

## PAPER



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# Solving the Schrödinger equation of the hydrogen molecule with the free-complement variational theory: essentially exact potential curves and vibrational levels of the ground and excited states of $\Pi$ symmetry†

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Following a previous study of the  $\Sigma$  states (*Phys. Chem. Chem. Phys.*, 2019, **21**, 6327), we solved the Schrödinger equation (SE) of the hydrogen molecule in the ground and excited  $\Pi$  states using the free complement (FC) variational method. This method is a general method to solve the SE: the energies obtained are highly accurate and the potential energy curves dissociate correctly. The calculated energies are upper bound to the exact energies, and the wave functions at any distance are always orthogonal and Hamiltonian-orthogonal to those in the different states calculated in this study. Using the essentially exact potential energy curves, the vibrational energy levels of each state were calculated by solving the vibrational Schrödinger equation.

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## 1. Introduction

A general method for solving the Schrödinger equation (SE) is important because quantum chemistry is governed by the SE. One author proposed the free complement (FC) theory<sup>1–5</sup> for solving the SE. The high potentiality of this theory was demonstrated by solving the SE of helium atoms and hydrogen molecules in the ground states.<sup>2,3</sup> The early-stage results were summarized in a review article.<sup>4</sup> Recently, this theory has been combined with the chemical formula theory (CFT)<sup>6,7</sup> and applied to the studies of the ground and highly excited states of Li and Be atoms.<sup>8</sup>

In a previous study, which is referred to as Paper I,<sup>9</sup> we studied the potential energy curves (PECs) of the hydrogen molecule in the ground and excited states of the  $\Sigma$  symmetry using the FC-variation principle (FC-VP) method. There, we studied the  $^1\Sigma_g$ ,  $^1\Sigma_u$ ,  $^3\Sigma_g$ , and  $^3\Sigma_u$  states. In this study, we study, using the same method, the highly accurate PECs of the hydrogen molecule of the  $\Pi$  symmetry in the ground and excited states: the  $^1\Pi_g$ ,  $^1\Pi_u$ ,  $^3\Pi_g$ , and  $^3\Pi_u$  states are studied by the FC variational method based on the analytical integral evaluations. Thereafter, we solve the vibrational SE of each state using the obtained theoretical PECs.

The study of the accurate wave functions of hydrogen molecules has a long history. In 1933, James and Coolidge (JC) succeeded in obtaining very accurate energy and equilibrium geometry of the hydrogen molecule.<sup>10</sup> In 1965, Kolos and Wolniewicz (KW) reported the accurate methods that were applied to various states of different spin and spatial symmetries.<sup>11</sup> However, their wave functions were not guaranteed to satisfy the orthogonality and Hamiltonian-orthogonality relationships, which are written as

$$\hat{H}(R)\psi_n(R) = E_n(R)\psi_n(R), \quad (1)$$

$$\langle\psi_n(R)|\psi_m(R)\rangle = \delta_{mn}, \quad (2)$$

and

$$\langle\psi_n(R)|\hat{H}(R)|\psi_m(R)\rangle = E_n(R)\delta_{mn}, \quad (3)$$

where  $\psi_n$  is the wave function of the state  $n$ ,  $E_n$  is its energy, and  $R$  the inter-hydrogen distance. These are the necessary conditions for the wave functions to be the exact solutions of the SE. The FC-VP wave functions satisfy these orthogonality and Hamiltonian-orthogonality conditions.<sup>1–5</sup>

Recently we have also calculated the PECs of the hydrogen molecule in various symmetries by the FC-LSE method,<sup>12</sup> which is based on a sampling method and is not variational. Many other studies are carried out on the PECs of the hydrogen molecule. Good reviews are found in ref. 13 including the theoretical studies on the PECs.

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## II. Free complement wave functions

### A. Free complement theory

The FC theory was derived from the scaled SE (SSE) that was introduced to overcome the divergence difficulty of the original SE.<sup>2,3</sup> It was explained in many papers published thereafter,<sup>4,6,7</sup> and also in Paper I.<sup>9</sup> So, here, we only briefly explain the method. The FC method starts from choosing the initial wave function  $\psi_0$ , which is arbitrary but has a large overlap with the target states: the choice of  $\psi_0$  affects the speed of the convergence to the exact solutions of the SE. In this respect, we recently proposed the chemical formula (CF) theory for constructing a good (set of) initial wave function(s)  $\psi_0$ .<sup>6,7</sup> In this study we chose them only intuitively as explained in Section B. Starting from  $\psi_0$ , the solution of the SE is obtained by the recursion formula called the simplest iterative complement interaction (SICI) formula<sup>2,3</sup> as,

$$\psi_{n+1} = [1 + C_n g(H - E_n)]\psi_n \quad (n = 0, 1, 2, \dots) \quad (4)$$

By increasing the order  $n$  of the SICI, we can obtain the exact solutions of the SE without meeting the divergence difficulty of the integrals. In eqn (4),  $C_n$  is a variational parameter,  $E_n$  is the energy of  $\psi_n$ , and  $H$  and  $g$  are the Hamiltonian and scaling functions that will be explained in Section C for the hydrogen molecule. The speed of the converging of eqn (4) is much accelerated if we rewrite eqn (4) by picking up linearly independent and non-diverging functions included in the right hand side of eqn (4) as  $\{\phi_i^{(n)} | i = 1, 2, \dots, M^{(n)}\}$ , where  $\phi_i^{(n)}$  is called the complement functions (cfs) at order  $n$  with  $M^{(n)}$  being the number of the cfs at order  $n$ . Then, we can rewrite eqn (4) by a linear combination of the cfs, which defines the FC wave function at order  $n$  as

$$\psi_n = \sum_i^{M^{(n)}} c_i^{(n)} \phi_i^{(n)}, \quad (5)$$

where  $c_i^{(n)}$  is the variational parameter determined by solving the variational secular equation, giving the total energy  $E_n$  at the same time.

