Vibrational Calculations for the HD_2 First-Excited Electronic State Using a Coordinate-Transformation Technique[†]

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We report calculations of the vibrational spectrum of HD_2 in its first-excited electronic state by using a coordinate-transformation technique. The implications of the geometric phase (GP) effect in the spectrum have been investigated. The results show that the lowest 45 vibrational levels calculated using the traditional Longuet−Higgins phase ($\phi/2$, where ϕ is the pseudorotation angle) are in good agreement with those obtained by using a single-surface generalized Born−Oppenheimer equation previously reported by the authors.

1. Introduction

About 40 years ago, Herzberg and Longuet-Higgins[1] showed that a real-valued electronic wave function changes sign when the nuclear coordinates traverse a closed path encircling a conical intersection. This implies a breakdown of the standard Born−Oppenheimer (BO) treatment[2] whenever such an intersection is present.[1,3−8] In 1979, Mead and Truhlar[9−11] showed that the single-surface BO treatment could be generalized by introducing a vector potential into the nuclear Schrödinger equation. Five years later, Berry[12] proved the GP effect (also known[13] as Berry's phase effect and Aharonov−Bohm[14] effect) in a wider context by showing that it can be present on the adiabatic evolution of other quantum systems.

It is well established that the GP effect plays a significant role in molecular spectra,[15−18] and scattering;[19−27] for reviews, see refs 13 and 28. In fact, it was shown in 1979 by Varandas, Tennyson, and Murrell[29] using ab initio calculations, that it may be present even when the system has no symmetry such as is the case for the ground electronic state of LiNaK. Thus, for accuracy, the GP effect must be taken into consideration whenever studying the nuclear dynamics using a single BO surface.

Two alternative schemes have been suggested to account for the GP effect in the case of homonuclear triatomic species (X_3). One consists of multiplying the real double-valued electronic wave functions by a complex phase factor that changes sign on encircling the conical intersection and hence makes the resulting complex electronic wave function to be single-valued.[21,30,31] Indeed, such a complex phase factor leads to the vector potential of Mead and Truhlar[9,11] mentioned above. However, in general, such an approach is difficult to apply[24,32] and its practical value may require further exploitation. The other method is due to Billing and Markovic[33] who have utilized hyperspherical coordinates to include the GP effect in X_3 systems having a single D_{3h} conical intersection seam. In this case, the complex phase factor is incorporated into the nuclear wave function so as to make the total electronuclear wave function single-valued. A similar method has been employed by us[15,17,18] to study the resonance and vibrational spectra of H_3 and Li_3. This work has recently been reviewed,[34] while $J = 0$ calculations of the vibrational states of Li_3 in its lowest electronic doublet state by using a reliable double many-body expansion[35,36] (DMBE) potential energy surface[37,38] and a minimum-residual filter diagonalization[39] (MFD) technique, both without consideration (NGP) and with consideration (GP) of the GP effect, can be found elsewhere.[17,18] Another system that has been much studied is H_3 and its isotopomers.[15,17,18,22,23,40−48] However, a complication arises when one investigates the GP effect in such isotopomers, which is due to the mass scaling involved in defining the hyperspherical coordinates. Kuppermann and Wu[22] studied the GP effect in DH_2 using a mass-scaled Jacobi-vectors[49] formula. More recently, we proposed a novel split-basis (SB) technique[50] to treat the same problem. In all such treatments, the GP angle has been assumed to be path-independent, and hence one must supplement another boundary condition to the nuclear wave functions for nonsymmetric isotopomers of X_3 systems since the conical intersection moves away from the D_{3h} line (see later).

