Quantum-defect analysis of 3p and 3d
H₃ Rydberg energy levels

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In this work, Rydberg energy levels of the triatomic hydrogen molecule (H₃) are studied with multichannel quantum-defect theory. We extract the body-frame p-wave quantum defects from highly accurate ab initio electronic potential surfaces and calculate the quantum defects of higher angular momentum states in a long-range multipole potential model. Laboratory-frame quantum defect matrices emerge from a rovibrational-frame transformation carried out with accurate rovibrational states of H⁺³. Finally, we use the laboratory-frame quantum defects to calculate Rydberg energy levels for the fundamental neutral triatomic molecule H₃.

I. INTRODUCTION

The triatomic hydrogen molecule (H₃) plays an important role in astrophysics because its cation H⁺³ acts as a proton donor in chemical reactions occurring in interstellar clouds. As the simplest triatomic neutral molecule, H₃ also attracts fundamental interest. Ever since its emission spectra were first observed by G. Herzberg in the 1980s [1], H₃ has been studied extensively. Herzberg and co-workers measured infrared and visible emission spectra of H₃ in discharges through hydrogen and assigned them to Rydberg-Rydberg transitions between n = 2 and n = 3 electronic states using empirical fits [1]. Helm and co-workers investigated the higher Rydberg states and ionization potentials of H⁺³ by analyzing the photoabsorption spectrum [2]. In 2003, building on previous work of Schneider, Orel and Suzor-Weiner [3], it was shown [4, 5] that intermediate Rydberg states of H₃ play an important role in the dissociative recombination (DR) process, H⁺³ + e⁻ → H₃ → H₂ + H or H + H + H. Prior to the study of Ref. [4, 5], the large discrepancy between the DR rate determined by experiment and previous theory had not been resolved. Refs. [1, 5] found that Jahn-Teller effects in H₃ neglected in previous theoretical studies couple the electronic and nuclear degrees of freedom and generate a relatively high DR rate via intermediate p-wave Rydberg-state pathways. A recent alternative formulation developed by Jungen and Pratt provides supporting evidence for this interpretation [6]. Vervloet and Watson improved both the experimental techniques and empirical fits and reinvestigated the low Rydberg states that G. Herzberg had observed [7]. Here we undertake an analysis of the Rydberg states with ab initio theory. One of the most successful techniques in treating Rydberg states with ab initio theory is multichannel quantum defect theory (MQDT) [8, 9]. Earlier studies [4, 10, 12] have utilized MQDT to successfully describe the DR process.

The application of MQDT to study molecular Rydberg energy levels treats the H₃ molecule as a Rydberg electron attached to a H⁺³ ion. The interaction between the Rydberg electron and the ion core is described through a smooth reaction matrix K or quantum defect matrix μ. K and μ are simply related, e.g., for a single-channel, K = tan(πμ). We extract a body-frame reaction matrix from ab initio electronic potential surfaces for p-wave Rydberg states and calculate the body-frame reaction matrix for Higher angular momentum states (l > 1) by using the long-range multipole potential model. For the higher angular-momentum states, we neglect short-range interactions due to the nonpenetrating nature of the high l states. Here l denotes the quantum number of the Rydberg electron orbital angular momentum. We then construct the total laboratory-frame reaction matrix K through a rovibrational frame transformation, obtaining

Kᵢ‴ = ∑₈₃ₙ₃ₘ₃ₗ₃ₛ₃ₙ‴ₘ‴ₗ‴ₜ‴(i) αα′ ⟨α′ | i‴⟩.

Here, Kᵢ‴ is the laboratory-frame reaction matrix element between the laboratory-frame eigenchannels |i⟩ and |i‴⟩, and K₂₃₉₃₈₃₉₃₀₉₃ₙ‴ₘ‴ₗ‴ₜ‴ is the body-frame reaction matrix element between body-frame eigenchannels |α⟩ and |α′⟩. The rovibrational frame transformation is specified by the unitary transformation Uᵢ‴ₘ‴₀‴ = (i) α⟩⟨α|.

The process of constructing the rovibrational transformation is similar to that described in Ref. [4] and is based on the rovibrational wave functions of H⁺³. To calculate them, there are two important approximations adopted in Ref. [4], the rigid rotator approximation and the adiabatic hyperspherical approximation. The nonadiabatic coupling between different adiabatic hyperspherical channels was included in later studies by using the slow variable discretization (SVD) approach in Ref. [13, 14]. In the present study, we abandon the rigid rotator approximation and consider the Coriolis interaction. In this way, we obtain very accurate rovibrational energy levels and wave functions of H⁺³ that allow us to construct the rovibrational transformation.

After the rovibrational transformation described by Eq. (1) is carried out, we obtain the laboratory-frame K matrix and calculate the eigenenergies E of the H₃ molecule by solving the secular equation [15]

det [tan(πν) + K] = 0,

where ν is a diagonal matrix with elements νᵢᵢ = 1/√2(Eᵢ‴₀‴ − Eᵢ‴). Here Eᵢ‴₀‴ denotes the ith rovibrational energy level.
The remaining of the article is organized as follows. Section 2 describes the detailed calculation of rovibrational states of \( H_3^+ \) and shows how to use them to construct the rovibrational transformation. Section 3 describes the calculation of the p-wave energy levels of \( H_3 \) using \textit{ab initio} quantum defects. Section 4 discusses the long-range multipole potential model for higher angular momentum Rydberg states, and Section 5 gives our conclusions.

II. ROVIBRATIONAL STATES OF \( H_3^+ \)

In the cation \( H_3^+ \), three protons interact with each other under a potential surface. The potential surface was created by Refs. [16] and is sub-micro-hartree accurate. With this potential surface, we solve the three-body Schrödinger equation in the adiabatic hyperspherical representation. We use the SVD method to include the nonadiabatic coupling through the Schrödinger equation Eq.(4) directly should in principle provide accurate rovibrational energy levels, but it would require extensive computational time and memory to diagonalize the full Hamiltonian matrix. Instead, we break the problem into two steps: first solve the hyperangular Schrödinger equation in the adiabatic representation, and then later include the nonadiabatic coupling through the SVD method.

