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Analytical Potential Curve from Non-Born-Oppenheimer Wave Function: Application to Hydrogen Molecular Ion

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Abstract. Although the concept of a potential curve is one of the important outgrowths of the Born-Oppenheimer (BO) approximation, we propose a method to obtain an analytical potential curve from the Non-Born-Oppenheimer (Non-BO) wave functions. The present proceeding reviews this method originally published in J. Chem. Phys. 139, 074105 (2013). A numerical examination was performed with hydrogen molecular ion, where the free complement method was employed to solve the Non-BO Schrödinger equation very accurately. Whereas an ordinary potential curve on the BO approximation is obtained as a numeric curve evaluated at many fixed nuclear coordinates and curve fitting is always required, the present method can describe the potential curve as an analytical continuous function. It indicates that a single Non-BO calculation principally draws the whole potential curve at any nuclear coordinates.

Keywords: Non-Born-Oppenheimer Schrödinger equation, potential curve, H_2^+ ion, interstellar molecules

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INTRODUCTION

The Born-Oppenheimer (BO) approximation [1] is one of the most favorable assumptions widely used in chemistry. The electronic Schrödinger equation on the BO approximation is given by

$$H_{elec.}(\mathbf{R}_{fix})\psi_{elec.}(\mathbf{r}; \mathbf{R}_{fix}) = E_{elec.}(\mathbf{R}_{fix})\psi_{elec.}(\mathbf{r}; \mathbf{R}_{fix}), \quad (1)$$

where $H_{elec.}(\mathbf{R}_{fix})$ denotes the Hamiltonian of electrons on the electron-nucleus Coulomb field. $\mathbf{r}$ and $\mathbf{R}$ represent the electronic and nuclear coordinates (subscript “fix” represents fixed coordinates), respectively. $\psi_{elec.}(\mathbf{r}; \mathbf{R}_{fix})$ and $E_{elec.}(\mathbf{R}_{fix})$ are the wave function of electrons and corresponding energy, respectively. Thus, electrons are, of course, treated quantum mechanically but nuclei are just fixed at given coordinates. One of the most important corollaries of the BO approximation, however, is the concept of the potential curve defined by $V(\mathbf{R}) = E_{elec.}(\mathbf{R}_{fix})$ in Eq.(1) at given nuclear coordinates $\mathbf{R}_{fix}$. Needless to say, potential curve plays a crucial role in studying chemical reaction. However, the potential curve on the BO approximation has several problems as listed in Table 1 and they become severer as molecule becomes more complicated.

TABLE 1. Lists of problems of the BO potential curve.

1. The resultant curve is numerical only at given $\mathbf{R}_{fix}$.
2. Curve fitting with artificial functions is required to get a smooth curve.
3. The analysis using a fitted curve highly depends on the set of employed points $\mathbf{R}_{fix}$ and choosing fitting function.
4. Huge number of calculations solving Eq.(1) at different $\mathbf{R}_{fix}$ are necessary.

On the other hand, the Non-Born-Oppenheimer (Non-BO) Schrödinger equation is given by

$$H(\mathbf{r}, \mathbf{R})\psi(\mathbf{r}, \mathbf{R}) = E\psi(\mathbf{r}, \mathbf{R}), \quad (2)$$

where all the electrons and nuclei are treated quantum mechanically and the Non-BO Hamiltonian $H(\mathbf{r}, \mathbf{R})$ includes all the electronic, vibrational, and rotational motions. $\psi(\mathbf{r}, \mathbf{R})$ is the Non-BO wave function as a function of both $\mathbf{r}$

and $\mathbf{R}$ and E is the corresponding energy. This Non-BO energy, however, is composed of discrete energy levels and just numerical values and someone may believe that Non-BO calculations loose significant information of potential curve and cannot be applied to studying ordinary chemical phenomena.

Against such a delusion of the Non-BO calculations, we recently proposed a simple method to describe an analytical potential curve from the Non-BO wave function [2]. It can also overcome the problems of the BO potential curve as listed in Table 1. There had never been a genuine analytical potential curve yet. The present proceeding briefly reviews and summarizes this theory and applications to hydrogen molecular ion [2,3].

