameters)* (physics/0606120)

[e] W. Kolos and C.C.J. Roothan (the BO ground state energy with 40 variational parameters)

[f] Sims and Hangstrom. 7034 James-Coolidge type terms (**best result**)

r_1 is the distance from 1st electron to the mid-point between protons.

Simple and compact few-parametric trial function(it can be modified to study different states)

Most accurate Born-Oppenheimer energy for H_2 **(based on few-parametric** (≤ 14) **trial functions)**

We were able to design a computer code for multidimensional numerical integration with high accuracy.

Trial Functions: $(B > 0)$

$$\psi^{(trial)} = A_1\psi_1 + A_2\psi_2 + A_3\psi_3$$

$$\begin{aligned}
\psi_1 &= (1+\sigma_e P_{12})(1+\sigma_{_N} P_{ab})\, e^{-\alpha_1 r_{1a} - \alpha_2 r_{1b} - \alpha_3 r_{2a} - \alpha_4 r_{2b} - B\beta_1 \frac{\rho_1^2}{4} - B\beta_2 \frac{\rho_2^2}{4} + \gamma_1 r_{12}}\,, \\
\psi_2 &= (1+\sigma_e P_{12}) e^{-\alpha_5 (r_{1a}+r_{2b}) - \alpha_6 (r_{1b}+r_{2a}) - B\beta_3 \frac{\rho_1^2}{4} - B\beta_4 \frac{\rho_2^2}{4} + \gamma_2 r_{12}}\,, \\
\psi_3 &= (1+\sigma_e P_{12}) e^{-\alpha_7 (r_{1a}+r_{1b}) - \alpha_8 (r_{2a}+r_{2b}) - B\beta_5 \frac{\rho_1^2}{4} - B\beta_6 \frac{\rho_2^2}{4} + \gamma_3 r_{12}}
\end{aligned}$$

$\sigma_e = 1$ spin singlet$(S = 0)$

$\sigma_e = -1$ spin triplet $(S = 1)$

$\sigma_N = 1$ nuclear gerade state

$\sigma_N = -1$ nuclear ungerade state

α_{1-8}, β_{1-6} and γ_{1-3} variational parameters

Total of variational parameters(20)

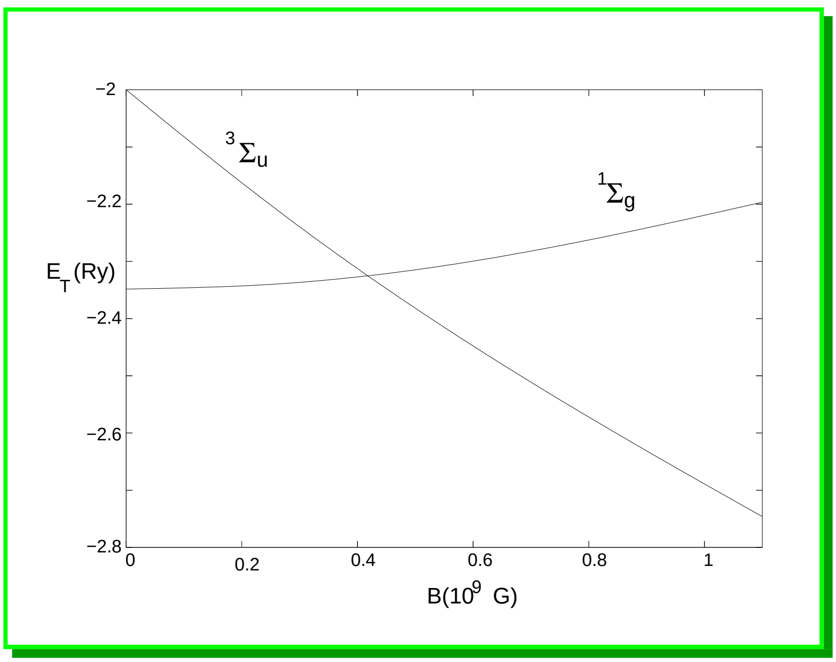
Low-lying states of H_2 in a weak magnetic field

