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ABSTRACT

The diatomic variational nuclear-motion program DUO is extended to calculate hyperfine-resolved spectra of homonuclear diatomic molecules. The hyperfine interactions considered include five nuclear magnetic dipole terms and one nuclear electric quadrupole term. Nuclear-exchange symmetry is explicitly incorporated, and the final hyperfine-resolved parity-adapted Hamiltonian is constructed in a complete angular-momentum basis. After diagonalization of this Hamiltonian, hyperfine-resolved line lists can be generated using transition electric dipole and quadrupole moment curves. To validate the implementation, we apply the extended program to H₂ and D₂, as well as ¹⁴N₂ and ¹⁴N₂⁺, and compare the calculated results with those from previous experimental and theoretical work and from the perturbative program PGOPHER; good agreement is obtained in all cases.

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I. INTRODUCTION

The nuclear spin of atoms in a molecule provides an additional source of angular momentum, which has often been neglected in theoretical treatments of infrared and vibronic spectra because the resulting splittings can be small and hard to resolve experimentally. However, in addition to new lines, hyperfine effects also lead to changes in selection rules where the selection rule for the total angular momentum quantum number including nuclear spin, F , namely $\Delta F = 0, \pm 1$, overrides the generally assumed selection rule on the total angular momentum J , $\Delta J = 0, \pm 1$. Indeed, when hyperfine effects are significant, transitions with $\Delta J > 1$ can be strong.¹ F is related to J by the vector addition expression $F = |\underline{J} + \underline{I}|$. Furthermore, the increasing precision with which high resolution spectra can be recorded has led to an increase in studies that are sensitive to individual hyperfine lines either because they are fully resolved or, at slightly lower resolution, because of their effect on the observed line shape. Such experimental progress needs to be matched by corresponding theoretical methods.

Qu *et al.*² adapted the diatomic variational nuclear motion program DUO³ to allow for the treatment of hyperfine effects in a single atom. This development allows the calculation of fully hyperfine-resolved rotational, rovibrational, and rovibronic spectra

of diatomic systems. The hyperfine-resolved version of DUO has been extensively applied to vanadium monoxide, ⁵¹V¹⁶O;^{4,5} the ⁵¹V nucleus has $I = \frac{7}{2}$ and particularly strong hyperfine effects.

In this study, we extend the hyperfine methodology of Qu *et al.*² to the important case of homonuclear diatomics comprising atoms with non-zero nuclear spin. As discussed below, there has been extensive theoretical work on this problem; see the comprehensive formulations by Cook and De Lucia,⁶ Kato,⁷ and Brown and Carrington (BC),⁸ for example. However, as far as we are aware, all previous studies have confined themselves to treating hyperfine effects as a perturbation; here we present a full formulation appropriate for use with a rigorous variational solution of the nuclear motion problem.

There are several advantages to our approach: First, a perturbative treatment might fail when there is strong state mixing, as in molecular Rydberg states.⁹ Second, our variational method requires fewer parameters, since the interactions are represented by R -dependent coupling curves and their vibrationally averaged matrix elements. It is therefore more suitable for molecules with large nuclear spins and strong hyperfine interactions, such as VO and V₂, where states with $|\Delta J|$ up to eight could be mixed. Similarly, as discussed below, our procedure automatically computes transition intensities with full allowance for J dependence.

In addition to deriving and implementing all the relevant matrix elements, we explicitly consider the important and fundamental hydrogen molecule in the form of H_2 and D_2 , as well as molecular nitrogen $^{14}N_2$ and its ion. Other species of interest for this approach for which hyperfine-resolved spectra have been observed include $^{23}Na_2$,^{10,11} $^{41}K_2$,¹² $^{85}Rb_2$,¹³ $^{133}Cs_2$,¹⁴ and $^{127}I_2$.^{15–17}

Ultra-high accuracy spectroscopic studies of molecular hydrogen are being increasingly used to probe fundamental physics.¹⁸ This has led to extensive theoretical studies of hyperfine effects in both H_2 and D_2 ,¹⁹ the construction of high accuracy beyond-Born–Oppenheimer potential energy curves (PECs),²⁰ and careful studies of electric field gradients.²¹ We make use of all of these studies below.

Similarly, for molecular nitrogen, there are careful theoretical studies of hyperfine structure,^{22,23} accurate potential curves,²⁴ and studies of fine structure effects in excited electronic states.²⁵ Quantum-logic spectroscopy of forbidden vibrational transitions in single nitrogen molecular ions (N_2^+) is being used for potential applications in quantum computers, atomic clocks, and quantum sensors.²⁶ Again, theoretical models of this system require a detailed understanding of the hyperfine structure^{27,28} and accurate potentials.²⁹

II. ALGORITHM OVERVIEW

The algorithm presented in this study extends the variational method by Qu *et al.*² to solve the total Hamiltonian for homonuclear diatomic molecules. The field-free Hamiltonian can be divided into two parts as

$$\mathcal{H}_{\text{tot}} = \mathcal{H}_{\text{rv}} + \mathcal{H}_{\text{hfs}}, \quad (1)$$

where $\mathcal{H}_{\text{rv}}$ is the rovibronic Hamiltonian used in the variational nuclear motion program DUO,³ and $\mathcal{H}_{\text{hfs}}$ is the hyperfine structure Hamiltonian considered in this study. Our algorithm first solves the eigenvalue problem of $\mathcal{H}_{\text{rv}}$ to obtain parity-conserved rovibronic eigenfunctions. These functions are then used as the basis for constructing and diagonalizing the hyperfine Hamiltonian. The details are presented in Subsections II A and II B.

A. Solution of rovibronic Hamiltonian

As implemented in DUO,³ the rovibronic Hamiltonian $\mathcal{H}_{\text{rv}}$ can be given as

$$\mathcal{H}_{\text{rv}} = \mathcal{H}_e + \mathcal{H}_v + \mathcal{H}_r + \mathcal{H}_{\text{fs}}, \quad (2)$$

where $\mathcal{H}_e$ is the electronic term, $\mathcal{H}_v$ is the vibrational term, $\mathcal{H}_r$ is the rotational term, and $\mathcal{H}_{\text{fs}}$ includes the additional terms in the rovibronic Hamiltonian caused by spin–orbit, spin–rotation, spin–spin, and Λ -doubling interactions.

As introduced in Sec. 2.1 of Ref. 3, DUO first solves the radial Schrödinger equation of each uncoupled electronic potential energy curve $V_{\text{state}}(R)$, as

$$\left[-\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + V_{\text{state}}(R) \right] \psi_v^{\text{state}}(R) = E_v^{\text{state}} \psi_v^{\text{state}}(R), \quad (3)$$

where $\hbar$ is the reduced Planck constant, μ is the reduced mass of the diatomic molecule, R is the internuclear distance, “state” denotes

a given electronic state, v labels the vibrational levels of this state, and E_v^{state} and $\psi_v^{\text{state}}(R)$ represent the vibrational energies and wave functions, respectively. A primitive basis set in the Hund’s case (a) representation is then constructed as

$$|k, J\rangle = |\text{state}, \Lambda, S, \Sigma\rangle |\text{state}, v\rangle |J, \Omega, M_J\rangle, \quad (4)$$

where S is the total electron spin; J is the total molecular angular momentum exclusive of nuclear spin; Σ , Λ , and Ω are, respectively, the projection of S , the total electronic orbital angular momentum L , and J along the internuclear axis; M_J is the projection of J along the space-fixed Z axis; $|\text{state}, \Lambda, S, \Sigma\rangle$ is the electronic eigenfunction; $|\text{state}, v\rangle$ is the vibrational eigenfunction of Eq. (3); and $|J, \Omega, M_J\rangle$ is the rotational eigenfunction of the symmetric-top. For convenience in what follows, we use index k to label the primitive basis functions for a given J . As M_J is not actually used in the field-free environment, we neglect it in this paper. The sum of $\mathcal{H}_e$ and $\mathcal{H}_v$ is diagonal in the basis set of Eq. (4), with the matrix elements equal to E_v^{state} . The matrix elements of $\mathcal{H}_r$ and $\mathcal{H}_{\text{fs}}$ are described in Ref. 3.

To account for the even (+) and odd (−) parity of the total molecular wave function under the space-fixed inversion, DUO forms the parity-conserved basis functions as linear combinations of basis functions in Eq. (4). In the current non-hyperfine rovibronic calculation in DUO, the field-free Hamiltonian is diagonalized in two parity-conserved blocks, regardless of whether the two nuclei are identical. These two blocks correspond to the two irreducible representations of the C_s point group. Diagonalizing each block gives the rovibronic eigenvalues and eigenfunctions.

However, the electronic states of homonuclear diatomics have an additional symmetry under inversion through the molecular center, conventionally denoted by gerade (g) and ungerade (u). In the absence of g/u-breaking interactions, we can assume there is no coupling between the g and u states. When the parity-conserved rovibronic eigenfunctions are passed to the hyperfine module, they are therefore further separated according to their g/u symmetry, giving four symmetry blocks. We use Γ to label these four irreducible representation blocks, which are related to A_1 , A_2 , B_1 , and B_2 in the representation of the C_{2v} point group. The rovibronic eigenvalues and eigenfunctions are then labeled as

$$\langle \phi_m^{\Gamma, J} | \mathcal{H}_{\text{rv}}^{\Gamma, J} | \phi_{m'}^{\Gamma, J} \rangle = \delta_{mm'} E_m^{\Gamma, J}, \quad (5)$$

where the index m labels the rovibronic eigenstates for a given (J , Γ) block. It should be emphasized that this four-block classification is only introduced when the rovibronic eigenfunctions are used to construct the hyperfine Hamiltonian. First, it allows the nuclear-spin basis to be filtered according to the permutation symmetry of the two identical nuclei, as discussed in Sec. II B. Second, it provides the symmetry labels required to apply the electric dipole (E1) and electric quadrupole (E2) transition selection rules, as described in Sec. IV.

B. Construction of hyperfine Hamiltonian

In the case of homonuclear diatomic molecules, the two identical nuclei with $I_1 = I_2$ have the same hyperfine coupling energies, so it is natural to adopt the equal coupling scheme

$$\begin{aligned} I_1 + I_2 &= I, \\ J + I &= F. \end{aligned} \quad (6)$$

As shown in Fig. 1, the two nuclear spins I_1 and I_2 are first coupled to give the total nuclear spin I , which is then coupled with the angular momentum J to obtain the total angular momentum F . The primitive basis is extended in the Hund's case (a_β) representation as

$$\begin{aligned} |k, J, I_1, I_2, I, F\rangle &= |k, J\rangle |J, I_1, I_2, I, F\rangle \\ &= |\text{state}, \Lambda, S, \Sigma\rangle |\text{state}, v\rangle |J, \Omega\rangle |J, I_1, I_2, I, F\rangle, \end{aligned} \quad (7)$$

where $I_1 = I_2$. β means the nuclear spin space is quantized in the laboratory frame. The matrix elements of the hyperfine Hamiltonian $\mathcal{H}_{\text{hfs}}$ under the primitive basis (7) are introduced in Sec. III. Although I_2 is equal to I_1 and does not explicitly appear in the matrix elements, we retain both labels of I_1 and I_2 in the basis to clarify the derivation process.

Due to the permutation symmetry of two identical nuclei, the nuclear spin states of homonuclear diatomic molecules can be classified into two symmetry species, conventionally denoted as ortho and para. Specifically, ortho nuclear-spin states satisfy $(-1)^{I-2I_1} = +1$, whereas para states satisfy $(-1)^{I-2I_1} = -1$. Because the total molecular wave function must obey the Pauli principle, only symmetry-allowed combinations of the nuclear spin and rovibronic parts can be retained. As a result, each symmetry block Γ only admits nuclear spin states with either even- I or odd- I , as summarized in Table I.