THEORY: ANALYTICAL POTENTIAL CURVE FROM NON-BO WAVE FUNCTION

Let us briefly explain the theory for an analytical potential curve from the Non-BO wave function [2]. The electronic and nuclear motions are coupled together and their coordinates are not separable in the Non-BO calculations. However, we can introduce the reduced density function, defined by

$$f(\mathbf{R}) = \int d\tau_r \cdot \psi(\mathbf{r}, \mathbf{R})^* \psi(\mathbf{r}, \mathbf{R}), \quad (3)$$

where $\psi(\mathbf{r}, \mathbf{R})$ is the normalized Non-BO wave function and $d\tau_r$ means the integration over only electron coordinates $\mathbf{r}$. Therefore, $f(\mathbf{R})$ is a function of the nuclear coordinates $\mathbf{R}$ and its square root

$$\varphi(\mathbf{R}) = \pm \sqrt{f(\mathbf{R})}, \quad (4)$$

corresponds to the vibrational rotational wave function.

Therefore, we assume here the vibrational rotational Schrödinger equation, given by

$$\left[-\frac{1}{2} \sum_A \frac{1}{M_A} \nabla_A^2 + V(\mathbf{R}) \right] \varphi(\mathbf{R}) = E \varphi(\mathbf{R}), \quad (5)$$

where A denotes nuclear index and M_A is the nuclear mass of A . On the ordinary BO approximation, the fitted potential curve $V(\mathbf{R})$ is first given and the vibrational rotational wave functions and corresponding energies are obtained after solving this Schrödinger equation of Eq.(5). On the other hand, in Non-BO case, $\varphi(\mathbf{R})$ and E are first given as input from the Non-BO wave function (through Eq.(4)) and corresponding energy (as eigenvalue of Eq.(2)). $V(\mathbf{R})$ is unknown and output and it is indeed the potential curve that we desire. Thus, this process is like solving an inverse problem. After just reformulating this equation, we can finally obtain

$$V(\mathbf{R}) = \frac{1}{2} \frac{1}{\varphi(\mathbf{R})} \sum_A \frac{1}{M_A} \nabla_A^2 \varphi(\mathbf{R}) + E. \quad (6)$$

This is the analytical potential curve from the Non-BO wave function and, principally, single Non-BO calculations can draw the whole potential curve at any $\mathbf{R}$ as an analytical function.

APPLICATIONS TO HYDROGEN MOLECULAR ION

We applied the present method to hydrogen molecular ion. This is the simplest system composed of two nuclei and one electron but suitable for examining the theory.

A. Solving the Non-BO Schrödinger equations

We first need to accurately solve the Non-BO Schrödinger equations of Eq.(2) and we employed the free complement (FC) method [4,5] for this purpose. In the FC method, we first prepare an appropriate initial function and apply the system's Hamiltonian iteratively and, then, construct the complement function space that is guaranteed to converge to the exact wave function space. The initial function we employed is given by

$$\psi_0 = (1 \pm P_{12}) \left[\sum_{j=1}^J \exp(-\alpha^{(j)} s) \exp(-\gamma^{(j)} (R - R_e^{(j)})^2) \right] \cdot Y_{L,M}^{l_1, l_2}(\mathbf{r}_1, \mathbf{r}_2), \quad (7)$$

where the Hylleraas-like coordinates $s = r_1 + r_2$, $t = r_1 - r_2$, and $R = r_{12}$ were employed (r_1 and r_2 are the distances from the electron to the first and second nuclei, respectively, and R is the inter-nuclear distance). J is the number of nonlinear parameter sets and we used $J=3$: $\{\alpha^{(1)} = 1.0, \gamma^{(1)} = 4.0, R_e^{(1)} = 2.0\}$, $\{\alpha^{(2)} = 0.5, \gamma^{(2)} = 1.0, R_e^{(2)} = 8.8\}$, and $\alpha^{(3)} = 1/3, \gamma^{(3)} = 1.0, R_e^{(3)} = 8.8$. In this initial function, $\exp(-\alpha^{(j)} s)$ mainly represents the electron motion by the ordinary Slater-type orbital. For the vibrational motion, a gauss-type function $\exp(-\gamma^{(j)} (R - R_e^{(j)})^2)$ should be an appropriate choice. The rotational motion of whole molecule is represented by the ordinary solid spherical

harmonics [6] as the exact eigenfunctions of the two-particle angular momentum operator. (L, M, l_1, l_2) is its quantum number. $(1 \pm P_{12})$ shows the symmetry or antisymmetry permutation operator for the nuclear spin.

