Chemical Physics Letters 761 (2020) 138041

Contents lists available at ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

Research paper

A quantum-mechanical non-Born–Oppenheimer model of a molecule in a strong magnetic field

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ABSTRACT

Interactions of a stationary external magnetic field with the spin and orbital magnetic momenta of a molecule are included in the quantum mechanical model where the Born–Oppenheimer approximation is not assumed. The model is used to calculate some of the lowest-lying internal bound states of the molecule for various strengths of the magnetic field. All-particle explicitly correlated Gaussian functions are used in the calculations.

1. Introduction

In recent works [1–3], we have presented a quantum-mechanical model for calculating states of a molecule in strong magnetic fields. In the model, the Born–Oppenheimer (BO) approximation is not assumed and all particles forming the molecular system are treated on an equal footing. The wave functions representing the states of the system in the model were expanded in terms of linear combinations of explicitly correlated Gaussian functions (ECGs) with shifted centers. These functions explicitly depend on the squares of the inter-particle distances through the Gaussian exponent. Only if such functions are used in the calculation can we effectively describe the highly correlated motion of the electrons contained in the molecule, as well as the correlated motion of the molecule's nuclei and the nucleus–electron correlated motion. The non-BO Hamiltonian used in the calculations of bound internal states of the molecule is obtained in an effective way by subtracting the operator representing the kinetic energy of the motion of the center of mass from the total laboratory-frame Hamiltonian of the system. This approach is different from the conventional approach used to separate out the center-of-mass motion, which typically involves a coordinate transformation resulting in the total Hamiltonian rigorously separating into a Hamiltonian representing the internal state of the system (the so-called internal Hamiltonian) and the center-of-mass Hamiltonian, which depends only on the laboratory-frame coordinates of the center of mass. More discussion on the construction of the effective non-BO Hamiltonian and on the ECGs is presented in the methodology section of this work.

The interest in quantum-mechanical calculations of ground and excited states of molecules exposed to strong magnetic fields is related to the significant alterations of some their chemical and physical properties in conditions where the magnetic interactions become comparable to the Coulombic interactions between the electrons and nuclei forming the molecules. Such conditions exist, for example, in the atmospheres of rapidly rotating compact stellar objects—white dwarfs (up to 100 kT), neutron stars (up to 100 MT), and magnetars (up to 100 GT) [4–6]. The field strengths that exist on such stellar objects cannot be generated in laboratories on Earth. Since the changes that occur in the chemical and physical properties of molecular systems in extremally strong magnetic fields cannot be probed experimentally, quantum-mechanical modeling is the only possible way to elucidate this phenomenon. An illustration of how strong magnetic fields affect chemical properties of molecules were given in Ref. [7]. The calculations performed in that work, using an approach based on the BO approximation and involving the full-CI electronic-structure method, showed that, as the strength of a perpendicularly applied magnetic field increases, the strength of the bonding in the $^3\Sigma_u^+(1\sigma_g 1\sigma_u^*)$ triplet state of the H_2 molecule also increases and its energy falls below that of the singlet zero-field ground state $^1\Sigma_g^+(1\sigma_g^2)$.

Over the years, many non-perturbative methods have been developed to study the behavior of molecules in a strong magnetic field—see, for example, Refs. [8–18]. However, almost all these methods are based on the BO approximation, assuming that the much faster motion of the electrons can be treated separately from the slower motion of the nuclei. Although this assumption is usually sufficient for most studies of molecules at Earth-like conditions, it may fail in conditions where the interactions with a very strong magnetic field cause the energy levels of the molecule to rearrange, resulting in acceleration of the nuclear

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https://doi.org/10.1016/j.cplett.2020.138041
Received 1 August 2020; Received in revised form 22 September 2020; Accepted 22 September 2020
Available online 23 September 2020

motion and deacceleration of the electronic motion. This, in turn, may cause the two motions to couple more significantly, necessitating a departure from the BO approximation. We here present a method that can address such increased electron–nucleus coupling.

In this work, we include the interactions of the magnetic field with the spin and angular magnetic momenta of the electrons and the nuclei in the non-BO model for a molecule in a strong stationary magnetic field developed in our previous works [1–3]. As all particles are treated on the same footing in non-BO calculations, the magnetic momenta associated with the electrons appear in the calculations in the same way as the spin and angular magnetic momenta of the nuclei.

There are two types of motion of the nuclei and electrons in an isolated molecule that can be distinguished. The first type is the synchronous translational motion of both nuclei and electrons of the molecule in space, which can be quantum-mechanically represented by a wave function dependent on the coordinates of the molecule's center of mass in the laboratory coordinate frame. The second type of motion is the coupled motion of the particles forming the molecule that does not cause the center of mass of the molecule to change its location. We call this the internal motion of the system; it can be approximately separated into rotational, vibrational, and electronic motions. When the BO approximation is not assumed, the rotational motion includes the synchronous rotation of all particles forming the molecule about the center of mass. Thus, the quantized bound states of the molecule corresponding to this motion, apart from including states that are conventionally attributed to rotation of the nuclear frame of the molecule, also include states corresponding to rotation of the electrons around the stationary nuclear frame and mixed electron–nucleus rotational states. As the total internal Hamiltonian for the molecule obtained by subtracting the center-of-mass translational Hamiltonian from the total laboratory-frame non-relativistic Hamiltonian commutes with the square of the total angular-momentum operator, the calculation of the bound states of the molecule can be separated into calculations each performed for a different total-angular-momentum quantum number. Each such calculation is carried out in a basis of functions that represent a different level of the rotation excitation of the system. The functions can describe angular excitations of different nuclei, or angular excitations of the electrons, or simultaneous excitations of both electrons and nuclei.

As showed by Schmelcher and Cederbaum [13], the separation of the translational and internal motion cannot be rigorously performed when a molecule is placed in a magnetic field. However, they also showed that, with the use of the so-called pseudo-momentum, one can perform a pseudo-separation of the two motions. The properties of the total pseudo-momentum expressed in terms of relative coordinates were exploited to partition the Hamiltonian operator of the system into an electronic part and a nuclear part.