### B. Initial wave function

The initial function  $\psi_0$  of the FC theory is chosen, considering the physical nature of the solution and the converging speed. In the present study, we employ

$$\begin{aligned} \psi_0 = \hat{A} \left[ \exp(-r_{1A} - r_{2B}) + \exp\left(-r_{1A} - \frac{1}{2}r_{2B}\right)(1 - r_{2B}) \right. \\ \left. + \exp\left(-r_{1A} - \frac{1}{3}r_{2B}\right)(1 - r_{2B} + r_{2B}^2) \right] (X_2 + Y_2 I)^A, \end{aligned} \quad (6)$$

as the initial wave function.  $r_{iA}$  represents the distance between electron  $i$  and nucleus A.  $X_i$  and  $Y_i$  are related to the  $x$  and  $y$  coordinates, respectively, perpendicular to the molecular axis,  $Z_i$  of electron  $i$ , as will be mentioned in Section C.  $A$  takes 1 for the  $\Pi$  states,  $\hat{A}$  is the symmetry-adaptation operator, which will be mentioned in Section D, and  $I$  is the imaginary unit. In Paper I for the  $\Sigma$  state, we employed the same function as eqn (6) but

$A$  took zero.<sup>9</sup> The second and third terms in the bracket in eqn (6) ensured that the wave function correctly dissociates to  $H(1s)-H(n=2)$ , and  $H(1s)-H(n=3)$  states, respectively. The wave functions which dissociate to  $H(1s)-H(n=4)$  and higher states are not included in the initial wave function. Thus the calculated results by the present method are highly reliable for up to the  $H(1s)-H(n=3)$  states, but less reliable for the higher states dissociating to  $H(1s)-H(n > 4)$  states. There is no state to dissociate to the  $H(1s)-H(1s)$  state in the  $\Pi$  symmetry, but we included the  $\exp(-r_{1A} - r_{2B})$  term in the initial wave function to make the present calculations comparable with the previous one.<sup>9</sup> We fixed the orbital exponents in eqn (6) in the whole regions of the PECs. This has three merits: the first is that the obtained PECs dissociate into the correct states, the second is that the PECs are smooth because we do not perform the non-linear optimization in the exponential functions, and the last merit is that we can save computational time. The demerit of the fixed exponents is that the description of the wave function in the bonding region is worse than that of the dissociating regions. This demerit is recovered by the FC method automatically as the FC order increases. These merits and demerits also apply to the previous calculations of the  $\Sigma$  states.<sup>9</sup>

### C. Hamiltonian and complement functions in the elliptic coordinates

The elliptic coordinates were employed in the actual calculations. In these coordinates, variables are defined as  $\lambda_i \equiv (r_{iA} + r_{iB})/R$  and  $\mu_i \equiv (r_{iA} - r_{iB})/R$ , where  $R$  is the distance between nuclei A and B, and  $\varphi_i$  is the azimuthal angle around the molecular axis ( $i = 1$  and  $2$ ). We further use supplementary variables,  $X_i$ ,  $Y_i$ , and  $\rho$ , which are defined as

$$X_i \equiv [(\lambda_i^2 - 1)(1 - \mu_i^2)]^{\frac{1}{2}} \cos \varphi_i \quad (7)$$

$$Y_i \equiv [(\lambda_i^2 - 1)(1 - \mu_i^2)]^{\frac{1}{2}} \sin \varphi_i \quad (8)$$

and

$$\rho \equiv \frac{2}{R} r_{12} \quad (9)$$

The  $X_i$  and  $Y_i$  are related to the Cartesian coordinates of electron  $i$  as  $X_i = \frac{2}{R} x_i$  and  $Y_i \equiv \frac{2}{R} y_i$ , respectively. These variables are useful to represent the  $\Pi$  and higher-angular momentum states.

Using the elliptic coordinates, the initial wave function (6) is written in a general form as

$$\begin{aligned} \psi_0 = \sum_i^{M^{(0)}} C_i \hat{A} \exp(-\alpha_{1i} \lambda_1 - \alpha_{2i} \lambda_2 - \beta_{1i} \mu_1 - \beta_{2i} \mu_2) \\ \times \lambda_1^{m_i} \lambda_2^{n_i} \mu_1^{j_i} \mu_2^{k_i} (X_2 + Y_2 I)^A. \end{aligned} \quad (10)$$

The exponents  $\alpha$ 's and  $\beta$ 's in eqn (10) change as the inter-nuclear distance changes in the elliptic coordinates, but they are essentially constants because they are related to the exponents kept constant in eqn (6).

The kinetic operator and the potential in the Hamiltonian are written as

$$\hat{V} = \frac{2}{R} \left[ -\frac{\lambda_1}{\lambda_1^2 - \mu_1^2} - \frac{\lambda_2}{\lambda_2^2 - \mu_2^2} + \frac{1}{\rho} + \frac{1}{2} \right] \quad (11)$$

and

$$\nabla_i^2 = \frac{4}{R^2(\lambda_i^2 - \mu_i^2)} \times \left[ \frac{\partial}{\partial \lambda_i} (\lambda_i^2 - 1) \frac{\partial}{\partial \lambda_i} + \frac{\partial}{\partial \mu_i} (1 - \mu_i^2) \frac{\partial}{\partial \mu_i} + \left( \frac{1}{\lambda_i^2 - 1} + \frac{1}{1 - \mu_i^2} \right) \frac{\partial^2}{\partial \varphi_i^2} \right], \quad (12)$$

respectively. The  $g$  function we employ in this study is

$$g = 1 + \frac{\lambda_1^2 - \mu_1^2}{\lambda_1} + \frac{\lambda_2^2 - \mu_2^2}{\lambda_2} + \rho. \quad (13)$$

When we utilize the kinetic operator, potential operator and the  $g$  function on  $\psi_0$  according to the FC scheme,<sup>2,3,5</sup> the function obtained is written as a sum of the following functions

$$\phi_i = \hat{A} \exp(-\alpha_{1i}\lambda_1 - \alpha_{2i}\lambda_2 - \beta_{1i}\mu_1 - \beta_{2i}\mu_2) \lambda_1^{m_i} \lambda_2^{n_i} \mu_1^{k_i} \mu_2^{p_i} \rho^{p_i} (X_2 + Y_2 I)^A. \quad (14)$$

This is the general expression of the complement function (cf). In the actual calculation, we neglect the  $Y_2 I$  terms from the cf, because the  $X_2$  and  $Y_2 I$  terms are orthogonal and that they have always the same coefficients. Note that the  $j$ ,  $k$ , and  $p$  (the power of  $\mu_1$ ,  $\mu_2$ , and  $\rho$ , respectively) take zero and positive integers and  $m$  and  $n$  (the power of  $\lambda_1$ , and  $\lambda_2$ , respectively) take negative, zero, and positive integers in the cfs. The cfs with negative powers of  $\lambda_1$  and/or  $\lambda_2$  have not been used in other studies.<sup>10,11</sup>