A. Adiabatic representation

In the adiabatic representation, the adiabatic potentials and channel functions are defined as solutions of the adiabatic eigenvalue equations,

\[
\left[ \frac{\Lambda^2}{2\mu R^2} + \frac{15}{8\mu R^2} + V(R, \theta, \varphi) \right] \Phi_\nu(\Omega; R) = U_\nu(R) \Phi_\nu(\Omega; R),
\]

whose solutions depend parametrically on \( R \). For each \( R \), the set of \( \Phi_\nu(\Omega; R) \) is orthogonal, complete, and can be used as a basis to expand the whole wave function, e.g.,

\[
\Psi_i(R, \Omega) = \sum_\nu R^{-5/2} F_i^\nu(R) \Phi_\nu(\Omega; R).
\]

Here we use \( \Omega \) to denote the Euler angles and the two hyperspherical angles. To solve Eq.(4) numerically, we expand \( \Phi_\nu(\Omega; R) \) in a set of basis \( \Phi_{N^+m^+g_l}^{j_{jm}K^+} \), such that

\[
\Phi_\nu(\Omega; R) = \sum_{j_{jm}K^+} \delta_{j_{jm}K^+}^{(\nu)}(R) \Phi_{N^+m^+g_l}^{j_{jm}K^+},
\]

where \( j, m_2, N^+, K^+ \) and \( g_l \) are quantum numbers labeling basis functions in different degrees of freedom. \( \Phi_{N^+m^+g_l}^{j_{jm}K^+} \) satisfies the permutation symmetry of a three-fermion system, e.g.,

\[
P_{12} \Phi_{j_{jm}K^+}^{N^+m^+g_l} = - \Phi_{j_{jm}K^+}^{N^+m^+g_l},
\]

and

\[
A \Phi_{j_{jm}K^+}^{N^+m^+g_l} = \Phi_{j_{jm}K^+}^{N^+m^+g_l},
\]

where

\[
A = 1 - P_{12} - P_{23} - P_{31} + P_{12}P_{31} + P_{12}P_{23}.
\]

The explicit form of the basis functions \( \Phi_{j_{jm}K^+}^{N^+m^+g_l} \) is given in Appendix A.
B. Slow variable discretization

With the help of the discrete variable representation (DVR) basis $\pi_n(R)$, effects of nonadiabatic couplings between different adiabatic potentials are included. The DVR basis has the following properties:

$$\int dR \pi_n(R) U_\nu(R) \pi_{n'}(R) \approx U_\nu(R_n) \delta_{nn'},$$

where $R_n$ are the quadrature abscissas used to generate the DVR basis. The SVD approximation expresses the expansion of Eq. (10) as

$$\Psi_i(R, \Omega) = \sum_{\nu,n} c_i^{\nu} \pi_n(R) \phi_\nu(\Omega; R_n),$$

reduces Eq. (10) as

$$\sum_{n,\mu} T_{nn'} O_{\nu,n',\mu} c_i^{\nu} \phi_\mu(\Omega; R_n) = 0,$$

where

$$T_{nn'} = \int dR \pi_n(R) \left( -\frac{1}{2 \mu} \frac{\partial^2}{\partial R^2} \right) \pi_{n'}(R) dR,$$

and $O_{\nu,n',\mu}$ is the overlap matrix given by

$$O_{\nu,n',\mu} = \left< \phi_\nu(\Omega; R_n) \right| \phi_\mu(\Omega; R_n').$$

Finally, Eq. (10) is solved for the expansion coefficients $c_i$ and $E_i^{\nu}$. The total rovibrational wave function is therefore given by

$$\Psi_i(R, \Omega) = \sum_{\nu,n} c_i^{\nu} \pi_n(R) \sum_{j_{m2}K^+} a_{j_{m2}K^+}^{(\nu)}(R_n) \phi_{j_{m2}K^+}^{N^+m^+g_i},$$

where $i$ is the set of good quantum numbers $N^+m^+v^+g_i\Pi^+$, where $v^+$ denotes the vibrational quantum numbers.

C. Accuracy of rovibrational energies of $H_3^+$

Next we compare our theoretical rovibrational energy levels $E_i^{\nu}$ of $H_3^+$ with experimental energy levels. Adopting the notation used in Ref. 19, we label the rovibrational states $i$ by quantum numbers $(N^+, G)\{v_1, v_2\}\{l|u\}$. $v_1$ is the symmetric-stretch vibrational quantum number, $v_2$ denotes the quantum number of the asymmetric-stretch mode, $l_2$ describes the quantum number of the vibrational angular momentum, and $G \equiv |K^+ - l_2|$. The fact that $G$ instead of $K^+$ is a good quantum number implies that the Coriolis interaction couples rotational and vibrational angular momenta and makes levels with the same $G$ nearly degenerate. However, for levels with $l_2 \neq 0$ and $(N^+ - |l_2|) \geq G \geq 1$, the degeneracy breaks, and we $u$ (or $l$) to denote the upper (or lower) energy level; these levels with a $u$ or an $l$ cannot be described by rigid rotator approximations.

Table I: Comparison of several calculated rovibrational energy levels of $H_3^+$ with experimental results [19]. Only states with $N^+ \leq 3$ for the $\{0, 0^0\}$ and $\{0, 1^1\}$ bands are shown here.

| Q.N. | $E_{cal}^{\nu}$ (cm$^{-1}$) | $E_{exp}^{\nu}$ (cm$^{-1}$) |
|------|----------------|----------------|
| (1, 1)$\{0, 0^0\}$ | 64.128 | 64.121 |
| (1, 0)$\{0, 0^0\}$ | 86.960 | 86.960 |
| (2, 0)$\{0, 0^0\}$ | 169.288 | 169.295 |
| (2, 1)$\{0, 0^0\}$ | 237.335 | 237.356 |
| (3, 0)$\{0, 0^0\}$ | 315.317 | 315.349 |
| (3, 1)$\{0, 0^0\}$ | 494.712 | 494.775 |
| (0, 1)$\{0, 1^1\}$ | 516.823 | 516.873 |
| (1, 2)$\{0, 1^1\}$ | 2521.411 | 2521.183 |
| (1, 2)$\{0, 1^1\}$ | 2574.996 | 2548.164 |
| (3, 1)$\{0, 1^1\}$ | 3025.941 | 3025.663 |

The quantities labeling the energy levels, in the notation $(N^+, G)\{v_1, v_2\}\{l|u\}$ described in the text.

Theoretical calculated results from this work.

Experimentally determined energies from Ref. 19.

Table 2 compares the rovibrational energy levels, calculated for $N^+ \leq 3$ states of the $\{0, 0^0\}$ and $\{0, 1^1\}$ bands, with the experimental results of Lindsay and McCall. The agreement is good, with a rms difference of 0.281 cm$^{-1}$ for the levels shown in the table. Higher-rovibrational energy-level calculations also exhibit good agreement. For our calculated energy levels up to around 9000 cm$^{-1}$ with $N^+ \leq 4$, the rms difference between our calculation and the experimental results of Ref. 19 is 0.657 cm$^{-1}$.