The question of the validity of the BO approximation for the hydrogen atom [19] and the diatomic hydrogen molecule [14,15] in a stationary magnetic field has been analyzed. There also exist investigations where the effect of a magnetic field on the rotations and vibrations of neutral diatomic molecules has been considered [16,20]. However, to our knowledge, our works [1–3] provided the first practical scheme for an effective separation of the center-of-mass motion from the internal motion in calculations of molecular systems in the presence of a magnetic field.

2. The method

The non-Born–Oppenheimer approach used in this work was introduced by Kozlowski and Adamowicz [21]. We start from the standard total non-relativistic Hamiltonian of an isolated molecule without a magnetic field. We use the laboratory Cartesian coordinate frame to describe the positions of particles forming the molecule (i.e., nuclei and electrons) in space. The position vectors are denoted as $\mathbf{R}_l$, $l = 1, \ldots, N$, where N is the sum of the number of the nuclei and the number of the electrons in the system. In atomic units, the laboratory-frame total Hamiltonian is the sum of the kinetic-energy operators of the particles forming the system and the potential-energy operators describing the Coulombic interactions between the particles:

$$\hat{H} = \hat{T} + \hat{V} = -\sum_{l}^{N} \frac{1}{2M_l} \nabla^2_{\mathbf{R}_l} + \sum_{k>l}^{N} \frac{Q_k Q_l}{R_{kl}}. \tag{1}$$

Here $\hat{T}$ and $\hat{V}$ are the kinetic-energy and potential-energy operators, respectively, and M_l and Q_l are the mass and the charge, respectively, of particle l. The distance between particle k and particle l is given by $R_{kl} = |\mathbf{R}_l - \mathbf{R}_k|$.

Next, the kinetic energy of the center-of-mass motion is written in terms of the $\mathbf{R}_l$, $l = 1, \ldots, N$, coordinates. The coordinates of the center of mass of the system are:

$$\mathbf{R}_{\mathrm{cm}} = \frac{\sum_l^N M_l \mathbf{R}_l}{M}, \tag{2}$$

with $M = \sum_l^N M_l$ is the total mass of the system. The operator representing the kinetic energy of the center-of-mass motion in the laboratory coordinate frame is given by

$$\hat{T}_{\mathrm{cm}} = -\frac{1}{2M} \nabla^2_{\mathbf{R}_{\mathrm{cm}}} = \frac{1}{2M} \hat{\mathbf{P}}^2_{\mathrm{cm}} = \frac{1}{2M} \Big(\sum_{l=1}^{N} \hat{\mathbf{p}}_l \Big)^2, \tag{3}$$

where $\hat{\mathbf{P}}_{\mathrm{cm}}$ is the center-of-mass momentum operator and $\hat{\mathbf{p}}_l$ the momentum of particle l. The effective laboratory-frame Hamiltonian representing the internal energy of the system, $\hat{H}_{\mathrm{int}}$, called the *internal Hamiltonian*, is simply the difference between the laboratory-frame Hamiltonian and the center-of-mass kinetic-energy Hamiltonian:

$$\hat{H}_{\mathrm{int}} = \hat{H} - \hat{T}_{\mathrm{cm}}. \tag{4}$$

The internal Hamiltonian is used in the present work to calculate internal bound states of the molecule.

We note that the effective internal Hamiltonian depends on the $3N$ laboratory coordinates of *all particles* (nuclei and electrons) forming the system. In this respect, it differs from the usual internal non-BO Hamiltonian obtained by expressing the laboratory-frame total Hamiltonian in a set of new coordinates and then separating the Hamiltonian into a Hamiltonian representing the center-of-mass kinetic energy (dependent only on the center-of-mass coordinates) and an internal Hamiltonian (independent of the center-of-mass coordinates). One possible set of coordinates in such an approach can consist of the three Cartesian laboratory-frame coordinates of the center of mass and $3N-3$ internal Cartesian coordinates that represent the positions of particles 2 to N relative to a reference particle 1 (usually the heaviest nucleus) [22]. The axes of the internal coordinate system are parallel to the axes of the laboratory coordinate system. The non-BO internal Hamiltonian then depends only on $3N-3$ coordinates, by three less than the effective internal Hamiltonian, $\hat{H}_{\mathrm{int}}$. Thus, while the wave function depends on $3N$ (laboratory-frame Cartesian) coordinates in the effective internal-Hamiltonian approach taken in this work, it depends only on $3N-3$ (internal) in the approach based on the coordinate transformation.

The calculations performed in this work concern internal states of hydrogen deuteride, HD, interacting with a stationary magnetic field oriented along the Z-axis. We choose HD rather than H_2 because proton and deuteron have different masses and different spins, making HD more interesting than H_2 for non-BO calculations, especially when the Zeeman interactions of the magnetic field with the spin and angular magnetic momenta of the particles forming the molecule are included.

The non-BO wave functions of the bound states of the effective internal Hamiltonian, which depend of spatial and spin coordinates of all particles forming the molecule, must be properly symmetrized (for bosons) and anti-symmetrized (for fermions). For the HD molecule, each wave function is a product of a spatial function and a spin function. As the HD non-BO wave function must be antisymmetric with respect to the permutation of the electron labels, the spatial part of

the wave function can either be symmetric (electronic singlet state) or antisymmetric (electronic triplet state). In this work we consider both types of states.

The total spatial wave functions representing singlet and triplet states of the HD molecule can be represented as $(1 + \hat{P}(1,2))\Psi(\mathbf{R}_d, \mathbf{R}_p, \mathbf{R}_1, \mathbf{R}_2)$ and $(1 - \hat{P}(1,2))\Psi(\mathbf{R}_d, \mathbf{R}_p, \mathbf{R}_1, \mathbf{R}_2)$, respectively, where indices d, p, 1, and 2 denote the deuteron, the proton, and the two electrons, respectively, and the operator $\hat{P}(1,2)$ permutes the electron labels. These spatial functions are multiplied by the corresponding spin wave functions, which are products of a deuteron spin function, a proton spin function, and either antisymmetric electronic spin function (for the singlet) or symmetric electronic spin function (for the triplet).

