The hydrogen molecule H$_2$ in inclined configuration in a weak magnetic field

A. Alijah

Université de Reims Champagne-Ardenne,
Groupe de Spectrométrie Moléculaire et Atmosphérique (UMR CNRS 7331), U.F.R. Sciences Exactes et Naturelles,
Moulin de la Housse B.P. 1039, F-51687 Reims Cedex 2, France

J.C. López Vieyra, D. J. Nader, and A.V. Turbiner
Instituto de Ciencias Nucleares, Universidad Nacional Autónoma de México,
Apartado Postal 70-543, 04510 Ciudad de México, México

H. Medel Cobaxin
Instituto Tecnológico de Estudios Superiores de Monterrey
Eugenio Garza Sada 2501, 64849 Monterrey, N.L., México

Highly accurate variational calculations, based on a few parametric physically adequate trial function, are carried out for the hydrogen molecule H$_2$ in inclined configuration, when the molecular axis forms an angle $\theta$ with respect to the direction of a uniform constant magnetic field $\mathbf{B}$, for $B = 0, 0.1, 0.2$ a.u. Three inclinations $\theta = 0^\circ, 45^\circ, 90^\circ$ are studied in details with emphasis to the ground state $^1g$. Diamagnetic and paramagnetic susceptibilities are calculated (for $\theta = 45^\circ$ for the first time), they agree very well with the experimental data and with other calculations. Potential energy curves $E$ vs $R$ are built for each inclination, are approximated by simple, two-point Pade approximant $Pade[2/6](R)$ with accuracy not less than 4 s.d. The energies of rovibrational states are calculated for the first time. It was found that the optimal configuration of the ground state for $B \leq 0.2$ a.u. corresponds always to the parallel configuration $\theta = 0$, thus, it is $^1\Sigma_g$ state.
More than fifty years have passed since it was predicted that extremely strong magnetic fields up to \( B = 10^{14} - 10^{16} \text{ G} \) \((B \sim 4 \times 10^{4-6} \text{ a.u.})\), which by far beyond those can be reach in the laboratory, could exist, as effect of the magnetic field flux compression, in the neutron star remnant of a supernova explosion \[1\] (see also \[2-4\]). As for magnetized white dwarfs the surface magnetic field can reach \( B \sim 10^9 \text{ G} \) (see e.g. \[5\] and references therein). Soon afterwards it was recognized that the structure of atoms and molecules might be qualitatively different under strong magnetic fields \( B \gtrsim B_0 \) \((B_0 = 1 \text{ a.u.} \equiv 2.35 \times 10^9 \text{ G})\) \[6-8\] than in field-free case. Electronic cloud gets the well-pronounced cigar-like form, molecules become oriented along magnetic line. Eventually, the problem becomes quasi-one-dimensional where longitudinal and transverse motions of electrons are almost separated. It gives hope to develop analytic theory in the domain of very strong magnetic fields. The situation gets much more complicated in the domain of intermediate magnetic fields, where quadratic corrections to linear Zeeman effect become significant, say, of order of \( B \sim 10^{-1} \text{ a.u.} \). This domain is ‘slightly’ above of magnetic fields reachable in the laboratory. In this case we do not see hope to develop analytic approaches in for this domain. We will call the fields \( 0.01 \lesssim B \lesssim 1 \text{ a.u.} \) the intermediate magnetic fields.

Due to mainly technical difficulties in solving the Schrödinger equation in the presence of intermediate and strong magnetic fields only a relatively small number of simple atomic and molecular systems has been studied. Naturally, the hydrogen atom \( \text{H} \) and the hydrogen molecular ion \( \text{H}_2^+ \) are the most studied systems, see e.g. \[9\] and \[10\], and references therein, respectively. The first quantitative study of the \( \text{H}_2 \) molecule was carried out by one of the authors at 1983 (see \[11\]). In the majority of studies of molecules and molecular ions all non-adiabatic terms in the Hamiltonian are neglected by assuming an infinite nuclear mass (what is usually called Born-Oppenheimer (BO) approximation of zeroth order). The fact is that in both \( \text{H} \) and \( \text{H}_2^+ \) systems the binding energy grows dramatically with an increase of

\[\text{I. INTRODUCTION}\]
the magnetic field strength. Other simple (traditional and exotic) compounds mainly formed by protons and/or α-particles (helium nuclei) and one-two electrons have been studied to a certain degree (for discussion, see [10] for one electron systems, and [12] for two electron systems).

Recently, a detailed study of the \( \text{H}_2^+ \) molecular ion in inclined configuration (when the molecular axis and the magnetic line form some angle) was carried out for intermediate and strong magnetic fields [10, 13]. It was shown that for the ground state the optimal configuration is always parallel, when the molecular axis and magnetic field direction coincide. The spectra of rovibrational states was exhaustively studied.

As for \( \text{H}_2 \) molecule it was found long ago that the minimal energy (ground) state evolves with magnetic field strength being realized by different states depending on the strength of the magnetic field [14, 15] and references therein. At zero and small magnetic fields the \( \text{H}_2 \) ground state is realized by the spin-singlet \( S = 0, ^1\Sigma_g \) state in parallel configuration, but with the magnetic field strength increase at \( B \gtrsim 0.2 \text{ a.u.} \) the ground state changes to a spin-triplet \( S = 1, ^3\Sigma_u \) which is the repulsive state (!) [14]. It corresponds to two hydrogen atoms are large distances with electron spins antiparallel to the magnetic field, hence, the hydrogen molecule does not exist as a compact system. However, for stronger magnetic fields \( B \gtrsim 12 \text{ a.u.} \) the ground state is realized by a spin triplet \( S = 1, ^3\Pi_u \) state [15] (and references therein). A similar behavior is observed in the case of the linear \( \text{H}_3^+ \) molecular ion in strong magnetic fields: the ground state evolves from the spin-singlet \( ^1\Sigma_g \) state for weak magnetic fields \( B \lesssim 5 \times 10^8 \text{ G} \approx 0.2 \text{ a.u.} \) to a weakly bound spin-triplet \( ^3\Sigma_u \) state for intermediate and strong fields and, eventually, to a spin-triplet \( ^3\Pi_u \) state for magnetic fields \( B \gtrsim 5 \times 10^{10} \text{ G} \approx 21 \text{ a.u.} \) (see [16]). In such studies the parallel configuration of the molecular axis and the magnetic field direction is explicitly assumed. Non-aligned configurations, where the molecular axis is not parallel to the magnetic field direction, have received much less attention. In particular, this is due to the fact that such configurations require a much larger computational efforts to reach the accuracies obtained in the parallel case. Present authors are not aware about any studies of included configurations for \( \text{H}_2 \) molecule for \( B \lesssim 0.2 \text{ a.u.} \).