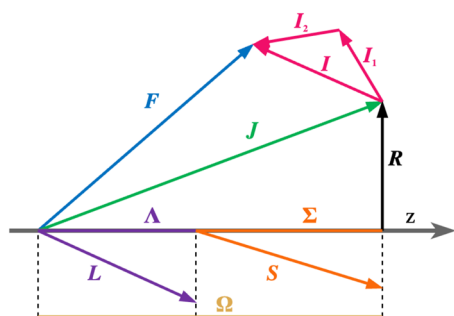


FIG. 1. Angular momentum coupling scheme used in the present study; the molecule is oriented along the z direction.

TABLE I. Four symmetry blocks used in the homonuclear hyperfine module and the corresponding allowed nuclear-spin states. Here, $\hat{E}^*$ denotes space-fixed inversion, which corresponds to reflection through the molecule-fixed xz plane in the molecule-fixed representation. $\hat{i}$ denotes inversion through the molecular center. $\hat{C}_2(y)$ is the geometric operation equivalent to the permutation $\hat{P}$ of the two identical nuclei when applied to all variables. Following Kato,⁷ $\hat{P} = \hat{C}_2(y) = \hat{\sigma}_v(xz)\hat{i} = \hat{E}^*\hat{i}$. Boson and Fermion refer to the quantum statistics of each identical nucleus. I_{tot} denotes the allowed values of the total nuclear spin I in each symmetry block.

Γ	$\hat{E}^*$	$\hat{i}$	$\hat{C}_2(y)$	Boson	Fermion	I_{tot}
A_1	+	g	s	Ortho	Para	Even
A_2	−	u	s	Ortho	Para	Even
B_1	−	g	a	Para	Ortho	Odd
B_2	+	u	a	Para	Ortho	Odd

We define the parity-conserved basis functions in the representation of the rovibronic eigenfunctions as

$$|\phi_m^{\Gamma,J}, I_1, I_2, I, F\rangle = \sum_k |k, J, I_1, I_2, I, F\rangle \langle k, J | \phi_m^{\Gamma,J} \rangle, \quad (8)$$

where $\langle k, J | \phi_m^{\Gamma,J} \rangle$ is the expansion coefficient of rovibronic eigenfunctions under the primitive basis set (4). The hyperfine Hamiltonian matrix is then transformed from the primitive basis set (7) to the parity-conserved basis set (8), which is given by

$$\begin{aligned} \langle \phi_m^{\Gamma,J}, I_1, I_2, I, F | \mathcal{H}_{\text{hfs}} | \phi_{m'}^{\Gamma,J'}, I_1, I_2, I', F \rangle \\ = \sum_{k,k'} \langle \phi_m^{\Gamma,J} | k, J \rangle \langle k, J, I_1, I_2, I, F | \mathcal{H}_{\text{hfs}} | k', J', I_1, I_2, I', F \rangle \langle k', J' | \phi_{m'}^{\Gamma,J'} \rangle. \end{aligned} \quad (9)$$

Accordingly, this transformation can be written in matrix form as

$$\mathbf{H}_{\text{hfs}}^{\Gamma,F} = (\Phi^{\Gamma,F})^\dagger \mathbf{H}_{\text{hfs}}^F \Phi^{\Gamma,F}, \quad (10)$$

where $\Phi^{\Gamma,F}$ is the transformation matrix with matrix elements of $\langle k, J | \phi_m^{\Gamma,J} \rangle$, while $\mathbf{H}_{\text{hfs}}^F$ and $\mathbf{H}_{\text{hfs}}^{\Gamma,F}$ are the hyperfine Hamiltonian matrices under the primitive basis set (7) and the parity-conserved basis set (8).

The total Hamiltonian can be obtained as the sum of the rovibronic and hyperfine Hamiltonian matrices, as

$$\mathbf{H}^{\Gamma,F} = \mathbf{H}_{\text{rv}}^{\Gamma,F} + \mathbf{H}_{\text{hfs}}^{\Gamma,F}. \quad (11)$$

Each block $\mathbf{H}^{\Gamma,F}$ is then diagonalized to give the hyperfine-resolved energies $E_l^{\Gamma,F}$ and wave functions $\psi_l^{\Gamma,F}$, as

$$\langle \psi_l^{\Gamma,F} | \mathcal{H}^{\Gamma,F} | \psi_{l'}^{\Gamma,F} \rangle = \delta_{ll'} E_l^{\Gamma,F}, \quad (12)$$

where the index l labels the hyperfine eigenstates for a given (F, Γ) block, and it can be written in matrix form as follows:

$$\mathbf{E}^{\Gamma,F} = (\mathbf{U}^{\Gamma,F})^\dagger \mathbf{H}^{\Gamma,F} \mathbf{U}^{\Gamma,F}, \quad (13)$$

with the matrix elements of $\mathbf{U}^{\Gamma,F}$ given as $\langle \phi_m^{\Gamma,J}, I_1, I_2, I, F | \psi_l^{\Gamma,F} \rangle$. Together with the transformation matrix, the final hyperfine wave functions can be represented as a matrix in the primitive Hund's case (a_β) basis set (7) as

$$\Psi^{\Gamma,F} = \Phi^{\Gamma,F} \mathbf{U}^{\Gamma,F}. \quad (14)$$

The matrix elements of $\Psi^{\Gamma,F}$ are $\langle k, J, I_1, I_2, I, F | \psi_l^{\Gamma,F} \rangle$, which are used when evaluating the transition moment matrix elements (see details in Sec. IV).

III. MATRIX ELEMENTS OF HYPERFINE HAMILTONIAN

In the absence of any external fields, the hyperfine structure Hamiltonian $\mathcal{H}_{\text{hfs}}$ includes several interaction terms following Brown and Carrington (BC),⁸ as

$$\mathcal{H}_{\text{hfs}} = \mathcal{H}_{\text{FC}} + \mathcal{H}_{\text{IL}} + \mathcal{H}_{\text{IJ}} + \mathcal{H}_{\text{IS}} + \mathcal{H}_{\text{II}} + \mathcal{H}_{\text{EQ}}, \quad (15)$$

where $\mathcal{H}_{\text{FC}}$ is the Fermi contact term, $\mathcal{H}_{\text{IL}}$ is the orbital hyperfine term, $\mathcal{H}_{\text{IJ}}$ is the nuclear spin-rotation term, $\mathcal{H}_{\text{IS}}$ and $\mathcal{H}_{\text{II}}$ denote the

electron–nuclear dipolar interaction and the nuclear–nuclear dipolar interaction, and $\mathcal{H}_{\text{EQ}}$ represents the nuclear electric quadrupole interaction. The physical meaning of these terms and their matrix elements in the primitive basis set (7) are given in Subsections III A–III F. These matrix elements are assumed to be diagonal in the electronic state such that

$$\text{state} = \text{state}', \quad S = S', \quad \text{and} \quad |\Lambda| = |\Lambda'|, \quad (16)$$

as we neglected any hyperfine coupling between different electronic states in the present study.

A. Fermi contact interaction

The Fermi contact interaction arises from the isotropic interaction between the electron and nuclear spin magnetic moments, which contributes only when the electron and the nucleus are at the same position in space. According to Eq. (7.144) of BC, the corresponding operator can be defined in the form of an irreducible spherical tensor as

$$\mathcal{H}_{\text{FC}} = \sum_n \sum_i \frac{2\mu_0}{3} g_S g_N \mu_B \mu_N T^1(\mathbf{i}_n) \cdot T^1(\mathbf{s}_i) \delta(r_{ni}), \quad (17)$$

where n labels the two nuclei and i runs over all electrons, μ_0 is the vacuum permeability, g_S is the free-electron g -factor, g_N is the nuclear g -factor, μ_B and μ_N are the Bohr magneton and the nuclear magneton, $T^1(\cdot)$ denotes a rank-1 tensor, $\mathbf{i}_n$ and $\mathbf{s}_i$ are the spins of nucleus n and electron i , and r_{ni} is the distance between them.

According to Eq. (5.173) of BC, the matrix elements of $\mathcal{H}_{\text{FC}}$ under the primitive basis can be decoupled in terms of two reduced matrix elements, as

$$\begin{aligned} &\langle k, J, I_1, I_2, I, F | \mathcal{H}_{\text{FC}} | k', J', I_1, I_2, I', F \rangle \\ &= \sum_n (-1)^{J'+I+F} \begin{Bmatrix} I & J & F \\ J' & I' & 1 \end{Bmatrix} \times \frac{2\mu_0}{3} g_S g_N \mu_B \mu_N \\ &\quad \times \langle I_1, I_2, I | T^1(\mathbf{i}_n) | I_1, I_2, I' \rangle \langle k, J | \sum_i T^1(\mathbf{s}_i) \delta(r_{ni}) | k', J' \rangle, \end{aligned} \quad (18)$$

where $\begin{Bmatrix} j_1 & j_2 & j_3 \\ j_4 & j_5 & j_6 \end{Bmatrix}$ is the Wigner 6- j symbol. The first reduced matrix element involving the nuclear spin is given in Eqs. (5.174) and (5.175) of BC, as

$$\begin{aligned} &\langle I_1, I_2, I | T^1(\mathbf{i}_1) | I_1, I_2, I' \rangle \\ &= (-1)^{I_1+I_2+I'+1} \sqrt{(2I+1)(2I'+1)} \begin{Bmatrix} I_1 & I & I_2 \\ I' & I_1 & 1 \end{Bmatrix} \langle I_1 | T^1(\mathbf{i}_1) | I_1 \rangle, \end{aligned} \quad (19)$$

for nucleus 1, and

$$\begin{aligned} &\langle I_1, I_2, I | T^1(\mathbf{i}_2) | I_1, I_2, I' \rangle \\ &= (-1)^{I_1+I_2+I+1} \sqrt{(2I+1)(2I'+1)} \begin{Bmatrix} I_2 & I & I_1 \\ I' & I_2 & 1 \end{Bmatrix} \langle I_2 | T^1(\mathbf{i}_2) | I_2 \rangle, \end{aligned} \quad (20)$$

for nucleus 2. Note that there is a difference between I' and I in their phase factors. Considering $I_1 = I_2$ for homonuclear species, the sum of Eqs. (19) and (20) can be taken as

$$\begin{aligned} &\langle I_1, I_2, I | T^1(\mathbf{i}_1) | I_1, I_2, I' \rangle + \langle I_1, I_2, I | T^1(\mathbf{i}_2) | I_1, I_2, I' \rangle \\ &= [(-1)^{I'} + (-1)^I] (-1)^{2I+1} \sqrt{(2I+1)(2I'+1)} \begin{Bmatrix} I_1 & I & I_1 \\ I' & I_1 & 1 \end{Bmatrix} \\ &\quad \times \sqrt{I(I+1)(2I+1)} \\ &= \delta_{II'} \sqrt{I(I+1)(2I+1)} = \langle I | T^1(I) | I' \rangle, \end{aligned} \quad (21)$$

which is equivalent to Eq. (30) of Qu *et al.*² In terms of two identical nuclei with equivalent coupling curves, the same simplification can be applied to the other rank-1 hyperfine interactions.