#### D. Symmetry adaptation

The symmetry adaptation operator,  $\hat{A}$ , in eqn (6) is defined as  $\hat{A} = \hat{P}_{\text{spin}} \hat{P}_{\text{space}}$ , where

$$\begin{aligned} \hat{P}_{\text{spin}} &\equiv 1 + \hat{P}_{12} \text{ (for singlet)} \\ &\equiv 1 - \hat{P}_{12} \text{ (for triplet)}. \end{aligned} \quad (15)$$

$$\begin{aligned} \hat{P}_{\text{space}} &\equiv 1 + \hat{P}_{AB} \text{ (for gerade)} \\ &\equiv 1 - \hat{P}_{AB} \text{ (for ungerade)}, \end{aligned} \quad (16)$$

and  $\hat{P}_{12}$  interchanges the electrons 1 and 2 as  $\hat{P}_{12} = \{\lambda_1 \leftrightarrow \lambda_2, \mu_1 \leftrightarrow \mu_2, X_1 \leftrightarrow X_2, Y_1 \leftrightarrow Y_2\}$  and  $\hat{P}_{AB}$  interchanges the nuclei A and B as  $\hat{P}_{AB} = \{\mu_1 \leftrightarrow -\mu_1, \mu_2 \leftrightarrow -\mu_2, X_1 \leftrightarrow -X_1, X_2 \leftrightarrow -X_2, Y_1 \leftrightarrow -Y_1, Y_2 \leftrightarrow -Y_2\}$ . The  $A$  takes 1 for the  $\Pi$  states, as mentioned before. Combinatorial use of these operators can express  $^1\Pi_g$ ,  $^1\Pi_u$ ,  $^3\Pi_g$ , and  $^3\Pi_u$  states from the common initial wave function.

#### E. Integral evaluation

To determine the wave function of each state, we need to construct the Hamiltonian matrix  $\mathbf{H}$  and overlap matrix  $\mathbf{S}$  defined by  $\mathbf{H}_{ij} \equiv \langle \phi_i | H | \phi_j \rangle$  and  $\mathbf{S}_{ij} \equiv \langle \phi_i | \phi_j \rangle$ , respectively, with respect to the cfs. The integrands, in both cases, can be a linear

combination of the following basic integrals:

$$\begin{aligned} I &= \int \exp(-\alpha_1 \lambda_1 - \alpha_2 \lambda_2 - \beta_1 \mu_1 - \beta_2 \mu_2) \\ &\times \lambda_1^m \lambda_2^n \mu_1^j \mu_2^k \rho^p X_1^{A_1} X_2^{A_2} d\lambda_1 d\lambda_2 d\mu_1 d\mu_2 d\varphi_1 d\varphi_2. \end{aligned} \quad (17)$$

where the  $j$ ,  $k$ , and  $p$  take zero or positive integers,  $m$  and  $n$  take negative, zero, or positive integers, and  $A_1$  and  $A_2$  take 0, 1, or 2; the integration range of each variable is  $1 \leq \lambda_i \leq \infty$ ,  $-1 \leq \mu_i \leq 1$ , and  $0 \leq \varphi_i \leq 2\pi$  ( $i = 1, 2$ ), and the Jacobian  $J \equiv \frac{R^6}{64} (\lambda_1^2 - \mu_1^2) (\lambda_2^2 - \mu_2^2)$  is already considered and expanded in the integrands. The  $X_1^{A_1} X_2^{A_2}$  term in eqn (17) is new, appearing in the calculations of the  $\Pi$  state.

To evaluate eqn (17), the  $X_1$  and  $X_2$  are replaced for  $\lambda_i$ ,  $\mu_i$ , and  $\varphi_i$  using eqn (7). The  $\rho^p$  is reduced to  $\rho^0$  when  $p$  is even or  $\rho^{-1}$  when  $p$  is odd using the relationship

$$\begin{aligned} \rho^2 &= \lambda_1^2 + \lambda_2^2 + \mu_1^2 + \mu_2^2 - 2\lambda_1 \lambda_2 \mu_1 \mu_2 \\ &- 2[(\lambda_1^2 - 1)(\lambda_2^2 - 1)(1 - \mu_1^2)(1 - \mu_2^2)]^{\frac{1}{2}} \cos(\varphi_1 - \varphi_2). \end{aligned} \quad (18)$$

The  $\rho^{-1}$  can be expanded using Neuman's expansion,

$$\rho^{-1} = \sum_{\tau=0}^{\infty} \sum_{N=0}^{\infty} D_{\tau}^N P_{\tau}^N \left( \frac{\lambda_1}{\lambda_2} \right) Q_{\tau}^N \left( \frac{\lambda_2}{\lambda_1} \right) P_{\tau}^N(\mu_1) P_{\tau}^N(\mu_2) \cos[N(\varphi_1 - \varphi_2)], \quad (19)$$

where  $D_{\tau}^0 = 2\tau + 1$ ,  $D_{\tau}^N = 2(2\tau + 1)[(\tau - N)!/(\tau + N)!]^2$  ( $N > 0$ ),  $P$  and  $Q$  are the associated Legendre functions of the first and second kinds, respectively, and we take the upper variables when  $\lambda_2 \geq \lambda_1$  and the lower ones otherwise. Then, the integrand in eqn (17) is decomposed into a sum of the products of the  $\lambda_1$  and  $\lambda_2$  part,  $\mu_1$  part,  $\mu_2$  part, and  $\varphi_1$  and  $\varphi_2$  part. We can integrate over these variables separately. In the  $\tau$  summation in eqn (19), we truncate it when the summed value reaches more than 60-digits accuracy. In integrating the  $\lambda_2$  part, we need to evaluate the integrals

$$\begin{aligned} I' &= \int_{\lambda_2=1}^{\infty} \exp(-\alpha \lambda_2) E_i(-\beta \lambda_2) \lambda_2^m \\ I'' &= \int_{\lambda_2=1}^{\infty} \exp(-\alpha \lambda_2) E_i(-\beta \lambda_2) \lambda_2^m \ln \left( \frac{\lambda_2 + 1}{\lambda_2 - 1} \right). \end{aligned} \quad (20)$$

with negative  $m$ . These integrations including the  $E_i$  functions were performed using Maple program.<sup>14</sup> The other calculations to construct the overlap and Hamiltonian matrices were performed using the GMP (GNU multiple precision arithmetic) library.<sup>15</sup>

### III. Convergence of the FC wave functions and potential curves

In Table 1, the number of the cfs  $M^{(n)}$  generated at the orders  $n = 0, 1, 2$ , and 3 is shown for the  $^1\Pi_g$ ,  $^1\Pi_u$ ,  $^3\Pi_g$ , and  $^3\Pi_u$  symmetries. A set of cfs at order  $n$  always includes those at lower orders  $m$  ( $m < n$ ). In the calculations for the  $\Pi$  symmetry,

