Hydrogen molecule ion: Path integral Monte Carlo approach

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Path integral Monte Carlo approach is used to study the coupled quantum dynamics of the electron and nuclei in hydrogen molecule ion. The coupling effects are demonstrated by comparing differences in adiabatic Born–Oppenheimer and non-adiabatic simulations, and inspecting projections of the full three-body dynamics onto adiabatic Born–Oppenheimer approximation.

Coupling of electron and nuclear quantum dynamics is clearly seen. Nuclear pair correlation function is found to broaden by 0.040 \( a_0 \) and average bond length is larger by 0.056 \( a_0 \). Also, non-adiabatic correction to the binding energy is found. Electronic distribution is affected less, and therefore, we could say that the adiabatic approximation is better for the electron than for the nuclei.

INTRODUCTION

There is a number of phenomena in molecular and chemical physics which are influenced by the quantum behavior of both nuclei and electrons, rovibrational dynamics being a good example, see Refs. [1, 2, 3] and references therein. In case of light-mass nuclei, protons in particular, treatment of the quantum nature of the nuclei is essential [4, 5, 6]. This has proven to be important in the description of hydrogen bond, for example [7].

Hydrogen molecule ion (H\(_2^+\)), being the simplest molecule, has been studied extensively [8] and it has often been used as an example or a test case for an improved method or accuracy [9, 10, 11, 12, 13]. In addition to the free molecule, H\(_2^+\) influenced by an electric or magnetic field is a well-studied subject [14, 15, 16, 17, 18, 19, 20]. Furthermore, there is interest in descriptions that do not restrict to Born–Oppenheimer (BO) or other adiabatic approximations [21, 22, 23, 24, 25, 26]. Such extensions can be easily realized by using quantum Monte Carlo (QMC) methods [27, 28], for example.

Among the QMC methods the path integral formalism (PIMC) offers a finite-temperature approach together with a transparent tool to trace the correlations between the particles involved. Though computationally extremely demanding, with some approximations it is capable of treating low-dimensional systems, such as small molecules or clusters accurately enough. Some examples found in literature are H [29], HD\(^+\) and H\(_2^+\) [30], H\(_2\) clusters [31], He clusters [32, 33, 34, 35] with special attention laid on \(^4\)He [36, 37, 38, 39, 40]. The approximations in these approaches relate to the \textit{ad hoc} type potentials describing the interactions between particles.

In this work we evaluate the density matrix of the full three-body quantum dynamics in a stationary state and finite-temperature. This is what we call “all-quantum” (AQ) simulation. Secondly, the electronic part only is evaluated as a function of internuclear distance in the spirit of BO approximation, and thereby, the adiabatic nuclear dynamics is evaluated in the BO potential curve. These allow us to demonstrate the non-adiabatic electron–nuclei coupling by a projection of the AQ dynamics onto the adiabatic approximations.

We need to approximate the \(-1/r\) Coulomb potential of electron–nucleus interaction at short range to make calculations feasible. We realize this with a carefully tested pseudopotential (PP). Also, the absent (ortho) or negligible (para) exchange interaction of nuclei is not taken into account. Finally, we have to simulate a finite temperature mixed state. For convenience, we have chosen 300 K, but this essentially restricts the system to its electronic ground state.

We begin with a brief introduction to the theory and methods in the next section. This includes description of the PP, and tools and concepts for the analysis in the following section. Then we carry on to the results.

THEORY AND METHODS

For a quantum many-body system in thermal equilibrium the partition function contains all the information of the system [41]. The local thermodynamical properties, however, are included in the density matrix from which all the properties of the quantum system may be derived [42]. The non-adiabatic effects are directly taken into account in PIMC. In addition, finite temperature and correlation effects are exactly included.