To evaluate the second reduced matrix element in Eq. (18) involving the electron spin, the spherical tensor of the electron spin should be transformed from the space-fixed frame to the molecule-fixed frame where the electron spin is quantized. According to (5.186) of BC, it can be written

$$\begin{aligned} &\langle k, J | \sum_i T^1(\mathbf{s}_i) \delta(r_{ni}) | k', J' \rangle \\ &= \langle k, J | \sum_i \sum_q \mathcal{D}_q^{(1)}(\omega)^* T_q^1(\mathbf{s}_i) \delta(r_{ni}) | k', J' \rangle \\ &= \sum_q (-1)^{J-\Omega} \sqrt{(2J+1)(2J'+1)} \begin{pmatrix} J & 1 & J' \\ -\Omega & q & \Omega' \end{pmatrix} \\ &\quad \times \langle \text{state}, v | \langle \text{state}, \Lambda, S, \Sigma | \sum_i T_q^1(\mathbf{s}_i) \delta(r_{ni}) \\ &\quad \times | \text{state}, \Lambda', S, \Sigma' \rangle | \text{state}, v' \rangle, \end{aligned} \quad (22)$$

where $\mathcal{D}_q^{(1)}(\omega)$ is the Wigner rotation matrix and $\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix}$ is a Wigner 3- j symbol. The Hund's case (a) basis is labeled by the total electron spin S instead of the individual one $\mathbf{s}_i$, so it is more convenient to project each $\mathbf{s}_i$ onto $\mathbf{S}$ as [see Eq. (7.150) of BC]

$$\mathbf{s}_i = \Phi_i^S \mathbf{S} = \frac{T_0^1(\mathbf{s}_i)}{\Sigma} \mathbf{S}, \quad (23)$$

where Φ_i^S is the projection operator for the spin of electron i onto the total electron spin $\mathbf{S}$. According to Eq. (8.374) of BC or Eq. (101) of Kato,⁷ there is

$$\begin{aligned} &\langle \text{state}, \Lambda, S, \Sigma | \sum_i T_q^1(\mathbf{s}_i) \delta(r_{ni}) | \text{state}, \Lambda', S, \Sigma' \rangle \\ &= \langle \text{state}, \Lambda, S, \Sigma | \sum_i \Phi_i^S \delta(r_{ni}) T_q^1(\mathbf{S}) | \text{state}, \Lambda', S, \Sigma' \rangle \\ &= (-1)^{S-\Sigma} \sqrt{S(S+1)(2S+1)} \begin{pmatrix} S & 1 & S \\ -\Sigma & q & \Sigma' \end{pmatrix} \\ &\quad \times \langle \text{state}, \Lambda | \sum_i \Phi_i^S \delta(r_{ni}) | \text{state}, \Lambda' \rangle. \end{aligned} \quad (24)$$

By combining Eqs. (21), (22), and (24) with Eq. (18), we obtain

$$\begin{aligned}
& \langle k, J, I_1, I_2, I, F | \mathcal{H}_{\text{FC}} | k', J', I_1, I_2, I', F \rangle \\
&= \sum_q \delta_{II'} \delta_{\Lambda\Lambda'} (-1)^{J'+I+F+J-\Omega+\Sigma-\Sigma'} \begin{Bmatrix} I & J & F \\ J' & I' & 1 \end{Bmatrix} \\
&\quad \times \begin{pmatrix} J & 1 & J' \\ -\Omega & q & \Omega' \end{pmatrix} \begin{pmatrix} S & 1 & S \\ -\Sigma & q & \Sigma' \end{pmatrix} \\
&\quad \times \sqrt{I(I+1)(2I+1)(2J+1)(2J'+1)S(S+1)(2S+1)} \\
&\quad \times \langle \text{state}, v | b_F(R) | \text{state}, v' \rangle, \quad (25)
\end{aligned}$$

where the Fermi contact constant $b_F(R)$ is defined as a function of internuclear distance R as

$$b_F(R) = \frac{2\mu_0}{3} g_{\text{SN}} \mu_B \mu_N \langle \text{state}, \Lambda | \sum_i \Phi_i^S \delta(r_{ni}) | \text{state}, \Lambda \rangle. \quad (26)$$

B. Orbital hyperfine interaction

The orbital hyperfine interaction originates from the coupling between the nuclear spin magnetic moment and the electronic orbital angular momentum, which is present only for electronic states with $\Lambda > 0$. According to Eqs. (1.68) and (1.69) of BC, it is defined as

$$\mathcal{H}_{\text{IL}} = \sum_n \sum_i 2g_N \mu_B \mu_N \frac{\mu_0}{4\pi} \mathbf{T}^1(\mathbf{i}_n) \cdot \mathbf{T}^1(\mathbf{i}_i) r_{ni}^{-3}, \quad (27)$$

where $\mathbf{i}_i$ is the orbital angular momentum of electron i . Following the derivation for the matrix element of $\mathcal{H}_{\text{FC}}$, the matrix elements of $\mathcal{H}_{\text{IL}}$ can be written as

$$\begin{aligned}
& \langle k, J, I_1, I_2, I, F | \mathcal{H}_{\text{IL}} | k', J', I_1, I_2, I', F \rangle \\
&= \delta_{II'} (-1)^{J'+F+I} \begin{Bmatrix} I & J & F \\ J' & I' & 1 \end{Bmatrix} \sqrt{I(I+1)(2I+1)} \\
&\quad \times 2g_N \mu_B \mu_N \frac{\mu_0}{4\pi} \langle k, J | \sum_i \mathbf{T}^1(\mathbf{i}_i) r_{ni}^{-3} | k', J' \rangle. \quad (28)
\end{aligned}$$

The reduced matrix element involving the electron orbital angular momentum is given as

$$\begin{aligned}
& \langle k, J | \sum_i \mathbf{T}^1(\mathbf{i}_i) r_{ni}^{-3} | k', J' \rangle \\
&= \langle k, J | \sum_i \sum_q \mathcal{D}_q^{(1)}(\omega)^* \mathbf{T}_q^1(\mathbf{i}_i) r_{ni}^{-3} | k', J' \rangle \\
&= \sum_q (-1)^{J-\Omega} \sqrt{(2J+1)(2J'+1)} \begin{pmatrix} J & 1 & J' \\ -\Omega & q & \Omega' \end{pmatrix} \\
&\quad \times \langle \text{state}, v | \langle \text{state}, \Lambda, S, \Sigma | \sum_i \mathbf{T}_q^1(\mathbf{i}_i) r_{ni}^{-3} \\
&\quad \times | \text{state}, \Lambda', S, \Sigma' \rangle | \text{state}, v' \rangle. \quad (29)
\end{aligned}$$

Similar to the projection of electron spin, each $\mathbf{i}_i$ is projected onto $\mathbf{L}$ as

$$\mathbf{i}_i = \Phi_i^L \mathbf{L} = \frac{\mathbf{T}_0^1(\mathbf{i}_i)}{\Lambda} \mathbf{L}, \quad (30)$$

where Φ_i^L is the projection operator for the orbital angular momentum of electron i . When the matrix elements off-diagonal in electronic states are ignored, only the $q = 0$ component is retained,

$$\begin{aligned}
& \langle \text{state}, \Lambda, S, \Sigma | \sum_i \mathbf{T}_0^1(\mathbf{i}_i) r_{ni}^{-3} | \text{state}, \Lambda', S, \Sigma' \rangle \\
&= \langle \text{state}, \Lambda, S, \Sigma | \sum_i \Phi_i^L r_{ni}^{-3} \mathbf{T}_0^1(\mathbf{L}) | \text{state}, \Lambda', S, \Sigma' \rangle \\
&= \delta_{\Sigma\Sigma'} \delta_{\Lambda\Lambda'} \Lambda \langle \text{state}, \Lambda | \sum_i \Phi_i^L r_{ni}^{-3} | \text{state}, \Lambda \rangle. \quad (31)
\end{aligned}$$

Together with Eqs. (28), (29), and (31), the matrix element of $\mathcal{H}_{\text{IL}}$ becomes

$$\begin{aligned}
& \langle k, J, I_1, I_2, I, F | \mathcal{H}_{\text{IL}} | k', J', I_1, I_2, I', F \rangle \\
&= \delta_{II'} \delta_{\Sigma\Sigma'} \delta_{\Lambda\Lambda'} \Lambda (-1)^{J'+F+I+J-\Omega} \begin{Bmatrix} I & J & F \\ J' & I' & 1 \end{Bmatrix} \begin{pmatrix} J & 1 & J' \\ -\Omega & 0 & \Omega' \end{pmatrix} \\
&\quad \times \sqrt{I(I+1)(2I+1)(2J+1)(2J'+1)} \\
&\quad \times \langle \text{state}, v | a(R) | \text{state}, v' \rangle, \quad (32)
\end{aligned}$$

where the orbital hyperfine constant $a(R)$ is defined as

$$a(R) = 2g_N \mu_B \mu_N \frac{\mu_0}{4\pi} \langle \text{state}, \Lambda | \sum_i \Phi_i^L r_{ni}^{-3} | \text{state}, \Lambda \rangle. \quad (33)$$

C. Nuclear spin-rotation interaction

The nuclear spin-rotation interaction arises from the coupling between the total nuclear spin and the total angular momentum exclusive of nuclear spin, which is defined in Eq. (8.170) of BC as

$$\mathcal{H}_{\text{IJ}} = c_I(R) \mathbf{T}^1(\mathbf{I}) \cdot \mathbf{T}^1(\mathbf{J}), \quad (34)$$

where $c_I(R)$ is the nuclear spin-rotation constant. The matrix element of $\mathcal{H}_{\text{IJ}}$ can be written as

$$\begin{aligned}
& \langle k, J, I_1, I_2, I, F | \mathcal{H}_{\text{IJ}} | k', J', I_1, I_2, I', F \rangle \\
&= (-1)^{J'+I+F} \begin{Bmatrix} I & J & F \\ J' & I' & 1 \end{Bmatrix} \sqrt{I(I+1)(2I+1)} \\
&\quad \times \langle k, J | c_I(R) \mathbf{T}^1(\mathbf{J}) | k', J' \rangle. \quad (35)
\end{aligned}$$

The reduced matrix element in Eq. (35) is much simpler, given that both $\mathbf{I}$ and $\mathbf{J}$ are quantized in the space-fixed frame and, therefore, need not be transformed to the molecule-fixed frame. By using Eq. (5.129) of BC, the matrix element of $\mathcal{H}_{\text{IJ}}$ becomes

$$\begin{aligned}
& \langle k, J, I_1, I_2, I, F | \mathcal{H}_{\text{IJ}} | k', J', I_1, I_2, I', F \rangle \\
&= \delta_{JJ'} \delta_{II'} \delta_{\Sigma\Sigma'} \delta_{\Lambda\Lambda'} (-1)^{J'+I+F} \begin{Bmatrix} I & J & F \\ J & I & 1 \end{Bmatrix} \\
&\quad \times \sqrt{I(I+1)(2I+1)J(J+1)(2J+1)} \\
&\quad \times \langle \text{state}, v | c_I(R) | \text{state}, v' \rangle. \quad (36)
\end{aligned}$$

Equivalently, Eq. (36) can be rewritten as

$$\begin{aligned} & \langle k, J, I_1, I_2, I, F | \mathcal{H}_{II} | k', J', I_1, I_2, I', F \rangle \\ &= \frac{1}{2} \delta_{JJ'} \delta_{II'} \delta_{\Sigma\Sigma'} \delta_{\Lambda\Lambda'} [F(F+1) - I(I+1) - J(J+1)] \\ & \times \langle \text{state}, v | c_I(R) | \text{state}, v' \rangle. \end{aligned} \quad (37)$$

D. Electron-nuclear dipolar interaction

The electron-nuclear dipolar interaction arises from the dipole interaction between the electron and nuclear spin magnetic moments, which depends on the orientation of the electron-nucleus separation vector and its magnitude. It is defined in Eq. (8.462) of BC as

$$\mathcal{H}_{IS} = \sum_n \sum_i -\sqrt{10} g_S \mu_B g_N \mu_N \frac{\mu_0}{4\pi} \mathbf{T}^1(\mathbf{i}_n) \cdot \mathbf{T}^1(\mathbf{s}_i, \mathbf{C}^2), \quad (38)$$

with the last rank-1 tensor defined in Eq. (8.377) of BC as

$$T_q^{(1)}(\mathbf{s}_i, \mathbf{C}^2) = \sum_{q_1, q_2} -\sqrt{3} (-1)^q T_{q_1}^1(\mathbf{s}_i) \frac{C_{q_2}^2(\theta_{ni}, \phi_{ni})}{r_{ni}^3} \begin{pmatrix} 1 & 2 & 1 \\ q_1 & q_2 & -q \end{pmatrix}, \quad (39)$$

where θ_{ni} and ϕ_{ni} are the spherical polar angles describing the direction from nucleus n to electron i in the molecule-fixed frame, and $C_{q_2}^2(\theta, \phi)$ is the normalized spherical harmonic

$$C_{q_2}^2(\theta, \phi) = \sqrt{\frac{4\pi}{5}} Y_{2q_2}(\theta, \phi). \quad (40)$$