D. Rovibrational-frame transformation

Next we describe in detail how to construct the rovibrational-frame transformation using the ionic rovibrational eigenstates. In the laboratory frame, the $H_3^+ + e^−$ system is described by the electron orbital angular momentum $l$ and its projection $\lambda$ onto the electronic $z$-axis, and by $N^+, m^+$, $g_i$, and parity of the ion core. Hence, we construct the wave function of the $H_3^+ + e^-$ system as a sum of products of the ionic rovibrational wave function and electronic wave function, of the form

$$\psi^{N^+m^+ g_i \Pi^+}(R, \Omega) Y_{\lambda \lambda}(\theta_e, \varphi_e),$$

where $\theta_e$ and $\varphi_e$ are spherical angles of the electron in the laboratory frame. The radial part of electronic wave function is not shown here since we apply the MQDT method for that degrees of freedom. Specifically, we want to construct the laboratory eigenchannel function $|i⟩$ with
a definite laboratory-frame total angular momentum $N$: 
\[ |i\rangle = |N^+, \nu^+\rangle (N, l, m, \Pi^+, gi) \]
In the position representation, it takes the form as,
\[ \sum_{\lambda} C_{N^+, m, +, \lambda}^{N, m} \Phi_{N^+, m^+, +, \lambda}^g Y_{N^+, m^+, +, \lambda} \] 
(21)
where $C_{N^+, m, +, \lambda}^{N, m}$ denotes the appropriate Clebsch-Gordan coefficient.

In the body-frame, the is specified state by the projection of the electron angular momentum on the molecular $Z$-axis $\Lambda$, by the total angular momentum of the system $N$ including the electron contribution $l$ and the projection $m$ of $N$ on the laboratory $z$-axis. Applying the transformation between body-frame and lab-frame
\[ Y_{\lambda} (\theta_e, \varphi_e) = \sum_{\Lambda} \left[ D_{\lambda\Lambda} (\alpha, \beta, \gamma) \right]^* \phi_{\lambda} (\theta_e', \varphi_e') \] 
(22)
the expansion of the product of two Wigner functions,
\[ D_{m+K+} D_{\lambda\Lambda} = \sum_{N} D_{mK}^{N} C_{N^+, K^+, +, \lambda}^{N, m} C_{N^+, m^+, +, \lambda}^{N, m} \] 
(23)
we have the following equation,
\[ \sum_{\lambda} C_{N^+, m, +, \lambda}^{N, m} \left[ D_{m+K^+}^{N^+} \right]^* Y_{\lambda} (\theta_e, \varphi_e) \] 
\[ = \sum_{\lambda} (\hat{D}^{-\Lambda}_{\lambda-\Lambda} D_{mK}^{N})^* Y_{\lambda} (\theta_e', \varphi_e') \] 
(24)
with some manipulation of algebra, where $\theta_e'$ and $\varphi_e'$ are the spherical angles of the electron in the laboratory frame. Using Eq. (24), we derive the transformation between the body-frame and laboratory-frame states as,
\[ \Psi_{N^+, v^+, \lambda}^{Nmg, \Pi^+, gi} = \psi_{N^+, v^+, \lambda}^{Nmg, \Pi^+, gi} \] 
(25)
where $\Psi_{N^+, v^+, \lambda}^{Nmg, \Pi^+, gi}$ is defined as,
\[ \Psi_{N^+, v^+, \lambda}^{Nmg, \Pi^+, gi} = \sum_{n\nu} c_{n\nu}^{(\nu)} \pi_1 (R) \times \sum_{jm2K^+} \phi_{jm2K^+}^{(\nu)} (R_n) \psi_{jm2N^+, K^+, \lambda}^{Nmg, \Pi^+, gi} \] 
(26)
The explicit form of $\psi_{jm2N^+, K^+, \lambda}^{Nmg, \Pi^+, gi}$ is given in Appendix A. The rovibrational frame transformation can be accomplished as follows:
\[ K_{N^+, v^+, \lambda}^{Nmg, \Pi^+, gi} = \sum_{\lambda\lambda'} \int dQ d\Omega E \hat{\Psi}_{N^+, v^+, \lambda}^{Nmg, \Pi^+, gi} \hat{K}_{\lambda\lambda'} (Q) \hat{\Psi}_{N^+, v^+, \lambda'}^{Nmg, \Pi^+, gi} \] 
(27)
where $\Omega$ denotes the Euler angles, and $Q$ contains the three vibrational degrees of freedom.

### III. P-WAVE ENERGY LEVELS OF $H_3$

The body-frame reaction matrix for a p-wave electron is described by the short-range interaction extracted from an ab initio calculation [20]. In practice, the quantum defects are smoother than the reaction matrix elements because the latter can have poles. Hence in this work, we extract the body-frame quantum defects $\mu (Q)$ from the ab initio energy surface directly. After replacing $K_{\lambda\lambda'} (Q)$ by $\mu_{\lambda\lambda'} (Q)$ in Eq. (27), we perform a rovibrational transformation to get the laboratory-frame quantum-defect matrix. Finally, we get the laboratory $K$ matrix by using the eigenvalues $\mu_e$ from the laboratory-frame quantum-defect matrix,
\[ K = U \tan (\pi \mu_e) U^T \] 
(28)

### A. Body-frame quantum defects for p-waves

Because of Jahn-Teller effects, the body-frame quantum-defect matrix is generally not diagonal in the electronic projections $\Lambda$, $\Lambda'$. Similar to the body-frame $K$ matrix proposed by Staib and Domcke [21], it has the form
\[ \mu (Q) = \begin{bmatrix} \mu_0 (Q) & 0 & 0 \\ 0 & \mu_{11} (Q) & \mu_{1-1} (Q) \\ 0 & \mu_{-1} (Q) & \mu_{-1-1} (Q) \end{bmatrix} \] 
(29)
We express each matrix element by using the vibrational symmetry coordinates $Q = (Q_1, Q_x, Q_y)$ as
\[ Q_1 = f \frac{1}{\sqrt{3}} (\Delta r_1 + \Delta r_2 + \Delta r_3) \] 
(30a)
\[ Q_x = f \frac{1}{\sqrt{3}} (2\Delta r_3 - \Delta r_2 - \Delta r_1), \]  
and
\[ Q_y = f (\Delta r_1 - \Delta r_2). \]

where \( f = 2.639 \, 255 \, \text{bohr}^{-1} \) is a constant and \( \Delta r_i \) describes displacements of the nuclei from the equilibrium geometry at which \( r_{12} = r_{23} = r_{31} = r_{\text{equi}} = 1.6504 \, \text{a.u.} \). For example, \( \Delta r_1 = r_{23} - r_{\text{equi}} \), \( Q_x \) and \( Q_y \) can be alternatively described by another pair of coordinates \( (\rho, \phi) \) as \( Q_x = \rho \cos \phi \) and \( Q_y = \rho \sin \phi \). \( Q_3 \) describes the symmetric stretch of the molecule, while \( (Q_x, Q_y) \) or \( (\rho, \phi) \) describe bends and the asymmetric stretch. These coordinates are very useful here for our Taylor expansion of the body-frame quantum defects around an equilibrium position.

