H₂⁺ in a weak magnetic field

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Abstract
The electronic energy of H₂⁺ in magnetic fields of up to B = 0.2B₀ (or 4.7 × 10⁴ T) is investigated. Numerical values of the magnetic susceptibility for both the diamagnetic and paramagnetic contributions are reported for arbitrary orientations of the molecule in the magnetic field. It is shown that both diamagnetic and paramagnetic susceptibilities grow with inclination, while paramagnetic susceptibility is systematically much smaller than the diamagnetic one. Accurate two-dimensional Born–Oppenheimer surfaces are obtained with special trial functions. Using these surfaces, vibrational and rotational states are computed and analyzed for the isotopologues H₂⁺ and D₂⁺.

Keywords: variational method, weak magnetic field, magnetic susceptibility, ro-vibrational states

(Some figures may appear in colour only in the online journal)

1. Introduction
Since the pioneering work of de Melo et al [1] on the molecular ion H₂⁺ in strong magnetic fields, B ≥ B₀ (B₀ = 2.35 × 10⁹ Gauss = 2.35 × 10⁵ T), many studies have been conducted for this system under such conditions (see for example [2–10] and references therein) where the electronic energy of the ground and first excited states as well as some rotation-vibrational states have been studied. H₂⁺ has been used as a test system for the investigation of the validity of approximations commonly made in field-free molecular physics, such as the Born–Oppenheimer approximation [11, 12]. Though H₂⁺ can be considered a benchmark molecule for the development of appropriate theoretical methods for the accurate computation of molecular structure and properties in magnetic fields that may be extended to more complex systems [7, 13–15], only a few studies have been reported in the range of small fields (0 ≤ B ≤ B₀) [16–19], where electronic energies of the ground state are presented besides some physical features such as a qualitative evolution of the rotational levels as function of the field.

The goal of the present study is to investigate the electronic ground state of the molecular system H₂⁺ placed in a weak magnetic field, B ≤ 0.2B₀. Overall in this domain of field strength, the effects of the magnetic field cannot be treated accurately via perturbation theory. In the first part of the present work we use physically motivated, specially tailored trial functions [5–7] to obtain sufficiently accurate estimates of the electronic energy over a range of field strengths up to B = B₀ and different inclinations of the molecular axis with respect to the field direction. In the second part we investigate the vibrational and rotational structure of H₂⁺ and D₂⁺ in the external magnetic field.

2. Hamiltonian
We consider a homonuclear molecular ion formed by two nuclei of charge q separated by a distance R, and one electron e placed in a uniform magnetic field B oriented along the z-axis. The reference point for coordinates is chosen to be at the midpoint of the line connecting the nuclei which in turn forms an angle θ with respect to the magnetic field direction (see
A set of physically adequate real trial functions introduced in [5–7] are used to calculate the total energy of the electronic Hamiltonian (3). Thus, the trial function employed in the present study is a linear superposition of three particular functions

$$\Psi = A_1 \Psi_1 + A_2 \Psi_2 + A_3 \Psi_3,$$

where

$$\Psi_1 = e^{-a_1(n_1+1)} e^{-i \tilde{B} \rho_1 \beta_1 \hat{x}^2 + \beta_1 (1-\xi)^2 \hat{y}^2},$$

is a Heitler–London type function,

$$\Psi_2 = (e^{-a_2 n} + e^{-a_1 n}) e^{-i \tilde{A} \rho \beta_1 \hat{x}^2 + \beta_1 (1-\xi)^2 \hat{y}^2},$$

is a Hund–Mulliken type function, and

$$\Psi_3 = (e^{-a_3 n} - a_1 n) e^{-i \tilde{A} \rho \beta_1 \hat{x}^2 + \beta_1 (1-\xi)^2 \hat{y}^2},$$

is a Guillaume–Zener type function, all multiplied with exponential terms that correspond to the lowest Landau orbital.

Without loss of generality one of the linear parameters $A_{1,2,3}$ may be set equal to one, hence the trial function consists of 13 variational parameters. For the parallel configuration the parameters are not independent and must obey the symmetry relations $\beta_{1z} = \beta_{1y}$, $\beta_{2z} = \beta_{2y}$, and $\beta_{3z} = \beta_{3y}$, reducing the number of variational parameters to ten. The trial function (4) defined in this way is expected to provide an accurate approximation to the exact electronic wave function of the ground state of molecular ion $H^+_2$ for a large variety of strengths and inclinations of the magnetic field.

Calculations are performed using the minimization package MINUIT from CERN-LIB. Numerical integrations were done with a relative accuracy of $\sim 10^{-6}$ using the adaptive NAG-LIB (D01FCF) routine.
3.2. Results

Using the trial function (5) presented in section 3.1, two-dimensional potential energy surfaces of the electronic energy have been obtained variationally as function of the internuclear distance, \( R \), and the inclination \( \theta \) (see figure 1).

As examples we show in figure 2 sections of the potential surface at different inclinations, \( \theta = 0^\circ \), \( \theta = 45^\circ \) (for the field \( B = 0.5B_0 \)) and \( \theta = 90^\circ \).