Following a strategy similar to Baer and Englman[51,52] (for a rebuttal of their work, see ref 53), we have recently[54] derived novel single-surface Born−Oppenheimer equations to study the nuclear dynamics in the coupled two-states problem at the vicinity of a conical intersection. Although such a formalism may be strictly valid in the vicinity of the conical intersection, we have conveyed generality to it by invoking the well-known[1,4−7] fact that such regions influence in a dominant way the nuclear dynamics even when energetics allows us to sample areas of configurational space far away from the crossing seam. It was found[54] that the GP angle, $A(\mathbf{R})$, is defined by the argument of the complex electronic vector state in the complex plane spanned by the two real-valued electronic components. Such an angle is identical (up to a constant) to the mixing angle $\gamma(\mathbf{R})$ of the orthogonal transformation that diagonalizes the diabatic potential matrix[46,55−59] in the coupled two-states problem. We have subsequently used this equation (for brevity referred to as VX) to study the GP effect in the vibrational spectra of H_3 and HD_2 systems.[54,60] Moreover, in a previous study with Baer,[48] we have employed a line-integral technique[52,61−71] to study the GP effect in two coupled-state hydrogenic systems. It was then found that the adiabatic−diabatic-transformation (ADT) angle[61−64,66] is also identical (up to a constant) to the mixing angle $\gamma(\mathbf{R})$. We have also discussed[72] the singularities in the Hamiltonian at the crossing seam and established the relationships linking the magnetic

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vector and electronic scalar gauge potentials to the mixing angle. In addition, the study of cyclic phases at N-fold electronic degeneracies has been examined by various authors.[73−75]

The paper is organized as follows. In section 2, we survey the methodology. The calculations of the vibrational spectrum for HD$_2$ are reported in section 3. The conclusions are in section 4.

2. Methodology

2.1. Coordinate-Transformation Treatment. As shown elsewhere,[48] for any isotopomer of a X$_3$ system, the crossing seam in hyperspherical coordinates (ρ,θ,ϕ) is generally defined at an arbitrary value of the hyperradius ρ by

$$\phi_s = \tan^{-1}\left[\frac{\cos\chi_{AC} - t\cos\chi_{AB} - \left(\frac{d_A}{d_C}\right)^2 + t\left(\frac{d_A}{d_B}\right)^2}{\sin\chi_{AC} + t\sin\chi_{AB}}\right] \tag{1}$$

$$\theta_s = 2\sin^{-1}\left[\frac{\left(\frac{d_A}{d_B}\right)^2 - 1}{\cos(\phi_s - \chi_{AB}) - \left(\frac{d_A}{d_B}\right)^2\cos\phi_s}\right] \tag{2}$$

where t is given by

$$t = \left[\left(\frac{d_A}{d_C}\right)^2 - 1\right]\left[\left(\frac{d_A}{d_B}\right)^2 - 1\right]^{-1} \tag{3}$$

and

$$d_X{}^2 = \frac{m_X}{\mu}\left(1 - \frac{m_X}{M}\right) \qquad \chi_{XY} = 2\tan^{-1}\left(\frac{m_Z}{\mu}\right)$$
$$\mu = \sqrt{\frac{m_A m_B m_C}{M}} \qquad M = m_A + m_B + m_C \tag{4}$$

with X, Y, and Z standing for atoms A, B, and C with masses m_A, m_B, and m_C. In case two atomic masses are equal, namely $m_B = m_C$, we get for θ_s the simplified expression

$$\theta_s = 2\sin^{-1}\left|\frac{m_B - m_A}{m_B + 2m_A}\right| \tag{5}$$

while ϕ_s assumes the value π (0) when $m_A > m_B$ and the value zero (π) when $m_A < m_B$; in this work, we have chosen the value $\phi_s = 0$ for $m_A < m_B$. For the case of HD$_2$, the equation for the (straight line) seam is therefore defined[48] by $\theta_s = 0.5048$ rad and $\phi_s = 0$. Since θ_s is different from zero, only closed paths with constant $\theta \geq \theta_s$ will enclose the seam: all other loops corresponding to $\theta < \theta_s$ will not satisfy such a requirement.