We use the following forms,
\[ \mu_{00} (Q) = \mu_{00} (Q = 0) + a_1 Q_1 + a_2 Q_1^2 + a_3 Q_1^3 + a_4 \rho^2, \]  
\[ \mu_{11} (Q) = \mu_{11} (Q = 0) + b_1 Q_1 + b_2 Q_1^2 + b_3 Q_1^3 + \delta \rho^2, \]

and
\[ \mu_{1-1} (Q) = \mu_{-11} (Q) = \lambda \rho. \]

The form of our off-diagonal matrix elements \( \mu_{1-1} (Q) \) and \( \mu_{-11} (Q) \) differs from the usual adopted form in Ref. [4] by a phase factor \( \exp (\pm i\phi) \). This different phase convention is due to the fact that the usual adopted form was derived in a body frame that is rotated from our body frame by \( \phi/2 \). We develop the detailed proof in Appendix B. The effective quantum numbers are calculated by diagonalizing the quantum defect matrix. This calculation gives,
\[ \nu_{n, n_{1/2}} (Q) = n - |\mu_{11} (Q) + |\mu_{1-1} (Q)||, \]

an expression that can be used to fit the effective quantum numbers calculated ab-initio in Ref. [2].

**B. 3p_1 energy levels of H_3**

We calculate the 3p_1 energy levels of H_3 and compare them with empirical fits from Ref. [7]. Quantum defect parameters in Eqs. (31–33) are extracted from the ab-initio calculation in Ref. [20]. To fit the experimental results, we shift the quantum defects at equilibrium positions \( \mu_{00} (Q = 0) = 0.0683 \) and \( \mu_{11} (Q = 0) = 0.4069 \) by a small amount, 0.0043 and 0.0021 correspondingly.

In Ref. [7], Vervloet and Watson studied the H_3 emission lines of (3s, 3p_0, 3d) \( \rightarrow \) 2p_0 bands and (3s, 3p_0, 3d) \( \rightarrow \) 3p_0 bands. They then fitted the lines with effective Hamiltonians of the following form,
\[ BN (N + 1) + (C - B) \, K^2 \]
\[ -D_N N^2 (N + 1)^2 \]
\[ -D_N K N (N + 1) K^2 \]
\[ -D_K K^4 + \ldots \]

**TABLE II: A comparison between several of our calculated 3p_1 H_3 energy levels with empirically fitted experimental energy levels.**

| Label \( N, g, U \) | \( E_{\text{cal}} \, \text{(cm}^{-1}) \) | \( E_{\text{fit}} \, \text{(cm}^{-1}) \) | Differences \( \text{(cm}^{-1}) \) |
|---------------------|-----------------|-----------------|-----------------|
| 0, 1, 1             | 12967.8         | 12966.836       | 0.9             |
| 1, 0, 1             | 12999.1         | 12998.196       | 0.9             |
| 1, 1, 1             | 13052.3         | 13050.966       | 1.3             |
| 1, 2, 1             | 13066.9         | 13068.700       | -1.8            |
| 2, 0, -1            | 13139.9         | 13138.608       | 1.3             |
| 2, 1, -1            | 13056.1         | 13056.588       | -0.5            |
| 2, 1, 1             | 13221.1         | 13219.125       | 1.9             |
| 2, 2, 1             | 13234.3         | 13235.522       | -1.2            |
| 2, -3, 1            | 13203.8         | 13212.055       | -8.3            |
| 3, 0, 1             | 13450.7         | 13446.072       | 4.6             |
| 3, 1, -1            | 13300.6         | 13300.119       | 0.5             |
| 3, 2, -1            | 13160.5         | 13165.030       | -4.5            |
| 3, 2, 1             | 13485.4         | 13483.545       | 1.9             |
| 3, 3, 1             | 13453.2         | 13460.934       | -7.7            |

The label denotes the values of \( N, g, U \) adopted in Ref. [7] to fit the experimental energy levels.

Empirical results calculated in this study.

Empirical fits for experimental energies determined in Ref. [7].

Differences theory - experiment.

where the explicit expressions can be found in Ref. [1] and Ref. [2]. Table 2 compares our MQDT result with the experimental energy levels calculated from the fitted effective Hamiltonians. The labels \( N, g, U \) are fitting parameters, where \( N \) is also the total angular momentum of H_3, and \( g \) is related to the quantum number \( G \) by \( G = |g| \). Evidently our calculations are in good agreement with the fitted and recalculated experimental results, with differences of around a few cm\(^{-1}\).

**IV. HIGHER ANGULAR-MOMENTUM STATES**

For higher electronic angular-momentum states with \( l > 1 \), the orbits are nonpenetrating and the short-range interaction is negligible. The long-range multipole potential model employing perturbation theory has successfully described the high orbital angular Rydberg states of H_2 [22,23]. In this work, we include the perturbations and interactions between levels of different \( n \) (principle quantum number) and \( l \) (angular-momentum quantum number) in a systematic fashion by incorporating the formalism of MQDT [24]. We use this long-range model to calculate the Rydberg states of H_3 with \( l \geq 2 \).