The most effective and accurate representation of a molecular non-BO wave function is obtained by expanding its spatial part in terms of functions that explicitly depend on the distances between the particles. Here we use *explicitly correlated Gaussians (ECGs)* with shifted centers of the form

$$\phi_k(\mathbf{R}) = \exp\left[-(\mathbf{R} - \mathbf{s}_k)' \underline{\mathbf{A}}_k (\mathbf{R} - \mathbf{s}_k)\right], \tag{5}$$

where prime denotes vector transposition, $\mathbf{R}$ is a $3N$ vector of laboratory-frame coordinates (for HD, concatenated from $\mathbf{R}_d$, $\mathbf{R}_p$, $\mathbf{R}_1$, and $\mathbf{R}_2$), $\mathbf{s}_k$ is a $3N$ vector of the Gaussian shifts, $\underline{\mathbf{A}}_k = \mathbf{A}_k \otimes \mathbf{I}_3$ is a $3N \times 3N$ symmetric, positive-definite Kronecker product of the 3×3 identity matrix $\mathbf{I}$ and the $N \times N$ symmetric positive-definite matrix $\mathbf{A}_k$ of Gaussian exponential factors. Positive definiteness of $\mathbf{A}_k$ is imposed by representing it in the Cholesky-factored form $\mathbf{A}_k = \mathbf{L}_k \mathbf{L}_k'$ with $\mathbf{L}_k$ being a lower triangular $N \times N$ matrix. The ECGs in (5) were used in our previous works [2,3].

In the present calculations, we use the variational approach to optimize the non-linear parameters of the Gaussians and the coefficients in the expansion of the spatial wave function in ECGs. The non-linear variational parameters are the elements of the $\mathbf{L}_k$ matrices and the coordinates of the $\mathbf{s}_k$ shift vectors of the Gaussians.

As shown by Lange at al. [7], the lowest-energy orientation of the bond axis of a diatomic molecule with respect to the direction of the magnetic field is perpendicular for the electronic triplet state and parallel for the singlet state. Thus, for the Z-direction of the magnetic field, the Gaussian shifts in the calculations for the triplet state are restricted to the XY plane and in the calculations for the singlet state they are restricted to the Z axis. In the first step, the Gaussians are optimized for the lowest electronic singlet and triplet states without the Zeeman interactions included in the Hamiltonian. The optimizations are carried out for three different strengths of the magnetic field oriented along the Z axis. For the triplet state, to approximately impose the axial symmetry of the wave function expanded in terms of ECGs (i.e., making it approximately symmetric in terms of rotations about the Z-axis), four ECGs are contracted to form a single basis function. The $\mathbf{L}_k$ matrices of all four Gaussians are the same, but the $\mathbf{s}_k$ shift vectors are different. In the first Gaussian, only the x-coordinates of the shift vector $\mathbf{s}_k$ are non-zero: $\mathbf{s}_{k1} = \{X_d^k, 0, 0, X_p^k, 0, 0, X_1^k, 0, 0, X_2^k, 0, 0\}$. The shift vectors of the other three Gaussians are: $\mathbf{s}_{k2} = \{-X_d^k, 0, 0, -X_p^k, 0, 0, -X_1^k, 0, 0, -X_2^k, 0, 0\}$, $\mathbf{s}_{k3} = \{0, X_d^k, 0, 0, X_p^k, 0, 0, X_1^k, 0, 0, X_2^k, 0\}$, and $\mathbf{s}_{k4} = \{0, -X_d^k, 0, 0, -X_p^k, 0, 0, -X_1^k, 0, 0, -X_2^k, 0\}$. The contraction coefficients of all four Gaussians are equal to +1. The contracted ECG function, Φ_k, can be written as:

$$\begin{aligned}\Phi_k = {} & \phi_{k1}(X_d^k, 0, 0, X_p^k, 0, 0, X_1^k, 0, 0, X_2^k, 0, 0) \\ & + \phi_{k2}(-X_d^k, 0, 0, -X_p^k, 0, 0, -X_1^k, 0, 0, -X_2^k, 0, 0) \\ & + \phi_{k3}(0, X_d^k, 0, 0, X_p^k, 0, 0, X_1^k, 0, 0, X_2^k, 0) \\ & + \phi_{k4}(0, -X_d^k, 0, 0, -X_p^k, 0, 0, -X_1^k, 0, 0, -X_2^k, 0).\end{aligned} \tag{6}$$

In the variational optimization, the elements of $\mathbf{L}_k$ and the X_d^k, X_p^k, X_1^k, and X_2^k coordinates are optimized. No contraction is used in the basis functions for the singlet state and, as mentioned, the basis functions have shifts located on the Z axis:

$$\Phi_k = \phi_k(0, 0, Z_d^k, 0, 0, Z_p^k, 0, 0, Z_1^k, 0, 0, Z_2^k). \tag{7}$$

Also, both parallel and antiparallel orientations of the HD bond axis with respect to the Z axis are represented in the Gaussians used as a starting point for the optimization. This means that, if Φ_k (7) is included in the starting basis set, the following Gaussian is also included as an independent function:

$$\Phi_k = \phi_k(0, 0, Z_p^k, 0, 0, Z_d^k, 0, 0, Z_1^k, 0, 0, Z_2^k) \tag{8}$$

and its parameters are optimized independently of the parameters of (7).