At perpendicular orientation an energy ridge shows up which can be interpreted as a barrier of a hindered rotation. This fact is shown in more detail in figure 3 where the electronic energy is plotted as a function of the inclination angle and field strengths of \( B = 0.1B_0 \) and \( 0.2B_0 \) for \( B \geq 10^3 T \) [7]. At perpendicular orientation an energy ridge shows up which can be interpreted as a barrier of a hindered rotation. This fact is shown in more detail in figure 3 where the electronic energy is plotted as a function of the inclination angle and field strengths of \( B = 0.1B_0 \) and \( 0.2B_0 \).

3.3. Magnetic susceptibility

An important quantity that describes the response of the molecular system with respect to the external field is the magnetic susceptibility. It is defined via a Taylor expansion of the electronic energy in powers of the magnetic field \( B \)

\[
E(\vec{B}) = E(0) - \sum_a \frac{1}{2} \sum_{\beta} \alpha_{\alpha\beta} B_\beta + \cdots
\]
For the electronic ground state, when the spin contributions are neglected, the first coefficient, \(e_s\), vanishes. The coefficient tensor \(\chi_{ab}\) is the magnetic susceptibility. The response of a molecule to an external magnetic field leads to a classification into two types (see for example [23–27]): diamagnetic and paramagnetic.

In the electronic Hamiltonian (3) there are two terms containing the magnetic field, \(B\), a linear and a quadratic one. Correspondingly, there are two contributions to the susceptibility: a paramagnetic contribution originating from the linear term of the Hamiltonian when treated by second order perturbation theory in \(B\), and a diamagnetic contribution coming from the quadratic term in the first order in perturbation theory in \(B\).

At first, let us proceed to the diamagnetic susceptibility. The diamagnetic susceptibility term \(\chi^d\) can be expressed as the expectation value with respect to the field-free wavefunction at equilibrium distance. Thus, in the symmetric gauge, \(\vec{A}_s = \frac{1}{2}\vec{B} \times \vec{r}\), the expression of the diamagnetic susceptibility tensor is

\[
\chi^d_{\alpha\beta} = -\frac{1}{4} \left[ \langle \vec{r}^2 \rangle \delta_{\alpha\beta} - \left\langle \vec{r}_n r_\beta \right\rangle \right],
\]

where \(\vec{r} = (x, y, z)\) is the position vector of the electron and \(r_n, \alpha = 1, 2, 3\), its components. If the magnetic field direction is chosen along the z-axis, \(\vec{B} = B\hat{z}\), the tensor \(\chi^d\) contains a single non-zero component, \(\chi^d_{zz} \equiv \chi^d\),

\[
\chi^d = -\frac{1}{4} \langle \rho^2 \rangle = -\frac{1}{4} \left[ \langle x^2 \rangle + \langle y^2 \rangle \right].
\]

Let us now consider the molecule in the x–z plane (it can be regarded as the definition of the x-direction). For different orientations of the molecule with respect to the z-axis, the expectation values change according to a rotation by the angle \(\theta\) around the y-axis \((x \rightarrow x \cos \theta + z \sin \theta, y \rightarrow y, z \rightarrow z \cos \theta - x \sin \theta)\)

\[
\chi^d = -\frac{1}{4} \left[ \langle x^2 \rangle (1 + \cos^2 \theta) + \langle z^2 \rangle \sin^2 \theta \right].
\]

where \(\langle x^2 \rangle_0\) and \(\langle z^2 \rangle_0\) are the expectation values at zero inclination, and where we have used the fact that \(x^2_0 \approx \langle y^2 \rangle_0\) and \(xz_0 = 0\). In table 2, the numerical values of the expectation values of the squares of the components of the position vector of the electron, and the diamagnetic susceptibility, \(\chi^d\), are presented, at equilibrium distance, as function of \(\theta\) and compared with results obtained by Hegstrom [28] for parallel and perpendicular orientations.

For strong fields, higher powers of \(B\) might need to be considered in the expansion (8). With our variational method, evaluation of higher order terms is straightforward as the trial functions depend parametrically on the field strength. To this end we define the function \(X(\vec{B}) = -\langle \rho^2 \rangle_{\vec{B}}/4\), where the expectation value is taken with the optimized, \(B\)-dependent trial function. In the limiting case when \(B \rightarrow 0\), the diamagnetic susceptibility is recovered, \(X(\vec{B}) \rightarrow \chi^d\). Numerical results of \(X(\vec{B})\) were obtained at the equilibrium distances for \(B = 0.0, 0.01 \ldots 0.2B_0\) and \(\theta = 0^\circ, 15^\circ \ldots 90^\circ\) and fitted (rms = 1.6 × 10\(^{-4}\)) to a simple functional form of the field strength \(B\) and inclination \(\theta\).

\[
X_B(\vec{B}) = -0.43795 + 0.013498B + 0.37103B^2
+ \left(0.11774 - 0.01577B - 0.141B^2\right)\cos^2 \theta.
\]

