The Ion H_3^+ in a Strong Magnetic Field in Linear Configuration

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Abstract

A first detailed study of the low-lying electronic states of the H_3^+ molecular ion in linear configuration, parallel to a magnetic field, is carried out for $B = 0 - 4.414 \times 10^{13}$ G in the Born-Oppenheimer approximation. The variational method is employed with a single, physically adequate trial function which includes, in particular, explicitly a correlation term in the form $\exp(\gamma r_{12})$, where γ is a variational parameter. The state of the lowest total energy (ground state) depends on the magnetic field strength. It evolves from spin-singlet $^1\Sigma_g$ for small magnetic fields $B \lesssim 5 \times 10^8$ G to weakly-bound spin-triplet $^3\Sigma_u$ for intermediate fields and eventually to spin-triplet $^3\Pi_u$ state for $B \gtrsim 5 \times 10^{10}$ G.

Formulation of the Problem

In the Born-Oppenheimer approximation where protons are infinitely massive, the Hamiltonian which describes the two-electron-three-proton system ($pppee$) in a constant uniform magnetic field $\mathbf{B} = (0, 0, B)$ is

$$\mathcal{H} = \sum_{\ell=1}^{2} (\hat{\mathbf{p}}_\ell + \mathcal{A}_\ell)^2 - \sum_{\substack{\ell=1,2 \\ \kappa=a,b,c}} \frac{2}{r_{\ell,\kappa}} + \frac{2}{r_{12}} + \frac{2}{R_+} + \frac{2}{R_-} + \frac{2}{R_+ + R_-} + 2\mathbf{B}\cdot\mathbf{S},$$

with protons situated along magnetic line (so called *parallel configuration*, see Fig.1). Here $\hat{\mathbf{p}}_\ell = -i\nabla_\ell$ is the 3-vector of the momentum of the ℓ-th-electron, the index κ runs over protons a, b and c; r_{12} is the interelectronic distance and $\mathbf{S} = \hat{\mathbf{s}}_1 + \hat{\mathbf{s}}_2$ is the operator of the total spin. $\mathcal{A}_\ell$ is a vector potential which corresponds to the constant uniform magnetic field $\mathbf{B}$. It is chosen in the symmetric gauge,

$$\mathcal{A}_\ell = \frac{1}{2}(\mathbf{B} \times \mathbf{r}_\ell) = \frac{B}{2}(-y_\ell,\ x_\ell,\ 0)\ .$$

Finally, the Hamiltonian can be written as

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

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

where $\hat{L}_z = \hat{l}_{z_1} + \hat{l}_{z_2}$ and $\hat{S}_z = \hat{s}_{z_1} + \hat{s}_{z_2}$ are the z-components of the total angular momentum and total spin, respectively, and $\rho_\ell = \sqrt{x_\ell^2 + y_\ell^2}$.

Goal

Recently, extended studies of possible one-electron molecular systems in strong magnetic field were performed (see Ref.1). Our present goal is to carry out a detailed study of the low lying electronic states of the molecular ion H_3^+ in parallel configuration in a magnetic field where the non-relativistic approximation is valid: $B = 0 - 4.414 \times 10^{13}$ G. We mention a single, semi-quantitative attempt to perform a similar study in the past (Ref.2). Presented results there can not be trusted.

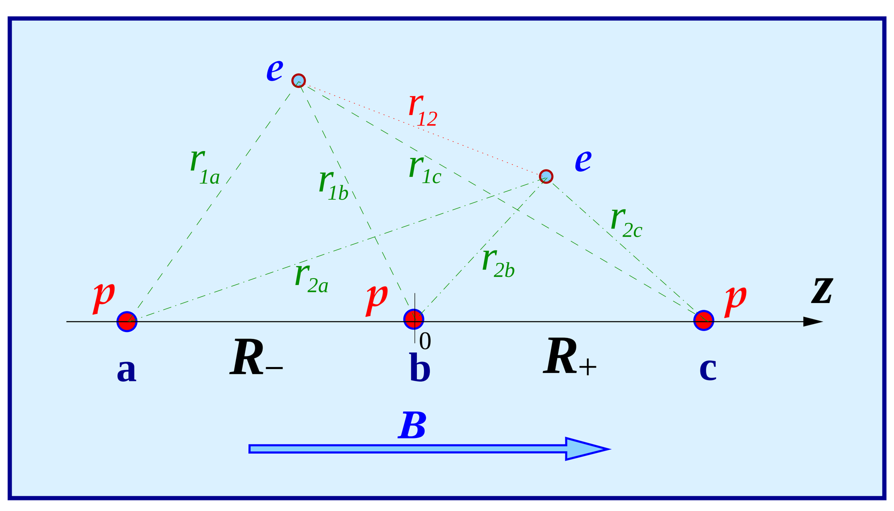

Fig. 1: The H_3^+ molecular ion in parallel configuration in a uniform constant magnetic field $\mathbf{B} = (0, 0, B)$.