**Table 1** The number of generated complement functions (cfs)

State	Order			
	0	1	2	3
$^1\Pi_g$	4	29	213	1050
$^1\Pi_u$	4	29	213	1050
$^3\Pi_g$	4	29	213	1044
$^3\Pi_u$	4	29	213	1044

the number of the cfs was smaller than that for the  $\Sigma$  symmetry.<sup>9</sup> This is because the terms representing the H(1s)–H(1s), H(1s)–H(2s), and H(1s)–H(3s) states at the dissociations vanish in the initial wave function of eqn (6) for the  $\Pi$  symmetry. The remaining three states, *i.e.*, H(1s)–H(2p), H(1s)–H(3p), and H(1s)–H(3d) states, are included in the initial wave function. In other words, the PECs are guaranteed to be exact only for these states at the dissociation limit.

We calculated the FC energies and wave functions, changing the inter-nuclear distance  $R$  at order  $n = 0, 1, 2$ , and  $3$ . We refer to the lowest eigenvalue in each symmetry as  $E_0$ , and second, third, ... solutions as  $E_1, E_2, \dots$  Fig. 1 shows the PECs of the  $^1\Pi_u$  state at  $n = 0, 1, 2$ , and  $3$ , and their detailed values are shown in Table 2 at the selected inter-nuclear distances. As the order  $n$  increases, the energies approached from above the reference values cited at the bottom of each distance in Table 2, and some energy values at  $n = 3$  were lower than them; for example, the energy of the first excited state ( $E_1(D)$  state) at  $R = 1.4$  a.u. was calculated as  $E = -0.623745005$  a.u.

by the FC method, while  $E = -0.623586924$  a.u. by Wolniewicz *et al.*<sup>17</sup>

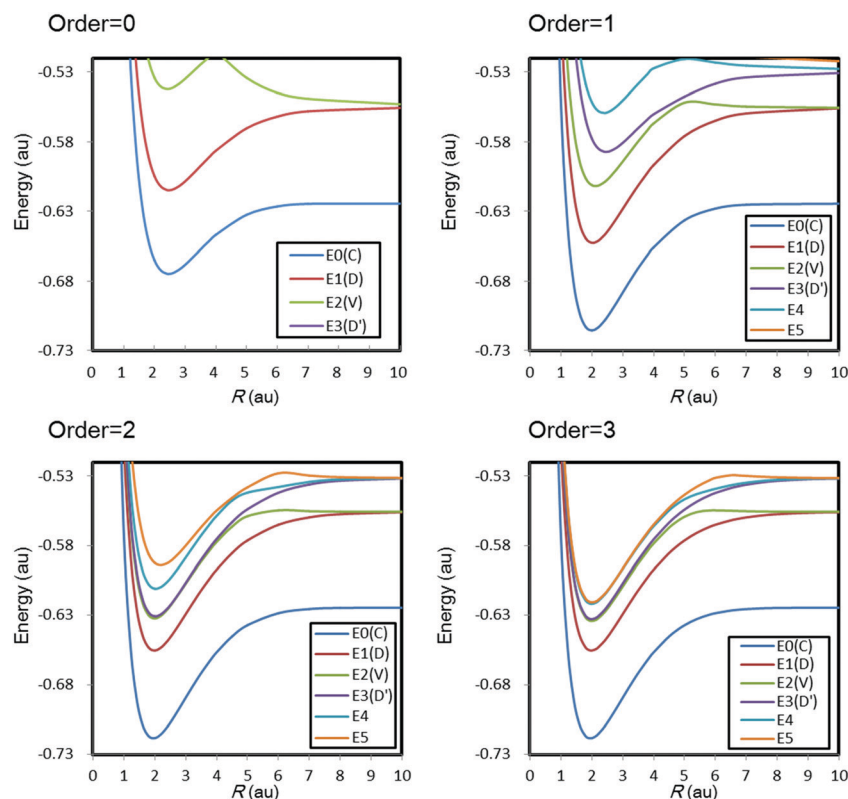
It is observed that the converging speed becomes faster as the inter-nuclear distance becomes longer in both the ground and excited states; for example in the  $E_0(C)$  state, the energy difference between orders  $n = 2$  and  $3$  is  $\Delta E = 0.000117399$  a.u. at  $R = 0.8$  a.u., while it is much decreased to  $\Delta E = 0.000001281$  a.u. at  $R = 10.0$  a.u. This was also observed in the calculation of the  $\Sigma$  symmetry. This is because our initial wave function (order  $n = 0$ ) is already exact when the inter-nuclear distance is infinity, as explained in Section II-B.

In the following discussion, we focus on the order  $n = 3$  results, if not specially mentioned.

## IV. Potential energy curves

In Fig. 2–5, the PECs of the six lowest states in the  $\Pi$  symmetry calculated by the FC method at order  $n = 3$  are plotted. All the calculated PECs are shown together in Fig. 6. The detailed values are given in Tables S1–S4 in the ESI.<sup>†</sup>

The lowest curves in Fig. 2–5 converge to the H(1s)–H(2p) state ( $E = -0.625$  a.u.), and the second and third lowest curves are converging to the H(1s)–H(3p) and H(1s)–H(3d) states ( $E = -0.555555 \dots$  a.u.). In the bonding regions, the FC energies are lower than the literature values at some points; for example, in the  $^3\Pi_u$  state at  $R = 2.0$  a.u., the FC energies are  $E_1 = -0.660716722$  and  $E_2 = -0.634903530$  a.u., while Staszewska

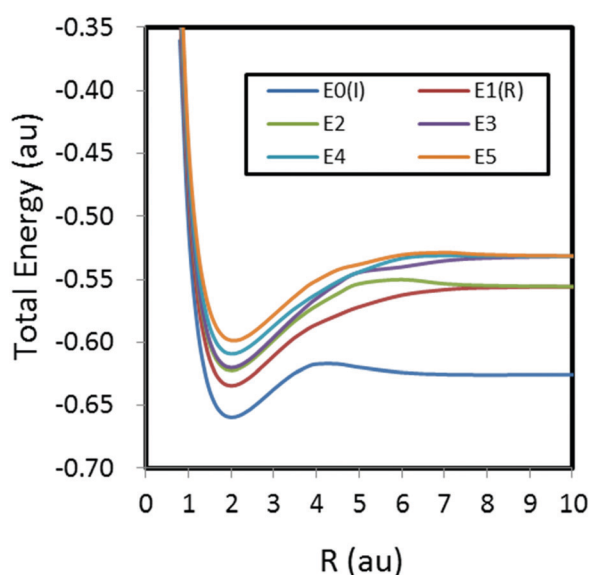


**Fig. 1** Convergence of the potential energy curves of the hydrogen molecule in the  $^1\Pi_u$  state calculated at order  $n = 0, 1, 2$ , and  $3$  of the FC-VP method.