For a Rydberg electron with high orbital angular momentum \( (l \geq 2 \text{ in the case of H}_3) \), the effects of core penetration are negligible. Hence, the interaction be-
TABLE III: Comparison between several of our calculated 3d energy levels of H$_3$ with experimentally-determined energy levels\[1\].

| Label\[a\] | $N^+, K^+, N$ | $E_{\text{cal}}$ \[b\] (cm$^{-1}$) | $E_{\text{fit}}$ \[c\] (cm$^{-1}$) | Differences\[d\] (cm$^{-1}$) |
|-----------|----------------|-----------------|-----------------|------------------|
| 2, 1, 0   | 17399.14       | 17415.86        | -15.89          |
| 2, 2, 0   | 17058.41       | 17039.61        | 18.80           |
| 1, 0, 1   | 17284.81       | 17296.57        | -11.76          |
| 3, 0, 1   | 17742.32       | 17741.29        | 1.03            |
| 1, 1, 1   | 17005.99       | 16991.72        | 14.28           |
| 2, 1, 1   | 17403.89       | 17412.83        | -8.94           |
| 3, 1, 1   | 17698.40       | 17700.43        | -2.02           |
| 2, 2, 1   | 17107.24       | 17094.12        | 13.13           |
| 3, 2, 1   | 17540.96       | 17557.32        | -16.35          |
| 3, 3, 1   | 17204.46       | 17188.48        | 15.98           |
| 1, 0, 2   | 17011.36       | 17001.08        | 10.27           |
| 3, 0, 2   | 17643.36       | 17655.58        | -12.21          |

\[a\]The label denotes the quantum numbers $N^+, K^+, N$.

\[b\]Theoretical results calculated in this work.

\[c\]Empirical fits to the experimental energies determined in Ref. [7].

\[d\]Differences between theoretical and experimental results.

Between the Rydberg electron and the ion core can be approximately described by two effects. First, the interaction potential between the Rydberg electron and the molecular ion is expanded into a multipole series, where the quadrupole moment of the H$_3^+$ core is the leading anisotropic term. Second, the induced dipole moment of the ion core interacts with the Rydberg electron by a potential characterized by the polarizability of the H$_3^+$ core. All higher angular momenta and higher-order polarizabilities are neglected here, as well as the anisotropic portion of the polarizability interaction.

In this approximation, the Hamiltonian is given in atomic units by

$$H = -\frac{1}{2} \nabla^2 - \frac{1}{r} + V_{\text{eff}} + H_{\text{core}},$$

where $H_{\text{core}}$ is the rovibrational energy of the $H_3^+$ core. $V_{\text{eff}}$ includes quadrupole and polarizability interactions:

$$V_{\text{eff}} = V_{\text{quad}} + V_{\text{pol}} = -\frac{Q_2}{r^3} P_2 (\cos \theta'_e) - \frac{\alpha}{2r^4} - \frac{3}{r^4} P_2 (\cos \theta'_e),$$

where $Q_2$, $\alpha$, and $\gamma$ are respectively the quadrupole moment, isotropic polarizability and the cylindrically-symmetric anisotropic polarizability. Other components of the quadrupole moment tensor vanish for the undistorted equilateral triangle configuration. For the vibrational ground state, $Q_2$, $\alpha$, and $\gamma$ are taken from table III of Ref. [25]. The polarizability and quadrupole interactions are much smaller than the Coulomb interaction and hence will be treated in perturbation theory. We also find that the quantum defect is small (of the order of 0.01), and the coupling between vibrational ground states of H$_3^+$ to excited vibrational states are negligible. Hence, in the rovibrational transformation, we only include the vibrational ground state. The body-frame reaction matrix thus can be written as

$$K_{\text{AA'}} \approx -\pi \int dr f_{nl} (r) \langle Y_{I\Delta}| V_{\text{eff}} | Y_{I'\Delta'} \rangle f_{nl} (r), \tag{38}$$

where $f_{nl}$ is the regular Coulomb function with $l = 1$ as the angular momentum quantum number and $n$ as the principal quantum number. As the quantum defect for $d$-wave electrons are small, we can use integers for $n$ in calculating the radial functions. Here, $r$ is the electronic radial coordinate. Again, we perform a rovibrational transformation (with only the vibrational ground states) to obtain the laboratory-frame $K$ matrix and finally, calculate the energy levels using the standard determinantal equation of MQDT.

Table 3 compares our theoretical calculations with the experimentally-determined 3d energy levels \[1\]. The agreement somewhat poorer than the p-wave case.

V. SUMMARY

In this work, we have calculated the Rydberg energy levels of H$_3$ molecules. Using an accurate ab-initio quantum-defect surface and ab-initio core energies of H$_3^+$, our theoretical results for the p-wave Rydberg states from the present MQDT calculations are in good agreement with experimental results from J. K. G. Watson \[1\]. We also study higher-momentum states by using a long-range multipole potential model in conjunction with MQDT, and find encouraging agreement with experimental results from Ref. \[2\].

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Appendix A: Permutation symmetry of the basis functions

For convenience, we first consider trial basis functions as

$$\Phi_{\mathrm{try}} = e^{im_2 \phi} R_{K_+m_+}^N (\alpha, \beta, \gamma) \Phi_{\gamma j} u_j (\theta), \tag{A1}$$

and use them to construct basis functions with proper permutation symmetry Eqs.\[12a,12b\]. The continuity condition for Smith-Whitten hyperspherical coordinates \[17,26\] requires that,

$$\Phi_{\mathrm{try}} (\theta, \varphi, \alpha, \beta, \gamma) = \Phi_{\mathrm{try}} (\theta, \varphi + 2\pi, \alpha, \beta, \gamma + \pi). \tag{A2}$$
TABLE IV: Permutation symmetry for basis functions in the different degrees of freedom.

| Permutation Operation | $e^{im_2 \varphi}$ | $R_{K^+m+}^{N^+}$ | $\Phi_{gl}$ |
|-----------------------|-------------------|-------------------|---------------|
| $P_{12}$              | $e^{4\pi/3} - e^{-2\pi/3}$ | $(-)^{N^+ + K^+} R_{K^+m+}^{N^+}$ | $e^{4\pi ig_1/3} \Phi_{gl}$ |
| $P_{23}$              | $e^{2\pi/3} - e^{-2\pi/3}$ | $(-)^{N^+ + K^+} R_{K^+m+}^{N^+}$ | $e^{2\pi ig_1/3} \Phi_{gl}$ |
| $P_{31}$              | $e^{2\pi/3} - e^{-2\pi/3}$ | $(-)^{N^+ + K^+} R_{K^+m+}^{N^+}$ | $e^{2\pi ig_1/3} \Phi_{gl}$ |
| $P_{12}P_{31}$        | $e^{4\pi/3} - e^{-2\pi/3}$ | $(-)^{K^+} R_{K^+m+}^{N^+}$ | $e^{4\pi ig_1/3} \Phi_{gl}$ |
| $P_{12}P_{23}$        | $e^{4\pi/3} - e^{-2\pi/3}$ | $(-)^{K^+} R_{K^+m+}^{N^+}$ | $e^{4\pi ig_1/3} \Phi_{gl}$ |

This boundary condition leads to the condition that $K^+/2 + m_2$ must be integral. Hence, if $K^+$ is even, $m_2$ must be integral; if $K^+$ is odd, $m_2$ must be half integral. We remark here that the parity $\Pi^+$ is determined by $K^+$ only; $\Pi^+ = +1$, if $K^+$ is even, and $\Pi^+ = -1$, if $K^+$ is odd. 

