The diagonal Born–Oppenheimer correction to molecular dynamical properties

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Abstract

We examine the effect of the diagonal Born–Oppenheimer correction on dynamics in two simple systems – the Hooke’s atom in an external harmonic potential and the collinear hydrogen exchange reaction. The transmission probability for the Hooke’s atom, calculated within the Born–Oppenheimer approximation, is simply shifted in energy with respect to the exact result, and this is corrected by the diagonal adiabatic contribution. The reaction probability for the H3 system reflects the fact, that the diagonal Born–Oppenheimer correction raises the barrier to the reaction by approximately 70 cm⁻¹.

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1. Introduction

The increase in accuracy and efficiency of ab initio quantum chemistry methods and the ability to study non-adiabatic molecular dynamics of small molecules brings attention to small corrections to the Born–Oppenheimer electronic potential surface. The state-of-the-art electronic structure calculations approach the accuracy of a few wave numbers [1]. The agreement of the best spectroscopic calculations with experiment can be better than a wave number [2,3]. Thus, the relativistic, adiabatic and non-adiabatic corrections become important. The non-adiabatic effect of ‘electrons following nuclei’ that does not involve transitions between the potential surfaces is often simulated by using atomic rather than nuclear masses for some of the degrees of freedom or even some intermediate between the atomic and nuclear masses [4,5]. The adiabatic diagonal Born–Oppenheimer correction (DBOC) is generally neglected. A few studies show that the effect of DBOC is, indeed, small for the equilibrium properties of small molecules, such as bond distances and fundamental frequencies. Several small molecules, such as H₂ and He₂⁺ were examined by Handy and coworkers [6,7]. The effect of DBOC was found to be small (change in bond length on the order of $10^{-4}$–$10^{-5}$ bohr) for HF, N₂, F₂, but a DBOC was essential to obtain an accurate dissociation energy of H₂. Moss [8] found the adiabatic correction to the bond length of H₂ to be about 0.3%, while the non-adiabatic correction was three orders of magnitude smaller. For the equilibrium configuration, the DBOC has weak dependence on the nuclear position (for the harmonic oscillator-like potential electronic surface it is constant).
However, one might expect more pronounced DBOC effects for reactive systems, where the electronic potential energy surface is poorly approximated by harmonic oscillator solutions in the interaction region of the potential surface. For example, the DBOC lowers the barrier to linearity of hydrogen sulfide is also raised by about 27 cm$^{-1}$ [9] and it raises the barrier for the reaction $F + H_2 \rightarrow FH + H$ by 17 cm$^{-1}$ [7]. The barrier to linearity of hydrogen sulfide is also raised by about 27 cm$^{-1}$ [10].

In this Letter, we examine the DBOC effects on dynamics of two simple systems by finding reaction probabilities. In Section 2, we find the transmission probability for an exactly soluble system, the Hooke’s atom in the parabolic external potential where the DBOC, indeed, compensates for the Hooke’s atom in the parabolic external potential. The correction is added to the LSTH influence of the single determinant approximation of the collinear hydrogen exchange reaction. The DBOC is calculated within a compact single-term BO approximation errors in the first order. Then, we look at the state-resolved reaction probabilities. In Section 2, we find the transmission probability for an exactly soluble system, the Hooke’s atom in the parabolic external potential.

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The standard way to solve the Schrödinger equation for a system with the electronic and nuclear degrees of freedom is to use the Born–Oppenheimer approximation to the total wave function $|\psi\rangle$. $|\psi\rangle$ is represented as a product $|\psi\rangle = |\chi\rangle|\phi\rangle$, where $|\phi\rangle = \phi(r; R)$ is the eigenfunction in the electronic coordinate $r$ of the electronic part of the Schrödinger equation, solved for fixed values of the nuclear coordinate $R$. The energy eigenvalue $V(R)$ is the electronic potential energy surface (PES) and $R$ appears as a parameter in $\phi(r; R)$. $|\chi\rangle = \chi(R)$ is the solution of the nuclear part of the Schrödinger equation in the potential $V(R)$. The general form of the diagonal BO correction [11], which is independent of the center of mass motion, is

$$V^c(R) = -\frac{\hbar^2}{2} \langle \phi| \sum_{\mu} \frac{1}{M_{\mu}} \nabla^2_{R_{\mu}}| \phi \rangle,$$ (1)

where $\mu$ is the index for nuclei and $M_{\mu}$ are the masses of nuclei. The nuclear masses also appear in the kinetic energy part of the nuclear Hamiltonian.