The goal of this paper is to study the hydrogen molecule \( \text{H}_2 \) arbitrarily oriented i.e. with the molecular axis forming an angle \( \theta \) with respect to the direction of a uniform magnetic field \( \mathbf{B} \) in its ground state \( 1_g \). The strength of the magnetic fields of interest in this work are
chosen to be $B = 0, 0.1, 0.2$ a.u. (equivalently, $0, 2.35 \times 10^8, 4.7 \times 10^8$ G), where the ground state is realized by the spin-singlet state ($^1\Sigma_g$ at $\theta = 0$). We use the variational method with trial functions designed following a criterion of physical adequacy [10, 17]. Three inclinations $\theta = 0^\circ, 45^\circ, 90^\circ$ will be studied in details and the potential energy curves for each inclination and each magnetic field will be constructed. This allows us to calculate for the first time the lowest rovibrational levels of the $\text{H}_2$ molecule in weak and intermediate magnetic fields, where $\text{H}_2$ molecule exists as a compact object. A study of the magnetic susceptibility of the $\text{H}_2$ molecule is also performed. We will follow in presentation to our previous work on $\text{H}_2^+$ in weak and intermediate magnetic fields [13]. Atomic units will be used through the text.

II. THE HAMILTONIAN AND GENERALITIES

We consider the Hydrogen molecule $\text{H}_2$ interacting with an external magnetic field $\mathbf{B}$. The origin of coordinates is chosen in the midpoint of the line connecting the nuclei (molecular axis). The molecular axis in turn forms an angle $\theta$ with respect to the magnetic field direction (chosen to coincide with the $z$-axis). A convenient gauge which describes a magnetic field oriented parallel to the $z$-axis, is the linear gauge

$$\hat{A} = B[(\xi - 1)y, \xi x, 0],$$

where $\xi$ is a parameter. If $\xi = 0$ the linear gauge is reduced to the Landau gauge, and if $\xi = 1/2$ then the symmetric gauge is obtained. In approximate variational calculations the parameter $\xi$ is considered as an extra variational parameter.

Since the nucleus mass is by far larger than the electron mass, we can neglect all non-adiabatic coupling terms in the Hamiltonian to obtain the order zero BO approximation. Thus, the electronic Hamiltonian in atomic units ($\hbar = m_e = c = 1$) is given by

$$\hat{H}_e = -\frac{1}{2} \sum_{i=1}^{2} \nabla_i^2 - iB \sum_{i=1}^{2} ((\xi - 1)y_i \partial_{x_i} + \xi x_i \partial_{y_i})$$
$$+ \frac{1}{2} B^2 \sum_{i=1}^{2} (\xi^2 x_i^2 + (\xi - 1)^2 y_i^2) - \sum_{i=1}^{2} \left( \frac{1}{r_{ia}} + \frac{1}{r_{ib}} \right) + \frac{1}{r_{12}} + \frac{1}{R},$$

where $\nabla_i$ is the Laplacian operator with respect to the coordinates of the $i$-th electron $\mathbf{r} = (x_i, y_i, z_i)$, $r_{ia,ib}$ are the distances from the $i$-th electron to the nucleus $a$ or $b$, respectively, $r_{ij}$ is the distance between the electrons and $R$ is the distance between the nuclei. As usual,
the contribution to the energy due to the Coulomb interaction between the nuclei \((1/R)\) is treated classically. Hence, \(R\) is considered an external parameter. In the particular case \(\theta = 0^\circ\) the component of the angular momentum in the \(z\)-axis is conserved.

Finally, the nuclear motion can be treated as vibrations and rotations following the BO approximation with the electronic energy acting as the potential.

### III. THE TRIAL FUNCTION

Following physical relevance arguments (see, e.g. [17]) we designed a spatial trial function which is a product of Landau orbitals, Coulomb orbitals and a correlation term in exponential form:

\[
\psi(r_1,r_2) = \prod_{k=1}^{2} \left( e^{-\alpha_{ka}r_{ka} - \alpha_{kb}r_{kb} - \frac{B\beta_{ka}r_{ka}^2}{4} - \frac{B\beta_{kb}r_{kb}^2}{4}} \right) e^{\alpha_{12}r_{12}}
\]

where \(\alpha_{ka,kb}, \beta_{kx,ky}\) with \(k = 1, 2\) as well as \(\alpha_{12}\) are variational parameters. In this expression the variational parameters \(\alpha_{ka,\alpha_{kb}} (k = 1, 2)\) have the meaning of screening (or anti-screening) factors (charges) for the nucleus \(a, b\) respectively, as it is seen from the \(k\)-th electron. The variational parameters \(\beta_{kx,\beta_{ky}}\) account for the screening (or anti-screening) factors for the magnetic field seen from \(k\)-th electron in \(x, y\) direction respectively, and the parameter \(\alpha_{12}\) “measures” the screening (or anti-screening) of the electron correlation interaction. This spatial function reproduces adequately the behavior of the electrons near the Coulomb singularities and the harmonic oscillator at long distances arising from the magnetic field. In a certain way the trial function (3) is a generalization of the trial function presented in [18] for the field free case. It reproduces two physical situations: for small internuclear distances the trial function (3) mimics the interaction \(H_{2}^+ + e\) (if \(\alpha_{1a} = \alpha_{1b}\) and \(\alpha_{2a} = \alpha_{2b}\)) and for large internuclear distances the trial function mimics the interaction \(H - H\) (if \(\alpha_{1a} = \alpha_{2b}\) and \(\alpha_{1b} = \alpha_{2a}\)).

We consider a trial function which is a superposition of three Ansätze: a general Ansatz of the type (3), a \(H - H\) type Ansatz and a \(H_{2}^+ + e\) type Ansatz

\[
\Psi = A_1 \psi + A_2 \psi_{H+H} + A_3 \psi_{H_{2}^+ + e},
\]

where \(A_{1,2,3}\) are linear variational parameters. Each Ansatz has its own set of variational parameters. Without loss of generality \(A_1\) may be set equal to the unity, therefore the
total number of variational parameters is 27 including the internuclear distance $R$ and $\xi$ as variational parameters.

In the singlet state ($S = 0$) the trial function (4) must be symmetric with respect to the exchange of the electrons and in the gerade (g) state the trial function (4) must be symmetric with respect to the exchange of nuclei. Therefore the operator

$$(1 + \hat{P}_{ab})(1 + \hat{P}_{12}),$$

where $\hat{P}_{ab}$ is the operator of symmetrization of nuclei and $\hat{P}_{12}$ is the operator of symmetrization of the electrons, must be applied to the trial function (4).

