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Non-Born-Oppenheimer potential energy curve: Hydrogen molecular ion with highly accurate free complement method

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Although the concept of a potential energy curve (PEC) originates from the outgrowth of the Born-Oppenheimer (BO) approximation, we propose the application of analysis methods for the physical PEC with non-Born-Oppenheimer (non-BO) wave functions. A numerical examination was performed with the highly accurate non-BO vibronic wave functions of hydrogen molecular ion, which were obtained in our previous studies with the free complement method. The reduced density function integrated over the electron coordinates plays an important role in understanding nuclear motion dynamics, since it corresponds to the wave function density of the vibrational and rotational motions. The maximum positions of this density indicate the high existence probability of nuclei and can be considered as a discrete representation of the PEC. Whereas an ordinary PEC with the BO approximation is obtained as a numeric curve after multiple electronic state calculations at fixed nuclear coordinates, we propose a new analytical expression of the PEC from a non-BO wave function. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4818161>]

I. INTRODUCTION

The potential energy curve (PEC) plays an important role in understanding chemical reactions and it is a corollary of the Born-Oppenheimer (BO) approximation at fixed nuclear coordinates.¹ In actual molecular calculations on the BO approximation, however, the PEC is usually described as an accumulation of numerical discrete points which are evaluated by solving the electronic Schrödinger equation at fixed nuclear coordinates. Some analytical fitting functions²⁻⁵ or numerical procedures, such as the discrete variable representation method,⁶⁻⁸ are required to proceed to a vibrational and/or rotational mode analysis. On the other hand, the non-Born-Oppenheimer (non-BO) or non-adiabatic wave functions include the coupled motion effects of every particle and can be considered to be the limit of nonrelativistic quantum mechanics. Compared to ordinary electronic state calculations on the BO approximation, however, the fully non-BO calculations are infrequently performed due to the difficulties of their computation and analysis. Their use has especially been avoided for understanding molecular reaction dynamics, as they are considered to possibly destroy an important feature typified by the PEC. Thus, novel analysis methods of the non-BO wave functions are required to extract important physical properties related to the PEC.

In a series of articles,^{9,10} we performed highly accurate non-BO calculations of hydrogen molecular ions for the ground and electronic, vibrational, and rotational excited states with the free complement (FC) method.¹¹⁻²⁰ One of the present authors proposed the FC method to accurately solve the Schrödinger equation of atoms and molecules. A

significant feature of this method is that the wave function is automatically constructed from the system's Hamiltonian. Therefore, it is applicable not only to the Schrödinger equation on the BO approximation but also to the relativistic Dirac equation,¹⁶ and it can be extended to non-BO calculations since each Hamiltonian takes care of its appropriate wave functions.^{9,10}

In the first paper of this series,⁹ very accurate non-BO wave functions of the ground and lower vibrational excited states for H₂⁺ and its isotopomers (D₂⁺, T₂⁺, HD⁺, HT⁺, and DT⁺) were obtained with the correct energies with up to more than 30 digits. That provides numeric proof that the FC method is applicable to the non-BO system and guaranteed to converge to the exact solutions without any theoretical difficulty. In our second paper,¹⁰ we extended these highly accurate calculations to the electronic, highly vibrational, and highly rotational (angular momentum) excited states. There have been few reports of these in the literature especially for the electronic and highly rotational excited states, even in the simplest H₂⁺ system. The precise theoretical spectra including nuclei in motion are valuable for the studies of astronomy observations and cryogenic science, where various quantum mechanical effects clearly appear.²¹⁻³⁶

Most quantum chemists believe that the non-BO calculation is difficult. However, using the above important feature of the FC method, the non-BO computation would be made much easier in some sense than the PEC analysis on the BO approximation. This latter case rather has a high computational cost for determining various molecular properties, such as the energy minimum structure, transition state, and vibrational frequency.

In the present study, we attempt to obtain a result from the analysis of physical properties related to the PEC using the highly accurate non-BO vibronic wave functions of hydrogen

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molecular ion. It is natural to imagine that the reduced density function integrated over the electron coordinates plays an important role in the present problem because the remaining coordinates consist of the nuclear coordinates. Several notations for the analysis can be defined for the non-BO PEC; for example, Hunter and Wilson provided their own definitions of the non-adiabatic PECs.^{37–40} Their PEC definitions, however, contained the molecular or pseudo-electronic Hamiltonian and the formulations are difficult. Here, we propose an alternative definition of the non-BO PEC using the property of the reduced density function. This is different from Hunter's and Wilson's definitions, and our definition of the PEC is rather straightforwardly obtained based on the Schrödinger equation of the nuclear motions.

The present paper is organized as follows. The theoretical formulations for the analysis methods of the non-BO PEC are provided in Sec. II. For the reference, Sec. III provides the highly accurate PECs of hydrogen molecular ion on the BO approximation, where the FC method is used again. Numerical examinations of the non-BO PECs of hydrogen molecular ion with the highly accurate non-BO wave functions are given in Sec. IV. We present concluding remarks in Sec. V.