First, let us look at a simple soluble problem – the one-dimensional Hooke’s atom, which is a system of a proton and an electron bound by a harmonic potential, in an external parabolic potential. The coordinate of the proton is $X$ and the mass of a proton is $M$. The coordinate of the electron is $x$ and the electronic mass is $1$. We use $\hbar = 1$ below. The Hamiltonian is

$$\hat{H} = -\frac{1}{2M} \frac{\partial^2}{\partial X^2} - \frac{1}{2} \frac{\partial^2}{\partial x^2} + \frac{k}{2} (X - x)^2 - \frac{g_p X^2}{2} - \frac{g_e x^2}{2},$$ (2)

where the proton–electron interaction is controlled by the parameter $k$ and the parameters of interaction with the external potential is $g_p$ for a proton, and $g_e$ for electron.

Solving the model exactly in the normal mode coordinates $(y, Y)$:

$$y = c \eta^{-1} x + (\lambda^+ - a) \eta^{-1} X,$$

$$Y = -(\lambda^- - a) \eta^{-1} x + c \eta^{-1} X,$$

$$\lambda^\pm = \sqrt{\frac{(a - b)^2}{4} + c^2} \pm \frac{a + b}{2},$$ (4)

$$a = k - g_e, \quad b = (k - g_p)/M, \quad c = -k/\sqrt{M},$$

$$\eta = \sqrt{(\lambda^+ - a)^2 + c^2}$$ (5)

gives a decoupled Hamiltonian

$$\hat{H} = -\frac{1}{2} \frac{\partial^2}{\partial Y^2} - \frac{1}{2} \frac{\partial^2}{\partial y^2} - \frac{\lambda^+ Y^2}{2} + \frac{\lambda^- y^2}{2}.$$ (6)
Under the conditions $k > 0$, $ge > 0$, $gp > 0$, $gegp \neq 0$ the motion is bounded in $y$, but is unbounded in $Y$. The ground state of the harmonic oscillator in the $y$ coordinate gives the energy of the top of the barrier in $Y$

$$V_0 = \sqrt{\lambda}^2/2.$$  \hfill (7)

The potential in $Y$ coordinate becomes $V = V_0 - w^2Y^2/2$ with the barrier frequency

$$w = \sqrt{\lambda}.$$  \hfill (8)

Solving the same problem in the BO approximation we have the barrier height for the electronic ground state

$$V_{BO}^e = \sqrt{k - ge}/2$$  \hfill (9)

and the barrier frequency

$$w_{BO} = \sqrt{\left(\frac{gp}{k - ge}\right)M^{-1}}.$$  \hfill (10)

The DBOC for the electronic ground state is

$$\epsilon = \frac{1}{2M} \left(\frac{\partial^2}{\partial X^2} |\phi^0\rangle = \frac{V_{BO}^e}{2M}\right).$$  \hfill (11)

Expanding in the first order of $1/M$ for $ge = 0$ we have

$$4V_0^2 = \lambda^+ \approx k + k/M, \quad w^2 = \lambda^- \approx gp/M - gp/M^2$$  \hfill (12)

for the exact solution and

$$4(V_{BO}^e)^2 = k, \quad (w_{BO}^e)^2 = gp/M.$$  \hfill (13)

The corrected barrier height within the BO approximation is

$$V_0^{BO} + \epsilon = \frac{\sqrt{k}}{2} \left(1 + \frac{1}{2M}\right),$$  \hfill (14)

which is in agreement within the first-order in $1/M$ with the exact result

$$V_0 \approx \frac{\sqrt{k}}{2} \left(1 + \frac{1}{2M} - \frac{1}{8M^2} \left(1 + \frac{4gp}{k}\right)\right).$$  \hfill (15)

The transmission probability for the parabolic barrier is [15]

$$N(E) = (1 + \exp(-2\pi\epsilon))^{-1},$$  \hfill (16)

where

$$\epsilon = (E - V_0)/w.$$  \hfill (17)