The calculation of the variational energy using the trial function (3) involves two major parts: (i) 6-dimensional numerical integrations which were implemented by an adaptive multidimensional integration C-language routine (cubature) [19], and (ii) a minimizer which was implemented with the Fortran minimization package MINUIT from CERN-LIB. Our C-Fortran hybrid program was parallelized using MPI. The 6-dimensional integrations were carried out using a dynamical partitioning procedure: the domain of integration is manually divided into sub-domains following the profile of the integrand. Then each sub-domain is integrated on separated processors using the routine CUBATURE. In total, we have a subdivision to 960 subregions for the numerator and $\sim 1000$ for the denominator of the variational energy. With a maximal number of sampling points $\sim 10^8$ for the numerical integrations for each subregion. The time needed for one evaluation of the variational energy (two integrations) takes $2 \times 10^3$ seconds ($\sim 37 \text{ min}$) with 96 processors at the cluster KAREN (ICN-UNAM, Mexico). It was checked that this procedure stabilizes the estimated accuracy to be reliable in the first three-four decimal digits. However, in order to localize domain, where minimal parameters are, the minimization procedure with much less number of sample points was used in each sub-domain and a single evaluation of the energy usually took $\sim 15 - 20 \text{ mins}$. Once a domain is roughly localized the number of sample points increased by a factor $\sim 10^2$. Typically, a minimization process required several hundreds of evaluations. As a general strategy, the variational energy corresponding to the general Ansatz only is calculated in first place. Then, either the $\text{H} - \text{H}$ type Ansatz or the $\text{H}_2^+ + e$ type Ansatz is added as a first correction (depending on which configuration yields better variational results) and the energy is minimized using the superposition of two Ansatze. Then, finally, the remaining configuration is included in the final trial function and a final minimization
is carried out. The whole process is very lengthy and cumbersome due to absence of fast minimization procedure. Computations were mainly performed in parallel with the cluster ROMEO from the University of Reims, France and the cluster KAREN (ICN-UNAM, Mexico) both with 96 processors.

IV. RESULTS

The electronic energies and the equilibrium distances of H\(_2\) in the 1\(g\) state are presented in Table I for magnetic fields with magnitude \(B = 0, 0.1\) and \(0.2\) a.u. We studied the geometrical configurations with angles \(\theta = 0^\circ, 45^\circ\) and \(90^\circ\) between the magnetic field direction and molecular axis with great details, while for the angles \(\theta = 15^\circ, 30^\circ\) and \(60^\circ, 75^\circ\) it was done as test calculations to check smoothness of angular dependence. For all inclinations the potential energy curve \(E\) vs \(R\) exhibits a well pronounced minimum at a finite internuclear distance \(R\). As the magnetic field increases, for given inclination the system becomes more bound (the binding energy increases) and more compact (the internuclear equilibrium distance reduces), see Table I. For a given magnetic field, the equilibrium distance \(R\) shows a small decrease with increase in the inclination angle increase from \(\theta = 0\) to \(90^\circ\). Such a decrease in \(R_{eq}\) is bigger for the larger magnetic field \(B = 0.2\) a.u. From the results collected in Table I, it is clear that for all magnetic fields studied, the optimal configuration corresponds to the parallel configuration as it is expected.

V. POTENTIAL ENERGY CURVES

Potential energy curves \(E\) vs \(R\) of the state \(1_g\) of the H\(_2\) molecule in magnetic fields \(B = 0, 0.1, 0.2\) a.u. and inclinations \(\theta = 0, 45^\circ, 90^\circ\) are built from variational results obtained in domain \(R \in [1, 2]\) a.u. and extended beyond following the procedure discussed in [21] for approximating potential curves in diatomic molecules (see also references therein). It is evident that the asymptotic behavior of the electronic energy of H\(_2\) at small distances \(R \to 0\) is given by

\[
E \approx \frac{1}{R} + E_{\text{He}}(B) + c_1 R + O(R^2),
\]

(6)

where \(E_{\text{He}}(B)\) is the ground state energy of the Helium atom in a magnetic field \((B)\) (the so-called united atom limit), and the coefficient in front of \(R\) depends on the magnetic field.
Table I: Total electronic energy and equilibrium distance of H\textsubscript{2} in the state 1\textsubscript{g} as a function of the magnetic field \(B\) and inclination \(\theta\) as described by the trial function (4). Results marked with a † from Ref. [14] and results marked with ‡ are from [20] (rounded). The binding energy for \(\theta = 0\) with respect to dissociation H+H shown. The energies for H atom in ground state taken from [9].

and the inclination \(\theta\),\( c_1 = c_1(B, \theta)\); at \(B = 0\) this coefficient vanishes \(c_1 = 0\) (see [21] and references therein). As for the asymptotic limit \(R \to \infty\), the expansion of the energy \(E\) is given by

\[
E \approx E_{2H}(B) + \frac{c_5}{R^5} - \frac{c_6}{R^6} + \frac{c_7}{R^7} + O\left(\frac{1}{R^8}\right),
\]

where \(E_{2H}(B)\) is the energy of two (infinitely separated) Hydrogen atoms in their ground state in the magnetic field of strength \(B\), the term \(\propto 1/R^5\) corresponds to the quadrupole-quadrupole interaction (repulsive for 0, 90° and attractive for 45°) between two separated Hydrogen atoms in the magnetic field (which is the leading order interaction at \(R \to \infty\)). The term \(\propto 1/R^6\) corresponds to the induced dipole-dipole interaction (in second order perturbation theory in \(1/R\) for \(B = 0\)) between two separated Hydrogen atoms (see [11] and [8]). The coefficients \(c_{5,6,7}\) can depend on the magnetic field strength and inclination \(c_{5,6,7} = c_{5,6,7}(B, \theta)\). In absence of a magnetic field \(c_{5,7} = 0\). In general, the quadrupole-quadrupole interaction energy (in a.u.) is given by

\[
E_Q = \frac{3}{4} \frac{Q_{zzz}(B) P_4(\cos \theta)}{R^5},
\]
where \( Q_{zz} \) is the quadrupole moment of the Hydrogen atom in a magnetic field of strength \( B \) (see [11]), \( P_4 \) is 4th Legendre polynomial. Thus, the coefficient \( c_5 \) is known. For weak magnetic fields \( B \) we use the approximation the quadrupole moment in perturbation theory (see [22])

\[
Q_{zz} = \frac{-5}{2}B^2 + \frac{615}{32}B^4 + \ldots .
\]  

(9)

Now we interpolate both asymptotic expansions (6) and (7) via the two-point Padé approximant \( \text{Pade}[N/N+4](R) \) with \( N = 2 \) as the minimal degree, which guarantees that the expansions (6) and (7) are described functionally correct,

\[
E(R) = \frac{1}{R} \left( \frac{a_0 + a_1 R + a_2 R^2}{(b_0 + b_1 R + b_2 R^2 + b_3 R^3 + b_4 R^4 + b_5 R^5 + b_6 R^6)} + E_{2H}(B) \right),
\]  

(10)

where the constraints

\[
b_0 = a_0, \quad b_1 = a_0 \left( E_{2H}(B) - E_{\text{He}}(B) \right) + a_1,
\]

are imposed in order to reproduce the first two leading terms in (6) exactly plus the condition \( c_5 = \frac{3}{4}Q_{zz}^2(B) \), it implies the relation

\[
a_2 = c_5 b_6 .
\]

Without loss of generality we can set \( a_0 = 1 \). Therefore, we have six free parameters \( a_1, b_2, b_3, b_4, b_5, b_6 \) to fit the variational energies at internuclear distances near the equilibrium, \( R \in [1, 2] \) a.u. for both \( B = 0.1, 0.2 \) a.u. and inclinations \( \theta = 0, 45^\circ, 90^\circ \). The value of the parameters is presented in Table II. The potential energy curves are presented in the Fig I

In general, the curves (10) reproduce four decimal digits (d.d.) in energy at \( R \in [1, 2] \) a.u.