In the present work, we use a coordinate-transformation approach[24] to treat the GP effect. First, we note that the hyperspherical coordinates are related to the Cartesian ones (x, y, z) by[76]

$$\begin{aligned} x &= \rho\sin\theta\cos\phi \\ y &= \rho\sin\theta\sin\phi \\ z &= \rho\cos\theta \end{aligned} \tag{6}$$

Then, we introduce the new set of internal coordinates

$$\begin{aligned} x' &= \rho'\sin\theta'\cos\phi' \\ y' &= \rho'\sin\theta'\sin\phi' \\ z' &= \rho'\cos\theta' \end{aligned} \tag{7}$$

and choose the origin ($x' = 0$, $y' = 0$) of this coordinate system to coincide with the location of the conical intersection, such that the z' axis passes through the conical intersection and ϕ' is the azimuthal (pseudorotation) angle about the conical intersection. The two coordinate systems are then related through an $O(3)$ rotation about the y axis by an angle θ_s

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{bmatrix} \cos\theta_s & 0 & \sin\theta_s \\ 0 & 1 & 0 \\ -\sin\theta_s & 0 & \cos\theta_s \end{bmatrix}\begin{pmatrix} x \\ y \\ z \end{pmatrix} \tag{8}$$

As a result, the transformed hyperspherical coordinates are given by

$$\begin{aligned} \rho' &= \rho \\ \theta' &= \cos^{-1}(-\sin\theta_s\sin\theta\cos\phi + \cos\theta_s\cos\theta) \\ \phi' &= \tan^{-1}\left(\frac{\sin\theta\sin\phi}{\cos\theta_s\sin\theta\cos\phi + \sin\theta_s\cos\theta}\right) \end{aligned} \tag{9}$$

with the conical intersection being in this coordinate system always located at $\theta' = 0$.

2.2. Calculation of Spectrum. The rovibrational energy states can be calculated by solving the time-independent Schrödinger equation

$$\hat{H}\chi = E\chi \tag{10}$$

where $\hat{H}$ is the system Hamiltonian. Because the Hamiltonian for zero total angular momentum should be invariant to rotations of the body-fixed coordinate system, it assumes in modified hyperspherical coordinates the form[15]

$$\hat{H} = -\frac{\hbar^2}{2\mu}\left\{\frac{\partial^2}{\partial\rho^2} + \frac{16}{\rho^2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{4\sin^2(\theta/2)}\frac{\partial^2}{\partial\phi^2}\right]\right\} + \frac{15\hbar^2}{8\mu\rho^2} + V(\rho,\theta,\phi) \tag{11}$$

where we have neglected all spin−orbit and spin−spin interactions. Note that we have omitted for simplicity in eq 11 (and will omit from here onward) the primes in the coordinates (ρ',θ',ϕ'). In turn, V is the potential energy surface of the system which depends only on the three internal coordinates (ρ,θ,ϕ). The hyperangles θ and ϕ are related[15] to the Smith−Whitten's (Θ,Φ) hyperangles[77] through the relations $\theta = \pi - 4\Theta$ and $\phi = 2\pi - 2\Phi$. Hence, the range of θ is extended from 0 to π, and hence Jacobi polynomials in $\cos\theta$ can be used as the finite basis representation (FBR) in θ.

The action of the Hamiltonian $\hat{H}$ on the nuclear wave function has been carried out using a mixed grid-basis method.[78] Accordingly, the nuclear wave function $|\chi\rangle$ has been expanded as

$$|\chi\rangle = \sum_{\alpha,j,m} C_{\alpha,j,m}|\rho_\alpha\rangle|jm\rangle \tag{12}$$

where $\{|\rho_\alpha\rangle\}$ is the grid point basis in ρ, and $|jm\rangle = |j;m\rangle|m\rangle$ are the hyperspherical harmonics defined by

$$\langle\theta|j;m\rangle = N_{jm}\sin^{|m|}\left(\frac{\theta}{2}\right)P^{(|m|,0)}_{l=j-|m|/2}(\cos\theta) \tag{13}$$

$$\langle\phi|m\rangle = \frac{1}{\sqrt{2\pi}}\exp(im\phi) \qquad (14)$$

where $P_l^{(|m|,0)}(\cos\theta)$ are the Jacobi polynomials and N_{jm} are the normalization constants. Use of such a nondirect type product basis can somehow ameliorate the difficulties encountered in the calculation of the vibrational spectra of HD_2 which arise due to the sigularity in eq 11 at $\theta = 0$.