As in the previous case, the matrix element of $\mathcal{H}_{IS}$ can be evaluated as

$$\begin{aligned} & \langle k, J, I_1, I_2, I, F | \mathcal{H}_{IS} | k', J', I_1, I_2, I', F \rangle \\ &= \delta_{II'} (-1)^{J'+F+I} \begin{Bmatrix} I & J & F \\ J' & I' & 1 \end{Bmatrix} \sqrt{I(I+1)(2I+1)} \\ & \times \sum_q (-1)^{J'-\Omega} \sqrt{(2J+1)(2J'+1)} \begin{pmatrix} J & 1 & J' \\ -\Omega & q & \Omega' \end{pmatrix} \\ & \times \sum_{q_1, q_2} \sqrt{30} g_S \mu_B g_N \mu_N \frac{\mu_0}{4\pi} (-1)^q \begin{pmatrix} 1 & 2 & 1 \\ q_1 & q_2 & -q \end{pmatrix} \\ & \times (-1)^{S-\Sigma} \begin{pmatrix} S & 1 & S \\ -\Sigma & q_1 & \Sigma' \end{pmatrix} \sqrt{S(S+1)(2S+1)} \langle \text{state}, v | \\ & \times \langle \text{state}, \Lambda | \sum_i \Phi_i^S C_{q_2}^2(\theta_{ni}, \phi_{ni}) r_{ni}^{-3} | \text{state}, \Lambda' \rangle | \text{state}, v' \rangle, \end{aligned} \quad (41)$$

where $q_2 = \Lambda' - \Lambda$ can take the values 0, ± 1 , and ± 2 . Note that the $q_2 = \pm 1$ terms are not included in this study, as they couple different electronic states with $\Delta\Lambda = \pm 1$. The matrix elements diagonal in Λ ($q_2 = 0$ and $q_1 = q$) are given as

$$\begin{aligned} & \langle k, J, I_1, I_2, I, F | \mathcal{H}_{IS} | k', J', I_1, I_2, I', F \rangle \\ &= \sum_q (-1)^q \delta_{II'} \delta_{\Lambda\Lambda'} (-1)^{J'+F+I+J-\Omega+\Sigma} \\ & \times \begin{Bmatrix} I & J & F \\ J' & I' & 1 \end{Bmatrix} \begin{pmatrix} J & 1 & J' \\ -\Omega & q & \Omega' \end{pmatrix} \begin{pmatrix} 1 & 2 & 1 \\ q & 0 & -q \end{pmatrix} \begin{pmatrix} S & 1 & S \\ -\Sigma & q & \Sigma' \end{pmatrix} \end{aligned}$$

$$\begin{aligned} & \times \sqrt{I(I+1)(2I+1)(2J+1)(2J'+1)S(S+1)(2S+1)} \\ & \times \sqrt{\frac{10}{3}} \langle \text{state}, v | c(R) | \text{state}, v' \rangle, \end{aligned} \quad (42)$$

where the diagonal electron-nuclear dipolar interaction constant $c(R)$ is defined as

$$c(R) = 3 g_S g_N \mu_B \mu_N \frac{\mu_0}{4\pi} \langle \text{state}, \Lambda | \sum_i \Phi_i^S C_0^2(\theta_{ni}, \phi_{ni}) r_{ni}^{-3} | \text{state}, \Lambda \rangle. \quad (43)$$

To account for the Λ -doubling terms of Π states, the matrix elements off-diagonal in Λ and Λ' ($q = \pm 1$, $q_1 = -q$ and $q_2 = 2q$) are

$$\begin{aligned} & \langle k, J, I_1, I_2, I, F | \mathcal{H}_{IS} | k', J', I_1, I_2, I', F \rangle \\ &= \sum_{q=\pm 1} (-1)^q \delta_{II'} (-1)^{J'+F+I+J-\Omega+\Sigma} \\ & \times \begin{Bmatrix} I & J & F \\ J' & I' & 1 \end{Bmatrix} \begin{pmatrix} J & 1 & J' \\ -\Omega & q & \Omega' \end{pmatrix} \begin{pmatrix} 1 & 2 & 1 \\ -q & 2q & -q \end{pmatrix} \begin{pmatrix} S & 1 & S \\ -\Sigma & -q & \Sigma' \end{pmatrix} \\ & \times \sqrt{I(I+1)(2I+1)(2J+1)(2J'+1)S(S+1)(2S+1)} \\ & \times (-\sqrt{5}) \langle \text{state}, v | d(R) | \text{state}, v' \rangle, \end{aligned} \quad (44)$$

where the off-diagonal electron-nuclear dipolar interaction constant d is defined as

$$\begin{aligned} d(R) &= -\sqrt{6} g_S g_N \mu_B \mu_N \frac{\mu_0}{4\pi} \\ & \times \langle \text{state}, \Lambda | \sum_i \Phi_i^S C_{\pm 2}^2(\theta_{ni}, \phi_{ni}) r_{ni}^{-3} | \text{state}, \Lambda' \rangle. \end{aligned} \quad (45)$$

E. Nuclear-nuclear dipolar interaction

Apart from the hyperfine interactions considered previously by Qu *et al.*,² the homonuclear diatomic molecule exhibits additional interactions between the spin magnetic moments of its two nuclei. The dipolar interaction between two nuclear spins is given in Eq. (8.9) of BC as

$$\mathcal{H}_{II} = g_N^2 \mu_N^2 \frac{\mu_0}{4\pi} \left[\frac{\mathbf{i}_1 \cdot \mathbf{i}_2}{R^3} - \frac{3(\mathbf{i}_1 \cdot \mathbf{R})(\mathbf{i}_2 \cdot \mathbf{R})}{R^5} \right], \quad (46)$$

or, equivalently, in the form of an irreducible rank-2 spherical tensor in Eq. (8.10) of BC as

$$\mathcal{H}_{II} = -\sqrt{6} g_N^2 \mu_N^2 \frac{\mu_0}{4\pi} \mathbf{T}^2(\mathbf{C}) \cdot \mathbf{T}^2(\mathbf{i}_1, \mathbf{i}_2). \quad (47)$$

Note that only the tensor (dipolar) interaction is included here. The scalar (or electron coupled) nuclear spin-spin interaction,³⁰ which has not yet been implemented in the current DUO, is expected to be much smaller³¹ than the dipolar interaction.

As in the previous treatment, it is convenient to decompose the matrix elements of $\mathcal{H}_{II}$ in terms of two reduced matrix elements as

$$\begin{aligned} & \langle k, J, I_1, I_2, I, F | \mathcal{H}_{II} | k', J', I_1, I_2, I', F \rangle \\ &= (-1)^{J'+I+F} \begin{Bmatrix} I & J & F \\ J' & I' & 2 \end{Bmatrix} \times (-\sqrt{6}) g_N^2 \mu_N^2 \frac{\mu_0}{4\pi} \\ & \times \langle I_1, I_2, I | \mathbf{T}^2(\mathbf{i}_1, \mathbf{i}_2) | I_1, I_2, I' \rangle \langle k, J | \mathbf{T}^2(\mathbf{C}) | k', J' \rangle. \end{aligned} \quad (48)$$

The first reduced matrix element involving i_1 and i_2 can be obtained from Eq. (8.14) of BC. Considering $I_1 = I_2$, it becomes

$$\begin{aligned} \langle I_1, I_2, I \| T^2(i_1, i_2) \| I_1, I_2, I' \rangle \\ = \sqrt{5} I_1 (I_1 + 1) (2I_1 + 1) \begin{Bmatrix} I_1 & I_1 & 1 \\ I_1 & I_1 & 1 \\ I' & I & 2 \end{Bmatrix} \sqrt{(2I_1 + 1)(2I' + 1)}. \end{aligned} \quad (49)$$

By transforming the tensor $T^2(C)$ from the space-fixed frame to the molecule-fixed frame, the second reduced matrix element becomes

$$\begin{aligned} \langle k, J \| T^2(C) \| k', J' \rangle \\ = \langle k, J \| \sum_q \mathcal{D}_q^{(2)}(\omega)^* T_q^2(C) \| k', J' \rangle \\ = \sum_q (-1)^{J-\Omega} \sqrt{(2J+1)(2J'+1)} \begin{Bmatrix} J & 2 & J' \\ -\Omega & q & \Omega' \end{Bmatrix} \\ \times \langle \text{state}, v, \Lambda, S, \Sigma | C_q^2(\theta_R, \phi_R) R^{-3} | \text{state}, v', \Lambda', S, \Sigma' \rangle, \end{aligned} \quad (50)$$

where θ_R and ϕ_R denote the spherical polar angles describing the direction of the internuclear axis. It is obvious that $\theta_R = 0$ in the molecule-fixed frame, leading to $q = 0$ and $C_0^2(\theta_R = 0, \phi_R) = 1$.

By substituting Eqs. (49) and (50) into Eq. (48), we obtain

$$\begin{aligned} \langle k, J, I_1, I_2, I, F | \mathcal{H}_{II} | k', J', I_1, I_2, I', F \rangle \\ = \delta_{\Sigma\Sigma'} \delta_{\Lambda\Lambda'} (-1)^{J'+I+F+J-\Omega} \begin{Bmatrix} I & J & F \\ J' & I' & 2 \end{Bmatrix} \\ \times \begin{Bmatrix} J & 2 & J' \\ -\Omega & 0 & \Omega' \end{Bmatrix} \begin{Bmatrix} I_1 & I_1 & 1 \\ I_1 & I_1 & 1 \\ I' & I & 2 \end{Bmatrix} \\ \times I_1 (I_1 + 1) (2I_1 + 1) \sqrt{(2J+1)(2J'+1)(2I_1+1)(2I'+1)} \\ \times (-\sqrt{30}) \langle \text{state}, v | g_N^2 \mu_N^2 \frac{\mu_0}{4\pi} R^{-3} | \text{state}, v' \rangle. \end{aligned} \quad (51)$$

We note that the nuclear–nuclear dipolar interaction can couple different nuclear spin states with $\Delta I = I' - I = \pm 2$, for example, between the $I = 0$ and $I' = 2$ states.

F. Nuclear electric quadrupole interaction

The nuclear electric quadrupole interaction arises from the coupling between the nuclear electric quadrupole moment and the electric field gradient at the nucleus, which is defined by Eq. (8.22) of BC as

$$\mathcal{H}_{EQ} = -e \sum_n T^2(\nabla E_n) \cdot T^2(Q_n), \quad (52)$$

where e is the elementary charge, ∇E_n is the electric field gradient at nucleus n , and Q_n is its nuclear electric quadrupole moment.