VI. MAGNETIC SUSCEPTIBILITY

Trial function (4) in spite of its simplicity incorporates accurately the major physical features of the \( H_2 \) molecule in a magnetic field. In order to verify this assertion for weak magnetic fields we calculated the magnetic susceptibility. For the estimation of such magnetic susceptibility we follow the recipe used in our previous work on \( H_2^+ \) [13]. The first step is to consider the definition of the magnetic susceptibility via the Taylor expansion of the electronic energy in powers of \( B \)

\[
E(B) = E(0) - \sum_\alpha c_\alpha B_\alpha - \frac{1}{2} \sum_{\alpha \beta} \chi_{\alpha \beta} B_\alpha B_\beta + \ldots ,
\]  

(11)
Figure 1: Potential Energy curves of the $1_g$ ground state of the H$_2$ molecule for $B = 0, 0.1, 0.2$ a.u. and inclinations $\theta = 0^\circ, 45^\circ, 90^\circ$. The insets show amplified energy curves for $B = 0.1, 0.2$ a.u. near the equilibrium distance.

Table II: Fitted parameters (rounded to 5 d.d.) in the Pade approximant (10) for the H$_2$ potential energy curves $E$ vs $R$ for $B = 0, 0.1, 0.2$ a.u., see Fig. 1.

| $B$(a.u.) | $\theta$ | $a_1$   | $b_2$   | $b_3$   | $b_4$   | $b_5$   | $b_6$   |
|-----------|----------|---------|---------|---------|---------|---------|---------|
| 0         | $0^\circ$| -1.28814| 1.09317 | -0.94343| 0.79009 | -0.28161| 0.04758 |
| 0.1       | $0^\circ$| -1.29188| 0.97020 | -0.64470| 0.51708 | -0.11715| 0.02136 |
|           | $45^\circ$| -1.29133| 1.16648 | -1.12137| 0.94652 | -0.34039| 0.05644 |
|           | $90^\circ$| -1.29330| 1.30768 | -1.38159| 1.13784 | -0.40315| 0.06395 |
| 0.2       | $0^\circ$| -1.30393| 1.04298 | -0.80653| 0.65880 | -0.22496| 0.03886 |
|           | $45^\circ$| -1.30284| 1.09918 | -0.99912| 0.90103 | -0.35196| 0.06408 |
|           | $90^\circ$| -1.30207| 1.13086 | -1.06132| 0.93558 | -0.35573| 0.06400 |

where $\chi_{\alpha\beta}$ is identified as tensor of the magnetic susceptibility. The response of the molecule to the external magnetic field is classified into two types: diamagnetic and paramagnetic susceptibilities. Correspondingly, there are two contributions to the susceptibility: a paramagnetic contribution $\chi^p$ originating from the linear Zeeman term of the Hamiltonian when
treated by second order perturbation theory in B, and a diamagnetic contribution $\chi^d$ coming from the quadratic Zeeman term. The total magnetic susceptibility is the addition of the two contributions $\chi = \chi^d + \chi^p$. In principle, the total magnetic susceptibility can be obtained directly using the Taylor expansion (11) of the energy potential curve $E = E(B, R, \theta)$ for fixed $\theta$ in powers of $B$, but taking into account that the equilibrium distance $R_{eq}(B, \theta)$ changes with $B$, it is a quite complicated procedure. It is easier to calculate numerically the energy evolution with $B$ at minimum of the energy potential curve at fixed inclination. Then we interpolate this curve $E(B)$ near the origin ($B = 0$) using a polynomial of finite degree in $B$. The total susceptibility $\chi$ will be related to the coefficient $E^{(2)}$, in front of $B^2$, as $\chi = -2E^{(2)}$.

As for the diamagnetic susceptibility term $\chi^d$, it can be expressed as the expectation value with respect to the field-free wavefunction at equilibrium distance. The expression of the diamagnetic susceptibility tensor is

$$\chi^d_{\alpha\beta} = -\frac{1}{4} \sum_{i=1}^{2} \left( \langle r_i \rangle \delta_{\alpha\beta} - \langle r_{i\alpha} r_{i\beta} \rangle \right),$$  \hfill (12)

where $r_i$ is the position vector of the $i$-th electron and $\alpha = 1, 2, 3$ marks its components. If the magnetic field direction is chosen along the $z$-axis, $B = B \hat{z}$, the tensor $\chi^d$ contains a single non-zero component, $\chi^d_{zz} \equiv \chi^d$,

$$\chi^d = -\frac{1}{4} \sum_{i=1}^{2} \left( \langle x_i^2 \rangle + \langle y_i^2 \rangle \right).$$ \hfill (13)

For identical electrons we can use the fact $\langle r_{1\alpha} \rangle = \langle r_{2\alpha} \rangle = \langle r_{\alpha} \rangle$ for all the components of the position vector. Finally, the paramagnetic contribution to the susceptibility can be evaluated as the difference $\chi^p = \chi - \chi^d$. In general, the paramagnetic susceptibility is much smaller than the diamagnetic part.

Susceptibilities are presented in Table III for different inclinations $\theta$ and compared with the experimental data, when possible, as well as with other calculations. In general, all susceptibilities grow with the inclination. For $\theta = 0$ our $\chi^d$ is larger than ones obtained in [23], [24], closer to experimental data being different from experimental data in one portion $\times 10^{-3}$. As for $\theta = 45^\circ$ susceptibilities are calculated for the first time. While for $\theta = 90^\circ$ our $\chi^d$ agrees in 2 d.d. with [24] and differs from experimental data in $2 \times 10^{-2}$, as for $\chi^p$ it is superior to the value calculated at [25] and differs from experimental data in $\sim 1\%$. 
Thus, our results of the susceptibility agree very well with the experimental data and with other calculations.

| \(\theta\) | \(\langle x^2 \rangle\) | \(\langle y^2 \rangle\) | \(\langle z^2 \rangle\) | \(\chi^d\) | \(\chi^p\) | \(\chi\) |
|---|---|---|---|---|---|---|
| 0° | 0.76465 | 0.76465 | 1.00929 | -0.7647 | 0.0 | -0.7647 |
| 0.7608^a | 0.7608^a | 0.9730^a | -0.7608^a | 0.0^a |
| 0.76169^b | 0.76169^b | 1.02297^b | -0.7617^b | 0.0^b |
| 45° | 0.88697 | 0.76465 | 0.88697 | -0.8258 | 0.0218 | -0.804 |
| 90° | 1.00929 | 0.76465 | 0.76465 | -0.8870 | 0.0660 | -0.821 |
| 0.9730^a | 0.7608^a | 0.7608^a | -0.8669^a |
| 1.02297^b | 0.76169^b | 0.76169^b | -0.8923^b |
| 0.0534^c |
| -0.913^{exp} | 0.0654^{exp} |

Table III: Paramagnetic \(\chi^d\) and total susceptibility \(\chi\) of \(\text{H}_2\) in the state \(1_g\) for different \(\theta\). Paramagnetic \(\chi^p\), obtained as \(\chi^p = \chi - \chi^d\), is included for completeness. The expectations values of the squared components (in a.u.) of the position vector are also included for \(B = 0\) at the equilibrium distance \(R_{eq} = 1.40\) a.u. using the optimal values of variational parameters. Experimental results taken from Table I in \[26\] for the diamagnetic susceptibility and from Table XIII in \[25\] for the paramagnetic susceptibility. Results marked as \(^a\) from \[23\], \(^b\) from \[24\], \(^c\) from \[25\].