Although $V_0$ agrees with $V_{BO}^e + \epsilon$ and $w$ agrees with $w_{BO}^e$ within the first-order of $1/M$, parameters $\epsilon$ for the exact and the BO corrected cases are different by

$$\epsilon - \epsilon' = \frac{1}{2\sqrt{M}} \frac{2E - \sqrt{k}}{2\sqrt{gp}}.$$  \hfill (18)

This is the effect of the overall motion of the proton and electron. The discrepancy is zero when $E$ is equal to the zero-point energy of the relative (vibrational) motion and it is large for energies that are either very high or very low compared to the barrier height. The absolute reaction probability is little affected by this error due to its functional dependence on $\epsilon$ (Eq. (16)), which may be a general feature of most chemical systems. We also note, that if the nuclear mass $M$ is replaced with the atomic mass $M^*$ in the BO corrected expressions (9) and (10), the resulting $\epsilon$ does agree with the exact $\epsilon$ within $O(1/M)$, which justifies the usage of the atomic mass rather than nuclear mass in molecular dynamics calculations. Nevertheless, the effect of using atomic rather than nuclear mass is small compared to the effect of the DBOC itself.

Fig. 1 compares the exact result with the BO approximation

![Fig. 1. Transmission probability, $N(E)$, for the Hooke’s atom in a parabolic potential calculated exactly, within BO approximation with and without the DBOC.](image)
and with the BO approximation with the DBOC

\[ \epsilon^\text{BO} = \left( E - V_0^\text{BO} \right) / w \]

and with the BO approximation with the DBOC

\[ \epsilon^e = \left( E - V_0^\text{BO} - V^e \right) / w \]

for the value of parameters \( M = 918 \) a.u., \( k = 0.38 \), \( g_p = 0.0647 \) and \( g_e = 0 \), which approximately corresponds to the H\(_3\) system using nuclear mass. For given parameters the effect of using atomic instead of nuclear mass is small: the maximal difference between exact and the Born–Oppenheimer probability with the DBOC is 0.031 hartree using nuclear or atomic mass. For given parameters the effect of using the DBOC correction is 1.05 if using nuclear mass and 2.7 \times 10^{-5} \text{ hartree} if using atomic mass. For our model with quadratic potentials the DBOC is independent of the nuclear position. So the Born–Oppenheimer approximation results in an overall shift of the barrier height, that is very accurately compensated by the diagonal correction in the first order in \( M^{-1} \). For chemical systems the DBOC does depend on the position of nuclei, even more so for systems far from equilibrium as demonstrated in the next section.

3. State-to-state reaction probability for collinear H\(_3\) system

In order to see the magnitude of the effect of the DBOC on dynamics, we calculate the state-to-state transition probabilities of the collinear hydrogen reaction for the two lowest vibrational states. We use the wave packet correlation formulation to calculate reaction probabilities for \( 0 \rightarrow 0 \) and \( 1 \rightarrow 1 \) reactive transitions. The incoming reactant and outgoing product wave packets are defined in the asymptotic region of the potential surface in Jacobi coordinates. The wave packets are defined as the direct products of Gaussians in the translational coordinate and the eigenstate of the Morse oscillator in the vibrational coordinate. The parameters of the reactant and product translational wave packets, \( \Phi_X(R) = \exp\left(-\alpha(R - R_0)^2 + \nu_p(R - R_0)\right) \), in the appropriate asymptotic region are \( \alpha = 6.0 \), \( R_0 = 6.0 \) and \( \nu_p = -7.0 \) in atomic units.

The wave packet parameters are the same for all calculations with and without the correction and using: (a) atomic and (b) nuclear masses. The probabilities are obtained from the ratio of the energy spectrum of the reactant/product wave packet correlation function to the spectrum of the reactant/reactant correlation function [16].