This surface is plotted in figure 6, while cuts at constant orientation angles are presented in figure 7. It can be seen that the \(X(\vec{B})\) is a smooth function of the orientation angle, \(\theta\), and the field strength, \(B\), and tends to the magnetic susceptibility \(X(\vec{B}) \rightarrow \chi^d\) as the field tends to zero. The points on the ordinate represent the value of the magnetic susceptibility \(\chi^d\) for various orientations and agree with the corresponding data obtained from the model (12), within the accuracy. At weak fields \(\leq 0.04B_0\), \(X\) is close to \(\chi^d\) as given

| \(B/B_0\) | \(\theta\) | \(R_{\text{eq}}/a_0\) | Energy/Eh | \(B/B_0\) | \(\theta\) | \(R_{\text{eq}}/a_0\) | Energy/Eh |
|---|---|---|---|---|---|---|---|
| 0 | — | 1.9971 | -0.602625 | 0.1 | 0° | 1.9920 | -0.601029 | 0.6 | 0° | 1.8705 | -0.550864 |
| 45° | 1.9897 | -0.600785 | 45° | 1.8201 | -0.543923 |
| 90° | 1.9882 | -0.600613 | 90° | 1.7968 | -0.539131 |
| 0.2 | 0° | 1.9786 | -0.596311 | 0.7 | 0° | 1.8399 | -0.534186 |
| 45° | 1.9687 | -0.595361 | 45° | 1.7800 | -0.525296 |
| 90° | 1.9637 | -0.594678 | 90° | 1.7535 | -0.519216 |
| 0.3 | 0° | 1.9566 | -0.588667 | 0.8 | 0° | 1.8096 | -0.515853 |
| 45° | 1.9379 | -0.586615 | 45° | 1.7411 | -0.504917 |
| 90° | 1.9283 | -0.585161 | 90° | 1.7112 | -0.497503 |
| 0.4 | 0° | 1.9301 | -0.578360 | 0.9 | 0° | 1.7799 | -0.496041 |
| 45° | 1.9013 | -0.574889 | 45° | 1.7027 | -0.482994 |
| 90° | 1.8862 | -0.572447 | 90° | 1.6721 | -0.474219 |
| 0.5 | 0° | 1.9019 | -0.565667 | 1.0 | 0° | 1.7563 | -0.474937 |
| 45° | 1.8610 | -0.560550 | 45° | 1.6687 | -0.459670 |
| 90° | 1.8413 | -0.556976 | 90° | 1.6348 | -0.449532 |
The angle the surface generated by (12) as function of the magnetic orientations. It can be obtained directly using the Taylor expansion (8) of the energy potential curve (see (12)). Turning now to the total susceptibility (11). It indicates that perturbation theory in (12) numerically the energy evolution with inclination. Then interpolate the angle between the molecular and the field strength \( \theta \). The energy correction quadratic in \( B \) is recovered in this way. The energy correction in powers of \( B \) is much smaller than the diamagnetic part. It grows with inclination. Concerning our statement that standard first order perturbation theory based on the field-free \( H^{(0)} \) problem should be applicable up to \( B \approx 0.04 B_0 \), we may now add that at least 92% of the total susceptibility is recovered in this way. The energy correction quadratic in \( B \) is accurate to \( -6 \times 10^{-5} E_h \).

4. Solving the nuclear Schrödinger equation

Substituting in the Hamiltonian (1) the electronic part (last three terms) by the potential energy surface, \( \bar{V}(R, \theta) \), we obtain the nuclear Hamiltonian. In the symmetric gauge, it can be written as

\[
\hat{H}_{\text{nuc}} = \frac{1}{M_r} \rho^2 - \frac{1}{M_s} \bar{B} \cdot \bar{L}_R + \frac{1}{8 M_s} \left[ B^2 \bar{R}^2 - \left( \bar{B} \cdot \bar{R} \right)^2 \right] + \bar{V}(R, \theta),
\]

where \( \bar{L}_R = \bar{R} \times \bar{\theta}_R \) is the angular momentum operator of the molecular frame. Transforming the Hamiltonian in spherical coordinates yields

\[
\hat{H}_{\text{nuc}} = -\frac{1}{M_s} \frac{\partial^2}{\partial \theta^2} R + \frac{2}{M_s R^2} \frac{\partial}{\partial R} R \bar{L}_R + \frac{1}{M_s} B \bar{L}_z \\
+ \frac{1}{8 M_s} B^2 R^2 \sin^2 \theta + \bar{V}(R, \theta),
\]

where \( \bar{L}_z \) is the projection of angular momentum along \( z \)-axis and \( \theta \) the angle between the molecular and the \( z \)-axis.