VII. ROVIBRATIONAL LEVELS

The lowest rovibrational states of \(\text{H}_2\) and \(\text{D}_2\) were calculated for the field strengths \(B = 0.1 B_0\) and \(B = 0.2 B_0\), where \(B_0 = 2.35 \times 10^9\) Gauss = \(2.35 \times 10^5\) T, as described in \[13\]. To keep the present paper self-contained, the method is briefly summarized below. Starting point is the nuclear Hamiltonian expressed in spherical coordinates,

\[
\hat{H}_{nuc} = -\frac{2}{M_s} \frac{\partial^2}{\partial R^2} R + \frac{2}{M_s R^2} \hat{L}_R^2 - \frac{1}{M_s} B \hat{L}_z + \frac{1}{8M_s} B^2 R^2 \sin^2 \theta + \tilde{V}(R, \theta). \tag{14}
\]

Here, \(M_s\) denotes the total mass of the nuclei, \(\hat{L}_z\) is the projection of angular momentum along \(z\)-axis and \(\theta\) the angle between the molecular and the \(z\)-axis. The two-dimensional
potential, $\tilde{V}(R, \theta)$, is parametrized as a hindered rotator, where only the lowest expansion term is maintained, to yield

$$\tilde{V}(R, \theta) = \tilde{V}(R, 0) + \sum_n \frac{V_{90,n}(R)}{2} [1 - \cos(2n\theta)]$$

$$\approx \tilde{V}(R, 0) + V_{90}(R) \sin^2 \theta \tag{15}$$

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

The rovibrational wave function can be expanded in terms of vibrational and rotational basis functions as

$$\Psi(R, \theta, \phi) = \sum_{v, L} c_v L M Y_L M (\theta, \phi) \tag{16}$$

where $\xi_v(R; \theta')$ are solutions of the vibrational part of Eq. (14) at the reference orientation $\theta'$, chosen as $\theta' = 0$. These are obtained numerically using the renormalized Numerov algorithm. The $Y_L^M(\theta, \phi)$ in the above equation are spherical harmonics.

In this basis, the matrix elements of the Hamiltonian in Eq. (14) are given by

$$\langle v' L' M | \hat{H}_{\text{nucl}} | v L M \rangle = E_v \delta_{v'v} \delta_{L'L} + \frac{2}{M_s} \left\langle v' \left| \frac{1}{R^2} \right| v \right\rangle L(L + 1) \delta_{v'v}$$

$$- \frac{B M}{M_s} \delta_{L'L} \delta_{v'v}$$

$$+ \left[ \frac{B^2}{12M_s} \left( v' \right| R^2 | v \right) + \frac{2}{3} \left( v' | V_{90}(R) | v \right) \right] \delta_{v'v}$$

$$- \left[ \frac{B^2}{12M_s} \left( v' \right| R^2 | v \right) + \frac{2}{3} \left( v' | V_{90}(R) | v \right) \right] \times (-1)^M \sqrt{(2L' + 1)(2L + 1)}$$

$$\times \left( \begin{array}{ccc} L & 2 & L' \\ 0 & 0 & 0 \end{array} \right) \left( \begin{array}{ccc} L & 2 & L' \\ M & 0 & -M \end{array} \right) \right) \tag{17}$$

The terms in parentheses are Wigner 3$j$-symbols. The matrix Eq. (17) is diagonal in $M$ as expected, since $M$ is an exact quantum number. $L$-functions are coupled in steps of 2, conserving $z$-parity, $\pi = (-1)^{L+M}$. Diagonalization of the Hamiltonian matrix, Eq. (17), yields the eigenvalues and eigenvectors of the rovibrational problem.

We have computed the lowest rovibrational states for $\text{H}_2$ and $\text{D}_2$. Allowed rovibrational states must obey the permutational symmetry of the two identical nuclei. In the case of $\text{H}_2$, with two fermions, the symmetry of the vibrational and rotational parts of the rovibrational wavefunction must be opposite, while in the case of $\text{D}_2$, with two bosons, it must be the
same. For a rovibrational state of given vibrational quantum number, \( v \), and projection of the angular momentum on the magnetic field axis, \( M \), the \( z \)-parities are thus

\[
\pi = (-1)^{M+v+1} = \begin{cases} 
-(-1)^M & \text{for } v \text{ even} \\
(-1)^M & \text{for } v \text{ odd}
\end{cases}
\]

(18)

for \( H_2 \), and

\[
\pi = (-1)^{M+v} = \begin{cases} 
(-1)^M & \text{for } v \text{ even} \\
-(-1)^M & \text{for } v \text{ odd}
\end{cases}
\]

(19)

for \( D_2 \).

The results of our calculations for the lowest vibrational states, \( v = 0, 1, 2, 3 \) and \( M \leq 5 \) are presented in Tables [VII][X] for \( H_2 \) and in Tables [VII][XI] for \( D_2 \), for the magnetic field strengths \( B = 0.1 B_0 \) and \( B = 0.2 B_0 \). As in our previous work on \( H_2^+ \), two models have been considered: the approximate model 1, in which off-diagonal terms in \( v \) are omitted when setting up the rovibrational matrix, Eq. (17), and model 2, in which they are included. The closeness of the two sets of results demonstrate that a simple expansion, with just one vibrational function, yields a good approximation of the final rovibrational wavefunction, at least for the lowest vibrational states. Therefore, in the full expansion of model 2, the coefficients \( c_{v,L} \) allow easy identification of the vibrational quantum number of each computed eigenstate.

All states are located above the rotational barrier, which is at \( E_{\text{barrier}} = -1.16971697 E_h \) for \( B = 0.1 B_0 \) and \( E_{\text{barrier}} = -1.15712721 E_h \) for \( B = 0.2 B_0 \), respectively, and hence, \( L \), which is an exact quantum number in the field-free case, can still be considered a “good” quantum number. It is interesting to analyse the orientation with respect to the magnetic field axis of the lowest rovibrational state. The lowest state of \( H_2 \), at the field strength of \( B = 0.1 B_0 \), is located 0.0101 \( E_h \), or 2222 cm\(^{-1}\), above the barrier. Yet only one of the basis functions of the expansion in Eq. (16) contributes effectively to its eigenvector, with coefficient \( c_{0,1} = 0.997 \). The eigenfunction of the lowest state is thus \( \Psi(R, \theta, \phi) \sim [\xi_v(R; \theta^x = 0)/R] Y_1^0(\theta, \phi) \sim [\xi_v(R; \theta^x = 0)/R] \cos \theta \), which shows that molecule essentially vibrates in the direction of the magnetic field.