Starting from this ψ_0 , the FC method can automatically construct accurate Non-BO wave functions by the Non-BO Hamiltonian itself. We performed the Non-BO calculations for 1S , 3P , 1D , 3F , 1G , 3H , and 1I symmetries ($L=0$ to 6) at $n=15$ with $M_n=22689$ for 1S and $n=6$ with $M_n=2757, 4167, 5118, 6204, 6915$, and 7713 for 3P , 1D , 3F , 1G , 3H , and 1I , respectively, where n is the number of iterations or order and M_n is the number of complement functions in the FC method [4,5]. We could successfully obtain extremely accurate wave functions and their corresponding absolute energies and excitation energies including all the electronic, vibrational, and rotational motions [3]. In the Non-BO calculations, all these states are simultaneously obtained at one diagonalization in each symmetry. For more details, see the original article of Ref. [3]

B. Analytical potential curve from the Non-BO wave function

After obtaining the accurate Non-BO wave functions, we next evaluate the reduced density functions $f(R)$ defined as Eq.(3) by integration over only the electron coordinates. For 1S symmetry, this corresponds to the density of the vibrational wave functions. For the vibrational level $v=0$, the shape of $f(R)$ looks like harmonic oscillator around equilibrium distance ($R_{eq}=2.0$ a.u.). As increasing v , anharmonicity and further Non-BO effects naturally appear. In higher v , the existence probability of electron moves to long distance near dissociation.

The Non-BO analytical potential curves $V(R)$ are easily formulated by Eq.(6) from $\phi(R) = \pm\sqrt{f(R)}$. Figure 1 shows the plots of the calculated Non-BO analytical potential curves using the Non-BO wave functions of $v=0, 1, 2, 13, 14$, and 15 of 1S symmetry belonging to the electronic ground state. In $v=0$, the obtained curve is almost overlap with the BO potential curve up to about $R=5$ a.u. Beyond 5 a.u., however, there is obviously unphysical behavior and numerical ambiguity. This is due to no information of the wave function at long distant R since large amplitude of the wave function of $v=0$ is only near equilibrium distance. As increasing v , the region of such an ambiguity gradually disappears and, in $v=15$, the obtained curve is almost on the BO potential curve up to $R=14$ a.u. On the other hand, unfortunately, there are v singular divergent points in the case of the vibrational level v . These singular points obviously come from the nodal positions of the vibrational wave functions due to the denominator of Eq.(6). Thus, vibrational highly excited states produce many singular positions in the potential curve but include physical information up to long distance R near dissociation for the Non-BO analytical potential curve.