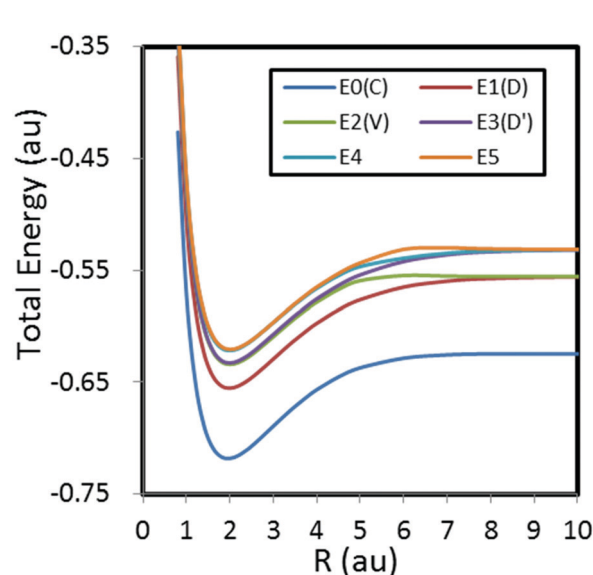
**Table 2** The energies of the hydrogen molecule at selected inter-nuclear distances in the  $^1\Pi_u$  state calculated with the FC-VP method at order  $n = 0, 1, 2$ , and  $3^a$

$R$ (a.u.)	Order	$E_0(C)$	$E_1(D)$	$E_2(V)$	$E_3(D')$	$E_4$	$E_5$
0.8	0	−0.207503679	−0.145335591	−0.080719121	0.778430492		
	1	−0.392128773	−0.324536086	−0.274772586	−0.124542597	−0.097363706	0.113727435
	2	−0.426025923	−0.358835752	−0.334353709	−0.329843374	−0.307715889	−0.269367589
	3	−0.426143322	−0.358968050	−0.335703794	−0.335264576	−0.323696706	−0.321483070
	Ref. <sup>b</sup>	−0.426144006	−0.358968509	−0.335762214	−0.335271730		
1.4	0	−0.584861085	−0.523660320	−0.456409759	0.052670701		
	1	−0.680101765	−0.614947775	−0.568638938	−0.498906325	−0.473827142	−0.282861572
	2	−0.688787663	−0.623725119	−0.600009590	−0.596823350	−0.576342599	−0.546231212
	3	−0.688818370	−0.623745005	−0.601448689	−0.600560621	−0.589376238	−0.587572335
	Ref. <sup>b</sup>	−0.688664532	−0.623586924	−0.601320038	−0.600402500		
2.0	0	−0.665039905	−0.604620553	−0.533960368	−0.236271942		
	1	−0.715534563	−0.652632771	−0.611179125	−0.577672517	−0.551575472	−0.386084631
	2	−0.718225797	−0.655320254	−0.632220183	−0.630646814	−0.610834079	−0.592339138
	3	−0.718242144	−0.655328191	−0.634036945	−0.632669650	−0.621700378	−0.620612402
	Ref. <sup>b</sup>	−0.718242330	−0.655328261	−0.634058929	−0.632670214		
3.0	0	−0.668337663	−0.608446301	−0.534785983	−0.433353887		
	1	−0.688312018	−0.628260028	−0.594184602	−0.580765258	−0.550374839	−0.439898207
	2	−0.689260931	−0.629092845	−0.607262464	−0.606739186	−0.588441485	−0.579951590
	3	−0.689273682	−0.629098846	−0.609246171	−0.607110340	−0.596612330	−0.596402470
	Ref. <sup>b</sup>	−0.689273777	−0.629098883	−0.609254852	−0.607111045		
6.0	0	−0.626515764	−0.561903716	−0.544838675	−0.498919184		
	1	−0.628050005	−0.564792428	−0.553120752	−0.538258760	−0.523108548	−0.518326923
	2	−0.628438756	−0.564982052	−0.554618297	−0.541928061	−0.537843221	−0.527924001
	3	−0.628452760	−0.564986575	−0.554668326	−0.542109754	−0.539119219	−0.531213377
	Ref. <sup>b</sup>	−0.628452782	−0.564986581	−0.554668394	−0.542110459		
10.0	0	−0.624473909	−0.555597166	−0.552946203	−0.495945798		
	1	−0.624547121	−0.555874695	−0.555521393	−0.530690432	−0.527735278	−0.522192678
	2	−0.624575449	−0.556002910	−0.555631706	−0.531700800	−0.531466448	−0.531316166
	3	−0.624576730	−0.556015017	−0.555635886	−0.531729411	−0.531592079	−0.531359626
	Ref. <sup>b</sup>	−0.624576730	−0.556014966	−0.555635880	−0.531729509		

<sup>a</sup> The complete data at order  $n = 3$  for the  $^1\Pi_g$ ,  $^1\Pi_u$ ,  $^3\Pi_g$ , and  $^3\Pi_u$  symmetries are listed in Tables S1–S4 in the ESI. <sup>b</sup> Ref. 16.



**Fig. 2** Potential energy curves of the hydrogen molecule in the  $^1\Pi_g$  state calculated by the FC-VP method at order  $n = 3$ .



**Fig. 3** Potential energy curves of the hydrogen molecule in the  $^1\Pi_u$  state calculated by the FC-VP method at order  $n = 3$ .