In general, within each \( L \)-layer, the rotational energy of a vibrational state increases with \( |M| \). Figures 3 and 5 show some exceptions for the states \( v = 1, 3 \) of \( H_2 \) and \( v = 0, 2 \) of \( D_2 \), where the \( M = 0 \) state corresponding to \( L = 2 \) is above \( |M| = 1 \). A similar effect has been
observed in the case of H$_2^+$ and D$_2^+$. It is due to strong coupling of the $L = 0$ and $L = 2$ basis functions, a kind of Fermi resonance of the zero-order states with well-defined $L$. The effect scales as $B^2$ and is not visible for the lower field strength, $B = 0.1 B_0$. No strong effect can be seen for the states $v = 0, 2$ of H$_2$ and $v = 1, 3$ of D$_2$, which have $L = 1, 3 \ldots$, where the $L = 1$ and $L = 3$ layers are sufficiently separated in energy.

Figure 2: Rotational structure, up to $L = 5$, of the four lowest vibrational states of H$_2$ in the presence of an external magnetic field $B = 0.1 B_0$.

VIII. CONCLUSIONS

We have investigated the problem of the hydrogen molecule vibrating and rotating in the presence of an external magnetic field for the field strengths of $B = 0.1$ a.u. ($2.35 \times 10^4$ T) and $B = 0.2$ a.u. ($4.7 \times 10^4$ T). Highly accurate variational calculations, based on a few parametric physically adequate trial function, are carried out for inclined configuration, when the molecular axis forms an angle $\theta$ with respect to the direction of a uniform constant magnetic field. We calculated diamagnetic and paramagnetic susceptibilities (for $\theta = 45^\circ$ for the first time), they closely described experimental data and agree very well (or superior) with other calculations. The two-dimensional potential energy surfaces were built for
Table IV: Rotational energy levels of $\text{H}_2$ 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 is diagonalized.

| $L$ | Energy/$E_h$ | $M$ | $\pi$ | Energy/$E_h$ |
|-----|--------------|-----|-------|--------------|
| $B = 0.0$ | model 1 | model 2 | model 1 | model 2 |
| -5 | 1 | -1.151400 | -1.151559 | -1.138417 | -1.138521 |
| 5 | 1 | -1.151672 | -1.151832 | -1.138962 | -1.139065 |
| -4 | -1 | -1.151551 | -1.151714 | -1.138858 | -1.138976 |
| 4 | -1 | -1.151769 | -1.151932 | -1.139294 | -1.139412 |
| -3 | 1 | -1.151673 | -1.151839 | -1.139193 | -1.139321 |
| $L = 5$ | -1.156268 | 3 | 1 | -1.151836 | -1.152002 | -1.139519 | -1.139648 |
| -2 | -1 | -1.151766 | -1.151934 | -1.139439 | -1.139576 |
| 2 | -1 | -1.151875 | -1.152043 | -1.139657 | -1.139794 |
| -1 | 1 | -1.151833 | -1.152002 | -1.139606 | -1.139748 |
| 1 | 1 | -1.151887 | -1.152057 | -1.139715 | -1.139857 |
| 0 | -1 | -1.151873 | -1.152043 | -1.139698 | -1.139841 |
| -3 | 1 | -1.156384 | -1.156405 | -1.143600 | -1.143607 |
| 3 | 1 | -1.156547 | -1.156569 | -1.143927 | -1.143934 |
| -2 | -1 | -1.156591 | -1.156615 | -1.144222 | -1.144235 |
| $L = 3$ | -1.160991 | 2 | -1 | -1.156700 | -1.156724 | -1.144440 | -1.144453 |
| -1 | 1 | -1.156715 | -1.156740 | -1.144497 | -1.144515 |
| 1 | 1 | -1.156769 | -1.156794 | -1.144606 | -1.144624 |
| 0 | -1 | -1.156774 | -1.156800 | -1.144658 | -1.144677 |
| -1 | 1 | -1.159240 | -1.159241 | -1.146789 | -1.146795 |
| $L = 1$ | -1.163671 | 1 | 1 | -1.159295 | -1.159295 | -1.146898 | -1.146904 |
| 0 | -1 | -1.159590 | -1.159591 | -1.147827 | -1.147830 |
| $L = 0$ | -1.164212 | 0 | -1 | -1.159944 | -1.159945 | -1.147954 | -1.147960 |
Figure 3: Rotational structure, up to $L = 5$, of the four lowest vibrational states of H$_2$ in the presence of an external magnetic field of $B = 0.2 \, B_0$.

Figure 4: Rotational structure, up to $L = 5$, of the four lowest vibrational states of D$_2$ in the presence of an external magnetic field $B = 0.1 \, B_0$. 
Table V: Rotational energy levels of H\textsubscript{2} in presence of a uniform magnetic field \(B\) for the vibrational state \(v = 1\). See Caption of Table IV for explications.

| \(L\) | Energy/\(E_h\) | \(M\) | \(\pi\) | Energy/\(E_h\) |
|-------|---------------|-------|--------|---------------|
|       | \(B = 0.0\)  |       |        | \(B = 0.1\)  | \(B = 0.2\)  |
|       | model 1       | model 2 | model 1 | model 2       | model 2       |
| \(-4\) | -1.135143     | -1.135210 | -1.121759 | -1.121789     |
| \(4\)  | -1.135361     | -1.135428 | -1.122195 | -1.122225     |
| \(-3\) | -1.135343     | -1.135412 | -1.122353 | -1.122392     |
| \(3\)  | -1.135506     | -1.135576 | -1.122679 | -1.122718     |
| \(L = 4\) | -1.140103 | \(-2\) | -1.135487 | -1.135558     | -1.122724 | -1.122771 |
| \(2\)  | -1.135596     | -1.135667 | -1.122941 | -1.122989     |
| \(-1\) | -1.135583     | -1.135655 | -1.122966 | -1.123019     |
| \(1\)  | -1.135637     | -1.135709 | -1.123075 | -1.123127     |
| \(0\)  | -1.135632     | -1.135705 | -1.123078 | -1.123132     |
| \(-2\) | -1.138876     | -1.138880 | -1.125748 | -1.125752     |
| \(2\)  | -1.138985     | -1.138989 | -1.125966 | -1.125970     |
| \(L = 2\) | -1.143635 | \(-1\) | -1.139176 | -1.139181     | -1.126658 | -1.126662 |
| \(1\)  | -1.139230     | -1.139236 | -1.126767 | -1.126771     |
| \(0\)  | -1.139240     | -1.139245 | -1.126508 | -1.126520     |
| \(L = 0\) | -1.145172 | \(0\)  | -1.140709 | -1.140710     | -1.128395 | -1.128400 |

magnetic fields for \(B = 0.1\) and 0.2 a.u. The parallel orientation of the H\textsubscript{2} molecule with respect to the magnetic field is the most stable one. This holds true also if the vibrational zero-point energy is taken into account. Though the rovibrational ground state is located well above the barrier to perpendicular orientation, the vibrating molecule remains in its parallel orientation. The lowest rovibrational states have then been calculated for the first time. Their energy values are reported for the four lowest vibrational states and rotational excitation up to \(M = 5\), for both the H\textsubscript{2} and D\textsubscript{2} isotopologues.
Table VI: Rotational energy levels of 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 IV for explications.