II. THEORY: NON-BORN-OPPENHEIMER POTENTIAL ENERGY CURVE

A. Reduced density function with integration over the electron coordinates

Principally in the non-BO calculation, the electronic and nuclear motions are coupled together and their coordinates are not separable. After obtaining the accurate non-BO wave functions, the reduced density function with integration over the electron coordinates is a physical quantity related to the nuclear motion dynamics corresponding to the internal vibrational and/or rotational motions. The wave function of the simplest hydrogen molecular ion with angular momentum S is represented by the internal radial coordinates r_1 , r_2 , and R , where r_1 and r_2 are the electron-nucleus distances and R is the nucleus-nucleus distance.^{9,10} The reduced density function of the S states of hydrogen molecular ion, therefore, is given by⁹

$$f(R) = \int d\tau'_R \cdot \psi(r_1, r_2, R) \psi^*(r_1, r_2, R), \quad (1)$$

where $\psi(r_1, r_2, R)$ is a normalized S -symmetry non-BO wave function and $d\tau'_R$ is defined as the integration over the electron coordinates. The density $f(R)$ is a function of R and corresponds to the density of the vibrational motion (due to the S symmetry), where $f(R)$ spontaneously contains the anharmonicity and non-BO effects originating from the much faster electron motion. Therefore, $f(R)$ becomes nonsymmetric to the equilibrium position, especially for the highly vibrational levels due to their large anharmonicity close to the dissociation. The regions with large $f(R)$ amplitude indicate the high existence probabilities of nuclei. The left and right maximum positions to the equilibrium, therefore, can be considered to be discrete representations corresponding to the PEC, and they should be used as one of the measurements of the PEC from the non-BO wave functions.

B. Analytical potential energy curve from the non-BO wave function

For the BO approximation, we first need to evaluate the electronic wave functions at various fixed nuclear coordinates, and then obtain a numerical PEC composed of the electronic total energies. The vibrational analysis which follows the PEC requires some analytical fitting or numerical procedures.^{2–8} Even in this manner, we cannot evaluate any non-BO effect coming from the negligible coupling between the electrons and nuclei motions. In contrast, with the non-BO case, we first obtain the physical reduced density function, defined in Eq. (1), including the anharmonicity and non-BO effects. At that stage we still do not have a PEC. However, by solving an inverse problem to determine an unknown potential function, $V(R)$, it is possible to obtain an analytical function corresponding to the PEC.

For the S -symmetry state of a diatomic molecule, if one assumes the vibrational wave function $\varphi(R)$ of the nuclear coordinate R , the Schrödinger equation of the nuclear motion can be given by

$$\left[-\frac{1}{2\mu} \frac{d^2}{dR^2} + V(R) \right] \varphi(R) = E \varphi(R), \quad (2)$$

where μ is the effective mass of two nuclei, $V(R)$ is a potential energy function that remains to be determined, and $\varphi(R)$ and E are the vibrational wave function and the corresponding energy eigenvalue, respectively. In the non-BO case, we first obtain $\varphi(R)$ and E by taking the root square of the reduced density function $f(R)$, given by

$$\varphi(R) = \sqrt{f(R)}. \quad (3)$$

Note that a phase factor can be ignored since it is canceled by the left and right hand sides in Eq. (2). Therefore, if we modify Eq. (2), the unknown potential energy function can be given by

$$V(R) = \frac{1}{2\mu} \frac{d^2 \varphi(R)}{dR^2} \frac{1}{\varphi(R)} + E, \quad (4)$$

where the energy eigenvalue and corresponding eigenfunction obtained in the non-BO calculations can be used as E and $\varphi(R)$, respectively. Since $\varphi(R)$ is an analytical function, $V(R)$ is also represented as an analytical function. A single non-BO state can describe $V(R)$ for the whole range of R , whereas the PEC on the BO approximation is just expressed by a numerical curve and a lot of calculations at various coordinates R are required. Equation (4) only contains the differential operators with respect to the nuclear coordinates (the differentiation of $\varphi(R)$ is always possible), and there is no further integration with respect to the Hamiltonian of the electronic coordinates since the integration over those coordinates has already occurred.

III. BORN-OPPENHEIMER POTENTIAL ENERGY CURVES OF HYDROGEN MOLECULAR ION

It is worthwhile to draw the PECs on the BO approximation to make a comparable reference with the non-BO PECs

TABLE I. The equilibrium distances and their total energies of the PECs on the BO approximation with the FC wave functions ($n = 14$, $M_n = 480$) and the averaged non-BO PECs for the electronic ground $1s\sigma_g$ and excited $3d\sigma_g$ states.

	Equilibrium distance: R_e (a.u.)	Energy (a.u.)
Electronic ground state: $1s\sigma_g$		
BO PEC	1.997 193 319 969 992 9	-0.602 634 619 106 539 869 378
Ref. 41	1.997 193 320	-0.602 634 619 107
$\mu_e \times E(\text{BO})^a$		-0.602 306 592 683
Non-BO PEC: $V(R)$	1.998 181 149	-0.602 384 343 986
Electronic excited state: $3d\sigma_g$		
BO PEC	8.834 164 503 179 200 609 421 533 521	-0.175 049 035 895 464 389 091 719 403 786 087 150
$\mu_e \times E(\text{BO})^a$		-0.174 953 753 103
Non-BO PEC: $V(R)$	8.838 382 428	-0.174 956 573 837

^aThe energy including the effective mass effect, where μ_e is the effective mass of nucleus and electron.

later discussed. In our previous works, we already presented the accurate numerical PECs of hydrogen molecular ion on the BO approximation with the FC method.^{10,19} Here, we further update the accuracies of the PECs with the higher order FC wave functions. We employed the same initial and g functions of the FC method for σ_g symmetry as given in our second paper of this series.¹⁰ The calculations were performed with $n = 14$ and $M_n = 480$, n being the order of the FC method and M_n being the number of complement functions, which are much highly accurate than the previous one: $n = 6$ and $M_n = 112$ in Ref. 10. The PECs of the three electronic states, ground and two excited states assigned to the $1s\sigma_g$, $2s\sigma_g$, and $3d\sigma_g$ states, were calculated and shown in Fig. 1. The intersystem crossing appears between the $2s\sigma_g$ and $3d\sigma_g$ states around $R = 4.0$ a.u. and the PEC of $2s\sigma_g$ becomes dissociative but that of $3d\sigma_g$ has a minimum around $R = 8.8$ a.u.