To treat the action of the associated kinetic energy operator $\partial^2/\partial\rho^2$, one employs a prime fast Fourier transform[15] (PFFT) method, with a uniform grid being then used for the coordinate ρ. Note that the singularity at $\rho = 0$ can be ignored, since the molecule has a highly repulsive potential energy at such a united-atom limit. Similarly, for the ϕ coordinate, a PFFT method is applied to the sine or cosine basis defined in the following paragraph. The GP effect is then treated during the action of the kinetic operator $\partial^2/\partial\phi^2$ as

$$\frac{\partial^2\chi}{\partial\phi^2} = \exp\left(\frac{i\phi}{2}\right)\,\mathrm{PFFT}^{-1}\left[-\left(n+\frac{1}{2}\right)^2 C_n\right] \qquad (15)$$

where C_n are the coefficients obtained by a forward PFFT of $\exp(-i\phi/2)\chi$, with χ being the nuclear wave function in the grid point basis.

The action of V on the nuclear wave function can be evaluated through the matrix transformation[78]

$$\mathbf{T} = \Theta^\dagger\Phi^\dagger\mathbf{V}\Phi\Theta \qquad (16)$$

where $\boldsymbol{V}$ is the diagonal matrix with elements defined by $V(\rho_\alpha,\theta_\beta,\phi_\gamma)\omega_\beta\omega_\gamma$, where ω_β and ω_γ are the weights corresponding to the quadrature points θ_β ($\beta = 0, 1, ..., N_\theta$) and ϕ_γ ($\gamma = 0, 1, ..., N_\phi$). Note that Φ is the collocation unitary matrix which associates the Gauss-Chebyshev quadrature of the first kind and has elements defined by

$$\Phi^\dagger_{m,\gamma} = \frac{1}{\sqrt{N_\phi}}\exp(-im\phi_\gamma) \qquad (17)$$

where $\phi_\gamma = 2\pi\gamma/N_\phi$. If the GP effect is considered, m is chosen to be a half-integer. Instead, m will be an integer if one ignores the GP effect. The elements of the Φ matrix can be further reduced in terms of molecular symmetry. Thus, for the HD_2 system, the symmetry adapted basis without consideration of the GP effect will be $\cos(2n\phi)$ ($n = 0, 1, ...$) for A_2 symmetry, and $\sin(2n\phi)$ ($n = 1, 2, ...$) for B_1 symmetry. Instead, the symmetry adapted basis with consideration of the GP effect will be $\cos[2(n + {}^1/_2)\phi]$ ($n = 0, 1, ...$) for A_2 symmetry, and $\sin[2(n + {}^1/_2)\phi]$ ($n = 0, 1, ...$) for B_1 symmetry. In turn, the elements of the collocation Θ matrix are given by

$$\Phi^\dagger_{j,\beta} = N_{jm}\sqrt{2\pi\omega_\beta}\,\sin^{|m|-j_{\min}}\left(\frac{\theta_\beta}{2}\right)P^{(|m|,0)}_{l=j-|m|/2}(\cos\theta_\beta) \qquad (18)$$

where $j = |m|/2, |m|/2 + 1, ..., N_\theta - |m|/2$, and $j_{\min}$ is the minimum value of $|m|$ in the FBR (finite basis representation) used for ϕ. For HD_2, without consideration of the GP effect, $j_{\min} = 0$ for A_2 symmetry, and $j_{\min} = 2$ for B_1 symmetry. In turn, $j_{\min} = 1$ for the cases of both A_2 and B_1 with consideration of the GP effect. The grid points θ_β and corresponding weights ω_β are determined by a Gauss-Jacobi quadrature method in terms of the Jacobi function with a fixed value $m = j_{\min}$.