| $L$ | Energy/$E_h$ | $M$ | $\pi$ | Energy/$E_h$ |   |
|-----|--------------|-----|-------|--------------|---|
|     | $B = 0.0$    |     |       |              |   |
|     | model 1      | model 2 | model 1 | model 2 |   |
| -5  | 1 -1.114753  | -1.114910 | -1.100650 | -1.100729 |   |
|  5  | 1 -1.115025  | -1.115182 | -1.101194 | -1.101274 |   |
| -4  | 1 -1.114933  | -1.115092 | -1.101233 | -1.101326 |   |
|  4  | 1 -1.115151  | -1.115310 | -1.101669 | -1.101762 |   |
| -3  | 1 -1.115076  | -1.115237 | -1.101653 | -1.101758 |   |
| $L = 5$ | -1.120036 | 3 | 1 | -1.115240 | -1.115400 | -1.101979 | -1.102085 |
|     | -2 | 1 | -1.115184 | -1.115346 | -1.101956 | -1.102072 |
|     | 2 | 1 | -1.115293 | -1.115455 | -1.102174 | -1.102290 |
|     | -1 | 1 | -1.115260 | -1.115422 | -1.102155 | -1.102277 |
|     | 1 | 1 | -1.115314 | -1.115477 | -1.102264 | -1.102386 |
|     | 0 | 1 | -1.115303 | -1.115466 | -1.102258 | -1.102382 |
|     | -2 | 1 | -1.119272 | -1.119294 | -1.105398 | -1.105404 |
|     | 3 | 1 | -1.119435 | -1.119457 | -1.105724 | -1.105731 |
|     | -2 | 1 | -1.119522 | -1.119546 | -1.106232 | -1.106241 |
| $L = 3$ | -1.124307 | 2 | 1 | -1.119631 | -1.119655 | -1.106450 | -1.106459 |
|     | -1 | 1 | -1.119664 | -1.119688 | -1.106487 | -1.106506 |
|     | 1 | 1 | -1.119718 | -1.119743 | -1.106596 | -1.106615 |
|     | 0 | 1 | -1.119730 | -1.119755 | -1.106723 | -1.106742 |
|     | -2 | 1 | -1.121889 | -1.121889 | -1.108515 | -1.108525 |
| $L = 1$ | -1.126729 | 1 | 1 | -1.121944 | -1.121944 | -1.108624 | -1.108634 |
|     | 0 | 1 | -1.122315 | -1.122315 | -1.109858 | -1.109860 |
| $L = 0$ | -1.127217 | 0 | 1 | -1.122583 | -1.122584 | -1.109910 | -1.109915 |
Table VII: 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 [IV] for explications.

| \( L \) | \( \text{Energy}/E_h \) | \( M \) | \( \pi \) | \( \text{Energy}/E_h \) |
|---|---|---|---|---|
| \( B = 0.0 \) | \( B = 0.1 \) | \( B = 0.2 \) |
| model 1 | model 2 | model 1 | model 2 |
| -4 | 1 | -1.100413 | -1.100469 | -1.085807 | -1.085827 |
| 4 | 1 | -1.100631 | -1.100687 | -1.086243 | -1.086262 |
| -3 | -1 | -1.100629 | -1.100688 | -1.086661 | -1.086666 |
| 3 | -1 | -1.100792 | -1.100852 | -1.086943 | -1.086943 |
| \( L = 4 \) | -1.105502 | -2 | 1 | -1.100782 | -1.100844 | -1.087016 | -1.087053 |
| | 2 | 1 | -1.100891 | -1.100953 | -1.087234 | -1.087271 |
| | -1 | -1 | -1.100882 | -1.100946 | -1.087315 | -1.087358 |
| | 1 | -1 | -1.100937 | -1.101000 | -1.087423 | -1.087467 |
| | 0 | 1 | -1.100934 | -1.100997 | -1.087430 | -1.087476 |
| -2 | 1 | -1.103791 | -1.103794 | -1.089541 | -1.089549 |
| 2 | 1 | -1.103900 | -1.103903 | -1.089759 | -1.089767 |
| \( L = 2 \) | -1.108932 | -1 | -1 | -1.104117 | -1.104121 | -1.090741 | -1.090742 |
| | 1 | -1 | -1.104171 | -1.104175 | -1.090850 | -1.090851 |
| | 0 | 1 | -1.104171 | -1.104176 | -1.090313 | -1.090334 |
| \( L = 0 \) | -1.110336 | 0 | 1 | -1.105501 | -1.105502 | -1.092510 | -1.092513 |

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Table VIII: Rotational energy levels of D$_2$ in presence of a uniform magnetic field $B$ for the vibrational state $v = 0$. See Caption of Table IV for explications.

| $L$ | $\frac{\text{Energy}}{E_h}$ | $M$ | $\pi$ | $B = 0.0$ | $B = 0.1$ | $B = 0.2$ |
|-----|----------------|-----|-----|---------|---------|---------|
|     |                 |     |     | model 1 | model 2 | model 1 | model 2 |
| 3   | -1.160092       | -1  | -1.160011 | -1.160026 | -1.147642 | -1.147648 |
| 4   | -1.159962       | 1   | -1.159867 | -1.159876 | -1.147366 | -1.147369 |
| 5   | -1.159853       | 1   | -1.159867 | -1.159876 | -1.147148 | -1.147151 |
| 6   | -1.158877       | 1   | -1.158867 | -1.158876 | -1.147151 | -1.147156 |
| 7   | -1.158000       | 1   | -1.158000 | -1.158000 | -1.147151 | -1.147156 |
| 8   | -1.157133       | 1   | -1.157133 | -1.157133 | -1.147151 | -1.147156 |
| 9   | -1.156265       | 1   | -1.156265 | -1.156265 | -1.147151 | -1.147156 |

$L = 3$ - $1.162594$

|     |                 |     |     | model 1 | model 2 | model 1 | model 2 |
| 0   | -1.164212       | 0   | -1.162909 | -1.162909 | -1.151185 | -1.151187 |
Table IX: Rotational energy levels of $D_2$ in presence of a uniform magnetic field $B$ for the vibrational state $v = 1$. 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 [IV] for explications.