We have solved the nuclear Schrödinger equation with Hamiltonian (16) numerically. To this end the Hamiltonian is divided in the two separate terms

\[
\hat{H}_1 = -\frac{2}{M_s} \frac{\partial^2}{\partial \theta^2} R + \bar{V}(R, \theta') + \frac{1}{8 M_s} B^2 R^2 \sin^2 \theta' \]

and

\[
\hat{H}_2 = \frac{2}{M_s R^2} L_R^2 - \frac{1}{M_s} B \bar{L}_z + \frac{1}{8 M_s} B^2 R^2 \left( \sin^2 \theta - \sin^2 \theta' \right) \\
+ \bar{V}(R, \theta) - \bar{V}(R, \theta'),
\]

which roughly correspond to a vibrational part of the molecule with reference orientation angle \( \theta' \), and a rotational part.
vibrational and rotational basis functions as

$$
\Psi(R, \theta, \phi) = \sum_{vL} \xi_v(R; \theta') \frac{Y_v^L(\theta, \phi)}{R} Y_v^L(\theta, \phi),
$$

where $\xi_v(R; \theta')$ are solutions of (17), obtained by numerical integration using the renormalized Numerov algorithm, and $Y_v^L(\theta, \phi)$ are spherical harmonics. The matrix elements of Hamiltonian (16) in this basis are

$$
\langle v'L'M | \hat{H}_{\text{muc}} | vLM \rangle = E_v(\theta') \delta_{LL} \delta_{\nu \nu} + \frac{2}{M_s} \left\langle \left| v \right| \frac{1}{R^2} \right| v \rangle \times L(L+1) \delta_{LL} - \frac{BM}{M_s} \delta_{LL} \delta_{\nu \nu}$$

$$+ \frac{B^2}{2M_s} \left\langle l'M' | \sin^2 \theta - \sin^2 \theta' \right| l'M \rangle \times \left\langle v' \left| R^2 \right| v \right\rangle + \left\langle v'L'M \left| \tilde{V}(R, \theta) \right. \right. - \tilde{V}(R, \theta') \right| vLM \rangle
$$

with $E_v(\theta')$ the eigenvalue of the vibrational operator (17). To evaluate these matrix elements, the potential $\tilde{V}(R, \theta)$ is presented as that of a hindered rotator

$$
\tilde{V}(R, \theta) = \tilde{V}(R, 0) + \sum_n \frac{V_{00,n}(R)}{2} \left[ 1 - \cos(2n\theta) \right]
$$

$$= \tilde{V}(R, 0) + V_{90}(R) \sin^2 \theta
$$

$V_{90}(R) = \tilde{V}(R, 90) - \tilde{V}(R, 0)$ is the barrier height for a given value of $R$.

Limitation of the above expansion to just one term is a good approximation of the potential at the field strengths considered in the present work, as we have verified numerically. The rms values for fits of $\tilde{V}(R_{eq}, \theta)$, using increments $\Delta \theta = 5^\circ$, are rms = 7.98 x 10^{-5} and rms = 3.66 x 10^{-6} for the one and two-term approximations and $B = 0.2B_0$. For $B = 0.1B_0$ the fitting error is reduced by a factor of four, approximately. Figure 8 shows the performance of the two approximations. The one-term approximation thus represents the potential energy surface to within the accuracy of the raw data of the electronic energy. An appealing feature is that just two slices, at $\theta = 0^\circ$ and $\theta = 90^\circ$, of the surface are needed explicitly. Within the one-term approximation and choosing

| $\theta$ | $(x^2)$ | $(y^2)$ | $(z^2)$ | $\chi^d$ | $\chi^p$ | $\chi$ |
|---|---|---|---|---|---|---|
| 0° | 0.640 36 | 0.640 36 | 1.111 31 | -0.320 18 | 0.000 00 | -0.320 18 |
| 15° | 0.671 92 | 0.640 37 | 1.079 76 | -0.328 07 | 0.000 22 | -0.327 85 |
| 30° | 0.758 10 | 0.640 35 | 0.993 59 | -0.349 61 | 0.002 16 | -0.347 45 |
| 45° | 0.875 83 | 0.640 40 | 0.875 83 | -0.379 06 | 0.009 92 | -0.369 14 |
| 60° | 0.993 57 | 0.640 30 | 0.758 11 | -0.408 49 | 0.020 62 | -0.387 87 |
| 75° | 1.079 71 | 0.640 42 | 0.671 96 | -0.430 03 | 0.030 90 | -0.399 13 |
| 90° | 1.111 25 | 0.640 41 | 0.640 41 | -0.437 92 | 0.034 47 | -0.403 45 |

The Condon–Shortley phase [29] convention has been adopted.