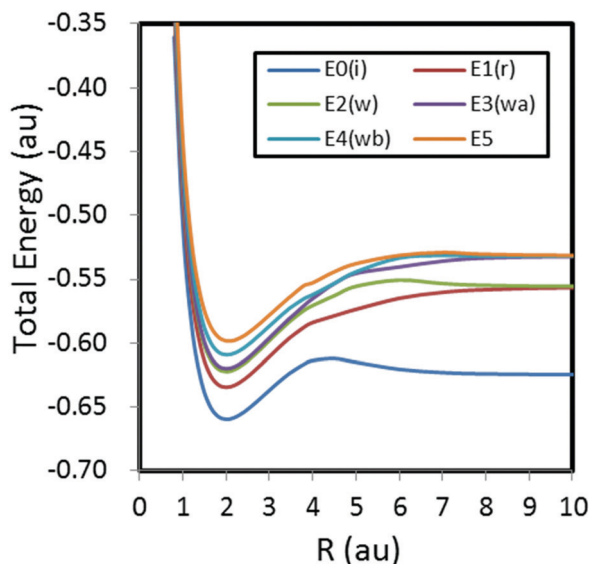


Fig. 4 Potential energy curves of the hydrogen molecule in the  $^3\Pi_g$  state calculated by the FC-VP method at order  $n = 3$ .

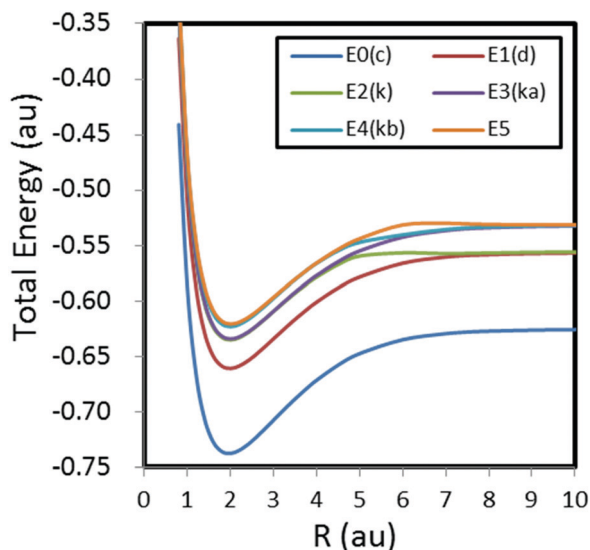


Fig. 5 Potential energy curves of the hydrogen molecule in the  $^3\Pi_u$  state calculated by the FC-VP method at order  $n = 3$ .

and Wolniewicz's energies are  $E_1 = -0.660716627$  and  $E_2 = -0.634901713$  a.u.<sup>16</sup> In the dissociating region, the FC energies agree with the Wolniewicz and Staszewska's values to more than 9 digits; for example, the energy differences between them at  $R = 20.0$  a.u. are  $\Delta E = 8 \times 10^{-11}$ ,  $-1.4 \times 10^{-9}$ , and  $2 \times 10^{-10}$  a.u. for the  $E_0(C)$ ,  $E_1(D)$ , and  $E_2(V)$  states, respectively, in the  $^1\Pi_u$  symmetry.<sup>16</sup> In short inter-nuclear regions, where the PEC is repulsive and steep, the FC energies seem to have more than 4-digit accuracies; for example at the worst case, the energy of the  $E_2(V)$  state at  $R = 0.8$  a.u. is  $E = -0.335704$  a.u., while Wolniewicz and Staszewska reported  $E = -0.335762$  a.u. In the previous calculation of the  $E_4$  state in the  $^1\Sigma_u$  symmetry, the FC energy has only 3-digit accuracy compared with the best

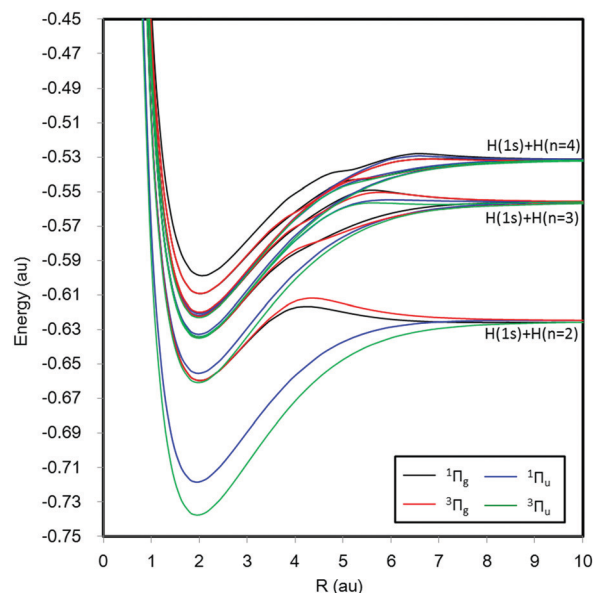


Fig. 6 Potential curves of all the  $\Pi$  states calculated by the FC-VP method at order  $n = 3$ . The black, blue, red, and green curves are for the  $^1\Pi_g$ ,  $^1\Pi_u$ ,  $^3\Pi_g$ , and  $^3\Pi_u$  symmetries, respectively.

literature value, even though the number of cfs in the  $\Sigma$  calculation is more than that in the present  $\Pi$  calculation. This is because, we suppose, the best literature values of the  $\Pi$  calculation are not so accurate compared with that of  $\Sigma$  calculation. Our calculations are not so accurate in the short region, because no special wave functions are included in the initial wave function to describe the short region. To study very short inter-nuclear regions, we need to increase the order of the FC wave function.

The fourth, fifth, and sixth lowest curves in Fig. 2–5, which must dissociate into the  $H(1s)-H(n=4)$  states, are not guaranteed to dissociate into the correct energy under the present conditions because we do not include the appropriate exponents in the initial wave function. However, the FC method produces qualitatively correct PECs for those states: it is observed that the fourth, fifth, and sixth lowest curves almost converge to the correct energy ( $E = -0.531250$  a.u.) to more than 3 digits at  $R = 20.0$  a.u. in all the  $\Pi$  calculations. For example, in the  $^1\Pi_g$  state, the fourth, fifth, and sixth lowest energies are  $E = -0.531320$ ,  $-0.531266$ , and  $-0.531261$  a.u., respectively, at  $R = 20.0$  a.u. In the bonding and short regions in the fourth states the FC energies have more than 3-digit accuracies; for example in the  $^1\Pi_u$  state,  $E = -0.335265$ ,  $-0.632670$ , and  $-0.607110$  a.u. for  $R = 0.8$ ,  $2.0$  and  $3.0$  a.u., respectively, while Wolniewicz and Staszewska reported  $E = -0.335272$ ,  $-0.632670$ , and  $-0.607111$  a.u., respectively.<sup>16</sup> For the sixth states of the  $^1\Pi_g$ ,  $^1\Pi_u$ , and  $^3\Pi_g$  symmetries that dissociate to  $H(1s)-H(n=4)$ , small wiggles are found in the regions between 3 and 6 a.u. The energies of these states are less reliable in the present calculation because the appropriate initial wave functions corresponding to these states were not included in the calculations as explained in Section II-B. Comparing the FC energies of the sixth states of  $^1\Pi_u$  symmetry at the order 3 of the FC calculations with those at order 2, the

energies seem not to converge yet. In order to calculate these states more accurately, we need to include the appropriate wave function in the initial wave function which dissociate into the  $H(1s)-H(n=4)$  states.