We also investigated the equilibrium distances R_e (energy minimum positions) and their total energies for the electronic ground $1s\sigma_g$ and excited $3d\sigma_g$ states. For the $1s\sigma_g$ state, $R_e = 2.0$ a.u. is often employed in the literatures of hydrogen molecular ion. The calculated energy at $R = 2.0$ a.u. was $-0.602\,634\,214\,494\,946\,237\,710$ a.u. with the present FC wave function. However, Bishop indicated more the precise equilibrium position as $R_e = 1.997\,193\,320$ a.u. with the total energy of $-0.602\,634\,619\,107$ a.u.⁴¹ In our calculations, we obtained more precise equilibrium distances of $R_e = 1.997\,193\,319\,969\,992\,9$ a.u. with the energy: $-0.602\,634\,619\,106\,539\,869\,378$ a.u. for the $1s\sigma_g$ state and $R_e = 8.834\,164\,503\,179\,200\,609\,421\,533\,521$ a.u. with the energy: $-0.175\,049\,035\,895\,464\,389\,091\,719\,403\,786\,087\,150$

a.u. for the $3d\sigma_g$ state, whose results are also summarized in Table I. On the BO approximation, they should be the most precise equilibrium distances and energies in the published literatures.

IV. NON-BORN-OPPENHEIMER POTENTIAL ENERGY CURVES OF HYDROGEN MOLECULAR ION WITH THE HIGHLY ACCURATE NON-BO WAVE FUNCTIONS

A. Free complement wave function of the $1S$ states

Let us first introduce the highly accurate free complement wave functions of the S-symmetry vibronic states in the non-BO Hamiltonian, which were calculated in our previous studies of this series (for details, see Refs. 9 and 10). The most accurate wave functions up to the highly vibrational levels were constructed from the initial function including the adequate exponents for both the electronic ground $1s\sigma_g$ and excited $3d\sigma_g$ states. The FC wave functions at the order $n = 15$ with its dimension $M_n = 22\,689$ are employed everywhere in this study.¹⁰ The form of the wave function is represented by

$$\psi = (1 \pm P_{12}) \left[\sum_{(a,b,c,j,l_1,l_2)} C_{(a,b,c,j,l_1,l_2)} \cdot s^a t^b R^c \cdot \exp(-\alpha^{(j)} s) \times \exp(-\gamma^{(j)} (R - R_e^{(j)})^2) \cdot Y_{L,M}^{l_1,l_2}(\mathbf{r}_1, \mathbf{r}_2) \right], \quad (5)$$

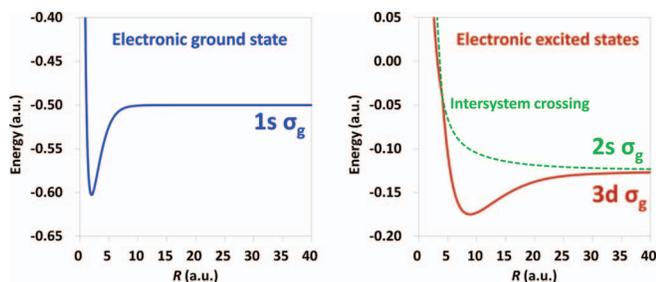


FIG. 1. The PECs on the BO approximation for the electronic ground $1s\sigma_g$ (left) and excited $2s\sigma_g$ and $3d\sigma_g$ (right) states, calculated by the FC method with $n = 14$ and $M_n = 480$ from $R = 0.5$ to 40 a.u. (0.1 a.u. interval).

where $Y_{L,M}^{l_1,l_2}(\mathbf{r}_1, \mathbf{r}_2)$ are the solid spherical harmonics⁴² and $L = M = l_1 = l_2 = 0$ for S symmetry. s and t are the Hylleraas coordinates, defined by $s = r_1 + r_2$ and $t = r_1 - r_2$. Here, $1 \pm P_{12}$ describes the nuclear spin states and its plus or minus sign represents a singlet or triplet nuclear spin, respectively. Three different sets of the nonlinear values $\alpha^{(j)}$, $\gamma^{(j)}$, and $R_e^{(j)}$ ($j = 1, 2$, and 3) were used to represent the electronic ground $1s\sigma_g$ and excited $3d\sigma_g$ states. The calculated energies up to the highly vibrational levels $v = 0$ to 15 for the $1s\sigma_g$ state, and $v = 0$ to 8 for the $3d\sigma_g$ state, are summarized in Tables II and III in Ref. 10, respectively, where v represents the vibrational level.

TABLE II. The length expectation values $\langle r_1 \rangle$ and $\langle R \rangle$ a.u. of the lowest 16 states ($v = 0$ to 15) of 1S ($L = 0, M = 0$) belonging to the electronic ground state $1s\sigma_g$, and 9 states ($v = 0$ to 8) belonging to the electronic excited state $3d\sigma_g$, with the FC wave functions at $n = 15$ with $M_n = 22\,689$.

V	Electronic ground state: $1s\sigma_g$		Electronic excited state: $3d\sigma_g$	
	$\langle r_1 \rangle$	$\langle R \rangle$	$\langle r_1 \rangle$	$\langle R \rangle$
0	1.692 966	2.063 913	5.694 663	8.931 296
1	1.764 752	2.199 125	5.788 739	9.117 154
2	1.839 368	2.339 751	5.884 357	9.305 935
3	1.917 243	2.486 623	5.981 577	9.497 762
4	1.998 905	2.640 771	6.080 467	9.692 773
5	2.085 014	2.803 480	6.181 102	9.891 124
6	2.176 407	2.976 382	6.283 569	10.092 987
7	2.274 159	3.161 577	6.387 964	10.298 560
8	2.379 674	3.361 813	6.494 399	10.508 064
9	2.494 826	3.580 773		
10	2.622 184	3.823 506		
11	2.765 369	4.097 166		
12	2.929 702	4.412 279		
13	3.123 396	4.785 144		
14	3.360 020	5.242 767		
15	3.664 258	5.834 398		

B. Length expectation values: $\langle r_1 \rangle$ and $\langle R \rangle$

A chemical reaction should occur with nonadiabatic state hopping among the vibrational and/or rotational levels. To analyze the nuclear motion dynamics, we first examine the length expectation values of $\langle r_1 \rangle (= \langle r_2 \rangle)$ and $\langle R \rangle$. Table II summarizes $\langle r_1 \rangle$ and $\langle R \rangle$ of the 16 states ($v = 0$ to 15) belonging to the electronic ground state $1s\sigma_g$ and the 9 states ($v = 0$ to 8) belonging to the electronic excited state $3d\sigma_g$.