| $L$ | Energy/$E_h$ | $M$ | $\pi$ | Energy/$E_h$ |
|-----|--------------|-----|-------|--------------|
|     | $B = 0.0$    |     |       | $B = 0.1$    |
|     | model 1      | model 2 | model 1 | model 2 |
| -5  | -1.144716    | -1.144750 | -1.131616 | -1.131629 |
| 5   | -1.144852    | -1.144887 | -1.131888 | -1.131901 |
| -4  | -1.144869    | -1.144906 | -1.132080 | -1.132098 |
| 4   | -1.144978    | -1.145015 | -1.132298 | -1.132316 |
| -3  | -1.144986    | -1.145024 | -1.132384 | -1.132407 |
|     | -1.137626    | 3    |       | -1.132547 |
| -2  | -1.145068    | -1.145071 | -1.132603 | -1.132630 |
| 2   | -1.145126    | -1.145165 | -1.132712 | -1.132739 |
| -1  | -1.145127    | -1.145166 | -1.132738 | -1.132767 |
| 1   | -1.145154    | -1.145194 | -1.132793 | -1.132822 |
|     | -1.145154    | -1.145194 | -1.132802 | -1.132832 |
|     | -1.147161    | -1.147165 | -1.134228 | -1.134231 |
| 3   | -1.147243    | -1.147246 | -1.134391 | -1.134394 |
| -2  | -1.147379    | -1.147384 | -1.134901 | -1.134904 |
|     | -1.142112    | 2    |       | -1.135010 |
| -1  | -1.147434    | -1.147438 | -1.135013 | -1.135013 |
| 1   | -1.147484    | -1.147489 | -1.134961 | -1.134970 |
|     | -1.147511    | -1.147517 | -1.135016 | -1.135025 |
| 0   | -1.147534    | -1.147539 | -1.135209 | -1.135216 |
|     | -1.148617    | -1.148618 | -1.136156 | -1.136161 |
|     | -1.144658    | 1    |       | -1.136211 |
| 0   | -1.148644    | -1.148645 | -1.136215 | -1.136215 |
|     | -1.148991    | -1.148992 | -1.137153 | -1.137154 |
|     | -1.145172    | 0    |       | -1.137162 |
|     | -1.149081    | -1.149082 | -1.137164 | -1.137164 |
Table X: Rotational energy levels of \( \text{D}_2 \) in presence of a uniform magnetic field \( B \) for the vibrational state \( v = 2 \). See Caption of Table IV for explications.

| \( L \) | Energy/\( E_h \) | \( M \) | \( \pi \) | Energy/\( E_h \) |
|-------|--------|-----|-----|--------|
|       | \( B = 0.0 \) | \( B = 0.1 \) | \( B = 0.2 \) |       |
|       | model 1 | model 2 | model 1 | model 2 |       |
|       |         |         |         |         |       |
| -4    | -1.132863 | -1.132879 | -1.119435 | -1.119439 |       |
| 4     | -1.132972 | -1.132988 | -1.119652 | -1.119657 |       |
| -3    | -1.133056 | -1.133073 | -1.120051 | -1.120057 |       |
| 3     | -1.133138 | -1.133155 | -1.120215 | -1.120220 |       |
|       | -1.122394 |         |         |         |       |
|       | -2     | -1.133183 | -1.133200 | -1.120303 | -1.120315 |       |
|       | 2     | -1.133237 | -1.133255 | -1.120412 | -1.120424 |       |
|       | -1    | -1.133262 | -1.133280 | -1.120535 | -1.120549 |       |
|       | 1     | -1.133290 | -1.133307 | -1.120590 | -1.120603 |       |
|       | 0     | -1.133327 | -1.133345 | -1.120583 | -1.120598 |       |
|       |       |         |         |         |       |
|       | -2    | -1.134741 | -1.134742 | -1.121613 | -1.121620 |       |
|       | 2     | -1.134795 | -1.134796 | -1.121722 | -1.121729 |       |
|       |       |         |         |         |       |
|       | -1    | -1.135039 | -1.135041 | -1.122536 | -1.122539 |       |
|       | 1     | -1.135067 | -1.135068 | -1.122591 | -1.122593 |       |
|       | 0     | -1.135030 | -1.135031 | -1.122043 | -1.122057 |       |
|       |       |         |         |         |       |
|       |       |       |         |         |       |
|       |       | -1.127217 | 0     | -1.135820 | -1.135820 | -1.123669 | -1.123671 |
Table XI: Rotational energy levels of D$_2$ in presence of a uniform magnetic field $B$ for the vibrational state $v = 3$. 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 IV for explications.

| $L$ | Energy/$E_h$ | $M$ | $\pi$ | Energy/$E_h$ |
|-----|--------------|-----|-------|--------------|
|     | $B = 0.0$    |     |       |              |
|     | model 1     | model 2 | model 1 | model 2 |
| -5  | -1.118947  | -1.118983 | -1.105014 | -1.105022 |
| 5   | -1.119083  | -1.119120 | -1.105287 | -1.105295 |
| -4  | -1.119117  | -1.119155 | -1.105592 | -1.105604 |
| 4   | -1.119226  | -1.119264 | -1.105810 | -1.105822 |
| -3  | -1.119245  | -1.119284 | -1.105931 | -1.105949 |
| $L = 5$ | -1.102915 |     |       |              |
| 3   | -1.119327  | -1.119365 | -1.106094 | -1.106112 |
| -2  | -1.119338  | -1.119377 | -1.106190 | -1.106212 |
| 2   | -1.119392  | -1.119431 | -1.106299 | -1.106321 |
| -1  | -1.119397  | -1.119437 | -1.106338 | -1.106364 |
| 1   | -1.119425  | -1.119464 | -1.106393 | -1.106418 |
| 0   | -1.119426  | -1.119466 | -1.106412 | -1.106438 |
|     | -1.121232  | -1.121236 | -1.107520 | -1.107524 |
| 3   | -1.121313  | -1.121318 | -1.107684 | -1.107688 |
| -2  | -1.121475  | -1.121481 | -1.108358 | -1.108359 |
| $L = 3$ | -1.107489 |     |       |              |
| 2   | -1.121530  | -1.121535 | -1.108467 | -1.108468 |
| -1  | -1.121583  | -1.121589 | -1.108278 | -1.108293 |
| 1   | -1.121610  | -1.121616 | -1.108333 | -1.108347 |
| 0   | -1.121639  | -1.121644 | -1.108672 | -1.108679 |
|     | -1.122616  | -1.122616 | -1.109602 | -1.109604 |
| $L = 1$ | -1.109872 |     |       |              |
| 1   | -1.122643  | -1.122643 | -1.109656 | -1.109659 |
| 0   | -1.123030  | -1.123031 | -1.110730 | -1.110730 |
| $L = 0$ | -1.110336 |     |       |              |
| 0   | -1.123096  | -1.123096 | -1.108965 | -1.108978 |
Figure 5: Rotational structure, up to $L = 5$, of the four lowest vibrational states of $D_2$ in the presence of an external magnetic field of $B = 0.2 B_0$. 
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