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4 We use $\sin^2 \theta = \frac{1}{2} - \frac{1}{2} \sqrt{1 - \cos^2 \theta}$ and the expression for the scalar product of three spherical harmonics, the Gaunt coefficients, $\int Y_{L'}^m(\Omega) Y_{L}^{m'}(\Omega) Y_{L''}^{m''}(\Omega) = (-)^{m+m'} \sqrt{\left(2L'+1\right)\left(2L+1\right)} \left\langle L' m' | L m \right\rangle L'' m''$. The Condon–Shortley phase [29] convention has been adopted.
Table 3. Rotational energy levels of H$_2^+$ in presence of a uniform magnetic field $B$ for the vibrational state $v = 0$. The pure vibrational state ($L = 0$ in the field-free case) is forbidden but shown here nevertheless as it corresponds to the origin of the rotational band. In the simple model 1, terms off-diagonal in $v$ are neglected. In model 2, the full matrix (22) is diagonalized.

| $L$ | Energy/Eh | $M$ | $\pi$ | $B = 0.1$ | Model 1 | Model 2 | $B = 0.2$ | Model 1 | Model 2 |
|-----|------------|-----|------|-----------|---------|---------|-----------|---------|---------|
|     |            |     |      |           |         |         |           |         |         |
| 0   | $-0.590 386$ | 0   | -1   | $-0.595 492$ | $-0.590 136$ | $-0.590 139$ | $-0.589 136$ | $-0.590 139$ | $-0.589 139$ |
| 5   | $-0.591 485$ | 5   | 1    | $-0.591 213$ | $-0.591 278$ | $-0.584 991$ | $-0.585 024$ | $-0.584 991$ | $-0.585 024$ |
| 4   | $-0.591 308$ | 4   | -1   | $-0.591 252$ | $-0.591 375$ | $-0.585 330$ | $-0.585 371$ | $-0.585 330$ | $-0.585 371$ |
| 3   | $-0.591 386$ | 3   | 1    | $-0.591 550$ | $-0.591 618$ | $-0.585 907$ | $-0.585 955$ | $-0.585 907$ | $-0.585 955$ |
|     | $-0.591 449$ | 2   | -1   | $-0.591 558$ | $-0.591 629$ | $-0.585 987$ | $-0.586 040$ | $-0.585 987$ | $-0.586 040$ |
|     | $-0.591 498$ | 1   | 1    | $-0.591 553$ | $-0.591 623$ | $-0.586 011$ | $-0.586 066$ | $-0.586 011$ | $-0.586 066$ |
|     | $-0.591 532$ | 0   | -1   | $-0.591 604$ | $-0.585 982$ | $-0.586 038$ | $-0.586 040$ | $-0.585 982$ | $-0.586 038$ |

\[ + \frac{2}{3} \langle \psi | V_0(R) | \psi \rangle \]
\[ \times (-1)^M \sqrt{(2L' + 1)(2L + 1)} \]
\[ \times \left( \begin{array}{cc} L & 2 \\ 2 & L' \end{array} \right) \left( \begin{array}{cc} 2 & L' \\ M & 0 \end{array} \right) \left( \begin{array}{cc} -M & L \\ 0 & 0 \end{array} \right) \] (22)

The terms in parentheses are Wigner 3j-symbols. The matrix (22) is diagonal in $M$ as expected, since $M$ is an exact quantum number. $L$-functions are coupled in steps of 2, conserving parity.

### 4.1. Results

For the isotopologues H$_2^+$ and D$_2^+$ we have computed the rovibrational eigenvalues of the nuclear Hamiltonian for the four lowest vibrational states and rotational excitation up to $L = 5$ with respect to the field-free case. Two levels of approximation are considered: a simplified model in which only the diagonal terms with respect to the vibrational basis are retained, and a second model which consists in diagonalizing the Hamiltonian (22) in the full basis. These data are presented in tables 3–10. The results obtained at the two levels of approximation agree to within \( \approx 7 \times 10^{-3} \) $E_a$.

If spin effects are neglected, rovibrational states of H$_2^+$ in a magnetic field can be classified in terms of three quantum numbers: the vibrational quantum number, $v$, the projection of the angular momentum of the molecular frame on the field axis, $M$, and the $z$-parity, $\pi$. The latter quantum number is due to the fact that positive and negative $z$-directions of the field are equivalent. If the wave function is reflected at the plane $z = 0$, $\theta$ is mapped to $\pi - \theta$ and $Y^L_\pi (\pi - \theta, \phi) = (-1)^L \pi^L_\pi (\theta, \phi)$. The $z$-parity of the state is thus $\pi = (-1)^{L + M}$. The nuclear wave function of a system of two fermions must be antisymmetric with respect to an exchange of the nuclei. The vibrational part of the wave function is symmetric for even vibrational quanta, $v = 0, 2, \ldots$ and antisymmetric for odd, $v = 1, 3, \ldots$. The symmetry of the rotational part can be derived from the properties of the spherical harmonics with respect to inversion, $(\theta, \phi \rightarrow \theta + \pi, \phi + \pi)$, $Y^L_\pi (\theta + \pi, \phi + \pi) = (-1)^L Y^L_\pi (\theta, \phi)$. Hence for even $v$ the rotational functions must have odd parity, while for odd $v$ they must have even parity, just as in the field-free case. The expression for the $z$-parity is

\[ \pi = (-1)^{M+v+1} \]
\[ \left\{ \begin{array}{ll} (-1)^M \quad \text{for } v \ \text{even}, \\ (-1)^M \quad \text{for } v \ \text{odd}. \end{array} \right. \] (23)