Now, let us consider the potential generated by an external magnetic field oriented along the Z-axis. The gauge-invariant kinetic momentum operator for particle l is:

$$\hat{\pi}_l = -i\hbar\nabla_l - Q_l \mathbf{A}(\mathbf{R}_l), \tag{9}$$

where Q_l is the charge of the particle and the magnetic vector potential $\mathbf{A}(\mathbf{R})$ represents the external magnetic field, $\mathbf{B} = \nabla \times \mathbf{A}(\mathbf{R})$. The vector potential for a stationary magnetic field may be written as:

$$\mathbf{A}(\mathbf{R}_l) = \frac{1}{2}\mathbf{B} \times (\mathbf{R}_l - \mathbf{g}), \tag{10}$$

where $\mathbf{g}$ is the gauge origin. Without the spin Zeeman interactions, the total kinetic energy operator is then given by:

$$\hat{T} = \sum_{l=1}^{N} \frac{\hat{\pi}_l^2}{2M_l} = \sum_{l=1}^{N} \left[-\hbar^2\nabla_l^2 + i\hbar Q_l \mathbf{B} \cdot ((\mathbf{R}_l - \mathbf{g}) \times \nabla_l) + Q_l^2 |\mathbf{A}(\mathbf{R}_l)|^2\right] / 2M_l. \tag{11}$$

The masses of the proton and the deuteron used in the present calculations are $1836.15267245 m_e$ and $3670.4829652 m_e$, respectively. Placing the gauge origin at the origin of the laboratory coordinate system, $\mathbf{g} = 0$, and the magnetic field vector along the z-axis $\mathbf{B} = (0, 0, B_Z)$, we can rewrite the kinetic-energy operator in the following form:

$$\hat{T} = -\sum_{l=1}^{N} \frac{\hbar^2}{2M_l}\nabla_l^2 + \hat{H}_{\text{Zeeman}}^{\text{orb}} + \hat{V} \tag{12}$$

where the first term represents the canonical kinetic energy, the second term the orbital Zeeman interaction of the particles with the magnetic field, and the third term the diamagnetic interaction of the particles with the field:

$$\hat{H}_{\text{Zeeman}}^{\text{orb}} = -\sum_{l=1}^{N} \frac{Q_l}{2M_l} B_Z \hat{L}_{Z_l}, \quad \hat{V} = \sum_{l=1}^{N} \frac{Q_l^2}{8M_l} B_Z^2 (X_l^2 + Y_l^2). \tag{13}$$

Here $\hat{L}_{Z_l} = -i\hbar\left(X_l\nabla_{Y_l} - Y_l\nabla_{X_l}\right)$ is the operator representing the Z coordinate of the angular momentum of particle l. The diamagnetic operator, $\hat{V}$, takes the form of a quadratic (harmonic) well about the Z-axis; it is proportional to the squared particle charge, the squared field strength, and the inverse particle mass. It squeezes the system and raises its energy.

The paramagnetic orbital Zeeman operator $\hat{H}_{\text{Zeeman}}^{\text{orb}}$ is linear in the charge and the field strength and inversely proportional to the mass of the particle; it may lower or raise the energy, reduce the symmetry of the wave function, and split energy levels. It must be supplemented by the spin Zeeman operator, which arises more naturally from a relativistic treatment. The total Zeeman operator then takes the form:

$$\hat{H}_{\text{Zeeman}} = \hat{H}_{\text{Zeeman}}^{\text{orb}} + \hat{H}_{\text{Zeeman}}^{\text{spin}} = B_Z \sum_{l=1}^{N} \frac{Q_l}{2M_l} \hat{L}_{Z_l} - B_Z \sum_{l=1}^{N} g_l \mu_l \hat{S}_{Z_l} \tag{14}$$

where μ_l is equal to minus the Bohr magneton $-\mu_B = -\frac{e\hbar}{2m_e}$ for electrons and to the nuclear magneton $\mu_N = \frac{e\hbar}{2m_p}$ for the nuclei, while g_l is the g factor of the particle: $g_e = 2.00231930436256$, $g_p = 5.5856946893$, and $g_d = 0.8574382338$. Therefore, in atomic units, the spin Zeeman interaction of electron l with the magnetic field oriented along the Z-axis is $B_Z \hat{S}_{Z_l}$, while the proton and deuteron spin Zeeman interactions are about three orders of magnitude smaller and of opposite sign:

$-(g_p/2m_p)B_Z\hat{S}_{Z_p}$ and $-(g_d/2m_p)B_Z\hat{S}_{Z_d}$. The possible values of the Z-component of the spin are $+\frac{1}{2}$ and $-\frac{1}{2}$ for an electron and the proton, and $+1$ and -1 for the deuteron.

In the calculations performed in this work, the Hamiltonian and overlap matrices with the ECGs (5) are constructed. These matrices are subsequently used to solve the matrix secular equation problem and to determine the energy of the considered state and the linear expansion coefficients of the ECGs in the corresponding wave function. The algorithms for calculating the matrix elements with operators in the diamagnetic operator were published before [2,23,24]. The algorithm for calculating this matrix elements of the orbital Zeeman operator is described in Appendix.

3. Illustration calculations

Our computer code is written in Fortran90 using MPI (message passing interface) to enable multiprocessor calculations. The integral algorithms for the Hamiltonian matrix elements are taken from our previous work [2,3]. The code contains a module for variational optimization of the non-linear parameters ($\mathbf{L}_k$ and $\mathbf{s}_k$) of the ECGs. The approach is employed to perform calculations of low-energy states of the HD molecule. The total Hamiltonian representing the internal energy of the molecule in an external magnetic field is a sum of the field-free internal Hamiltonian, $\hat{H}_{\text{int}}$, the diamagnetic Hamiltonian, $\hat{V}$, and the Zeeman Hamiltonian, $\hat{H}_{\text{Zeeman}}$:

$$\hat{H} = \hat{H}_{\text{int}} + \hat{V} + \hat{H}_{\text{Zeeman}}. \tag{15}$$

As mentioned, the illustration calculations are performed for the HD molecule. They involved the following steps:

1. In the first step, Hamiltonian $\hat{H}_{\text{int}} + \hat{V}$ is used in the variational optimization of three basis sets for the triplet electronic state and three for the singlet state. The three basis sets for each state are generated for the following three different field strengths, $B_Z = 0.1B_0$, $0.2B_0$, and $0.3B_0$, where $B_0 \approx 235kT$ (one atomic unit field strength). For the triple state, the basis set consists of six contracted ECGs (6) with centers (Gaussian shifts) located in the plane (i.e. the XY plane) perpendicular to the orientation of the field (i.e. the Z axis). For the singlet state, the basis set consists of twelve uncontracted ECGs with the centers located on the Z axis. The wave functions of the singlet and triplet states for the three field strengths are used to calculate the expectation values of the proton–deuteron distance and its square ($\langle r_{pd}\rangle$ and $\langle r_{pd}^2\rangle$).
2. Next, the electronic part of the spin Zeeman interaction $\hat{H}^{\text{el spin}}_{\text{Zeeman}}$ is added to the Hamiltonian and the energy of the system is calculated. Two electronic spin states are considered: the singlet state with $S = 0$ and $M_S = 0$ and the triplet state in the energetically most favorable orientation of electronic spin vector with respect to the direction of the field, i.e. the $S = 1$ and $M_S = -1$ state. While the spin Zeeman interaction vanishes for the singlet, it stabilizes the chosen triplet component. The stabilization increases with the field. The energy contribution from the $\hat{H}^{\text{el spin}}_{\text{Zeeman}}$ interaction has a constant value for each electronic spin state. It only depends on states M_S value, but is independent on the spatial wave function of the state. Thus, no reoptimization of the basis set is needed at this stage.
3. Next, the nuclear spin Zeeman Hamiltonian, $\hat{H}^{\text{nuc spin}}_{\text{Zeeman}}$, is included in the Hamiltonian and the energies of the singlet and triplet states of the molecule are calculated for all possible orientations of the spins of the proton ($\frac{1}{2}$ and $-\frac{1}{2}$)) and the deuteron (-1 and 1) with respect to the direction of the field.
4. Finally, $\hat{H}^{\text{orb}}_{\text{Zeeman}}$ is added to the Hamiltonian and the total energies of the above described states are calculated by again solving the secular equation (i.e., without reoptimizing the non-linear parameters of the Gaussians). The energies obtained in the calculations now include the effect due to the interaction between the magnetic field and the orbital momenta of the proton, the deuteron, and the electrons. As, in this case, the Hamiltonian matrix becomes complex Hermitian, a complex secular-equation solver is used to obtain the energies and the corresponding wave functions.

   The basis sets are also not reoptimized in this case and the adjustment of the wave functions and the corresponding energies due to the inclusion of the Zeeman orbital interaction with the field are only accounted for by the reoptimization of the (now complex) linear expansion coefficients. We should note that the Zeeman orbital interaction manifests itself by coupling states with different angular momenta. For example, the zero-field ground state, which is fully symmetric and corresponds to a superposition of the HD ground electronic state, the ground vibrational state, and the ground (fully symmetric) rotational state couples with states whose rotational components correspond to non-zero angular momenta—for example, components of the D symmetry. These components give non-zero off-diagonal matrix elements of $\hat{H}^{\text{orb}}_{\text{Zeeman}}$ with the rotational component of the ground state. The spherical symmetry of the field-free system, whose states are eigenstates of the $\hat{L}^2$ operator, is broken by the diamagnetic term. In a non-zero field, the symmetry becomes cylindrical with respect to the Z-axis, which is required because the $\hat{L}_Z$ quantum number is a good quantum number. The gauge origin being placed in the center of the coordinate system ensures that the proper symmetry of the internal Hamiltonian and the wave function is maintained. The lowest-energy wave function obtained in the calculations is used to calculate the expectation value of the $\hat{H}^{\text{orb}}_{\text{Zeeman}}$ operator in order to estimate the Zeeman orbital interaction.

   In the calculations with the complete internal Hamiltonian (including $\hat{H}^{\text{orb}}_{\text{Zeeman}}$), the non-linear parameters of the Gaussians are not reoptimized and only the linear expansion coefficients of the wave function are adjusted to reflect the orbital Zeeman interaction. To allow for the mixing of states of the different symmetries, the contracted basis functions for the electronic triplet state are separated into individual components (note that contraction is not used for the singlet state). These components are used as separate basis functions in the calculation. As each contracted triplet Gaussian comprises four components, the size of the basis set upon de-contraction increases from 6 to 24. The 24×24 matrix of the $\hat{H}^{\text{orb}}_{\text{Zeeman}}$ operator constructed using the uncontracted basis functions is Hermitian, but the off-diagonal matrix elements are very small because of very small overlap between any two components when their centers (shifts) are located on different axes. This results in very small values of the $\hat{H}^{\text{orb}}_{\text{Zeeman}}$ matrix elements and in the Zeeman orbital interaction with the field being negligibly small for the particular case being studied in this work.

The results of the calculations are shown in Table 1. The above-described levels of including the Zeeman effects are shown in the table. The results shown in the table correspond to the lowest singlet and triplet electronic states of HD. The first set of results (level one) are obtained with Hamiltonian that does not include the spin-dependent effects. The difference in the energies of the singlet and triplet states originates from the different permutational symmetries of the singlet and triplet electronic wave functions. As expected, the energies of both single and triplet electronic states of the system increase with the increasing value of B_Z and, for all considered values of B_Z, the singlet has lower energy than the triplet.

Adding the Zeeman interaction of the magnetic field with the spins of the electrons does not change the results for the singlet state, as the Zeeman interaction in this case is zero. However, the energies obtained

Table 1
Total internal energies of the lowest electronic singlet and triplet states (E_s and E_t) and the expectation values of the proton–deuteron distances and their squares ($\langle r_{pd}\rangle$ and $\langle r_{pd}^2\rangle$) of the HD molecule placed in a magnetic field oriented along the Z axis with the strengths of $B_Z = 0.1,\ 0.2,$ and $0.3B_0$. For the singlet, a parallel orientation of the HD molecule with respect to the field is assumed, while for the triplet a perpendicular orientation is assumed. The energies are calculated for different levels of including the Zeeman effects. At the first level, only the quadratic spin-independent Zeeman effects are included, at the second level, the interaction of the field with the electron spins is included, and at the third level the interaction of the field with the spins of the proton and deuteron is included. At the latter level the total internal energy is calculated for all possible spin orientations of the proton and the deuteron with respect to the direction of the field. The orientations are designated by the proton and deuteron s_Z quantum numbers, $(s_Z^p,\ s_Z^d)$. The Hamiltonians used in the different levels are shown in the first column. The energies are given in hartrees and the expectation values of the proton–deuteron distances in a.u.