In the same way as stated earlier, the matrix elements of $\mathcal{H}_{EQ}$ can be written as

$$\begin{aligned} \langle k, J, I_1, I_2, I, F | \mathcal{H}_{EQ} | k', J', I_1, I_2, I', F \rangle \\ = \sum_n (-1)^{J'+I+F} \begin{Bmatrix} I & J & F \\ J' & I' & 2 \end{Bmatrix} \langle I_1, I_2, I \| e T^2(Q_n) \| I_1, I_2, I' \rangle \\ \times \langle k, J \| -T^2(\nabla E_n) \| k', J' \rangle. \end{aligned} \quad (53)$$

The first reduced matrix element of Q_n can be further reduced as

$$\begin{aligned} \langle I_1, I_2, I \| e T^2(Q_1) \| I_1, I_2, I' \rangle = (-1)^{I_1+I_2+I'+2} \sqrt{(2I_1+1)(2I'+1)} \\ \times \begin{Bmatrix} I_1 & I & I_2 \\ I' & I_1 & 2 \end{Bmatrix} \langle I_1 \| e T^2(Q_1) \| I_1 \rangle, \end{aligned} \quad (54)$$

for $n = 1$, and

$$\begin{aligned} \langle I_1, I_2, I \| e T^2(Q_2) \| I_1, I_2, I' \rangle = (-1)^{I_1+I_2+I'+2} \sqrt{(2I_1+1)(2I'+1)} \\ \times \begin{Bmatrix} I_2 & I & I_1 \\ I' & I_2 & 2 \end{Bmatrix} \langle I_2 \| e T^2(Q_2) \| I_2 \rangle, \end{aligned} \quad (55)$$

for $n = 2$. Note that the phase factors in Eqs. (54) and (55) differ by I' and I , respectively. The reduced matrix element for a single nucleus is defined in Eq. (8.491) of BC

$$\langle I_1 \| e T^2(Q_1) \| I_1 \rangle = \frac{eQ_1}{2} \begin{pmatrix} I_1 & 2 & I_1 \\ -I_1 & 0 & I_1 \end{pmatrix}^{-1}. \quad (56)$$

The two nuclei are equivalent in homonuclear diatomics, so the same expression applies to nucleus 2. In the following, we therefore denote Q_1 by Q . The second reduced matrix element about the electric field is obtained as

$$\begin{aligned} \langle k, J \| -T^2(\nabla E_n) \| k', J' \rangle \\ = \langle k, J \| -\sum_q \mathcal{D}_q^{(2)}(\omega)^* T_q^2(\nabla E_n) \| k', J' \rangle \\ = \sum_q (-1)^{J-\Omega} \sqrt{(2J+1)(2J'+1)} \begin{Bmatrix} J & 2 & J' \\ -\Omega & q & \Omega' \end{Bmatrix} \\ \times \langle \text{state}, v | \langle \text{state}, \Lambda, S, \Sigma | -T_q^2(\nabla E_n) \\ \times | \text{state}, \Lambda', S, \Sigma' \rangle | \text{state}, v' \rangle. \end{aligned} \quad (57)$$

Like the electron–nuclear dipolar interaction, the matrix elements of $\mathcal{H}_{EQ}$ should also be separated into diagonal and off-diagonal terms in Λ . By substituting Eqs. (54)–(57) into Eq. (53), the diagonal term is given as

$$\begin{aligned} \langle k, J, I_1, I_2, I, F | \mathcal{H}_{EQ} | k', J', I_1, I_2, I', F \rangle \\ = (-1)^{J'+2I_1+I+F+J-\Omega} \begin{Bmatrix} I & J & F \\ J' & I' & 2 \end{Bmatrix} \begin{Bmatrix} J & 2 & J' \\ -\Omega & 0 & \Omega' \end{Bmatrix} \\ \times \sqrt{(2J+1)(2J'+1)} [(-1)^{J'} + (-1)^I] \begin{Bmatrix} I_1 & I & I_1 \\ I' & I_1 & 2 \end{Bmatrix} \\ \times \begin{Bmatrix} I_1 & 2 & I_1 \\ -I_1 & 0 & I_1 \end{Bmatrix}^{-1} \sqrt{(2I_1+1)(2I'+1)} \\ \times \frac{1}{4} \langle \text{state}, v | eQ q_0(R) | \text{state}, v' \rangle, \end{aligned} \quad (58)$$

and the off-diagonal term is given as

$$\begin{aligned} & \langle k, J, I_1, I_2, I, F | \mathcal{H}_{\text{EQ}} | k', J', I_1, I_2, I', F \rangle \\ &= (-1)^{J'+2I_1+I+F+J-\Omega} \begin{Bmatrix} I & J & F \\ J' & I' & 2 \end{Bmatrix} \begin{Bmatrix} J & 2 & J' \\ -\Omega & \pm 2 & \Omega' \end{Bmatrix} \\ & \times \sqrt{(2J+1)(2J'+1)} [(-1)^{I'} + (-1)^I] \begin{Bmatrix} I_1 & I & I_1 \\ I' & I_1 & 2 \end{Bmatrix} \\ & \times \begin{Bmatrix} I_1 & 2 & I_1 \\ -I_1 & 0 & I_1 \end{Bmatrix}^{-1} \sqrt{(2I+1)(2I'+1)} \\ & \times \frac{1}{4\sqrt{6}} \langle \text{state}, v | eQ q_2(R) | \text{state}, v' \rangle, \end{aligned} \quad (59)$$

where the electric field gradient constants $q_0(R)$ and $q_2(R)$ are defined as

$$q_0(R) = -2 \langle \text{state}, \Lambda, S, \Sigma | T_0^2(\nabla E_n) | \text{state}, \Lambda, S, \Sigma \rangle, \quad (60)$$

and

$$q_2(R) = -2\sqrt{6} \langle \text{state}, \Lambda, S, \Sigma | T_{\pm 2}^2(\nabla E_n) | \text{state}, \Lambda', S, \Sigma \rangle. \quad (61)$$

In the homonuclear case considered in the present study, both nuclei ($n = 1, 2$) share the same $q_0(R)$ and $q_2(R)$. Likewise, the nuclear electric quadrupole interaction can couple different nuclear spin states with $\Delta I = I' - I = \pm 2$.

IV. LINE INTENSITY OF HYPERFINE TRANSITIONS

In the line-intensity module, DUO calculates the Einstein A coefficients for hyperfine-resolved transitions. These coefficients can then be passed to EXOCROSS³² or PYEXOCROSS³³ to compute temperature-dependent line intensities. In this section, we discuss only the calculation of Einstein A coefficients.

Let the lower and upper hyperfine states be denoted by

$$i \equiv (\Gamma'', F'', I''), \quad f \equiv (\Gamma', F', I'). \quad (62)$$

The Einstein coefficient of spontaneous emission from the upper hyperfine state f to the lower hyperfine state i is given as

$$A_{fi} = \frac{16\pi^3 \times 10^6}{3h\epsilon_0} \bar{\nu}_{fi}^3 \frac{1}{2F'+1} S_{fi}, \quad (63)$$

for the electric dipole (E1) transition and

$$A_{fi} = \frac{8\pi^5 \times 10^{10}}{5h\epsilon_0} \bar{\nu}_{fi}^5 \frac{1}{2F'+1} S_{fi}, \quad (64)$$

for the electric quadrupole (E2) transition, where ϵ_0 is the vacuum permittivity in $\text{F} \cdot \text{m}^{-1}$, h is the Planck constant in $\text{J} \cdot \text{s}$, $\bar{\nu}_{fi}$ is the transition frequency in cm^{-1} , and F' is the total angular momentum quantum number of the upper state. The transition line strength is in the unit of $\text{C}^2 \cdot \text{m}^2$ and $\text{C}^2 \cdot \text{m}^4$ for E1 and E2 transitions, respectively, and it is defined as

$$\begin{aligned} S_{fi} &= \left| \sum_{k', k''} \sum_{J', J''} \sum_{I', I''} \langle \Psi_{I', F'}^{\Gamma', F'} | k', J', I_1, I_2, I', F' \rangle \right. \\ & \times \langle k', J', I_1, I_2, I', F' | T^\lambda(X) | k'', J'', I_1, I_2, I'', F'' \rangle \\ & \times \langle k'', J'', I_1, I_2, I'', F'' | \Psi_{I'', F''}^{\Gamma'', F''} \rangle \left. \right|^2, \end{aligned} \quad (65)$$

where the summations run over all primitive hyperfine basis functions contributing to the upper and lower hyperfine eigenstates. The coefficients $\langle \Psi_{I', F'}^{\Gamma', F'} | k', J', I_1, I_2, I', F' \rangle$ and $\langle k'', J'', I_1, I_2, I'', F'' | \Psi_{I'', F''}^{\Gamma'', F''} \rangle$ are the matrix elements of $(\Psi^{\Gamma', F'})^\dagger$ and $\Psi^{\Gamma'', F''}$, respectively, as introduced in Sec. II B.

The reduced matrix elements of the transition moments under the primitive basis set (7) are given by

$$\begin{aligned} & \langle k', J', I_1, I_2, I', F' | T^\lambda(X) | k'', J'', I_1, I_2, I'', F'' \rangle \\ &= \delta_{I' I''} (-1)^{J'+I'+F''+\lambda} \sqrt{(2F'+1)(2F''+1)} \begin{Bmatrix} J'' & F'' & I' \\ F' & J' & \lambda \end{Bmatrix} \\ & \times \sum_{q=-\lambda}^{\lambda} (-1)^{J'-\Omega'} \sqrt{(2J'+1)(2J''+1)} \begin{Bmatrix} J' & \lambda & J'' \\ -\Omega' & q & \Omega'' \end{Bmatrix} \\ & \times \langle \text{state}', v' | X_q(R) | \text{state}'', v'' \rangle, \end{aligned} \quad (66)$$

where

$$X_q(R) = \langle \text{state}', \Lambda', S', \Sigma' | T_q^\lambda(X) | \text{state}'', \Lambda'', S'', \Sigma'' \rangle. \quad (67)$$

For the E1 transitions, there is $\lambda = 1$ and $X_q(R)$ becomes the electric dipole moment curve $\mu_q(R)$, as described in Ref. 3. The E1 transition selection rules are

$$\begin{aligned} F: \quad \Delta F &= 0, \pm 1, & F' + F'' &\geq 1, \\ \Gamma: \quad A_1 &\leftrightarrow A_2, & B_1 &\leftrightarrow B_2. \end{aligned} \quad (68)$$

For the E2 transition, there is $\lambda = 2$, and $X_q(R)$ becomes the electric quadrupole moment curve $Q_q(R)$, as described in Ref. 34. The E2 transition selection rules are

$$\begin{aligned} F: \quad \Delta F &= 0, \pm 1, \pm 2, & F' + F'' &\geq 2, \\ \Gamma: \quad A_1 &\leftrightarrow A_1, & A_2 &\leftrightarrow A_2, & B_1 &\leftrightarrow B_1, & B_2 &\leftrightarrow B_2. \end{aligned} \quad (69)$$

V. CODE VERIFICATION

To verify the present hyperfine implementation for homonuclear diatomic molecules, we calculated the hyperfine-resolved spectra for H_2 , D_2 , $^{14}\text{N}_2^+$, and $^{14}\text{N}_2$ molecules. The numerical input settings used in these calculations ensure that the rovibronic energies are converged to 10^{-6} cm^{-1} , while the hyperfine shifts are converged to 10^{-9} – 10^{-11} cm^{-1} . To check our calculation, we compared the results of DUO with those in previous theoretical or experimental work. As an additional check, we also performed calculations with the perturbation-theory-based program PGOPHER.³⁵ The details of the verification are given in Subsections V A–V C.

A. $X^1\Sigma_g^+$ state of H_2 and D_2

Using DUO, we calculated the hyperfine-resolved spectra of the $X^1\Sigma_g^+$ state of H_2 and D_2 . The potential energy curve (PEC)

is obtained from Ref. 20. For H₂, only two hyperfine terms need to be considered: the nuclear spin–rotation interaction and the nuclear–nuclear dipolar interaction. The nuclear spin–rotation constant curve is obtained from Jóźwiak *et al.*¹⁹ We flipped the sign of this curve for use as input to DUO as in Sec. 8.2.1 of BC, where the nuclear spin–rotation interaction is defined as a positive operator but with a negative value for the coefficient *c*_I. This is equivalent to the sign correction given in the corrigendum of Jóźwiak *et al.*³⁶ It is also worth noting that the expression of the nuclear–nuclear dipolar interaction derived in this study is consistent with that corrected in the same corrigendum. For D₂, there is an additional hyperfine term, namely the nuclear electric quadrupole interaction. The

electric quadrupole moment is set as 0.285 98 fm² for the deuteron. The electric field gradient curve at the nucleus is taken from Ref. 21. Since our definition of electric field gradient differs from that in Ref. 21, we multiply this curve by a factor of two.