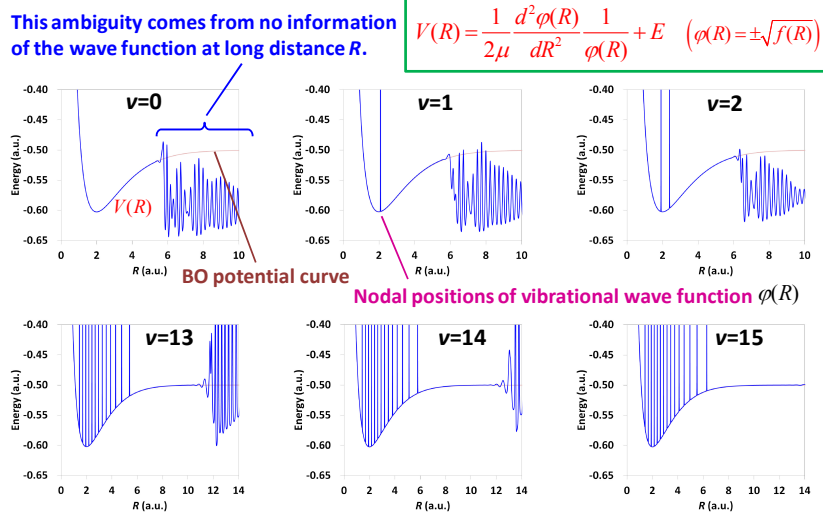


FIGURE 1. Plots of the Non-BO analytical potential energy curves of the vibrational levels $v=0, 1, 2, 13, 14$, and 15 of 1S symmetry belonging to the electronic ground state $1s\sigma_g$. The BO potential curve is shown with the pale red line. The analytical form of $V(R)$ for hydrogen molecular ion is given in the right upper side.

To avoid such a nodal problem, we also proposed another possibility of an alternative unique definition of $V(R)$. That is to simply average all the $V(R)$ over the vibronic states belonging to the same electronic state since the nodal points are different in different v and all the curves can complement the nodal positions each other. Figure 2 shows the averaged Non-BO analytical potential curves of the electronic ground ($1s\sigma_g$) and excited states ($3d\sigma_g$). They completely overlap with the BO potential curves on this graph scale.

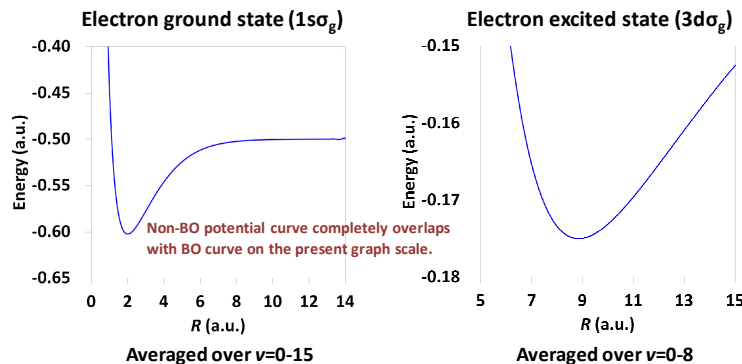


FIGURE 2. Averaged Non-BO analytical potential curves for the electronic ground state over $v=0$ to 15 (left hand side) and excited state over $v=0$ to 8 (right hand side).

CONCLUSIONS

We proposed a new simple method to obtain an analytical potential curve from the Non-BO wave function. Since the square root of the reduced density function integrated over only the electron coordinates corresponds to the vibrational rotational wave function, we easily formulate the potential curve as an inverse problem from the vibrational rotational Schrödinger equation. The features of the Non-BO analytical potential curve are summarized in Table 2: First, the potential curve is obtained analytically and as a continuous function without any artificial curve fitting. Second, single Non-BO calculation can draw the whole potential curve at any $\mathbf{R}$ without huge number of calculations at $3N-6$ hyper surface as needed in the BO approximation (N : Number of nuclei). Third, one can define different potential curves at each vibrational rotational state and it makes possible take a thermal average of these curves. Fourth, complicated equilibrium geometries, local minima, and transition states may be obtained analytically.

Thus, even in the Non-BO framework, the concept of potential curve can be introduced for studying chemical phenomena. The present methods are general not only for diatomic molecules but also for any molecule. The most difficult task, however, is to obtain accurate Non-BO wave functions and this task can be accomplished with the FC method. For future study, hydrogen clusters, such as H_2 , H_3^+ , H_5^+ , etc., are next good challenging targets since they are important key molecules in astrochemistry. We also hope accurate Non-BO calculations are more familiar for general molecules and the present method will be applicable to ordinary chemistry with a new physical concept of potential curve.

TABLE 2. Features of the Non-BO analytical potential curve.

1. Analytical and continuous potential curve as function of $\mathbf{R}$ without any artificial curve fitting.
2. In principle, single Non-BO calculation can draw the whole potential curve at any $\mathbf{R}$ without huge number of calculations at $3N-6$ hyper surface as needed in the BO approximation.
3. Definable different potential curves from different vibrational rotational states.
4. Applicable to complicated systems to analytically search equilibrium geometry, local minima, and transition states.

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