Hamiltonian	B_Z		Singlet			Triplet		
			E_s	$\langle r_{pd}\rangle$	$\langle r_{pd}^2\rangle$	E_t	$\langle r_{pd}\rangle$	$\langle r_{pd}^2\rangle$
$\hat{H}_{int} + \hat{V}$								
	0.1		−1.14060349	1.45	2.15	−0.95555737	4.62	21.65
	0.2		−1.12887841	1.44	2.12	−0.91543685	3.76	14.26
	0.3		−1.11001969	1.42	2.06	−0.85673820	3.30	10.98
$+\hat{H}^{\text{el spin}}_{\text{Zeeman}}$								
	0.1		−1.14060349			−1.05567333		
	0.2		−1.12887841			−1.11566871		
	0.3		−1.11001969			−1.15708609		
		$(s_Z^p,\ s_Z^d)$						
$+\hat{H}^{\text{nuc spin}}_{\text{Zeeman}}$								
	0.1	(1/2, 1)	−1.14070289			−1.05577273		
		(1/2, 0)	−1.14067954			−1.05574938		
		(1/2, −1)	−1.14065619			−1.05573770		
		(−1/2, 1)	−1.14055078			−1.05562063		
		(−1/2, 0)	−1.14052744			−1.05559728		
		(−1/2, −1)	−1.14050409			−1.05557393		
	0.2	(1/2, 1)	−1.12907721			−1.11586751		
		(1/2, 0)	−1.12903051			−1.11582081		
		(1/2, −1)	−1.12898381			−1.11577412		
		(−1/2, 1)	−1.12877300			−1.11556330		
		(−1/2, 0)	−1.12872631			−1.11551661		
		(−1/2, −1)	−1.12867961			−1.11546991		
	0.3	(1/2, 1)	−1.11031789			−1.15738430		
		(1/2, 0)	−1.11024785			−1.15731425		
		(1/2, −1)	−1.11017780			−1.15724420		
		(−1/2, 1)	−1.10986158			−1.15692799		
		(−1/2, 0)	−1.10979154			−1.15685794		
		(−1/2, −1)	−1.10972149			−1.15678789		

for the triplet state (we only consider the most energetically favorable alignment of the electron spins with the field) decrease with the field strength. At $B_Z = 0.1B_0$ the energy of singlet state is still lower than the energy of the triplet, but that changes with increasing field strength. Just above $B_Z = 0.2B_0$, the triplet state becomes the ground state of the HD molecule. This effect was observed before for the hydrogen molecule by Detmer et al. and the Turbiner's group [20,25,26], as well as in our work [7]. For H_2, Detmer at al. determined the single-triplet-crossing value of the field strength to be $0.18B_0$. A more refined value obtained by the Turbiner's group is $0.178B_0$. The addition of the spin Zeeman interaction that involves the spins of the proton and deuteron lowers the energy of both states. However, the relative order of the states remains the same — that is, just above the B_Z value of $0.2B_0$ the triplet energy dips below the energy of the singlet and the triplet becomes the ground state.

The addition of the interaction of the spins of the proton and the deuteron with the field splits both singlet and triplet energy levels into four levels corresponding to the possible combinations of the s_Z^p and s_Z^d quantum numbers. As expected, the splitting increases with the increasing field strength. The splitting due to the proton is almost by an order of magnitude larger than the splitting due to the deuteron.

The calculated average values of the proton–deuteron distance shown in Table 1 provide an interesting insight into the interaction of the singlet and triplet states of the HD molecule with the field. As expected, due to much weaker bonding, the average distance is significantly larger for the triplet state than for the singlet for each of the three field strengths. At $B_Z = 0.1B_0$, $\langle r_{pd}\rangle$ is equal to 1.45 a.u. for the singlet and 4.62 a.u. for the triplet. Also, for both states, the distance decreases with increasing B_Z. However, while for the singlet in going from $B_Z = 0.1B_0$ to $B_Z = 0.3B_0$, $\langle r_{pd}\rangle$ decreases to 1.42 a.u., for the triplet the decrease is much larger and at $B_Z = 0.3B_0$ $\langle r_{pd}\rangle$ shrinks to 3.30 a.u.

4. Summary

Our computational model for calculating bound states of molecular systems placed in a strong static magnetic field is augmented to include the interaction of the magnetic field with the spin and orbital magnetic momenta of the particles forming the system. In the model, the Born–Oppenheimer approximation is not assumed. The Hamiltonian representing the internal states of the molecule is obtained by subtracting the operator representing the kinetic energy of the center-of-mass motion from the laboratory-frame Hamiltonian. The wave functions of the molecule are expanded in terms of all-particle explicitly correlated Gaussian functions. The model is illustrated and tested in the calculations concerning the HD molecule. As noted before [7], the model predicts that at strong fields the HD ground state switches from the singlet state to the triplet state. Also, the calculations predict splitting of both singlet and triplet energy levels into four sublevels resulting from the interactions of the magnetic field with different spin states of the proton and the deuteron. As expected, the splitting increases with the strength of the field and it is significantly higher for the proton than for the deuteron. The difference results from the different values of the proton and deuteron g factors and from their different masses. Both of these factors make the proton splitting larger than the deuteron splitting.

CRediT authorship contribution statement

Ludwik Adamowicz: Methodology, Software, Data curation, Visualization, Writing. **Monika Stanke:** Software, Calculations, Methodology. **Erik Tellgren:** Supervision, Writing - review & editing. **Trygve Helgaker:** Supervision, Writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This work was supported by the Norwegian Research Council through its Centres of Excellence Scheme (project no. 262695) and through the European Research Council under the European Union Seventh Framework Program through the Advanced Grant ABACUS, ERC Grant Agreement no. 267683. This work was also supported by funds from the Polish National Science Centre granted on the basis of Decision no. DEC-2013/10/E/ST4/00033. and by the National Science Foundation, grant no. 1856702. LA thanks the Hylleraas Centre for supporting his visits to Oslo.