$^1\Sigma_g$, $^3\Sigma_u$ states

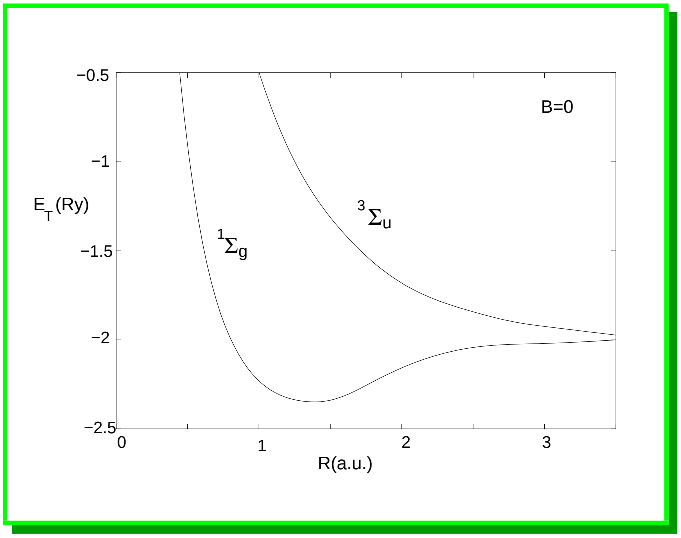
B(a.u.)	E_T ($^1\Sigma_g$)	R_{eq}	$E_T(^3\Sigma_u)$
0	-2.34839	1.4	-2.0
	-2.34778^a		
0.1	-2.34097	1.397	-2.1901
	-2.33930^a		
0.2	-2.31869	1.385	-2.3615
	-2.317532^a		
0.5	-2.17884	1.332	-2.7888
	-2.17816^a		
1.0	-1.78083	1.237	-3.3247
	-1.78067^a		