We also calculated the Einstein *A* coefficient for the electric quadrupole transition within the *X* ¹Σ_g⁺ state. The electric quadrupole moment curve is also taken from Jóźwiak *et al.*¹⁹ Note that the quadrupole curve is given by Jóźwiak *et al.* in terms of the Cartesian components in the Buckingham convention, but DUO requires the curve provided in the spherical tensor representation in the Shortley convention.³⁴ This transformation of conventions introduces a factor of $\sqrt{\frac{2}{3}}$.

TABLE II. Comparison of the hyperfine shifts and line intensities for the Q(1) line of the 1-0-band electric-quadrupole transition of H₂. The upper and lower level energies *E'* and *E''* are given in cm^{−1}. The hyperfine shifts are given in MHz. The line intensities are calculated via ExoCross,³² given in units of 10^{−27} cm/molecule at 296 K.

<i>F'</i> ← <i>F''</i>	<i>E'</i>	<i>E''</i>	Hyperfine shift		Line intensity	
			DUO	Reference 19	DUO	Reference 19
2 ← 0	4272.828 305 171 5	118.429 205 637 3	−0.600 99	−0.600 98	2.409 00	2.411 13
2 ← 1	4272.828 305 171 5	118.429 187 408 0	−0.054 48	−0.054 48	5.420 26	5.425 04
2 ← 2	4272.828 305 171 5	118.429 185 560 3	0.000 91	0.000 91	4.215 76	4.219 47
1 ← 1	4272.828 307 096 6	118.429 187 408 0	0.003 23	0.003 23	1.806 75	1.808 35
1 ← 2	4272.828 307 096 6	118.429 185 560 3	0.058 62	0.058 62	5.420 26	5.425 04
0 ← 2	4272.828 324 743 6	118.429 185 560 3	0.587 66	0.587 65	2.409 00	2.411 13

TABLE III. Comparison of the hyperfine shifts and line intensities for the S(2) line of the 2 – 0 band electric-quadrupole transition of D₂. The upper and lower level energies *E'* and *E''* are given in cm^{−1}. The hyperfine shifts are given in MHz. The line intensities are calculated via ExoCross,³² given in units of 10^{−33} cm/molecule at 296 K.

<i>F'</i> ← <i>F''</i>	<i>E'</i>	<i>E''</i>	Hyperfine shift		Line intensity	
			DUO	Reference 19	DUO	Reference 19
4+ ← 2+	6417.863 322 032 7	178.974 316 735 5	−0.171 98	−0.171 98	2340.85	2343.26
4+ ← 3	6417.863 322 032 7	178.974 314 725 7	−0.111 72	−0.111 72	9876.85	9887.14
2 ← 2+	6417.863 324 423 9	178.974 316 735 5	−0.100 29	−0.100 29	4081.16	4085.41
3 ← 2+	6417.863 325 617 3	178.974 316 735 5	−0.064 51	−0.064 51	17 855.1	17 873.7
2 ← 3	6417.863 324 423 9	178.974 314 725 7	−0.040 04	−0.040 03	568.991	569.583
6 ← 4	6417.863 320 509 3	178.974 310 752 8	−0.038 29	−0.038 29	115 063	115 182
5 ← 3	6417.863 324 767 5	178.974 314 725 7	−0.029 74	−0.029 74	73 020.5	73 096.5
3 ← 3	6417.863 325 617 3	178.974 314 725 7	−0.004 26	−0.004 26	6638.23	6645.13
4+ ← 2+	6417.863 327 917 2	178.974 316 735 5	0.004 44	0.004 44	55 381.6	55 439.3
4+ ← 4	6417.863 322 032 7	178.974 310 752 8	0.007 38	0.007 38	1154.44	1155.64
4+ ← 2−	6417.863 322 032 7	178.974 310 554 3	0.013 33	0.013 33	66 286.6	66 355.6
2 ← 1	6417.863 324 423 9	178.974 312 681 1	0.021 26	0.021 26	21 242.3	21 264.4
3 ← 1	6417.863 325 617 3	178.974 312 681 1	0.057 04	0.057 03	26 552.9	26 580.5
2 ← 0	6417.863 324 423 9	178.974 311 337 5	0.061 54	0.061 54	15 931.7	15 948.3
4+ ← 3	6417.863 327 917 2	178.974 314 725 7	0.064 69	0.064 69	21 417.7	21 439.9
2 ← 4	6417.863 324 423 9	178.974 310 752 8	0.079 07	0.079 07	9.0316	9.041 00
2 ← 2−	6417.863 324 423 9	178.974 310 554 3	0.085 02	0.085 02	2421.59	2424.11
5 ← 4	6417.863 324 767 5	178.974 310 752 8	0.089 37	0.089 37	24 340.2	24 365.5
3 ← 4	6417.863 325 617 3	178.974 310 752 8	0.114 84	0.114 84	316.106	316.435
3 ← 2−	6417.863 325 617 3	178.974 310 554 3	0.120 79	0.120 79	10 594.5	10 605.5
4+ ← 4	6417.863 327 917 2	178.974 310 752 8	0.183 79	0.183 79	2503.36	2505.97
4+ ← 2−	6417.863 327 917 2	178.974 310 554 3	0.189 74	0.189 74	356.091	356.473

We compare our calculation results with the values of Jóźwiak *et al.*,¹⁹ who use perturbation theory to predict hyperfine effects. Note that the non-hyperfine-resolved rovibrational transition frequencies by Jóźwiak *et al.*¹⁹ were not calculated based on the PEC in Ref. 20, so we only focus on the hyperfine shift relative to those transition frequencies. As the nuclear spin of the H nucleus is $\frac{1}{2}$, the total nuclear spin of H_2 can be 0 and 1 for the para and ortho states, respectively. To study the hyperfine structure, only the ortho states with $I = 1$ need to be considered. For the $X^1\Sigma_g^+$ state of H_2 , the electronic and vibrational parts are symmetric under nuclear exchange, and the rotational part has exchange symmetry $(-1)^J$. Since the protons are fermions, the ortho states with $I = 1$ occur only for odd J . Meanwhile, the nuclear spin of the D nucleus is 1, so the total nuclear spin of D_2 can be 0, 1, and 2. We focus only on the ortho states with $I = 0$ and 2, where the nuclear electric quadrupole interaction leads to coupling between $I = 0$ and $I = 2$. Therefore, the hyperfine state of $F = J$ has two components coming from $I = 0$ and $I = 2$. We use labels + and - to denote the higher and lower levels, respectively. Similarly, only rovibrational states with even J exist in the $X^1\Sigma_g^+$ state of ortho- D_2 . Here, we take the Q(1) line of the 1-0 band of H_2 and the S(2) line of the 2-0 band of D_2 as examples. The non-hyperfine-resolved transition frequencies of these two lines are $4154.399\,119\,580\,9\text{ cm}^{-1}$ and $6238.889\,011\,033\,7\text{ cm}^{-1}$; these values were calculated using the non-hyperfine rovibronic module of DUO. As shown in Tables II and III, the hyperfine shifts agree very well. The line intensities were calculated using EXOCROSS³² from the Einstein A coefficients obtained with DUO; the small relative differences between the Duo and reference values arise mainly from the use of different rovibrational transition frequencies in the calculations. Another source for this discrepancy is the approximate treatment of rovibrational mixing, especially for high- J states; see Appendix B.

B. $X^2\Sigma_g^+$ and $B^2\Sigma_u^+$ states of N_2^+

Compared with the $^1\Sigma$ states discussed earlier for H_2 and D_2 , open-shell Σ states have additional magnetic hyperfine interactions, including the Fermi contact and electron-nuclear dipolar interactions, which are usually much stronger than the nuclear spin-rotation and nuclear-nuclear dipolar terms considered in Sec. V A.

To test these electron-spin-dependent terms, we calculated the hyperfine-resolved level energies for the $X^2\Sigma_g^+$ state of N_2^+ . We also included the excited state $B^2\Sigma_u^+$ to check the implementation of the four irreducible-representation blocks. The PECs are obtained from Ref. 29, with an updated curve for the $X^2\Sigma_g^+$ state supplied by Prof. Andrey Stolyarov from the Faculty of Chemistry, Moscow State University. The spin-rotation constant and the corresponding hyperfine constants are taken from Mansour *et al.*,^{27,28} For the $X^2\Sigma_g^+$ state, the spin-rotation constant γ_{SR} is set to 276.922 53 MHz, while the hyperfine constants b_F , c , eQq_0 , and c_I are set to 100.6040, 84.5838, 0.7079, and 0.011 32 MHz, respectively. For the $B^2\Sigma_u^+$ state, the parameters γ_{SR} and b_F are set to 0.023 934 and $0.023\,27\text{ cm}^{-1}$, respectively.

We compared our calculated results for the $X^2\Sigma_g^+$ state with the measurements of Mansour *et al.*²⁷ Although the rotational quantum number N in Hund's case (b) is not adopted in DUO explicitly, it is still useful for assigning the rovibrational levels. For the $X^2\Sigma_g^+$ state of $^{14}N_2^+$, the para species corresponds to odd N , while the ortho

species corresponds to even N . As illustrated in Fig. 2, each rotational level N is split into the spin-rotation components $J = N \pm 1/2$, and each J level is split into hyperfine levels labeled by I and F . As listed in Table IV, the magnetic-dipole transition frequencies of $\Delta J = \pm 1$ are in good agreement between DUO and the experimental values of Mansour *et al.*,²⁷ with rms residuals of about 12 kHz and maximum residuals below 25 kHz. The remaining discrepancies mainly arise from two differences in the Hamiltonian. First, Mansour *et al.* used the nuclear spin-rotation operator $c_I \mathbf{I} \cdot \mathbf{N}$, whereas DUO uses $c_I \mathbf{I} \cdot \mathbf{J}$. Second, Mansour *et al.* neglected couplings between different N blocks, while these couplings are included in DUO.

To check the implementation of the E1 transition-intensity calculation, we considered the hyperfine-resolved electric-dipole transition between the $X^2\Sigma_g^+$ and $B^2\Sigma_u^+$ states and calculated the transition frequencies and Einstein A coefficients for the $B-X$ (0, 1) band. The R -dependent $B-X$ transition dipole moment curve was taken from the *ab initio* calculation of Ref. 37. In DUO, this curve is directly integrated with the vibrational wave functions. For the $B-X$ (0, 1) band, the resulting vibrational transition moment is $0.963\,286\,199\text{ D}$. We compared the results with those obtained from PGOPHER, which requires the vibrationally averaged spectroscopic constants. The rotational constants B_v obtained from DUO are $1.903\,416\,70\text{ cm}^{-1}$ for $X^2\Sigma_g^+$ with $v'' = 1$ and $2.074\,755\,26\text{ cm}^{-1}$ for $B^2\Sigma_u^+$ with $v' = 0$. The corresponding centrifugal distortion constants D_v are directly taken from Ref. 28, with values of $5.9813 \times 10^{-6}\text{ cm}^{-1}$ and $6.3242 \times 10^{-6}\text{ cm}^{-1}$, respectively.