Appendix

A.1. Algorithm for calculating the $\hat{\mathrm{L}}_{Z_j}$ matrix element

The integral to be calculated is:

$$\langle\phi_k|\hat{\mathrm{L}}_{Z_j}|\phi_l\rangle$$

$$\hat{L}_{Z_j} = (\mathbf{R}_j \times \mathbf{p}_j)^Z = -i\left(R_j^X \nabla_{\mathbf{R}_j}^Y - R_j^Y \nabla_{\mathbf{R}_j}^X\right) \tag{16}$$

$$\langle\phi_k|\hat{\mathrm{L}}_{Z_j}|\phi_l\rangle = -i\left\{\langle\phi_k|R_j^X\nabla_{\mathbf{R}_j}^Y|\phi_l\rangle - \langle\phi_k|R_j^Y\nabla_{\mathbf{R}_j}^X|\phi_l\rangle\right\}$$
$$\equiv -i\left\{\langle\phi_k|\mathbf{R}^T\underline{\mathbf{M}}\nabla_{\mathbf{R}}|\phi_l\rangle - \langle\phi_k|\mathbf{R}^T\underline{\mathbf{N}}\nabla_{\mathbf{R}}|\phi_l\rangle\right\} \tag{17}$$

If $n = 2$ and $j = 1$ then:

$$\mathbf{R}^T\underline{\mathbf{M}}\nabla_{\mathbf{R}} = \mathbf{R}^T\underline{\mathbf{E}}_{12}\nabla_{\mathbf{R}} = \begin{pmatrix} X_1\\ Y_1\\ Z_1\\ X_2\\ Y_2\\ Z_2\end{pmatrix}^T \begin{pmatrix} 0&1&0&0&0&0\\ 0&0&0&0&0&0\\ 0&0&0&0&0&0\\ 0&0&0&0&0&0\\ 0&0&0&0&0&0\\ 0&0&0&0&0&0\end{pmatrix} \begin{pmatrix} \nabla_{X_1}\\ \nabla_{Y_1}\\ \nabla_{Z_1}\\ \nabla_{X_2}\\ \nabla_{Y_2}\\ \nabla_{Z_2}\end{pmatrix}$$

$$= \begin{pmatrix}0&X_1&0&0&0&0\end{pmatrix}\begin{pmatrix} \nabla_{X_1}\\ \nabla_{Y_1}\\ \nabla_{Z_1}\\ \nabla_{X_2}\\ \nabla_{Y_2}\\ \nabla_{Z_2}\end{pmatrix} = \mathbf{R}_1^X\nabla_{\mathbf{R}_1^Y}$$

$$\mathbf{R}^T\underline{\mathbf{N}}\nabla_{\mathbf{R}} = \mathbf{R}^T\underline{\mathbf{E}}_{21}\nabla_{\mathbf{R}} = \begin{pmatrix} X_1\\ Y_1\\ Z_1\\ X_2\\ Y_2\\ Z_2\end{pmatrix}^T \begin{pmatrix} 0&0&0&0&0&0\\ 1&0&0&0&0&0\\ 0&0&0&0&0&0\\ 0&0&0&0&0&0\\ 0&0&0&0&0&0\\ 0&0&0&0&0&0\end{pmatrix} \begin{pmatrix} \nabla_{X_1}\\ \nabla_{Y_1}\\ \nabla_{Z_1}\\ \nabla_{X_2}\\ \nabla_{Y_2}\\ \nabla_{Z_2}\end{pmatrix}$$

$$= \begin{pmatrix}Y_1&0&0&0&0&0\end{pmatrix}\begin{pmatrix} \nabla_{X_1}\\ \nabla_{Y_1}\\ \nabla_{Z_1}\\ \nabla_{X_2}\\ \nabla_{Y_2}\\ \nabla_{Z_2}\end{pmatrix} = \mathbf{R}_1^Y\nabla_{\mathbf{R}_1^X}$$

If $n = 2$ and $j = 2$ then

$$\mathbf{R}^T\underline{\mathbf{M}}\nabla_{\mathbf{R}} = \mathbf{R}^T\underline{\mathbf{E}}_{45}\nabla_{\mathbf{R}} = \begin{pmatrix} X_1\\ Y_1\\ Z_1\\ X_2\\ Y_2\\ Z_2\end{pmatrix}^T \begin{pmatrix} 0&0&0&0&0&0\\ 0&0&0&0&0&0\\ 0&0&0&0&0&0\\ 0&0&0&0&1&0\\ 0&0&0&0&0&0\\ 0&0&0&0&0&0\end{pmatrix} \begin{pmatrix} \nabla_{X_1}\\ \nabla_{Y_1}\\ \nabla_{Z_1}\\ \nabla_{X_2}\\ \nabla_{Y_2}\\ \nabla_{Z_2}\end{pmatrix}$$

$$= \begin{pmatrix}0&0&0&0&X_2&0\end{pmatrix}\begin{pmatrix} \nabla_{X_1}\\ \nabla_{Y_1}\\ \nabla_{Z_1}\\ \nabla_{X_2}\\ \nabla_{Y_2}\\ \nabla_{Z_2}\end{pmatrix} = \mathbf{R}_2^X\nabla_{\mathbf{R}_2^Y}$$

$$\mathbf{R}^T\underline{\mathbf{N}}\nabla_{\mathbf{R}} = \mathbf{R}^T\underline{\mathbf{E}}_{54}\nabla_{\mathbf{R}} = \begin{pmatrix} X_1\\ Y_1\\ Z_1\\ X_2\\ Y_2\\ Z_2\end{pmatrix}^T \begin{pmatrix} 0&0&0&0&0&0\\ 0&0&0&0&0&0\\ 0&0&0&0&0&0\\ 0&0&0&0&0&0\\ 0&0&0&1&0&0\\ 0&0&0&0&0&0\end{pmatrix} \begin{pmatrix} \nabla_{X_1}\\ \nabla_{Y_1}\\ \nabla_{Z_1}\\ \nabla_{X_2}\\ \nabla_{Y_2}\\ \nabla_{Z_2}\end{pmatrix}$$

$$= \begin{pmatrix}0&0&0&Y_2&0&0\end{pmatrix}\begin{pmatrix} \nabla_{X_1}\\ \nabla_{Y_1}\\ \nabla_{Z_1}\\ \nabla_{X_2}\\ \nabla_{Y_2}\\ \nabla_{Z_2}\end{pmatrix} = \mathbf{R}_2^Y\nabla_{\mathbf{R}_2^X}$$