With the high vibration levels, both $\langle r_1 \rangle$ and $\langle R \rangle$ become large as v increases. With the approach to the dissociation, the electron locates near either proton. However, since the two nuclei are not distinguishable due to the symmetrization of the identical protons, the wave function is expressed by a superposition (resonance) of two identical configurations: $H^+ + H$ and $H + H^+$. Therefore, $\langle r_1 \rangle$ does not increase rapidly. $\langle R \rangle$ for the vibrational ground level belonging to the electronic ground state $1s\sigma_g$ was 2.064 a.u., which was close to the equilibrium distance of the PEC on the BO approximation, $R_e = 1.997$ a.u. (see Table I). However, due to the anharmonicity, it was slightly larger than its minimum. The effect of the anharmonicity becomes large as v increased. $\langle R \rangle$ for $v = 15$ was achieved at 5.834 a.u., which was more than twice the distance of $v = 0$. $\langle R \rangle$ for the vibrational ground level belonging to the electronic excited state $3d\sigma_g$ was 8.931 a.u., which was also slightly larger than the minimum of the PEC on the BO approximation, $R_e = 8.834$ a.u. (see Table I). Figures 2(a) and 3(a) show the plots of $\langle R \rangle$, described by the red circles, with respect to the non-BO energies with the PEC on the BO approximation for the electronic ground $1s\sigma_g$ and excited $3d\sigma_g$ states, respectively. As v increases, $\langle R \rangle$ becomes large but it is always located on the inside of the dissociation curve on the BO approximation, and this quantity does not show a perfect correspondence to the PEC.

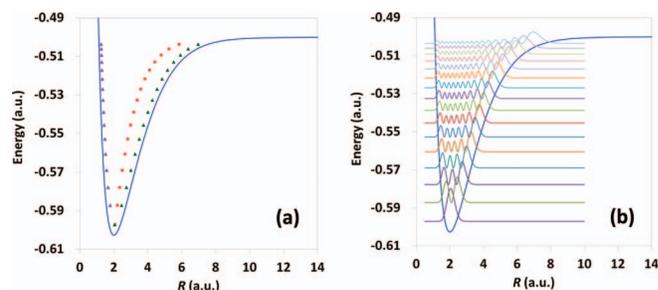


FIG. 2. (a) Plots of $\langle R \rangle$ (red circles) and the left (purple triangles) and right (green triangles) maximum positions of the reduced density function $f(R)$ to the equilibrium position $R_e = 2.0$ a.u., for the electronic ground state $1s\sigma_g$ with respect to the non-BO energies. (b) Plots of $f(R)$ for the electronic ground state with respect to the non-BO energies. The blue lines in both (a) and (b) show the PEC of the electronic ground state on the BO approximation.

C. Reduced density functions up to the high vibrational levels

Figures 4 and 5 show plots of the reduced density functions $f(R)$ of the non-BO wave functions at levels $v = 0$ to 15 for the electronic ground state $1s\sigma_g$ and $v = 0$ to 8 for the electronic excited state $3d\sigma_g$. In both cases, $f(R)$ includes a single maximum and no node for $v = 0$, and two maximums and single node for $v = 1$. Generally, $f(R)$ for the vibrational level v has $v + 1$ maximums and v nodes. Due to the anharmonicity, the center of $f(R)$ moves to the right side from the equilibrium distances R_e as v increases, and the maximum peak of the right side is larger than that of the left side for any level of v except for $v = 0$. For large v , $f(R)$ becomes broad and the probability of the right hand side is quite larger than that of the left peak. This indicates that the vibrational motion approaches the dissociation limit. For the electronic excited state (Fig. 5), $f(R)$ has a wider range than that of the electronic ground state due to the smaller force constant.

Figures 2(a) and 3(a) also include plots of the left and right maximum positions of $f(R)$ with respect to the non-BO energies for the electronic ground and excited states, respectively. Figures 2(b) and 3(b) show the plots of $f(R)$ with respect to the non-BO energies with the PEC on the BO approximation. Interestingly, the left and right maximum positions of $f(R)$ locate almost on the PEC. This is physically

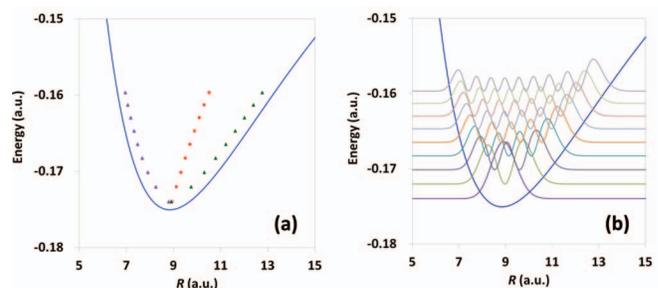


FIG. 3. (a) Plots of $\langle R \rangle$ (red circles) and the left (purple triangles) and right (green triangles) maximum positions of the reduced density function $f(R)$ to the equilibrium position $R_e = 8.8$ a.u., for the electronic excited state $3d\sigma_g$ with respect to the non-BO energies. (b) Plots of $f(R)$ for the electronic excited state with respect to the non-BO energies. The blue lines in both (a) and (b) show the PEC of the electronic excited state on the BO approximation.