In the  $\Sigma$  states, deep double-well type potential curves are found; for example, in the EF  $^1\Sigma_g$ , GK  $^1\Sigma_g$ , H $\bar{H}$   $^1\Sigma_g$ , and B''B  $^1\Sigma_u$  states.<sup>9,13</sup> In the  $\Pi$  states, on the other hand, no deep double-well type potential curves are found in the lowest six states of each symmetry. Very shallow minimums due to the van der Waals interaction were found at 8.2 a.u. in the I  $^1\Pi_g$  PEC with  $162.5\text{ cm}^{-1}$  depth, at 6.96 a.u. in the k  $^3\Pi_u$  PEC with  $395.0\text{ cm}^{-1}$  depth, and at about 12 a.u. in the w  $^3\Pi_g$  PEC with  $7.5\text{ cm}^{-1}$  depth. In the  $\Sigma$  states, a repulsive PEC was found in the b  $^3\Sigma_u$  state and no vibrational state exists there, while no repulsive PEC was found in the six lowest electronic states of  $\Pi$  states. This is because two electrons in the six lowest  $\Pi$  states occupy the  $\sigma$  and  $\pi$  orbitals which do not exhibit the anti-bonding interaction.

## V. Vibrational energy levels

We calculated the vibrational energy levels of all the calculated electronic states in the same way as the previous paper,<sup>9</sup> using the Level 8 program,<sup>17</sup> which can solve the radial Schrödinger equation for bound and quasi-bound levels. The calculated vibrational energy levels  $E_v$ , the expectation value of the nuclear distances  $\langle R \rangle$ , and those of the squared values  $\langle R^2 \rangle$  associated with the calculated potential energy curves are summarized in Table 3 for the  $E_0(C)$   $^1\Pi_u$  state. The vibrational energy splitting ( $E_v - E_{v-1}$ ) of the  $E_0(C)$   $^1\Pi_u$  state calculated by our method has more than 3-digit accuracies compared with the experimental value, as shown in Table 3. In the study by Kolos and Wolniewicz,<sup>18</sup> ten vibrational levels were calculated for the  $E_0(C)$   $^1\Pi_u$  states, while we obtained 13 vibrational levels with the FC method. Note that we do not include the non-adiabatic effects to calculate the vibrational levels. To study high

vibrational levels, non-adiabatic effects become important. In such cases, a non-BO treatment will become necessary to obtain accurate energy levels.<sup>20</sup>

The complete data for all the calculated vibrational levels associated with all the PECs of the ground and excited states of the  $^1\Pi_g$ ,  $^1\Pi_u$ ,  $^3\Pi_g$ , and  $^3\Pi_u$  symmetries are listed in Tables S5–S8 of the ESI.† All the vibrational energy levels are plotted in Fig. 7. In Fig. 8, all the ground and excited PECs in the  $^1\Pi_g$ ,  $^1\Pi_u$ ,  $^3\Pi_g$ , and  $^3\Pi_u$  symmetries and vibrational levels associated with each PEC are shown in different colors. These results are helpful for further investigations in theoretical and experimental studies in future.

## VI. Summary

We have solved the Schrödinger equation of the hydrogen molecule with high accuracy for the ground and excited states of the  $\Pi$  symmetries,  $^1\Pi_g$ ,  $^1\Pi_u$ ,  $^3\Pi_g$ , and  $^3\Pi_u$  states, using the free complement (FC) variational method within the Born–Oppenheimer approximation. We calculated the potential energy curves (PECs) of the ground and excited states and the associated vibrational energy levels. The calculations were systematic within the FC-VP theory and all the PECs were obtained in a common comprehensive manner. The ground and excited energies and the wave functions were obtained simultaneously as the eigenvalues and the eigenvectors of the same secular equations, which guarantees that the wave functions in different states are orthogonal and Hamiltonian orthogonal to each other, and that the energies are the upper bound to the exact energies.

The initial wave function we employed in the present study is a sum of the products of the two exact wave functions of the hydrogen atoms in the ground and/or excited states in the dissociation limit, *i.e.*,  $H(1s)-H(n=2)$ , and  $H(1s)-H(n=3)$  states, which ensures that the potential energy curves correctly dissociate to these states. We did not include the wave function

**Table 3** Vibrational energy levels  $E_v$  ( $\text{cm}^{-1}$ ) of the ground  $E_0(C)$   $^1\Pi_u$  states calculated from the PECs of the FC-VP method at the order  $n=3$  and the comparison with other studies<sup>a</sup>

State	$\nu$	FC method				Ref. (theoretical) <sup>d</sup>	Ref. (experimental) <sup>e</sup>
		$\langle R \rangle^b$	$\langle R^2 \rangle^b$	$E_v^c$	$E_v - E_{v-1}$	$E_v - E_{v-1}$	$E_v - E_{v-1}$
$^1\Pi_u$	0	1.06675	1.15220	−156453.28			
	1	1.13572	1.33325	−154145.20	2308.08	2310.62	2308.67
	2	1.20781	1.53332	−151971.81	2173.39	2176.04	2174.67
	3	1.28385	1.75607	−149929.62	2042.19	2044.98	2043.14
	4	1.36474	2.00603	−148016.24	1913.38	1915.03	1913.07
	5	1.45140	2.28874	−146231.31	1784.94	1789.08	1783.87
	6	1.54538	2.61250	−144576.13	1655.18	1655.81	1654.33
	7	1.64904	2.99002	−143053.42	1522.70	1523.20	1522.56
	8	1.76602	3.44107	−141667.79	1385.63	1386.41	1386.09
	9	1.90217	3.99862	−140425.98	1241.81	1242.75	1242.27
	10	2.06797	4.72343	−139338.68	1087.30	1088.54	1087.85
	11	2.28274	5.73571	−138421.43	917.24		
	12	2.59278	7.34115	−137698.08	723.35		
	13	3.17123	10.80733	−137208.95	489.13		

<sup>a</sup> The complete data for all the calculated vibrational levels associated with all the PECs of the ground and excited states of the  $^1\Pi_g$ ,  $^1\Pi_u$ ,  $^3\Pi_g$ , and  $^3\Pi_u$  symmetries are listed in Tables S5–S8 of the ESI. <sup>b</sup> The expectation value of the nuclear distance  $R$  in Å and that of the squared value.