The permutation symmetries for the basis functions chosen for each degree of freedom are shown in Table 4. Here, $\Phi_{gl}$ is the nuclear-spin basis function defined as in Ref. [4]. $g_1$ equals zero for the ortho state, and ±1 for the para state. The rotational part $R_{K^+m+}^{N^+} (\alpha, \beta, \gamma)$ is given by,

$$R_{K^+m+}^{N^+} (\alpha, \beta, \gamma) = \sqrt{\frac{2N^+ + 1}{8\pi^2}} D_{m+K^+}^{N^+} (\alpha, \beta, \gamma)$$

where $D_{m+K^+}^{N^+}$ are the Wigner D functions of the Euler angles. The phase of the Wigner function is chosen as in Varshalovich et al. [27]. $N^+$ is the total angular momentum of the ion, $K^+$ is the projection of $N^+$ onto the body frame z-axis, and $m^+$ is the projection onto the laboratory frame Z-axis. We also use a set of fifth-order basis splines $u_j (\theta)$ to expand the wave function in $\theta$. Since $u_j (\theta)$ is unaffected by permutations, it is not shown in Table 4.

Application of the antisymmetrization operator $A$ in Eq. (13) to Eq. (11) leads to:

$$A\Phi_{\text{try}} = u_j (\theta) \left[ 1 + (-)^{K^+} e^{i\pi (m_2 + g_1)} + e^{i\pi (m_2 + g_1)} \right]$$

$$\times \left[ e^{im\varphi} R_{K^+m+}^{N^+} \Phi_{g_1l} - e^{2\pi i (m_2 + g_1)} (-)^{N^+} \right]$$

$$\times e^{-im\varphi} R_{K^+m+}^{N^+} \Phi_{g_1l}$$

Following the fact that $m_2$ is integral (half integral) if $K^+$ is even (odd), and that $g_1$ equals 0 or ±1, we see that the factors in the second line of the right hand side of Eq. (A4) vanish unless,

$$m_2 + g_1 = 3n \text{ if } K^+ \text{ is even},$$

$$m_2 + g_1 = 3n + 3/2 \text{ if } K^+ \text{ is odd},$$

where $n$ is any integer. Under the conditions Eqs. (A5a), (A5b), the factors in the first line of the right hand side of Eq. (A4) vanish if $m_2 = 0, g_1 = 0, K^+ = 0$ when $N^+$ is even. Therefore, the basis functions that obey the permutation symmetry are:

$$\Phi_{gl}^{N^+m^+g_1} = u_j (\theta) e^{im_2 \varphi} R_{K^+m+}^{N^+} \Phi_{gl},$$

(A6)

if $m_2 = 0$, $K^+ = 0$, $g_1 = 0$, and $N^+$ is odd, otherwise,

$$\Phi_{gl}^{N^+m^+g_1} = \frac{1}{\sqrt{2}} u_j (\theta) \left[ e^{im_2 \varphi} R_{K^+m+}^{N^+} \Phi_{gl}$$

$$- (-)^{N^+ + K^+} e^{-im_2 \varphi} R_{K^+m+}^{N^+} \Phi_{gl} \right]$$

(A7)

where $m_2$, $g_1$ and $K^+$ obey the relations Eqs. (A5a), (A5b).

The explicit form of $\Phi_{gl}^{N^+m^+g_1}$ in Eq. (20) is closely related to $\Phi_{gl}^{N^+m^+g_1}$. Insertion of Eq. (24) into Eq. (21) yields

$$\Phi_{j_{m_2N^+K^+}\lambda}^{N^+g_1} = u_j (\theta) (-)^{-\lambda} e^{im_2 \varphi}$$

$$\times \Phi_{g_1l}^{C_{l,-\lambda;N,K}R_{K^+m^+}}$$

(A8)

with $K = K^+ + \lambda$, if $m_2 = 0, g_1 = 0, K^+ = 0$ and $N^+$ is odd. Otherwise,

$$\Phi_{j_{m_2N^+K^+}\lambda}^{N^+g_1} = \frac{1}{\sqrt{2}} u_j (\theta) (-)^{-\lambda}$$

$$\times \left[ e^{im_2 \varphi} \Phi_{g_1l}^{C_{l,-\lambda;N,K}R_{K^+m^+}} - (-)^{N^+ + K^+} \times e^{-im_2 \varphi} \Phi_{g_1l}^{C_{l,-\lambda;N,K}R_{K^+m^+}} \right]$$

(A9)

where $K = -K^+ + \lambda$.

Appendix B: Body-frame quantum defect matrix elements

The form of reaction matrix $K$ describing the Jahn-Teller coupling of the p-wave electron can be written as

$$K_{\Lambda \Lambda'} = \begin{pmatrix} K_{00} & K_{01} & K_{0-1} \\ K_{10} & K_{11} & K_{1-1} \\ K_{-10} & K_{-11} & K_{-1-1} \end{pmatrix}.$$

(B1)

In perturbation theory, the matrix elements of the reaction matrix near the equilibrium position obey,

$$K_{\Lambda \Lambda'} \approx -\pi \int dr' \bar{f}_{l\Lambda} (r') \bar{f}_{l\Lambda'} (r')$$

$$\times \int \omega' Y_{l\Lambda}^* (\theta', \varphi') \Delta V_e (Q; r_e') Y_{l\Lambda'} (\theta', \varphi')$$

(B2)

where $\Delta V_e = V_e (Q; r_e') - V_e (Q = 0; r_e')$, and $V_e (Q, r_e')$ is the interaction between the ion and the Rydberg electron excluding the Coulomb potential, $Q$. 


are the vibrational symmetry coordinates, and $r_e' = (r', \theta_e', \varphi_e')$ are the spherical coordinates of the electron in the body-frame. $f_{\ell \Lambda}(r')$ is the regular phase-renormalized Coulomb wave function defined by, $f_{\ell \Lambda} = f_{\ell \Lambda}(r') = g_{\ell \Lambda}(r') + \sqrt{\frac{2}{3\pi}} \cos (\pi \mu_{\Lambda \Lambda} (Q = 0)) - g_{\ell \Lambda}(r')$, where $\{f_{\ell \Lambda}, g_{\ell \Lambda}\}$ are the usual Coulomb wave functions with energy $\epsilon$ and angular momentum $\ell$. $\mu_{\Lambda \Lambda} (Q = 0)$ are the constant zero-order term of the diagonal quantum defect matrix elements.