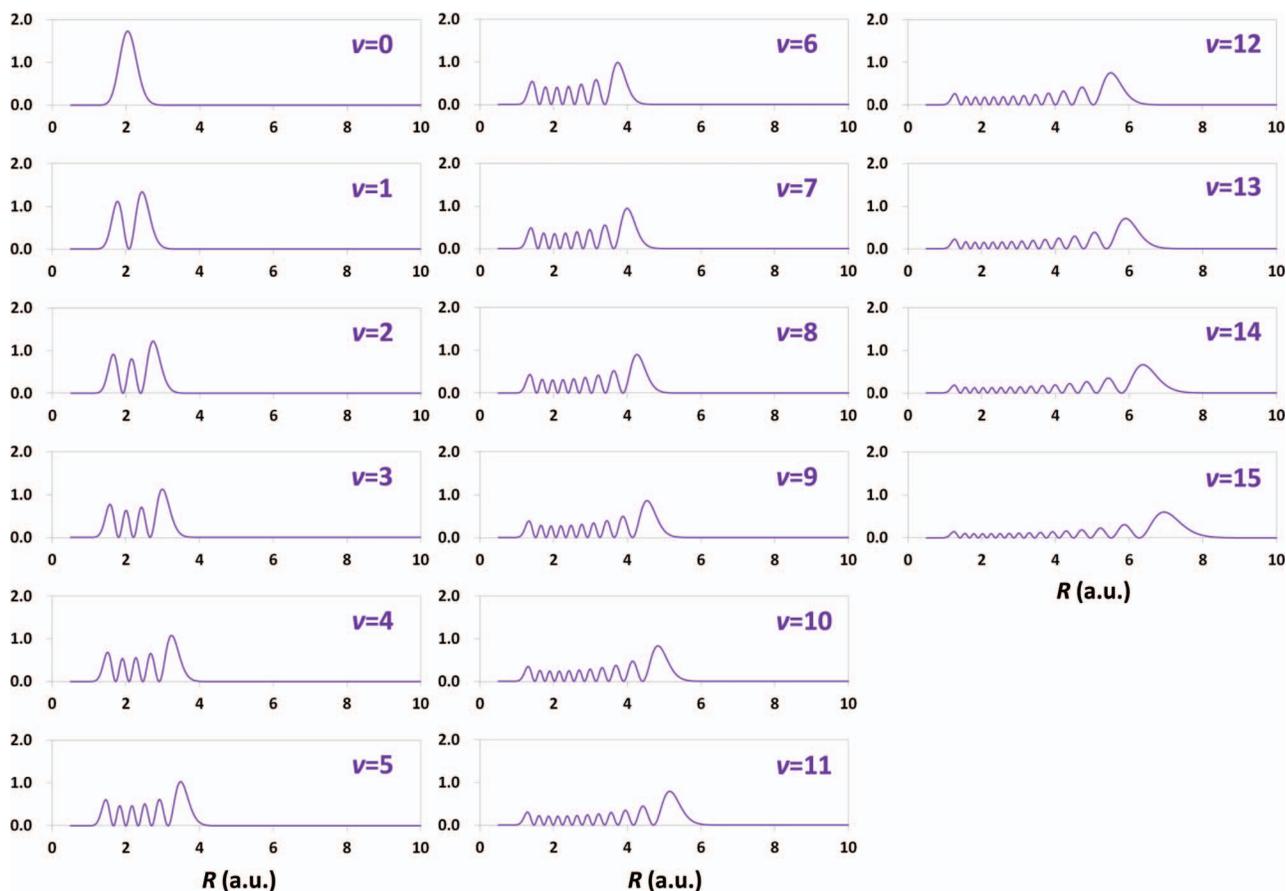


FIG. 4. Plots of the reduced density functions $f(R)$ of the non-BO wave functions $v = 0$ to 15 for the electronic ground state $1s\sigma_g$.

understandable since the positions with the largest probability of nuclei should correspond to the PEC. As a result, the left and right maximum positions of $f(R)$ can be considered to be a discrete representation of the PEC.

D. Analytical potential energy curves with the non-BO wave functions

From the accurate reduced density function, $f(R)$, the potential energy function $V(R)$, defined in Eq. (4), can be ob-

tained as an analytical function of R . On the BO approximation, the PEC is in common among the vibrational states belonging to the same electronic state. In the non-BO case, however, $V(R)$ can be defined for each of the states even if they belong to the same electronic state. We formulated $V(R)$ of the vibrational levels $v = 0$ to 15 for the electronic ground state $1s\sigma_g$, and $v = 0$ to 8 for the electronic excited state $3d\sigma_g$.

Figures 6 and 7 show plots of $V(R)$ for the $1s\sigma_g$ and $3d\sigma_g$ states, respectively. In Fig. 6, $V(R)$ for $v = 0$ is in good agreement with the PEC on the BO approximation up to around