For D$_2^+$, a system with two bosonic nuclei, vibrational and rotational parts of the wavefunction must have the same
Table 4. Rotational energy levels of \( \text{H}_2^+ \) in presence of a uniform magnetic field \( B \) for the vibrational state \( v = 1 \). See caption of table 3 for explications.

| \( L \) | Energy/\( E_b \) | \( M \) | \( \pi \) | \( B = 0 \) | \( B = 0.1 \) | \( B = 0.2 \) |
|---|---|---|---|---|---|---|
| | | | | Model 1 | Model 2 | Model 1 | Model 2 |
| \( L = 0 \) | | | | | | | |
| \( L = 1 \) | | | | | | | |
| \( L = 2 \) | | | | | | | |
| \( L = 3 \) | | | | | | | |
| \( L = 4 \) | | | | | | | |

Table 5. Rotational energy levels of \( \text{H}_2^+ \) in presence of a uniform magnetic field \( B \) for the vibrational state \( v = 2 \). The pure vibrational state \( (L = 0 \) in the field-free case) is forbidden but shown here nevertheless as it corresponds to the origin of the rotational band. See caption of table 3 for explications.

| \( L \) | Energy/\( E_b \) | \( M \) | \( \pi \) | \( B = 0 \) | \( B = 0.1 \) | \( B = 0.2 \) |
|---|---|---|---|---|---|---|
| | | | | Model 1 | Model 2 | Model 1 | Model 2 |
| \( L = 0 \) | | | | | | | |
| \( L = 1 \) | | | | | | | |
| \( L = 2 \) | | | | | | | |
| \( L = 3 \) | | | | | | | |
| \( L = 4 \) | | | | | | | |

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The calculated rovibrational states in tables 3–10 are labeled with the exact quantum numbers. Graphical analysis of the $\text{H}_2^+$ rovibrational states, figures 9 and 10, shows that they remain grouped according to the field-free quantum number $L$ which is explained by the fact that all rovibrational states are located above the rotational barrier, for the two isotopologues. $B = 0.2B_0$, or 47000 T, is a strong field but of modest size in atomic units, hence $L$ may be considered a good quantum number. The main effect of the magnetic field in this region of field strengths is on the electronic energy.

Table 6. Rotational energy levels of $\text{H}_2^+$ in presence of a uniform magnetic field $B$ for the vibrational state $v = 3$. See caption of table 3 for explications.

| $L$ | Energy/Eh | $M$ | $\pi$ | $B = 0.1$ | $B = 0.2$ |
|-----|-----------|-----|-------|-----------|-----------|
|     |           |     |       | Model 1   | Model 1   |
|     |           |     |       | Model 2   | Model 2   |
| $B = 0.0$ |          |     |       |           |           |
| 4   | 0.596047  | -2  | 1     | -0.559 197 | -0.559 201 |
| 4   | 0.564730  | -2  | 1     | -0.558 247 | -0.558 263 |
| 3   | 0.564678  | -1  | -1    | -0.558 029 | -0.558 045 |
| 2   | 0.564674  | -1  | -1    | -0.558 257 | -0.558 275 |
| 1   | 0.564737  | -1  | -1    | -0.558 366 | -0.558 384 |
| 0   | 0.564737  | 0   | 1     | -0.558 332 | -0.558 353 |
| $L = 4$ | 0.566912  | -2  | 1     | -0.590 197 | -0.590 201 |
| 2   | 0.566268  | -1  | 1     | -0.560 019 | -0.560 019 |
| 1   | 0.566323  | -1  | 1     | -0.560 128 | -0.560 128 |
| 0   | 0.566297  | 0   | 1     | -0.559 640 | -0.559 653 |
| $L = 0$ | 0.569134  | 0   | 1     | -0.561 037 | -0.561 037 |

Table 7. Rotational energy levels of $\text{D}_2^+$ in presence of a uniform magnetic field $B$ for the vibrational state $v = 0$. See caption of table 3 for explications.

| $L$ | Energy/Eh | $M$ | $\pi$ | $B = 0.1$ | $B = 0.2$ |
|-----|-----------|-----|-------|-----------|-----------|
|     |           |     |       | Model 1   | Model 1   |
|     |           |     |       | Model 2   | Model 2   |
| $B = 0.0$ |          |     |       |           |           |
| 4   | 0.595 506 | -2  | 1     | -0.589 494 | -0.589 496 |
| 4   | 0.595 615 | -2  | 1     | -0.589 712 | -0.589 714 |
| 3   | 0.595 598 | -1  | -1    | -0.589 871 | -0.589 874 |
| 3   | 0.595 680 | -1  | -1    | -0.590 035 | -0.590 037 |
| 2   | 0.595 717 | -1  | -1    | -0.590 122 | -0.590 128 |
| 1   | 0.595 733 | -1  | -1    | -0.590 221 | -0.590 227 |
| 0   | 0.595 729 | 0   | 1     | -0.590 197 | -0.590 205 |
| $L = 4$ | 0.597 576 | -2  | 1     | -0.590 494 | -0.590 496 |
| 2   | 0.595 706 | -1  | -1    | -0.590 166 | -0.590 173 |
| 1   | 0.595 733 | -1  | -1    | -0.590 221 | -0.590 227 |
| 0   | 0.595 729 | 0   | 1     | -0.590 197 | -0.590 205 |
| $L = 0$ | 0.598 908 | 0   | 1     | -0.590 512 | -0.590 512 |