As listed in Table V, the transition frequencies obtained by DUO and PGOPHER agree very well, while the Einstein A coefficients show small differences. Only selected low- J transitions are

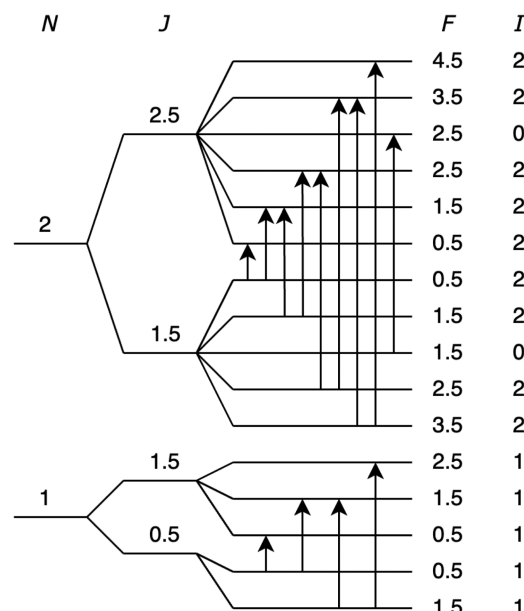


FIG. 2. Schematic energy-level diagram for the hyperfine-resolved energy levels of $N = 1, 2$ in the $X^2\Sigma_g^+$ state of $^{14}N_2^+$. The arrows indicate the magnetic-dipole transitions listed in Table IV. Note that the vertical positions are schematic and not drawn to scale.

TABLE IV. Comparison of the magnetic-dipole transition frequencies within the $X^2\Sigma_g^+$ state of $^{14}\text{N}_2^+$ with experimental values and uncertainties from Mansour *et al.*²⁷ The hyperfine-resolved upper and lower energies, E' and E'' , are given in cm^{-1} . Transition frequencies and uncertainties are given in MHz.

N	I	$(J', F') \leftarrow (J'', F'')$	E'	E''	Transition frequency			
					DUO	Fit ²⁷	Obs. ²⁷	Unc. ²⁷
1	1	1.5, 0.5 $\leftarrow$ 0.5, 0.5	2178.830 727 329	2178.818 657 060	361.858	361.866	361.866	0.011
1	1	1.5, 1.5 $\leftarrow$ 0.5, 0.5	2178.832 534 586	2178.818 657 060	416.038	416.040	416.043	0.009
1	1	1.5, 1.5 $\leftarrow$ 0.5, 1.5	2178.832 534 586	2178.818 533 119	419.753	419.748	419.748	0.011
1	1	1.5, 2.5 $\leftarrow$ 0.5, 1.5	2178.834 418 431	2178.818 533 119	476.230	476.219	476.222	0.009
2	2	2.5, 0.5 $\leftarrow$ 1.5, 0.5	2186.447 257 964	2186.429 051 431	545.818	545.834	545.836	0.009
2	2	2.5, 1.5 $\leftarrow$ 1.5, 0.5	2186.448 537 640	2186.429 051 431	584.182	584.193	584.195	0.009
2	2	2.5, 1.5 $\leftarrow$ 1.5, 1.5	2186.448 537 640	2186.428 190 677	609.987	609.997	610.000	0.010
2	2	2.5, 2.5 $\leftarrow$ 1.5, 1.5	2186.450 281 216	2186.428 190 677	662.258	662.262	662.259	0.009
2	2	2.5, 2.5 $\leftarrow$ 1.5, 2.5	2186.450 281 216	2186.427 133 100	693.963	693.963	693.961	0.009
2	2	2.5, 3.5 $\leftarrow$ 1.5, 2.5	2186.452 149 661	2186.427 133 100	749.978	749.973	749.967	0.009
2	2	2.5, 3.5 $\leftarrow$ 1.5, 3.5	2186.452 149 661	2186.426 201 661	777.901	777.882	777.884	0.012
2	2	2.5, 4.5 $\leftarrow$ 1.5, 3.5	2186.453 838 123	2186.426 201 661	828.520	828.495	828.496	0.009
2	0	2.5, 2.5 $\leftarrow$ 1.5, 1.5	2186.451 021 434	2186.427 928 222	692.317	692.311	692.315	0.009

TABLE V. Comparison of hyperfine-resolved transition frequencies and Einstein A coefficients for the $B-X(0, 1)$ band of $^{14}\text{N}_2^+$. All listed transitions satisfy $\Delta N = \Delta J = \Delta F = -1$. The first two rows correspond to the $P(1)$ branch, while the remaining rows correspond to the $P(2)$ branch. Frequencies are given in cm^{-1} and Einstein A coefficients are in s^{-1} . PGO stands for PGOPHER.

I	$J' \leftarrow J''$	$F' \leftarrow F''$	Transition frequency		Einstein A coefficient	
			DUO	PGO	DUO	PGO
1	0.5 $\leftarrow$ 1.5	0.5 $\leftarrow$ 1.5	23 376.171 476 60	23 376.171 477	8.6385×10^5	8.6371×10^5
1	0.5 $\leftarrow$ 1.5	1.5 $\leftarrow$ 2.5	23 376.204 497 76	23 376.204 498	1.8590×10^6	1.8587×10^6
0	0.5 $\leftarrow$ 1.5	0.5 $\leftarrow$ 1.5	23 372.724 904 70	23 372.724 905	2.4754×10^6	2.4747×10^6
0	1.5 $\leftarrow$ 2.5	1.5 $\leftarrow$ 2.5	23 372.737 712 48	23 372.737 712	2.2298×10^6	2.2291×10^6
2	1.5 $\leftarrow$ 2.5	0.5 $\leftarrow$ 1.5	23 372.705 291 28	23 372.705 291	8.5852×10^5	8.5827×10^5
2	0.5 $\leftarrow$ 1.5	1.5 $\leftarrow$ 2.5	23 372.714 557 49	23 372.714 557	1.1345×10^6	1.1341×10^6
2	1.5 $\leftarrow$ 2.5	1.5 $\leftarrow$ 2.5	23 372.737 960 03	23 372.737 960	7.3955×10^5	7.3934×10^5
2	0.5 $\leftarrow$ 1.5	2.5 $\leftarrow$ 3.5	23 372.703 580 15	23 372.703 580	1.8178×10^6	1.8173×10^6
2	1.5 $\leftarrow$ 2.5	2.5 $\leftarrow$ 3.5	23 372.748 000 36	23 372.748 000	1.3001×10^6	1.2997×10^6
2	1.5 $\leftarrow$ 2.5	3.5 $\leftarrow$ 4.5	23 372.758 165 80	23 372.758 166	1.8584×10^6	1.8579×10^6

listed in Table V. As J becomes higher, the differences in the Einstein A coefficients become larger as well. In DUO, the line strength is evaluated using variational eigenfunctions constructed from the complete angular momentum basis, whereas the PGOPHER calculation is based on a perturbation Hamiltonian for a given vibrational level. Therefore, an approximate treatment of rovibrational mixing can lead to small differences in the line intensities, especially for high- J states; see Appendix B.

C. $B^3\Pi_g$ state of N_2

Compared with the Σ states discussed earlier, the orbital hyperfine interaction needs to be considered for the electronic states with non-zero Λ . In addition, the Π state with $|\Lambda| = 1$ also involves additional off-diagonal hyperfine coupling terms between the $\Lambda = \pm 1$

components. It is worth checking whether the symmetry treatment and the corresponding off-diagonal matrix elements are correctly implemented in the code.

Accordingly, we calculated the hyperfine-resolved rovibrational levels for the $B^3\Pi_g$ state of the N_2 molecule using DUO. The PEC of the $B^3\Pi_g$ state used in DUO is obtained from the *ab initio* curve in Ref. 24. The parameters of the fine structure are estimated artificially based on the values given in Ref. 25. The spin-orbit coupling constant A_{SO} , which separates the different Ω components, is set to 40 cm^{-1} . The spin-spin constant λ_{SS} is set to -0.3 cm^{-1} . Note that the corresponding input for DUO should be $f_{\text{SS}} = \frac{2}{3}\lambda_{\text{SS}} = -0.2 \text{ cm}^{-1}$. The Λ -doubling constants o and p are set to -1.16 and -0.01 cm^{-1} , respectively. The spin-rotation constant γ_{SR} and the last Λ -doubling constant q are small enough to be ignored.

TABLE VI. Comparison of hyperfine level shifts for the $B^3\Pi_g$ state of N_2 with $J = 2$. The hyperfine interactions are divided into three groups. The first group includes only $a = 0.1\text{ cm}^{-1}$, the second group includes $b_F, c, d = 0.06, 0.03, 0.07\text{ cm}^{-1}$, and the third group includes $eQq_0, eQq_2 = 0.02, 0.08\text{ cm}^{-1}$. The rovibronic energies E_{rv} are given in cm^{-1} , while the hyperfine shifts $E_{\text{hfs}} - E_{rv}$ are given in GHz. The label τ denotes the parity of $\pm$. PGO stands for PGOPHER.

Ω	τ	E_{rv}	I	F	$E_{\text{hfs}} - E_{\text{rv}}$					
					a		$b_F + c + d$		$eQq_0 + eQq_2$	
					DUO	PGO	DUO	PGO	DUO	PGO
0	+	8.928 860 0	2	0	−0.059 00	−0.059 00	−1.757 49	−1.757 50	−0.316 46	−0.316 46
			2	1	−0.045 28	−0.045 27	−1.469 54	−1.469 55	−0.158 57	−0.158 57
			2	2	−0.024 65	−0.024 64	−0.897 10	−0.897 10	0.275 72	0.275 72
			2	3	−0.010 81	−0.010 82	−0.046 76	−0.046 77	0.180 94	0.180 92
			2	4	−0.024 22	−0.024 22	1.072 42	1.072 42	−0.090 81	−0.090 81
			0	2	0.000 00	0.000 00	0.000 00	0.000 00	−0.207 94	−0.207 94
	−	6.660 863 9	1	1	0.000 87	0.000 87	0.156 27	0.156 25	0.139 67	0.139 67
			1	2	0.029 19	0.029 20	0.082 15	0.082 14	−0.139 61	−0.139 61
			1	3	0.002 17	0.002 16	−0.095 57	−0.095 57	0.039 74	0.039 75
1	+	49.321 901 4	2	0	−2.996 09	−2.996 10	1.064 81	1.064 83	−0.702 27	−0.702 26
			2	1	−2.487 31	−2.487 29	0.885 07	0.885 08	−0.351 54	−0.351 54
			2	2	−1.478 23	−1.478 22	0.528 49	0.528 50	0.609 92	0.609 93
			2	3	0.013 22	0.013 22	0.000 99	0.001 02	0.400 54	0.400 55
			2	4	1.957 54	1.957 55	−0.688 20	−0.688 20	−0.201 10	−0.201 10
			0	2	0.000 00	0.000 00	0.000 00	0.000 00	−0.460 97	−0.460 96
	−	49.270 245 8	1	1	−1.489 71	−1.489 73	−0.464 12	−0.464 14	−0.206 79	−0.206 80
			1	2	−0.490 16	−0.490 16	−0.150 67	−0.150 68	0.208 40	0.208 39
			1	3	0.985 28	0.985 27	0.310 34	0.310 35	−0.059 64	−0.059 66
2	+	82.715 114 4	2	0	−5.938 68	−5.938 68	−4.104 00	−4.103 98	0.270 08	0.270 08
			2	1	−4.955 15	−4.955 15	−3.423 37	−3.423 36	0.134 98	0.135 00
			2	2	−2.985 46	−2.985 45	−2.060 18	−2.060 17	−0.235 18	−0.235 16
			2	3	−0.024 29	−0.024 28	−0.010 55	−0.010 55	−0.154 30	−0.154 27
			2	4	3.936 51	3.936 51	2.731 36	2.731 38	0.076 92	0.076 93
			0	2	0.000 00	0.000 00	0.000 00	0.000 00	0.177 27	0.177 27
	−	82.714 766 2	1	1	−2.969 40	−2.969 38	−2.064 12	−2.064 10	−0.156 05	−0.156 04
			1	2	−0.996 09	−0.996 09	−0.690 69	−0.690 69	0.156 15	0.156 16
			1	3	1.970 59	1.970 60	1.373 41	1.373 41	−0.044 69	−0.044 70

To isolate the contributions from different hyperfine interactions, we divided the hyperfine terms into three groups. Since our purpose is not to reproduce the experimental spectrum, the hyperfine constants were set to artificial values much larger than the expected experimental values. The first group includes only $a = 0.1\text{ cm}^{-1}$. The second group includes $b_F, c, d = 0.06, 0.03, 0.07\text{ cm}^{-1}$. Note that the Fermi contact constant b_F is different from b used in PGOPHER, which satisfies $b_F = b + \frac{1}{3}c$. The third group includes $eQq_0, eQq_2 = 0.02, 0.08\text{ cm}^{-1}$. These artificial constants produce hyperfine splittings on the GHz scale. They are not intended to be realistic, but make it easier to test the implementation.