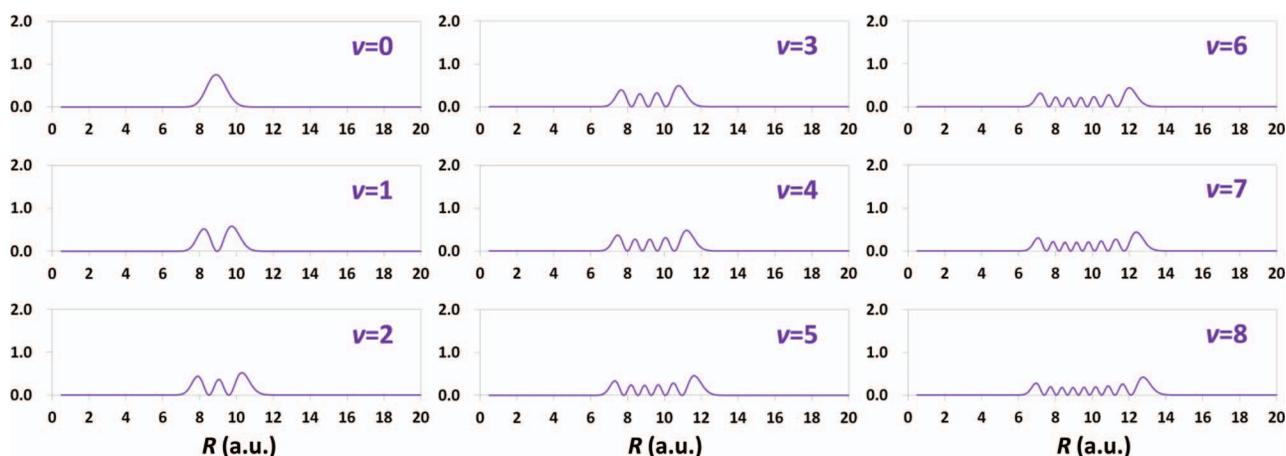


FIG. 5. Plots of the reduced density functions $f(R)$ of the non-BO wave functions $v = 0$ to 8 for the electronic excited state $3d\sigma_g$.

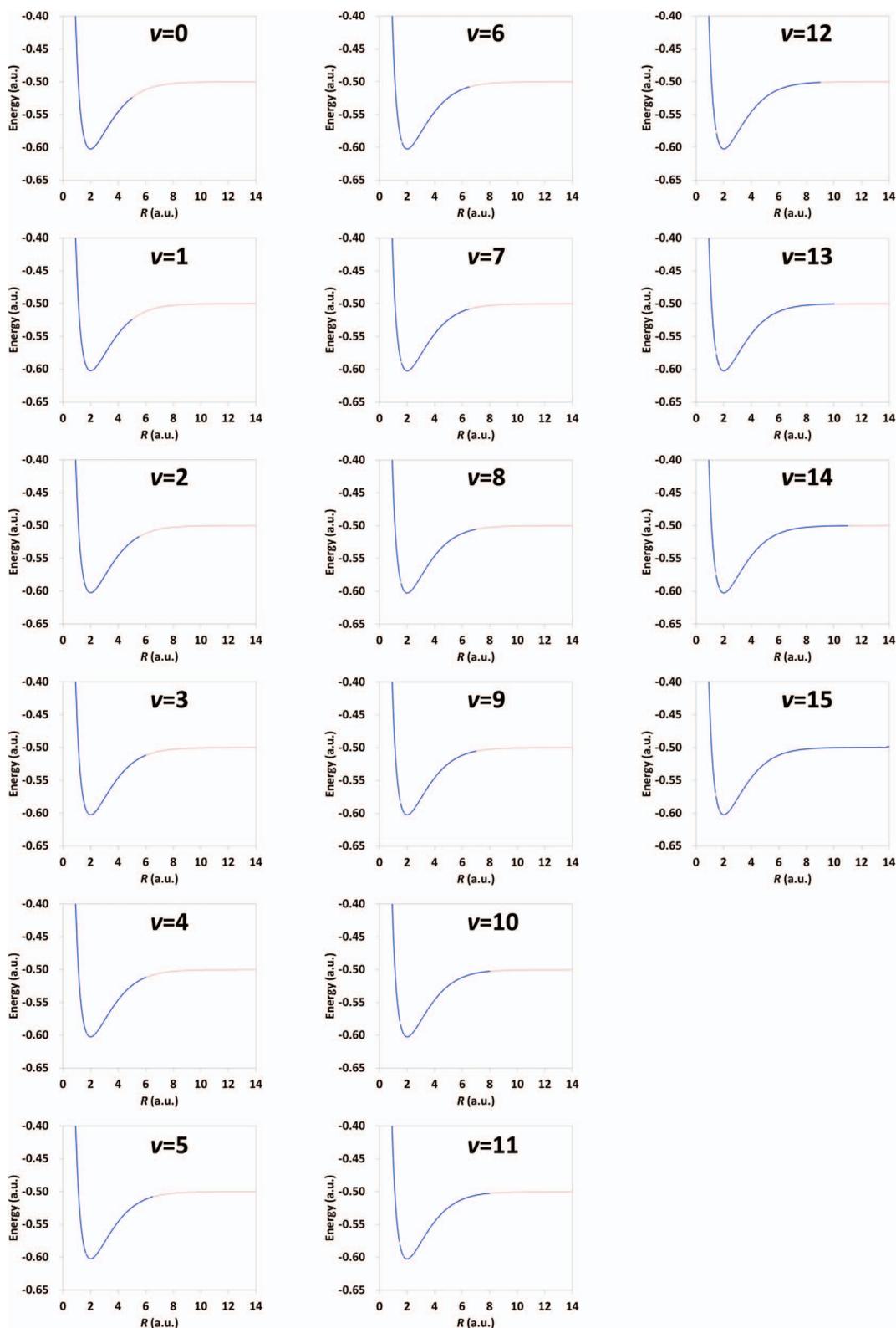


FIG. 6. Plots of the potential energy functions $V(R)$, defined in Eq. (4), of the vibrational levels $v = 0$ to 15 for the electronic ground state $1s\sigma_g$. The PEC on the BO approximation is shown with the pale red line. The unphysical regions of R , i.e., larger R for small v and near nodal positions ($R_{node} \pm 0.025$ a.u.), are omitted.