Variational Calculus

Take $\psi_{trial}(x, \{\alpha\})$ and find a potential for which it is an exact solution

$$V_{trial}(x, \{\alpha\}) = \frac{\Delta\psi_{trial}}{\psi_{trial}}\ ,\ E_{trial} = 0$$

where $\{\alpha\}$ are variational parameters. So, we know the Hamiltonian for which ψ_{trial} is the exact eigenfunction

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

then

$$\begin{aligned} E_{var} &= \min_{\{\alpha\}} \int \psi^*_{trial}\ H\ \psi_{trial} \\ &= \int \psi^*_{trial}\ \underbrace{H_{trial}\ \psi_{trial}}_{=0} + \int \psi^*_{trial}\,(H - H_{trial})\,\psi_{trial} \\ &= 0 + \int \psi^*_{trial}\,(V - V_{trial})\,\psi_{trial}\ \text{“} + \ldots\text{”} \end{aligned}$$

- Hence, the variational energy is the sum of the first two terms of a perturbative theory with perturbation potential

$$(V - V_{trial})\,.$$

- Choosing different ψ_{trial} we can get a convergence of the PT series (if possible) and also to control a rate of convergence trying to get it as fast as possible. Minimization is not always leading to an increase the rate of convergence.
- In practice, Ψ_{trial} is chosen in such a way to contain as much as possible physical properties of the problem we study as well.

Trial Function

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

where $\sigma_e = \pm 1$ stands for spin singlet ($S = 0$) and triplet states ($S = 1$), respectively.
For S_3-permutationally symmetric case $\sigma_N = \sigma_{N_a} = \pm 1$.
P_{ac} interchanges the two extreme protons a and c, and α_{1-6}, β_{1-2} and γ are variational parameters.
The operators P_{12} interchanges electrons $(1 \leftrightarrow 2)$,

Classification of States

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

$2S + 1$ is the electronic total spin multiplicity, it is 1 for spin-singlet ($S = 0$) and 3 for spin-triplet ($S = 1$); $M = m_1 + m_2$ is the total magnetic quantum number, $M = 0, -1, -2$ it is denoted by Σ, Π, Δ, respectively; p (the spatial parity) denotes gerade ($p = +1$), ungerade ($p = -1$) states.

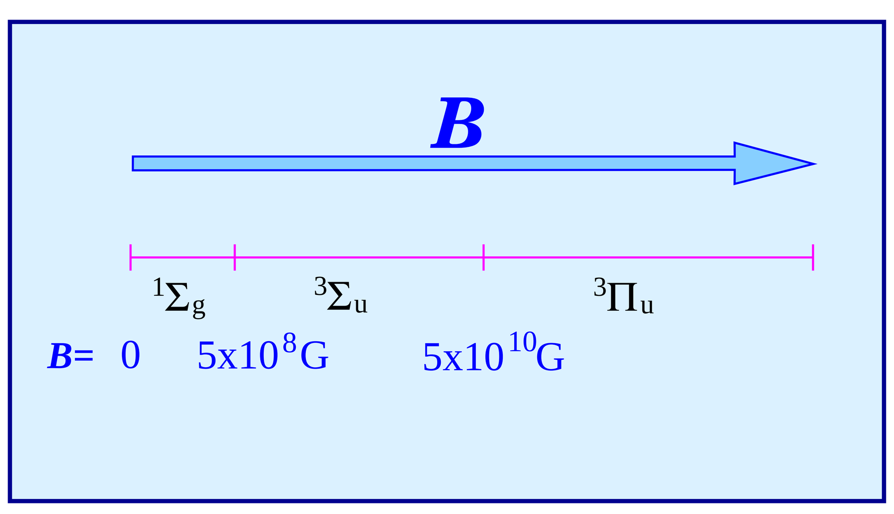

Fig. 2: Ground state evolution for the H_3^+-ion in parallel configuration as a function of the magnetic field strength.