The calculations of the eigenenergies have been carried out by using the MFD technique.[39] Two steps are then carried out: first, the calculation of the filtered states created by the Green operator $(\hat{H} - E)^{-1}$ from an initial random vector using a minimum residual algorithm[39] in a Lanczos subspace; second, the diagonalization of the smaller Hamiltonian matrix represented in the space of such filtered states to get the eigenvalues. Note that, similarly to the simple Lanczos algorithm, the MFD approach has low storage requirements (only two iteration vectors) and utilizes just a single Lanczos recursion for the eigenvalue problem. Furthermore, it can eliminate spurious and ghost eigenvalues.[79]

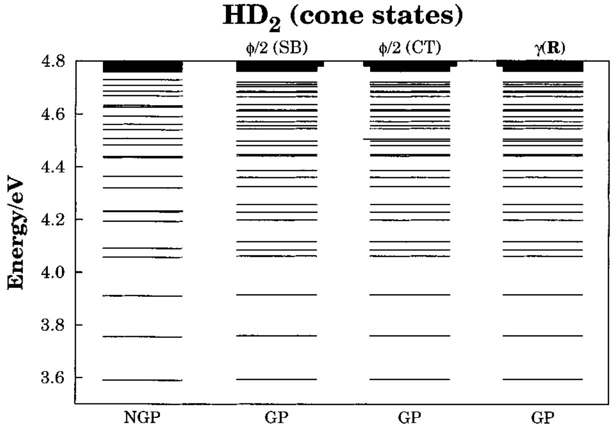

Figure 1. Comparison of the lowest states ($E \leq 4.80$ eV) of HD_2 calculated without consideration (NGP) and with consideration (GP) of the geometric phase effect. Shown by the larger lines are the levels which assume different values in the two sets of GP calculations. See the text.

3. Results and Discussion

All calculations reported in this work have employed the accurate H_3 potential energy surface[80] obtained from the double many-body expansion (DMBE) method (for a recent review, see ref 36). Figure 1 compares the results obtained from four sets of calculations over the range of energies ($E \leq 4.80$ eV). One, denoted NGP, corresponds to the case where we have simply ignored the GP effect. The other three include the GP effect according to distinct schemes. Of these, two employ the traditional[1,4,9,11,17,18,24] Longuet−Higgins phase $\phi/2$, and different techniques to account for the fact that the crossing seam moves away from the $\theta = 0$ line when one employs mass-dependent hyperspherical coordinates. The results obtained by using a recently proposed[50] split-basis technique are indicated in the second column, while those obtained from the coordinate-transformation technique of the present work are shown by the third set of lines and denoted CT. The remaining set of calculations is based on the VX equation[54] and employs the $\mathbf{R}$-dependent GP angle $\gamma(\mathbf{R})$. For completeness, the results obtained from the CT calculations of the present work are also defined numerically in Table 1 (all quoted decimal figures for the eigenvalues are thought to be significant from the analysis of the associated error norms), while similar tabulations can be found in the original papers[50,60] for the SB and $\gamma(\mathbf{R})$ methods. Note that in the SB technique one uses different expansions of the nuclear wave function for $\theta < \theta_s$ and $\theta > \theta_s$. According to such an approach, the wave function for $\theta < \theta_s$ is expanded in terms of a cosine-type basis which allows to impose the total electronuclear wave function to be symmetric with respect to permutation of the two D atoms. Conversely, for $\theta > \theta_s$, one uses a sine-type basis to impose antisymmetry in the nuclear wave function and hence make the total electronuclear wave function symmetric with respect to permutation of the two D atoms. Clearly, the most interesting comparisons are CT versus

TABLE 1: Vibrational Energy Levels (eV) of HD$_2$ Calculated Using the Coordinate-Transformation Technique from the Present Work