To explore the symmetry properties of $K_{\Lambda \Lambda'}$, we write the Taylor expansion in terms of $Q = \{Q_i, Q_{+}, Q_{-}\}$, where $Q_{+} = pe^{+i\varphi}$ and $Q_{-} = pe^{-i\varphi}$,

$$K_{\Lambda \Lambda'} = \sum_{\nu} K_{\Lambda \Lambda'}^{\nu} Q_{\nu} + \frac{1}{2} \sum_{\nu \mu} K_{\Lambda \Lambda'}^{\nu \mu} Q_{\nu} Q_{\mu} + \ldots \quad \text{(B3)}$$

where each summation is over the subscripts $1, +$ and $-$. However, the expansion Eq. (B3) is not valid in our body frame coordinates because $\Delta V_c (\hat{Q}; \hat{r}_e')$ is not single-valued at $Q_{+} = Q_{-} = 0$. This fact is demonstrated in the following discussion of our body frame coordinates.

The body frame coordinates used here are the same as the coordinates defined in Eq. (7) of Ref. [17], but we denote them as $x'y'z'$ instead of $x'y'z$ to make our notations consistent. The $z'$-axis is perpendicular to the plane defined by the three nuclei and the $x'$-axis is associated with the smallest moment of inertia. After manipulating Eqs.(2), (3), and Eq.(7) of Ref. [17] with some algebra, we can write down the cartesian coordinates of the positions of the $i$th nuclei $(x_i', y_i', z_i')$ as

$$x_i' = \frac{2}{3d} R \cos \left( \frac{\theta_i - \pi}{4} \right) \cos \left( \frac{\varphi_i}{2} + \vartheta_i \right), \quad \text{(B4a)}$$

$$y_i' = -\frac{2}{3d} R \sin \left( \frac{\theta_i - \pi}{4} \right) \sin \left( \frac{\varphi_i}{2} + \vartheta_i \right), \quad \text{(B4b)}$$

$$z_i' = 0. \quad \text{(B4c)}$$

where $\vartheta_1 = 5\pi/6, \vartheta_2 = -\pi/2$ and $\vartheta_3 = \pi/6$. When $\theta$ is very small, following Eqs. (B4a) and Eqs. (B4b), the two sets of coordinates $\{Q_1, \rho, \phi\}$ and $\{R, \theta, \varphi\}$ have the following relationship,

$$Q_1 = 3^{1/4} f (R - R_0), \quad \text{(B5a)}$$

$$\rho = 3^{1/4} f R \theta/2, \quad \text{(B5b)}$$

$$\phi = \varphi - 2\pi/3. \quad \text{(B5c)}$$

where $R_0 = 3^{1/4} \rho_{\text{equi}}$. Therefore, when $Q_{+} = Q_{-} = 0$, and hence $\rho = 0$, the positions of the $i$th nuclei $(x_i', y_i', z_i')$ can be written as,

$$x_i'(Q_1, Q_{+} = 0, Q_{-} = 0) = \sqrt{\frac{2}{3d}} \left( R_0 + \frac{Q_1}{3^{1/4} f} \right) \cos \left( \frac{\phi_i}{2} + \vartheta_i + \frac{\pi}{3} \right), \quad \text{(B6a)}$$

$$y_i'(Q_1, Q_{+} = 0, Q_{-} = 0) = \sqrt{\frac{2}{3d}} \left( R_0 + \frac{Q_1}{3^{1/4} f} \right) \sin \left( \frac{\phi_i}{2} + \vartheta_i + \frac{\pi}{3} \right), \quad \text{(B6b)}$$

$$z_i'(Q_1, Q_{+} = 0, Q_{-} = 0) = 0. \quad \text{(B6c)}$$

These equations show that the positions of the three nuclei can not be expressed by $Q_1, Q_{+}$ and $Q_{-}$ when $\rho = 0$, and hence the expansion Eq. (B3) is not valid as $\Delta V_c (\hat{Q}; \hat{r}_e')$ is not single-valued at $Q_{+} = Q_{-} = 0$ and therefore is not infinitely differentiable. However, if we define another set of $x', y', z'$-axes by a passive rotation through $\phi/2$ about $z'$-axis, the positions of nuclei have defined values when $Q_{+} = Q_{-} = 0$ in this new frame:

$$\tilde{x}_i'(Q_1, Q_{+} = 0, Q_{-} = 0) = \sqrt{\frac{2}{3d}} \left( R_0 + \frac{Q_1}{3^{1/4} f} \right) \cos \left( \vartheta_i + \frac{\pi}{3} \right), \quad \text{(B7a)}$$

$$\tilde{y}_i'(Q_1, Q_{+} = 0, Q_{-} = 0) = \sqrt{\frac{2}{3d}} \left( R_0 + \frac{Q_1}{3^{1/4} f} \right) \sin \left( \vartheta_i + \frac{\pi}{3} \right), \quad \text{(B7b)}$$

$$\tilde{z}_i'(Q_1, Q_{+} = 0, Q_{-} = 0) = 0. \quad \text{(B7c)}$$

Hence, the following expansion is valid,

$$\tilde{K}_{\Lambda \Lambda'} = \sum_{\nu} \tilde{K}_{\Lambda \Lambda'}^{\nu} Q_{\nu} + \frac{1}{2} \sum_{\nu \mu} \tilde{K}_{\Lambda \Lambda'}^{\nu \mu} Q_{\nu} Q_{\mu} + \ldots, \quad \text{(B8)}$$

and therefore using the analysis of Longuet-Higgins [23] in which $K_{\Lambda \Lambda}$ is expanded to third order in $Q_1$ and second order in $\rho$, gives:

$$\tilde{K}_{\Lambda \Lambda} = \tilde{K}^{1}_{\Lambda \Lambda} Q_1 + \tilde{K}^{11}_{\Lambda \Lambda} Q_1^2 + \tilde{K}^{111}_{\Lambda \Lambda} Q_1^3 + \tilde{K}^{++}_{\Lambda \Lambda} \rho^2. \quad \text{(B9)}$$