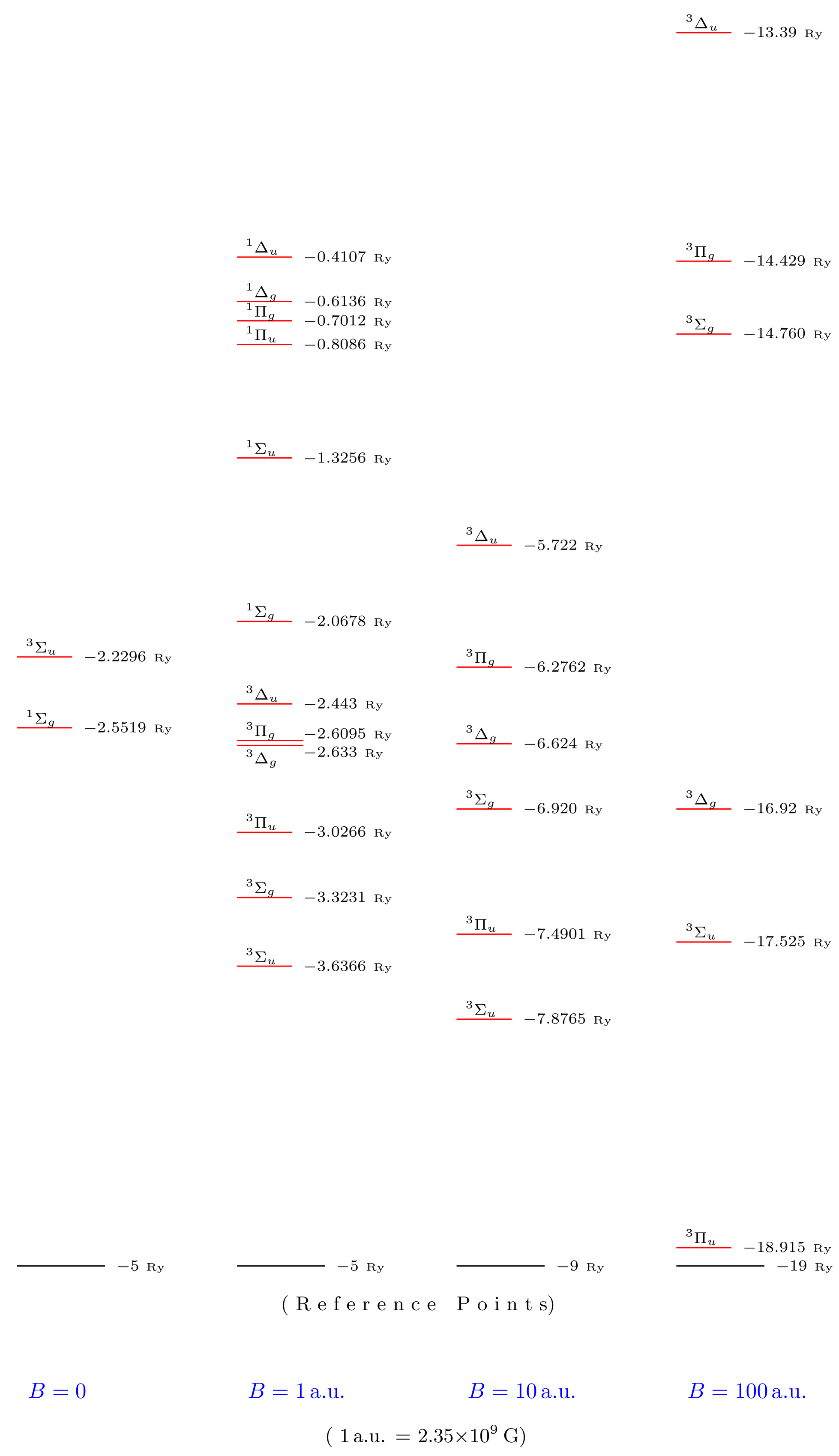

Fig.3: Low-lying electronic states of the H_3^+ ion in a magnetic field in linear, parallel configuration. For $B = 0$ the most accurate total energy for $^3\Sigma_u$ is -2.2322 Ry (Ref.3)

RESULTS

1. *It is found that in the Born-Oppenheimer approximation, for the system (pppee) in parallel configuration in a magnetic field ranging in $B = 0 - 4.414 \times 10^{13}$ G, the total energy curves display a well pronounced minimum at finite internuclear distances at $R_+ = R_- = R_{eq}$ (see Fig.1) for the lowest states with magnetic quantum numbers $M = 0, -1, -2$, total spin $S = 0, 1$ and parity $p = \pm 1$.*
2. *For all studied states as the magnetic field increases the internuclear distance R_{eq} decreases and the system becomes more compact, while the total energies of spin-singlet states increase and of spin-triplet states decrease.*
3. *The state of the lowest total energy (ground state) depends on the magnetic field strength. It evolves from spin-singlet $^1\Sigma_g$ for small magnetic fields $B \lesssim 5 \times 10^8$ G to weakly-bound spin-triplet $^3\Sigma_u$ state for intermediate fields and eventually to spin-triplet $^3\Pi_u$ state for $B \gtrsim 5 \times 10^{10}$ G.*

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