For the electronic structure calculations, we use a large 7s5p1d basis, with the innermost s function being a contraction of five primitives, and the rest of the functions uncontracted. The values of the DBOC changed only marginally with the addition of more primitives, so our basis is essentially complete within the accuracy of this Letter. The electronic structure calculations were used only to determine the DBOC which was added to the LSTH potential energy surface. We have used a modified version of Q-Chem software package for the DBOC calculation [17]. A larger error in the DBOC comes from the single determinant approximation to the electronic wave function. The DBOC has a singularity in the asymptotic H+H\(_2\) region at 2.36 bohr (RHF \( \rightarrow \) UHF instability) in H\(_3\). This is an artifact of the single determinant approximation. Fortunately, we found this discontinuity to be high enough on the potential surface to have a negligible effect on the two lowest transitions studied in this Letter. The investigation of the single determinant approximation was done by comparing the DBOC calculated with UHF wave function and perturbatively to the leading order with the UMP2 wave function [18]. They agree within 3–4\% in the asymptotic region and within 1–2\% in the barrier region in the low-energy region of the potential surface, shown in Fig. 2. Overall, we compared reaction probabilities for three different DBOCs. The first one is the DBOC within UHF theory, calculated for the bond distances \( 0.66 < X < 8.9 \) bohr, \( 0.66 < Y < 4.05 \) bohr and set to zero elsewhere. Note, that this DBOC contains the singularity region of PES. The second calculation is DBOC obtained from the UMP2 wave function calculated for \( 0.66 < X < 8.9 \) bohr, \( 0.66 < Y < 2.36 \) bohr and set to zero elsewhere. This calculation does not contain the afore-mentioned singularity. The third calculation uses DBOC of the second calculation, but with the singularity smoothed over and with the correction
extrapolated outside the calculated region. All three corrections are added to the same LSTH potential surface. The resulting three reaction probabilities are insensitive to the differences of the corrections as shown on Fig. 3. This shows that the wave packet never reaches the singularity region, which is quite high in energy, and that the UHF wave function is adequate for DBOC in the low energy region of PES.

The effect of DBOC on dynamics is defined by the changes in the interaction region relative to the changes in the asymptotic region. The BO correction raises the minimum of the potential surface by 168 cm\(^{-1}\). This is equivalent to the energy shift by 112 cm\(^{-1}\) for \(H_2\) and is consistent with the results of Kolos and Rychlewski [19] 114.6 cm\(^{-1}\) for the distance of \(R = 1.4\) bohr. The barrier is raised by an additional 72 cm\(^{-1}\). The relative shift of the barrier height determines the main change in the \(0 \rightarrow 0\) reaction probability shown on Fig. 4. Fig. 5

Fig. 2. DBOC for the asymptotic and barrier regions (\(X = 8.5\) bohr and \(X = Y\) in bond coordinates, respectively) calculated with UHF and UMP2 wave functions.

Fig. 3. Reaction probability for the collinear \(H_3\) system for \(0 \rightarrow 0\) transition calculated with UHF, UMP2 and with the smoothed UMP2 corrections using nuclear mass.

Fig. 4. Reaction probability for the collinear \(H_3\) system for \(0 \rightarrow 0\) transition calculated within BO approximation without DBOC using nuclear and atomic masses and with DBOC using nuclear mass. The probability obtained with the DBOC is shifted by about 70 cm\(^{-1}\).

Fig. 5. Reaction probability for the collinear \(H_3\) system for \(1 \rightarrow 1\) transition calculated with and without DBOC using nuclear mass.
shows the reaction probability of $1 \rightarrow 1$ transmission for which the difference between the BO probability and the corrected probability is more complicated than a mere shift.

The Born–Oppenheimer approximation implies that the nuclear masses are used. In practice, atomic masses are used to mimic the ‘electron following the nucleus’ effect. We repeated the calculations using atomic masses instead of nuclear masses and found a very small shift of the spectrum of about $-0.5 \text{ cm}^{-1}$, which is an order of magnitude smaller than the DBOC effect. This is shown on Fig. 4 for calculations without the DBOC, and the curves obtained with atomic and with nuclear masses are indistinguishable.

4. Summary

The diagonal Born–Oppenheimer correction to electronic potential surfaces becomes important in the context of high accuracy theoretical and experimental methods of physical chemistry. It can be readily incorporated into ab initio calculation of the electronic potential surfaces. Though the DBOC has small effect on the equilibrium properties of molecules, the DBOC in the barrier region has a noticeable effect on reaction probabilities, as was demonstrated for the example of collinear $\text{H}_3$. The DBOC does shift the barrier height by a small but noticeable amount on the order of $10^2 \text{ cm}^{-1}$ for $\text{H}_3$.

The DBOC was calculated perturbatively using UHF and UMP2 wave functions. We conclude that a single determinant UHF wave function is adequate for describing the DBOC in the barrier region. The effect of the mass substitution (atomic versus nuclear) on the reaction probabilities is negligible at low energies, as follows from the analysis of both systems, the harmonic model and the collinear $\text{H}_3$.

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