<sup>c</sup> Absolute energies in  $\text{cm}^{-1}$ . <sup>d</sup> Ref. 18. <sup>e</sup> Ref. 19.

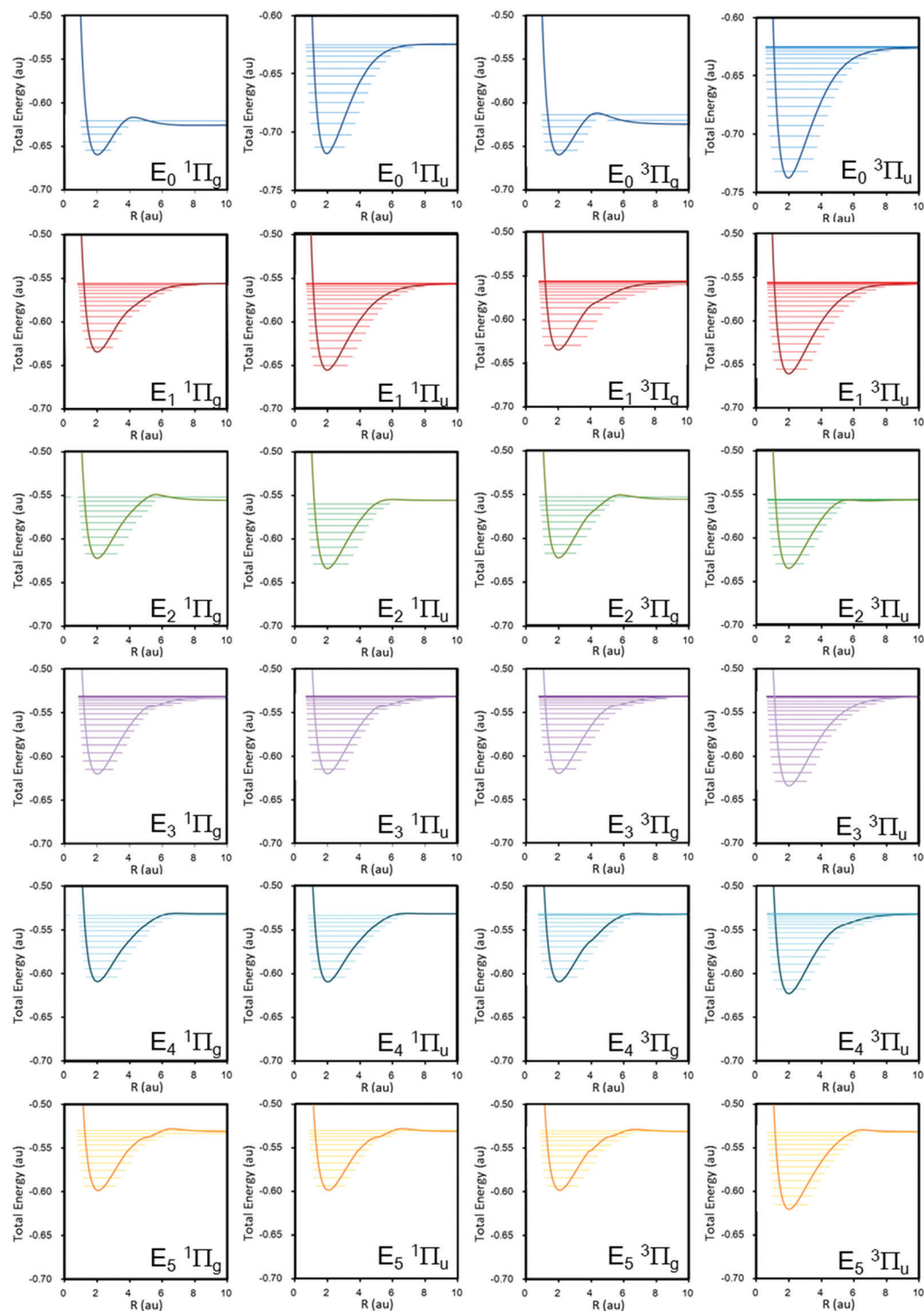


Fig. 7 All vibrational energy levels associated with each PEC calculated by the FC-VP method at order  $n = 3$ . The numerical data are listed in Tables S5–S8 of the ESI.†

which dissociates to the  $H(1s)-H(n = 4)$  state in the initial wave function. However, it was observed that the fourth, fifth, and sixth lowest curves corresponding to the  $H(1s)-H(n = 4)$  state almost converge to the correct energy to more than three digits at  $R = 20.0$  a.u. For the three lowest curves, it was observed that the energy values have three- to six-digit accuracies in the

whole region of the PECs, and that the energies become more accurate as the inter-nuclear distance increases.

Using the Born–Oppenheimer potential-energy curves calculated with the FC method, we calculated the vibrational wave functions and the energy levels associated with all the potential curves of different symmetries. The energy values of the



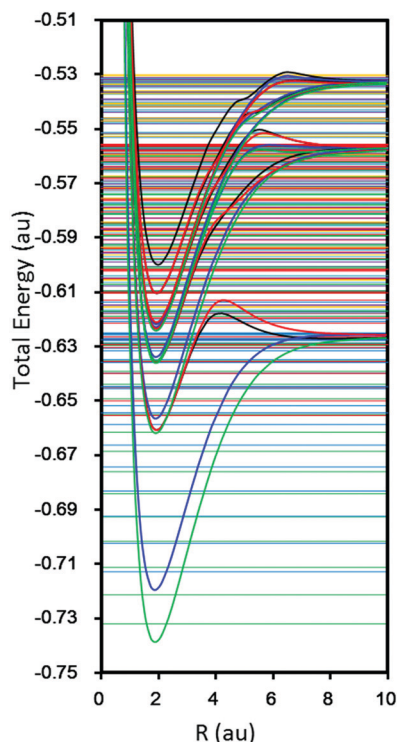


Fig. 8 All ground and excited potential energy curves (PECs) in the  $1\Pi_g$  (black),  $1\Pi_u$  (blue),  $3\Pi_g$  (red), and  $3\Pi_u$  (green) symmetries and vibrational levels associated with each PEC.

potential curves and the associated vibrational levels are given in the supplemental results. They should be useful as highly accurate reference data. See ESI† for detailed energy values.

## Conflicts of interest

There are no conflicts of interest to declare.

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