We also have

$$\tilde{K}_{\Lambda \Lambda \pm 1} = \tilde{K}_{\Lambda \pm 1 \Lambda} = 0, \quad \text{(B10)}$$

and

$$\tilde{K}_{\Lambda \Lambda \pm 2} = \tilde{K}^{1}_{\Lambda \Lambda \pm 2} \rho e^{\mp i\phi}, \quad \text{(B11)}$$

to first order in $\rho$. The matrix elements of $\tilde{K}_{\Lambda \Lambda'}$ also obey

$$\tilde{K}_{\Lambda \Lambda'} \approx -\pi \int dr' \tilde{f}_{\ell \Lambda} (r') \tilde{f}_{\ell' \Lambda'} (r') \times \int d\tilde{t} \tilde{Y}_{\ell \Lambda}^{*} (\tilde{\theta}_e, \tilde{\varphi}_e) V_c (\hat{Q}, \hat{r}_e') \tilde{Y}_{\ell' \Lambda'} (\tilde{\theta}_e, \tilde{\varphi}_e), \quad \text{(B12)}$$

where we use the tilde notation to stress that these are expressed in terms of coordinates in the new frame. The rotation to the new frame from our original one has the
following effects: $\tilde{\theta}_e = \theta_e$ and $\tilde{\varphi}_e = \varphi_e - \phi/2$. Hence a comparison with Eq. (B2) gives

$$K_{\Lambda \Lambda'} = K_{\Lambda \Lambda'} e^{i(\Lambda - \Lambda') \phi/2}. \quad (B13)$$

Because the reaction matrix $K$ and quantum defect ma-
trix $\mu$ are related by $\mu = \mu(Q = 0) + \arctan(K)/\pi \approx \mu(Q = 0) + K/\pi + O(K^3)/\pi + \ldots$, at least to first order, the $K$ matrix and $\mu$ matrix have the same symmetry properties, and hence we write the form of $\mu$ matrix as Eq. (29) and Eqs. (31-33).

[1] I. Dabrowski, G. Herzberg, Can. J. Phys. 58, 1238–1249 (1980). G. Herzberg, J. K. G. Watson, Can. J. Phys. 58, 1250–1258 (1980). G. Herzberg, H. Lew, J. J. Sloan, J. K. G. Watson, Can. J. Phys. 59, 428–440 (1981). G. Herzberg, J. T. Hougen, J. K. G. Watson, Can. J. Phys. 60, 1261–1284 (1982).
[2] H. Helm, Phys. Rev. Lett. 56, 42–45 (1986). H. Helm, Phys. Rev. A. 38, 3425–3429 (1988).
[3] A.E. Orel, I.F. Schneider, and A. Suzor-Weiner, Philos. Trans. R. Soc. London, Ser. A 385, 2445 (2000). I.F. Schneider, A.E. Orel, and A. Suzor-Weiner, Phys. Rev. Lett. 85, 3785 (2000).
[4] V. Kokoouline and C. H. Greene, Phys. Rev. A. 68, 012703 (2003).
[5] V. Kokoouline, C.H. Greene, and B.D. Esry, Nature (London) 412, 891 (2001).
[6] Ch. Jungen, and S. T. Pratt, Phys. Rev. Lett. 102, 023201 (2009).
[7] M. Vervloet and J. K. G. Watson, J. Mol. Spectrosc. 217, 255–277 (2003).
[8] M.J. Seaton, Rep. Prog. Phys. 46, 167–257 (1983)
[9] C.H. Greene and Ch. Jungen, Adv. At. Mol. Phys. 21, 51 (1985)
[10] H. Takagi, J. Phys. B 26, 4815 (1993)
[11] O. Motapon, F. O. W. Tamo, X. Urbain, and I. F. Schneider, Phys. Rev. A 77, 052711 (2008)
[12] A. Giusti, J. Phys. B 13, 3867 (1980)
[13] O.I. Tolstikhin, S. Watanabe and M. Matsuzawa, J. Phys. B: At. Mol. Opt. Phys. 29, L389–L395 (1996).
[14] S. F. Santos and V. Kokoouline and C. H. Greene, J. Chem. Phys. 127, 124309 (2007).
[15] M. Aymar, C.H. Greene, and E. Luc-Koenig, Rev. Mod. Phys. 68, 1015 (1996).
[16] W. Cencek, J. Rychlewski, R. Jaquet, and W. Kutzelnigg, J. Chem. Phys. 108, 2831 (1998). R. Jaquet, W. Cencek, W. Kutzelnigg, and J. Rychlewski, J. Chem. Phys. 108, 2837 (1998).
[17] H. Suno and B. D. Esry, C.H. Greene, J. P. Burke, Jr., Phys. Rev. A 65, 042725 (2002).
[18] B.R. Johnson, J. Chem. Phys. 73, 5051 (1980). B.K. Kendrick, R.T. Pack, R.B. Walker, and E.F. Hayes, J. Chem. Phys. 110, 6673 (1999). R.C. Whitten and F.T. Smith, J. Math. Phys. 9, 1103 (1968). B. Lepetit, Z. Peng, and A. Kuppermann, Chem. Phys. Lett. 166, 572 (1990).
[19] C. M. Lindsay and B. J. McCall, J. Mol. Spectrosc. 210, 60–83 (2001).
[20] I. Mistrik, R. Reichle, U. Müller, H. Helm, M. Jungen, and J. A. Stephens, Phys. Rev. A 61 033410 (2000).
[21] A. Staib and W. Domecke, Z. Phys. D: At., Mol. Clusters 16, 275 (1990).
[22] E. Eyler and F. M. Pipkin, Phys. Rev. A. 27, 2462 (1983).
[23] G. Herzberg and Ch. Jungen, J. Chem. Phys. 77, 5876-5884 (1982). Ch Jungen, I. Dabrowski, G. Herzberg, and D.J.W. Kendall, J. Chem. Phys. 91, 3926-3933 (1989).
[24] N. R. Badnell and M.J. Seaton, J. Phys. B. 32, 3955–3964 (1999).
[25] J. D. Augspurger and C.E. Dykstra, J. Chem. Phys. 88, 3817–3825 (1988). J. D. Augspurger and C.E. Dykstra, J. Chem. Phys. 91, 1384 (1989).
[26] B. K. Kendrick, R. T. Pack, R. B. Walker, and E.F. Hayes, J. Chem. Phys. 110, 6673 (1999).
[27] D.A. Varshalovich, A.N. Moskalev, and V.K. Khersonskii, Quantum Theory of Angular Momentum (World Scientific, Singapore, 1988)
[28] H.C. Longuet-Higgins, in Advances in Spectroscopy, edited by H.W. Thompson (Interscience, New York, 1961), Volume II, page 429–472.