The calculated rovibrational states in tables 3–10 are labeled with the exact quantum numbers. Graphical analysis of the $\text{H}_2^+$ rovibrational states, figures 9 and 10, shows that they remain grouped according to the field-free quantum number $L$ which is explained by the fact that all rovibrational states are located above the rotational barrier, for the two isotopologues. $B = 0.2B_0$, or 47000 T, is a strong field but of modest size in atomic units, hence $L$ may be considered a good quantum number. The main effect of the magnetic field in this region of field strengths is on the electronic energy.
Table 8. Rotational energy levels of D$_2^+$ in presence of a uniform magnetic field $B$ for the vibrational state $\nu = 1$. See caption of table 3 for explanations.

| $L$ | Energy/$E_h$ | $M$ | $\pi$ | $B = 0.0$ | $B = 0.1$ | $B = 0.2$ |
|-----|--------------|-----|-------|----------|----------|----------|
|     |              |     |       | Model 1  | Model 2  | Model 1  | Model 2  |
| $L = 5$ | -0.589 802 | -3  | 1     | -0.582 812 | -0.588 813 | -0.582 680 | -0.582 683 |
|      |              | 3   | 1     | -0.588 989 | -0.588 895 | -0.582 844 | -0.582 847 |
|      |              | -2  | 1     | -0.588 938 | -0.588 939 | -0.583 179 | -0.583 181 |
| $L = 3$ | -0.590 947 | 2   | 1     | -0.588 992 | -0.588 994 | -0.583 288 | -0.583 290 |
|      |              | -1  | 1     | -0.588 999 | -0.589 001 | -0.583 114 | -0.583 122 |
|      |              | 1   | 1     | -0.589 026 | -0.589 028 | -0.583 168 | -0.583 177 |
|      |              | 0   | -1    | -0.589 033 | -0.589 035 | -0.583 374 | -0.583 379 |
| $L = 1$ | -0.591 589 | -1  | 1     | -0.589 548 | -0.589 548 | -0.583 868 | -0.583 870 |
|      |              | 1   | 1     | -0.589 575 | -0.589 575 | -0.583 922 | -0.583 925 |
|      |              | 0   | -1    | -0.589 757 | -0.589 757 | -0.584 512 | -0.584 513 |
| $L = 0$ | -0.591 718 | 0   | -1    | -0.589 795 | -0.589 796 | -0.583 503 | -0.583 511 |

Table 9. Rotational energy levels of D$_2^+$ in presence of a uniform magnetic field $B$ for the vibrational state $\nu = 2$. See caption of table 3 for explanations.

| $L$ | Energy/$E_h$ | $M$ | $\pi$ | $B = 0.0$ | $B = 0.1$ | $B = 0.2$ |
|-----|--------------|-----|-------|----------|----------|----------|
|     |              |     |       | Model 1  | Model 2  | Model 1  | Model 2  |
| $L = 4$ | -0.583 590 | -4  | 1     | -0.581 345 | -0.581 350 | -0.574 886 | -0.574 889 |
|      |              | 4   | 1     | -0.581 454 | -0.581 459 | -0.575 104 | -0.575 106 |
|      |              | -3  | 1     | -0.581 458 | -0.581 463 | -0.575 341 | -0.575 343 |
| $L = 2$ | -0.584 451 | -2  | 1     | -0.581 533 | -0.581 539 | -0.575 442 | -0.575 450 |
|      |              | 2   | 1     | -0.581 587 | -0.581 593 | -0.575 551 | -0.575 559 |
|      |              | -1  | 1     | -0.581 582 | -0.581 588 | -0.575 649 | -0.575 656 |
|      |              | 1   | -1    | -0.581 609 | -0.581 616 | -0.575 703 | -0.575 710 |
|      |              | 0   | -1    | -0.581 607 | -0.581 614 | -0.575 643 | -0.575 654 |
| $L = 0$ | -0.584 823 | -2  | 1     | -0.582 282 | -0.582 282 | -0.576 120 | -0.576 124 |
|      |              | 2   | 1     | -0.582 336 | -0.582 336 | -0.576 229 | -0.576 233 |
|      |              | -1  | 1     | -0.582 453 | -0.582 453 | -0.576 748 | -0.576 749 |
|      |              | 1   | -1    | -0.582 480 | -0.582 480 | -0.576 803 | -0.576 804 |
|      |              | 0   | -1    | -0.582 446 | -0.582 447 | -0.577 428 | -0.577 429 |
which is at $E = -0.595678\, \text{Eh}$. An interesting feature can be observed for $L = 2$ states with odd $v$: the $M = 0$ state is located above the $M = 1$ and $M = -1$ states. This can be understood with the help of perturbation theory. The lowest $L$ value, $L = 0$ has a single $M$ component, $M = 0$, which interacts, in a zero-order picture, with the $L = 2$, $M = 0$ state and shifts it upwards. The size of this perturbation is proportional to $B^2$. At $B = 0.1\, B_0$, it has no strong effect. For even $v$ one does not see such an irregularity either because the two lowest $L$ shells, $L = 1$ and $L = 3$, are already well separated energetically, see the $L(L+1)$ term in equation (22).