1	3.5939	35	4.7650	69	4.8188
2	3.7591	36	4.7661	70	4.8193
3	3.9150	37	4.7686	71	4.8209
4	4.0614	38	4.7697	72	4.8240
5	4.0851	39	4.7727	73	4.8256
6	4.1158	40	4.7729	74	4.8271
7	4.1981	41	4.7750	75	4.8294
8	4.2285	42	4.7758	76	4.8310
9	4.2571	43	4.7760	77	4.8351
10	4.3248	44	4.7776	78	4.8367
11	4.3606	45	4.7803	79	4.8544
12	4.3870	46	4.7808	80	4.8565
13	4.4407	47	4.7812	81	4.8581
14	4.4475	48	4.7832	82	4.8603
15	4.4810	49	4.7837	83	4.8643
16	4.4974	50	4.7842	84	4.8673
17	4.5054	51	4.7864	85	4.8693
18	4.5449	52	4.7870	86	4.8718
19	4.5564	53	4.7877	87	4.8756
20	4.5718	54	4.7889	88	4.8931
21	4.5897	55	4.7917	89	4.9119
22	4.6114	56	4.7926	90	4.9182
23	4.6157	57	4.7965	91	4.9210
24	4.6360	58	4.7970	92	4.9283
25	4.6656	59	4.7988	93	4.9311
26	4.6815	60	4.8010	94	4.9361
27	4.6852	61	4.8021	95	4.9783
28	4.7037	62	4.8061	96	4.9905
29	4.7115	63	4.8071	97	4.9929
30	4.7193	64	4.8089	98	4.9960
31	4.7602	65	4.8099	99	5.0113
32	4.7607	66	4.8119	100	5.0177
33	4.7636	67	4.8134		
34	4.7648	68	4.8169		

SB, and CT versus $\gamma(\mathbf{R})$, and hence we focus on them in the remainder of this section. It is seen that the CT results from the present work are in excellent agreement (they agree to all quoted figures) with the $\gamma(\mathbf{R})$ ones for the lowest 45 levels. For higher energies, there are differences, as indicated by the larger lines in Figure 1. Such lines have been drawn so as to extend toward the set being compared with the CT one. For example, the larger lines in CT pointing to the right-hand-side and those in $\gamma(\mathbf{R})$ pointing to the left-hand-side refer to the CT versus $\gamma(\mathbf{R})$ comparison. Similarly, those in CT pointing to the left-hand-side and those in SB pointing to the right-hand-side refer to the CT versus SB analysis. Note that all lines indicate that the assigned levels assume different energies even if their values coincide up to the third decimal figure. Such differences may be tentatively explained as follows. In the case of the CT and $\gamma(\mathbf{R})$ sets of calculations, we note that a similar situation has been encountered[54] for the vibrational spectra of H$_3$, and hence the differences encountered are also attributed here to the use of different geometric phase angles. Of course, the two phases become identical as one approaches the crossing seam, where they both have the value of $\phi/2$. As for the CT versus SB comparison, we note that, except for level 17 in SB at $E = 4.5054$ eV which is absent, all other levels of both sets up to number 45 show excellent agreement with each other. Thus, except for the small numerical inaccuracies that are unavoidable (and likely to increase with energy), we can only attribute such a discrepancy to the distinct algorithms in which the two approaches are based. A final remark to note is that one may be tempted to conclude that an exact calculation employing the various methods would probably yield identical results, which would provide in itself a manifestation of the fact that physical quantities such as vibrational levels should be gauged invariant with respect to different functional forms for the angle around the conical intersection. Of course, such an issue can only be clarified when converged results are also obtained for the high-lying energy levels.

4. Conclusions

In the present work, we have used the traditional Longuet–Higgins GP angle and a novel coordinate transformation technique to study the GP effect in the vibrational spectra of HD$_2$ first-excited electronic state. Except for one missing vibrational level, numerical calculations have shown that the lowest 45 levels are in very good agreement with the corresponding results obtained via a split-basis technique.[50] Moreover, the results from the present work are found to be in excellent agreement with those obtained[60] by using the VX equation[54] with an **R**-dependent GP angle. For high energy levels, one observes significant differences that are in this case mostly due to differences in the two considered GP angles.

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