Now we define some symbols used in the subsequent equations:

$$\underline{\mathbf{A}}_k + \underline{\tilde{\mathbf{A}}}_l = \underline{\mathbf{A}}_{kl} \tag{18}$$

$$\underline{\mathbf{A}}_k\mathbf{s}_k = \mathbf{e}_k \tag{19}$$

$$\underline{\tilde{\mathbf{A}}}_l\tilde{\mathbf{s}}_l = \tilde{\mathbf{e}}_l \tag{20}$$

$$\mathbf{e}_k + \tilde{\mathbf{e}}_l = \mathbf{e} \tag{21}$$

$$-\mathbf{s}_k^T\underline{\mathbf{A}}_k\mathbf{s}_k - \tilde{\mathbf{s}}_l^T\underline{\tilde{\mathbf{A}}}_l\tilde{\mathbf{s}}_l = -\eta \tag{22}$$

$$\underline{\mathbf{A}}_{kl}^{-1}\mathbf{e} = \mathbf{s} \tag{23}$$

$$\mathbf{e}^T\underline{\mathbf{A}}_{kl}^{-1}\mathbf{e} - \eta = \mathbf{s}^T\underline{\mathbf{A}}_{kl}\mathbf{s} - \eta = \gamma \tag{24}$$

$$-\eta = \gamma - \mathbf{s}^T\underline{\mathbf{A}}_{kl}\mathbf{s} \tag{25}$$

The ECG with shifted centers used in the present work can be written in the following form:

$$\phi_k = \exp\left[-\mathbf{R}^T\underline{\mathbf{A}}_k\mathbf{R} + 2\mathbf{R}^T\underline{\mathbf{A}}_k\mathbf{s}_k - \mathbf{s}_k^T\underline{\mathbf{A}}_k\mathbf{s}_k\right]. \tag{26}$$

Now the derivative of ϕ_k with respect to $\mathbf{R}$ is calculated:

$$\nabla_{\mathbf{R}}\phi_k \equiv \partial_\alpha\phi_k = -2\left[\underline{\mathbf{A}}_k\left(\mathbf{R} - \mathbf{s}_k\right)\right]_\alpha\phi_k, \tag{27}$$

and used to calculate expression (17):

$$\langle\phi_k|\mathbf{R}^T\underline{\mathbf{M}}\nabla_{\mathbf{R}}|\phi_l\rangle = -2\langle\phi_k|\mathbf{R}^T\underline{\mathbf{M}}\underline{\mathbf{A}}_l\left(\mathbf{R} - \mathbf{s}_l\right)\ |\phi_l\rangle \equiv$$
$$\equiv -2\langle\phi_k|\mathbf{R}^T\underline{\mathbf{W}}\left(\mathbf{R} - \mathbf{s}_l\right)\ |\phi_l\rangle, \tag{28}$$

We need integral of type $\langle\phi_k|\mathbf{R}^T\underline{\mathbf{W}}\left(\mathbf{R} - \mathbf{s}_n\right)\ |\phi_l\rangle$, where $\underline{\mathbf{W}} = \underline{\mathbf{M}}\underline{\mathbf{A}}_l$ or $\underline{\mathbf{W}} = \underline{\mathbf{N}}\underline{\mathbf{A}}_l$:

$$\langle\phi_k|\mathbf{R}^T\underline{\mathbf{W}}\left(\mathbf{R} - \mathbf{s}_l\right)\ |\phi_l\rangle = \langle\phi_k|\left(\mathbf{R}^T\underline{\mathbf{W}}\,\mathbf{R}\right)|\phi_l\rangle - \langle\phi_k|\mathbf{R}^T\underline{\mathbf{W}}\mathbf{s}_l\ |\phi_l\rangle =$$
$$= -\exp\left[-\eta\right]\partial_\beta\int_{-\infty}^{\infty}d^3R$$
$$\times\exp\left[-\mathbf{R}^T\left(\underline{\mathbf{A}}_{kl} + \beta\underline{\mathbf{W}}\right)\mathbf{R} + 2\left(\underline{\mathbf{A}}_k\mathbf{s}_k + \underline{\tilde{\mathbf{A}}}_l\tilde{\mathbf{s}}_l\right)^T\mathbf{R}\right]|_{\beta=0} +$$
$$-\exp\left[-\eta\right]\partial_\alpha\int_{-\infty}^{\infty}d^3R\ \exp\left[-\mathbf{R}^T\underline{\mathbf{A}}_{kl}\mathbf{R} + 2\left(\mathbf{e} + \frac{\alpha}{2}\underline{\mathbf{W}}\,\mathbf{s}_n\right)^T\mathbf{R}\right]|_{\alpha=0} =$$
$$= \langle\phi_k|\phi_l\rangle\left\{\frac{1}{2}\mathrm{R}^T\left[\underline{\mathbf{A}}_{kl}^{-1}\underline{\mathbf{W}}\right] + \left(\mathbf{s}^T\underline{\mathbf{W}}\,\mathbf{s}\right)\right\} - \langle\phi_k|\phi_l\rangle\left(\mathbf{s}^T\underline{\mathbf{W}}\ \ \mathbf{s}_l\right) =$$
$$= \langle\phi_k|\phi_l\rangle\left\{\ \frac{1}{2}\mathrm{R}^T\left[\underline{\mathbf{A}}_{kl}^{-1}\underline{\mathbf{W}}\right] + \left(\mathbf{s}^T\underline{\mathbf{W}}\ \ (\mathbf{s} - \mathbf{s}_l)\right)\right\}, \tag{29}$$

where $\langle\phi_k|\phi_l\rangle$ is the overlap integral. This concludes the derivation.

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