### 5. Conclusions

We have investigated the problem of $\text{H}_2^+$ and $\text{D}_2^+$ in an external magnetic field of up to $B = 0.2\, B_0$ or $4.7 \times 10^4$ T by exact and approximate methods. This includes a thorough

#### Table 10. Rotational energy levels of $\text{D}_2^+$ in presence of a uniform magnetic field $B$ for the vibrational state $v = 3$. See caption of table 3 for explications.

| $L$ | Energy/$\text{E}_h$ | $M$ | $\pi$ |
|-----|---------------------|-----|-------|
|     | $B = 0.1$          |     |-------|
|     | Model 1            | Model 2 |       |
| -5  | -0.574 069         | -0.574 083 | -0.567 312 | -0.567 315 |
| 5   | -0.574 205         | -0.574 219 | -0.567 585 | -0.567 588 |
| -4  | -0.574 176         | -0.574 190 | -0.567 733 | -0.567 736 |
| 4   | -0.574 285         | -0.574 299 | -0.567 951 | -0.567 954 |
| -3  | -0.574 257         | -0.574 271 | -0.567 927 | -0.567 935 |
|     | $B = 0.2$          |     |-------|
|     | Model 1            | Model 2 |       |
| -3  | -0.574 203         | -0.574 205 | -0.568 648 | -0.568 651 |
| 3   | -0.574 285         | -0.574 286 | -0.568 811 | -0.568 814 |
| -2  | -0.574 354         | -0.574 355 | -0.569 236 | -0.569 236 |
|     | $L = 3$            | -0.577 502 |       |
| -1  | -0.574 417         | -0.574 419 | -0.569 941 | -0.569 942 |
| 1   | -0.574 444         | -0.574 446 | -0.569 996 | -0.569 997 |
| 0   | -0.574 457         | -0.574 459 | -0.569 426 | -0.569 430 |
|     | $L = 1$            | -0.578 097 |       |
| -1  | -0.575 911         | -0.575 911 | -0.569 061 | -0.569 071 |
| 1   | -0.575 938         | -0.575 938 | -0.569 115 | -0.569 126 |
| 0   | -0.576 160         | -0.576 160 | -0.570 634 | -0.570 634 |
|     | $L = 0$            | -0.578 216 |       |
| -1  | -0.576 183         | -0.576 183 | -0.569 491 | -0.569 498 |

**Figure 9.** Rotational structure, up to $L = 5$, of the four lowest vibrational states of $\text{H}_2^+$ in the presence of an external magnetic field of $B = 0.1\, B_0$. All states are located above the rotational barrier, which is at $E = -0.600\, 613\, \text{Eh}$.

**Figure 10.** As figure 9, but for the field strength of $B = 0.2\, B_0$. The rotational barrier is at $E = -0.595678\, \text{Eh}$. An interesting feature can be observed for $L = 2$ states with odd $v$: the $M = 0$ state is located above the $M = 1$ and $M = -1$ states. This can be understood with the help of perturbation theory. The lowest $L$ value, $L = 0$ has a single $M$ component, $M = 0$, which interacts, in a zero-order picture, with the $L = 2$, $M = 0$ state and shifts it upwards. The size of this perturbation is proportional to $B^2$. At $B = 0.1\, B_0$, it has no strong effect. For even $v$ one does not see such an irregularity either because the two lowest $L$ shells, $L = 1$ and $L = 3$, are already well separated energetically, see the $L(L+1)$ term in equation (22).
analysis of the electronic energy as function of field strength and orientation of the molecule with respect to the external field as well as of the rovibrational structure of \( \text{H}_2^+ \) and \( \text{D}_2^+ \). The electronic problem has been solved by the variational method with physically adequate trial functions. It is shown that both diamagnetic and paramagnetic susceptibilities grow with inclination, while paramagnetic susceptibility is systematically much smaller than the diamagnetic one. Evaluation of the magnetic susceptibility shows that first-order perturbation theory based on zero-field trial functions may no longer be accurate at a field strength of above \( B \approx 0.04 B_0 \). To solve the ro-vibrational problem, the hindered rotor approximation, in which the potential energy surface is approximated by a zero-inclination potential curve, is employed. The ro-vibrational problem has been solved by the variational method with physically adequate trial functions. It is shown that both diamagnetic and paramagnetic susceptibilities grow with inclination, while paramagnetic susceptibility is systematically much smaller than the diamagnetic one.

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