$R = 5$ a.u. However, for larger R , $V(R)$ was obviously physically meaningless because $f(R)$ for $v = 0$ should localize near the equilibrium distance around $R_e = 2.0$ a.u., and it does not contain sufficient information to describe the PEC for larger R . Similar to the case where $v = 0$, $V(R)$ for $v = 1$ could

also reproduce the PEC up to around $R = 6$ a.u. This was slightly longer than the $v = 0$ case; however, there is one indefinable point around $R = 2.1$ a.u. which obviously comes from the nodal position of $f(R)$ (Fig. 4). However, since such a nodal region is sufficiently narrow, it does not cause any

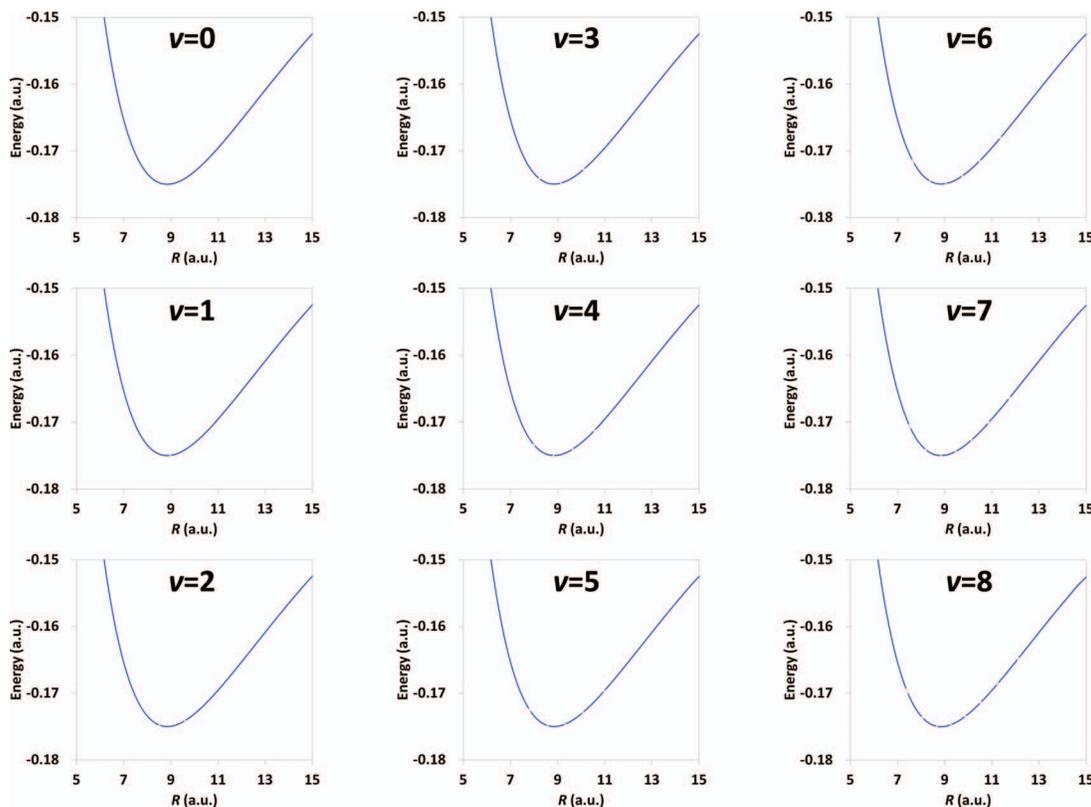


FIG. 7. Plots of the potential energy functions $V(R)$, defined in Eq. (4), of the vibrational levels $v = 0$ to 8 for the electronic ground state $3d\sigma_g$. The unphysical regions of R , i.e., near nodal positions ($R_{node} \pm 0.05$ a.u.), are omitted.

severe problem to investigate equilibrium positions or transition states or to understand chemical reactions. For $v = 2$, there are two indefinable points also coming from the nodes of $f(R)$, but the correspondence region to the PEC on the BO approximation becomes longer than in the $v = 0$ and 1 cases. Generally, as v increases, the region is physically meaningful as the PEC enlarges to a longer distance, since our non-BO wave functions for large v have nonzero amplitude even at large R . For $v = 13$, $V(R)$ overlapped with the PEC on the BO approximation up to $R = 10$ a.u. in the scope of Fig. 6, except for the nodal positions. For $v = 15$, its correspondence enlarges up to around $R = 14$ a.u.

Since the non-BO wave functions belonging to the $3d\sigma_g$ state might lack the diffuse complement functions to represent the longer region for $R > 16$ a.u., we only plot $V(R)$ in the region $R = 5$ to 15 a.u. in Fig. 7. Similar to $V(R)$ for the $1s\sigma_g$ state, the obtained $V(R)$ almost overlap with the PEC on the BO approximation in the scope of Fig. 7, even for small v . For the vibrational level v , there are v indefinable points corresponding to the nodal positions of $f(R)$. Thus, the non-BO wave functions belonging to the electronic excited state spontaneously reproduced the potential energy function $V(R)$ corresponding to the PEC of the electronic excited state.

Note that, in Figs. 6 and 7, the unphysical regions of R , i.e., larger R for small v and near nodal positions ($R_{node} \pm 0.025$ a.u. and $R_{node} \pm 0.05$ a.u. for the $1s\sigma_g$ and $3d\sigma_g$ states, respectively), are omitted since $V(R)$ on their regions

of R should be obviously unphysical. Nevertheless, the entire shapes of the PECs were well-described.