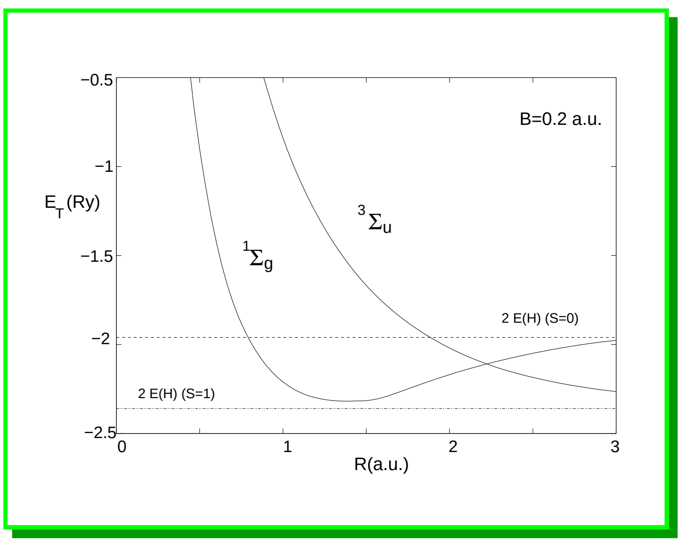
[a] Heidelberg group

Crossing between the $^1\Sigma_g$ and $^3\Sigma_u$ states

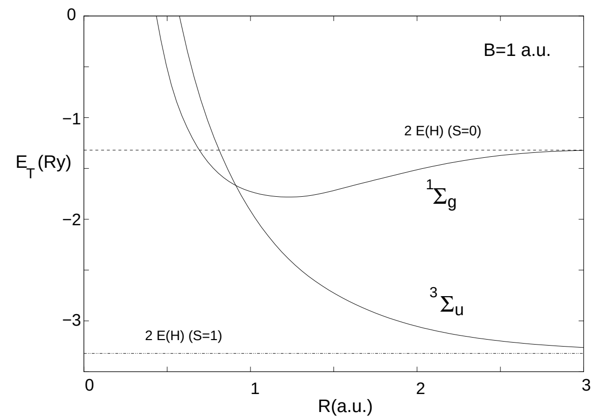


Low-lying states of H_2 in a weak magnetic field

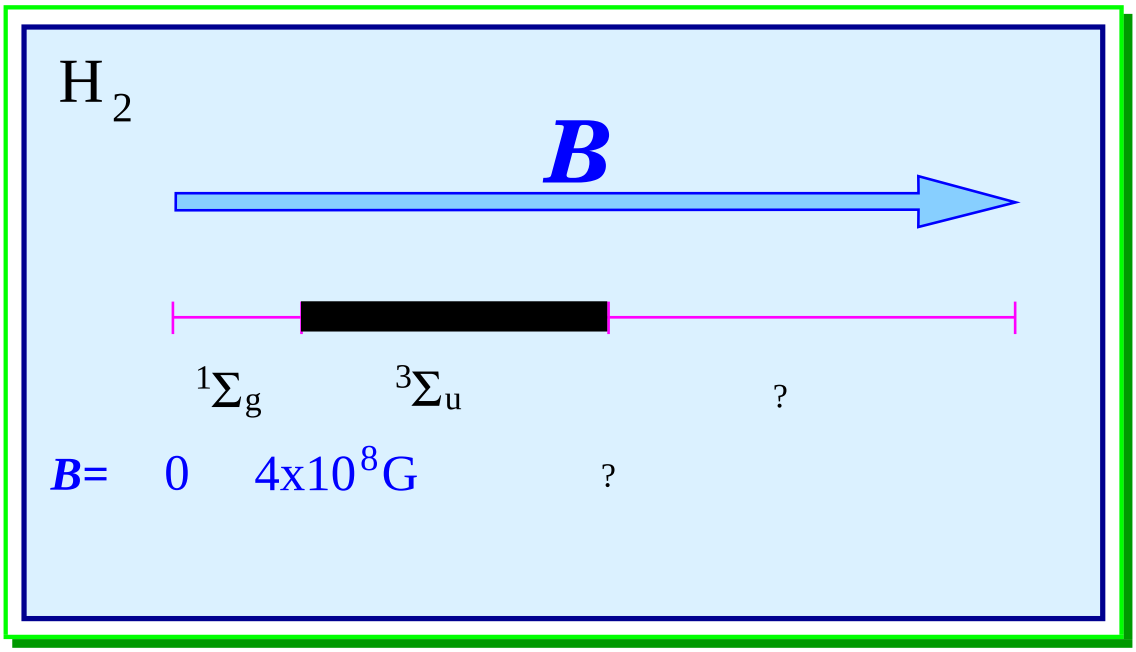




Low-lying states of H_2 in a weak magnetic field



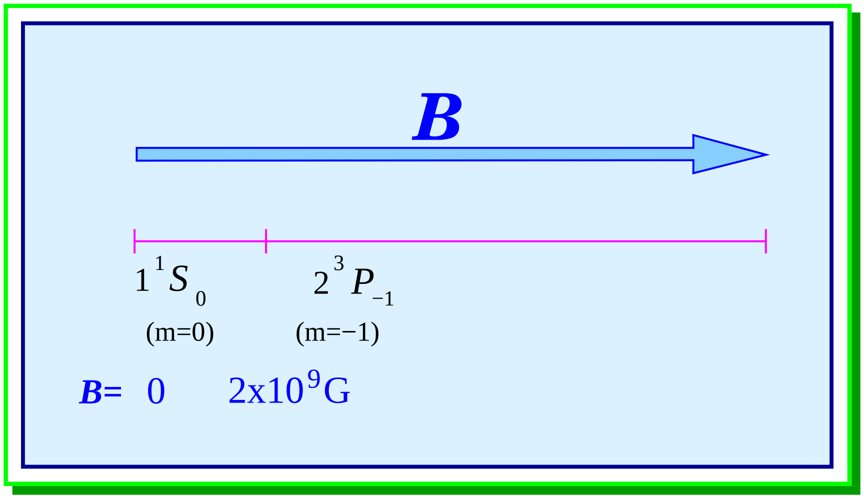
Hydrogen Molecule: Ground State



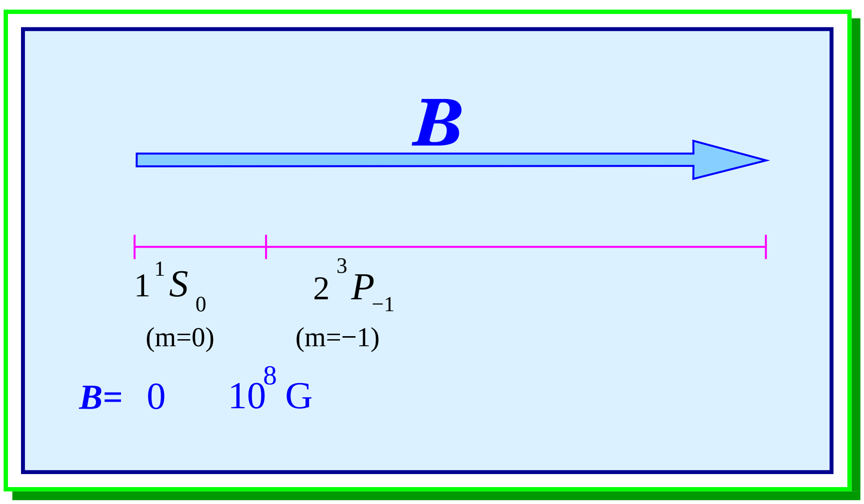
Parallel configuration is the optimal one,

Two-electron atomic systems

He: Ground state



H^-: Ground state



Schmelcher et al
Phys. Rev. A 61, 063413(2000), J. Phys. B, 32, 1557(1999),
J. Phys. B, 33, 545(2000)

Conclusions

1. *Simple and physically adequate trial function can give high accuracy for the energy in the variational calculations.*
2. *Quantum numbers of the ground state depend on the magnetic field strength: for weak magnetic fields* ($^1\Sigma_g \rightarrow {}^3\Sigma_u$) *for the hydrogen molecule.*
3. *The hydrogen molecule that exists for the field-free case becomes unbound for stronger magnetic field* ($B \geq 0.18 a.u.$)

   Is the $^3\Sigma_u$ *state the ground state for stronger magnetic field?*

   Do all two-electron hydrogen molecular systems(H_3^+ *and* H_4^{2+}) *show the same behavior?*

Future:

Studies of other two-electron molecular systems:
$H_4^{2+}, H_5^{3+}, (H - He - H)^{2+}, (He - H - He)^{3+}, He_3^{4+}$, etc.