We performed an independent calculation with PGOPHER to check the DUO results. Since PGOPHER is based on perturbation theory, we only calculated the rotational states for one vibrational level with $v = 0$. Accordingly, we only used one contracted basis in

DUO and calculated the rotational constant B_v , which is $1.620\,419\,70\text{ cm}^{-1}$. This value was passed to PGOPHER for the perturbation calculation. As shown in Table VI, we take the rotational level of $J = 2$ as an example, which contains the $\Omega = 0, 1, 2$ components and both parity symmetries. We focus on the hyperfine shifts $E_{\text{hfs}} - E_{rv}$ rather than the absolute hyperfine-resolved energies. The hyperfine shifts calculated by DUO agree with those from PGOPHER to the sixth decimal place in cm^{-1} , that is, the printed precision of the PGOPHER output.

VI. CONCLUSION

We have extended the variational method program DUO to perform hyperfine structure calculations for homonuclear diatomic molecules. The updated code is implemented in the equal coupling

scheme under the Hund's case (a_β) representation, where I_1 and I_2 are first coupled to the total nuclear spin I , and then I is coupled with J to form F . The primitive basis functions in the Hund's case (a_β) are then transformed to the parity-conserved basis set, where the g/u symmetry and the nuclear-exchange symmetry are considered, so only physically allowed nuclear-spin states are retained.

We consider the main hyperfine interactions such as the nuclear magnetic dipole interaction and nuclear electric quadrupole interaction. The rank-1 hyperfine interactions, including the Fermi contact term, orbital hyperfine term, nuclear spin-rotation term, and electron-nuclear dipolar interaction term, have the same analytical form as those given by Qu *et al.*,² with I now interpreted as the total nuclear spin of the two identical nuclei. The last two hyperfine interaction terms, namely the nuclear-nuclear dipolar interaction and nuclear electric quadrupole interaction, can contribute to the coupling between different nuclear spin states with $\Delta I = I' - I = \pm 2$.

For homonuclear molecules, the electric dipole (E1) transitions within a single electronic state are forbidden by symmetry. Therefore, electric-quadrupole (E2) transitions, and in some cases magnetic-dipole (M1) transitions, can play an important role in the observable rovibrational spectra. In the present study, we extended the hyperfine transition intensity module to calculate the Einstein A coefficients of both E1 and E2 transitions for homonuclear diatomics.

To verify the implementation, we calculated the hyperfine-resolved spectra for the $X^1\Sigma_g^+$ state of H_2 and D_2 , the $X^2\Sigma_g^+$ and $B^2\Sigma_u^+$ states of $^{14}N_2^+$, and the $B^3\Pi_g$ state of $^{14}N_2$. Comparison of our results with previous theoretical and experimental studies and with independent PGOPHER calculations all showed very good agreement.

There are several natural directions for future work. The first is to extend the code to treat heteronuclear diatomic molecules with two non-zero nuclear spins. This development will require a more general coupling scheme, since the two nuclei are no longer equivalent. The second is to consider the Zeeman interactions in an external magnetic field. For weak magnetic fields, this extension should be relatively straightforward, as the present basis can be expanded by introducing M_F . For strong magnetic fields, a different treatment would be required because F is no longer a good quantum number. We should use the basis set labeled by M_J and M_I instead. Another possible direction is to include the weak symmetry-breaking interactions that mix ortho and para states, such as the antisymmetric off-diagonal components of the nuclear spin-rotation interaction³⁸ and the relativistic nuclear spin-orbit interaction,³⁹ which are not considered in the current implementation.

SUPPLEMENTARY MATERIAL

The [supplementary material](#) provides the four files containing the inputs to DUO used for the calculations presented in this study. Files are in standard DUO format; see <https://duo.readthedocs.io>.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Yide Yin: Data curation (lead); Formal analysis (lead); Investigation (lead); Methodology (equal); Validation (lead); Visualization (lead); Writing – original draft (lead); Writing – review & editing (equal). **Sergei N. Yurchenko:** Software (equal); Writing – review & editing (equal). **Jonathan Tennyson:** Conceptualization (equal); Supervision (equal); Writing – original draft (equal); Writing – review & editing (equal).

DATA AVAILABILITY

The open-source version of DUO is available at <https://github.com/ExoMol/Duo>.

APPENDIX A: ERRATA TO REF. 2

We would like to correct several errors in the published expressions of Qu *et al.*²

1. The original form of Eq. (40) should contain

$$(-1)^{\mp 1} \sqrt{30} \begin{pmatrix} 1 & 2 & 1 \\ \pm 1 & \mp 2 & \pm 1 \end{pmatrix} = -\sqrt{6}, \quad (A1)$$

and

$$\begin{aligned} & (-1)^{S-\Sigma} \begin{pmatrix} S & 1 & S \\ -\Sigma & \pm 1 & \Sigma' \end{pmatrix} \sqrt{S(S+1)(2S+1)} \\ & = \langle S, \Sigma | T_{\pm 1}^1(S) | S, \Sigma' \rangle = \langle S, \Sigma | \mp \frac{1}{\sqrt{2}} S_{\pm} | S, \Sigma' \rangle \\ & = \mp \frac{1}{\sqrt{2}} \sqrt{S(S+1) - \Sigma'(\Sigma' \pm 1)} = \mp \frac{1}{\sqrt{2}} \sqrt{S(S+1) - \Sigma(\Sigma \mp 1)}. \end{aligned} \quad (A2)$$

Therefore, the correction is simply

$$\Sigma(\Sigma \pm 1) \longrightarrow \Sigma(\Sigma \mp 1), \quad (A3)$$

in both Eqs. (40) and (41), as

$$\begin{aligned} & \langle \text{state}, v, \Lambda, S, \Sigma, J, \Omega, I, F | \mathcal{H}_{\text{dip}} | \text{state}, v', \Lambda', S, \Sigma', J', \Omega', I, F \rangle \\ & = (-1)^{J'+F+I} \begin{Bmatrix} I & J' & F \\ J & I & 1 \end{Bmatrix} \sqrt{I(I+1)(2I+1)} \\ & \quad \times (-1)^{J-\Omega} \begin{pmatrix} J & 1 & J' \\ -\Omega & \mp 1 & \Omega' \end{pmatrix} \sqrt{(2J+1)(2J'+1)} \\ & \quad \times \frac{\sqrt{S(S+1) - \Sigma(\Sigma \mp 1)}}{\mp \sqrt{2}} \langle \text{state}, v | d(R) | \text{state}, v' \rangle, \end{aligned} \quad (A4)$$

and

$$d(R) = -\sqrt{6}g_S g_N \mu_B \mu_N \frac{\mu_0}{4\pi} \times \langle \text{state}, \Lambda, S, \Sigma |$$

$$\times \sum_i \frac{C_{\mp 2}^{(2)}(\theta_{1i}, \phi_{1i})}{r_{1i}^3} \frac{\mp \sqrt{2}T_{\pm 1}^1(\mathbf{s}_i)}{\sqrt{S(S+1) - \Sigma(\Sigma \mp 1)}} | \text{state}, \Lambda', S, \Sigma' \rangle. \quad (\text{A5})$$

2. The Wigner-3j symbol and corresponding phase factor should not appear in Eq. (42); it is unnecessary to rotate $T^1(J)$ to the molecule-fixed frame for the nuclear spin-rotation term. Therefore, Eq. (42) of Qu *et al.* should be written correctly as

$$\langle \text{state}, v, \Lambda, S, \Sigma, J, \Omega, I, F | \mathcal{H}_{\text{IJ}} | \text{state}, v', \Lambda', S, \Sigma', J', \Omega', I, F \rangle$$

$$= (-1)^{J'+F+I} \begin{Bmatrix} I & J' & F \\ J & I & 1 \end{Bmatrix} \sqrt{I(I+1)(2I+1)}$$

$$\times \delta_{\Lambda, \Lambda'} \delta_{\Sigma, \Sigma'} \delta_{JJ'} \sqrt{J(J+1)(2J+1)}$$

$$\times \langle \text{state}, v | \mathcal{C}_I(R) | \text{state}, v' \rangle. \quad (\text{A6})$$

It is worth noting that, although there were typographical errors in these two terms, the corresponding matrix elements in the previous version of DUO were coded correctly.

APPENDIX B: ROVIBRATIONAL MIXING EFFECTS AT HIGH J

To further quantify the difference between our variational treatment and the perturbative model based on an effective Hamiltonian, we performed additional comparisons of hyperfine-resolved line positions and intensities for high- J states. The high- J behavior of hyperfine-resolved line positions has been illustrated previously by Qu *et al.*² As shown in their Table V, the differences increase with J . Here, we focus on the corresponding behavior of the line intensities.

We compare the intensities calculated via DUO and EXOCROSS with the reference data of Jóźwiak *et al.*¹⁹ for the O branch of H_2 from the 2-0 to 6-0 bands. For each rovibronic transition line, we calculate the relative root-mean-square error (RMSE) over all hyperfine components,

$$\Delta_{\text{RMSE}}^I = \left[\frac{1}{N} \sum_{i=1}^N \left(\frac{I_i^{\text{Duo}} - I_i^{\text{ref}}}{I_i^{\text{ref}}} \right)^2 \right]^{1/2}, \quad (\text{B1})$$

where N is the number of hyperfine components, I_i^{Duo} is the intensity calculated with DUO and EXOCROSS, and I_i^{ref} is the corresponding reference intensity.

As shown in Fig. 3, the relative RMSE increases systematically with the lower-state rotational quantum number J'' . This suggests that the differences in the hyperfine-resolved intensities are mainly associated with rovibrational mixing at high- J states.

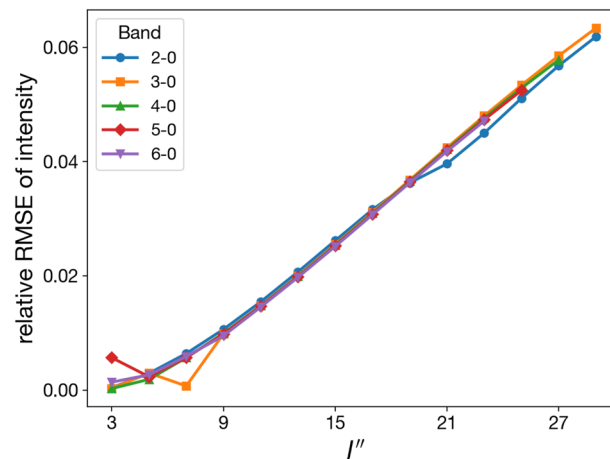


FIG. 3. Relative RMSE Δ_{RMSE}^I of intensities as a function of the lower-state rotational quantum number J'' for the O branch from the 2-0 to 6-0 bands of H_2 . For each rovibronic transition, the RMSE is calculated over all hyperfine components.

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