In a practical usage of the present method, one may ask which vibrational level should be employed for the analysis of the non-BO PEC. Since each non-BO state implicitly reflects the anharmonic vibrational motion, a low vibrational level can only describe the nuclei motion around the bottom of the PEC but the wave function corresponding to a high vibrational level much spreads to the wide range due to its large anharmonicity. Therefore, ordinarily, $V(R)$ from a higher vibrational level would be favorable. If the PEC of the target state forms an unusual shape such as double well or inter-system crossing, the wave function of a low vibrational level only describes local area and it might not have sufficient information of the whole PEC. In the present system, this was numerically confirmed up to $v = 15$ for the electronic ground state as shown in Fig. 6. Unfortunately, we cannot numerically examine $V(R)$ for $v > 15$ since their wave functions are not sufficiently accurate due to the lack of diffuse exponents in the initial function (see Ref. 10). However, it is quite interesting to see whether the vibrational levels near the dissociation limit and of the quasi-bound states above the dissociation limit, for example, have information of the entire PEC. If the answer is yes, then it might be said that even almost dissociative atoms potentially have information of the bound states. However, it might be impossible since their anharmonic vibrational motions are almost weighted toward the dissociation. We will focus in our subsequent paper of this series on such highly

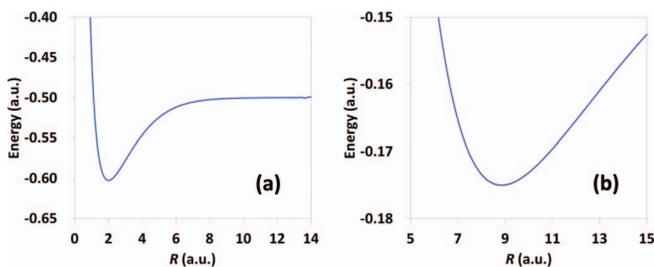


FIG. 8. Averaged potential energy curves including all range of R for (a) the electronic ground ($v = 0$ to 15) and (b) excited states ($v = 0$ to 8).

vibronic states and examine this topic with extensive numerical examinations.⁴³

We also propose another possibility of an alternative unique definition of $V(R)$, that is to simply average $V(R)$ over vibronic states belonging to the same electronic state. They would cover the wide range of the PEC when the various vibrational levels are included. Figures 8(a) and 8(b) illustrate the analytically averaged $V(R)$ over $v = 0$ to 15 and $v = 0$ to 8 for the electronic ground $1s\sigma_g$ and excited $3d\sigma_g$ states, respectively, where the above unphysical regions of R are still omitted in each v case. These averaged PECs are smooth at any positions of R including the nodal positions in the vertical scope of Fig. 8 since the nodal positions of each state are complemented by the other vibrational levels.

Finally, we investigated the equilibrium distances R_e , i.e., minimum positions of $V(R)$, of the averaged non-BO PEC for both the $1s\sigma_g$ and $3d\sigma_g$ states. Table I summarizes the R_e and $V(R_e)$ values and compared to those on the BO approximation. The differences of R_e between the non-BO and BO cases appear in mH digits both for the $1s\sigma_g$ and $3d\sigma_g$ states and the non-BO R_e are larger than those of the BO case. This tendency may reflect a non-BO effect that R is more likely to be repulsive due to the kinetic energy of the nuclei. The non-BO $V(R_e)$ values were higher than the energies of the BO case, $E(\text{BO})$. However, the values of $\mu_e \times E(\text{BO})$, which include the effective mass effect for total energy, come close to the non-BO $V(R_e)$ values, where μ_e is the effective mass of the nucleus and the electron. This indicates that $V(R)$ originally contains the energy corrections of the effective mass.

V. CONCLUSION

We proposed analysis methods to extract the physical PEC from the accurate non-BO wave functions. For the reference, before going to the non-BO analysis, we described the very accurate PEC of hydrogen molecular ion on the BO approximation with the FC method and searched the equilibrium positions and their energies, which showed the most precise values in the published literatures. The numerical examinations were performed with the highly accurate non-BO wave functions of hydrogen molecular ion, which were obtained with the free complement method in our previous study in this series.¹⁰ The reduced density function $f(R)$ integrated over the electron coordinates becomes an important physical quantity in nuclear motion dynamics. In the numerical examination of the non-BO wave functions of hydrogen molecu-

lar ion, their maximum positions on the left and right sides of the equilibrium position showed good agreement with the PEC on the BO approximation. They can be considered as a discrete representation of the PEC. We also proposed a new definition of the potential energy function $V(R)$ which was representable as an analytic function from the non-BO wave functions. $V(R)$ can be defined for each vibrational level v . For the lower v states, however, $V(R)$ for large R has no physical nature since their non-BO wave functions are localized near the equilibrium distance. For higher v states, their wave functions can cover a range of R wide enough to provide a physical $V(R)$, although the indefinable points appear at the nodal positions of $f(R)$. However, such nodes do not present an obstacle. Practically, we recommend to use the $V(R)$ function obtained from the higher vibrational level since its wave function covers the wider region of R than those of the lower vibrational levels. In the present system, this was numerically confirmed up to $v = 15$ for the electronic ground state but we could not examine it for $v > 15$ due to the lack of the accuracies in the wave functions. We will focus on such highly vibronic states in our next paper to see whether their states that locate very close to and even above the dissociation limit (like quasi-bound state) have information of the entire PEC.⁴³ Alternatively, we also recommend the analytically averaged $V(R)$ over the vibronic states belonging to the same electronic state. It should contain sufficient information for the wide range of R when the various vibrational levels are included. The differences of the equilibrium distances and their energies between the BO and non-BO PECs (the averaged $V(R)$) appear in mH digits. These differences may reflect a non-BO effect and the latter originally contains the energy corrections of the effective mass of the nucleus and the electron.

Thus, even on the non-BO framework, the properties related to the PEC can be analyzed. The present methods are general not only for diatomic molecules but also for any general molecule, without presenting any theoretical difficulty. Surely, preparing the accurate non-BO wave functions is the most significant task needed to obtain physically correct properties from their wave functions, and this task can be accomplished with the FC method. We will further extend the accurate non-BO applications of the FC method to a more general molecule in future studies. As an example, hydrogen clusters, which are an important species in astrochemistry and low-temperature physics,^{21–36} should include a lot of complicated local minimums in their PECs and the present methods are worth applying to them. Exotic systems including particles lighter than protons are also interesting for a more significant non-BO effect. We hope the accurate non-BO calculations based on the FC method would provide simpler solutions and that the present analysis methods help us understand their chemistry.

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