Path integral Monte Carlo approach

According to the Feynman formulation of the statistical quantum mechanics [43] the partition function for interacting distinguishable particles is given by the trace of the density matrix,

\[
Z = \text{Tr} \hat{\rho}(\beta) = \lim_{M \to \infty} \int dR_0 dR_1 dR_2 \ldots dR_{M-1} \prod_{i=0}^{M-1} e^{-S(R_i, R_{i+1}; \tau)},
\]

(1)
where \( \hat{\rho}(\beta) = e^{-\beta \hat{H}} \), \( S \) is the action, \( \beta = 1/k_B T \), \( \tau = \beta/M \) and \( R_M = R_0 \). \( M \) is called the Trotter number and it characterizes the accuracy of the discretized path. In the limit \( M \to \infty \) we are ensured to get the correct partition function \( Z \), but in practice sufficient convergence at some finite \( M \) is found, depending on the steepness of the Hamiltonian \( \hat{H} \).

In the primitive approximation scheme of the PIMC formalism the action is written as [44]

\[
S(R_i, R_{i+1}; \tau) = \frac{3N}{2} \ln(4\pi \lambda \tau) + \frac{(R_i - R_{i+1})^2}{4\lambda \tau} + U(R_i, R_{i+1}; \tau),
\]

where \( U(R_i, R_{i+1}; \tau) = \frac{\tau}{2} [V(R_i) + V(R_{i+1})] \) and \( \lambda = \hbar^2/2m \).

Sampling of the configuration space is carried out using the Metropolis procedure [45] with the bisection moves [46]. This way the kinetic part of the action is sampled accurately and only the interaction part is needed in the Metropolis algorithm. Level of the bisection sampling ranges from 3 to 6 in our simulations, respectively with the increase in the Trotter number. The bisection sampling turns out to be essential with large Trotter numbers to achieve feasible convergence, for nuclei in particular. Total energy is calculated using the virial estimator [47].

\section*{Extrapolation of expectation values}

The Trotter scaling procedure [30] for expectation values is used to obtain estimates for energetics in the limit \( M \to \infty \). To use this procedure one needs expectation values with several different Trotter numbers. For the Trotter number \( M \) the scaling scheme is

\[
\langle \hat{A} \rangle_{\infty} = \langle \hat{A} \rangle_M + \sum_{i=1}^{N} \frac{c_{2i}}{M^{2i}},
\]

where coefficients \( c_{2i} \) are constants for a given temperature and \( N \) represents the order of extrapolation. In this paper \( N = 2 \) has been used for the energies of \( H_2^+ \), and \( N = 3 \) for hydrogen atom energies, see Figs. 1 and 2.

\section*{Pseudopotential of the electron}

For the hydrogen molecule ion the potential energy is

\[
V(r_1, r_2, R) = -\frac{1}{r_1} - \frac{1}{r_2} + \frac{1}{R},
\]

where \( r_i = |r - R_i| \), \( R = |R_1 - R_2| \), \( r \) being the coordinates of the electron and \( R \) the internuclear distance. Eq. (4) sets challenges for PIMC arising from the singularity of the attractive Coulomb interaction [48, 49].

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{(Color online) Hydrogen atom total energies with different Trotter numbers: infinite nuclear mass (triangle) and AQ (circle). Extrapolated ground state energies are \(-0.4947(1) \text{ Ha} \) and \(-0.4938(3) \text{ Ha} \) for infinite nuclear mass and AQ simulations, respectively.}
\end{figure}

which in this work is replaced by a PP of the form [50]

\[
V_{\text{PP}}(r) = -\frac{\text{erf}(\alpha r)}{r} + (a + b r^2) e^{-ar^2}.
\]

The parameters \( \alpha_c = 3.8638 \), \( \alpha = 7.8857 \), \( a = 1.6617 \) and \( b = -18.2913 \) were fitted using direct numerical solution to give the exact ground state energy of hydrogen atom and the wave function accurately outside a cut-off radius of about 0.6 \( a_0 \). Also, a number of lowest energy orbitals of the hydrogen atom are obtained accurately outside the same cut-off radius [51]. Because the bond length of \( H_2^+ \) is about 2 \( a_0 \), it is expected that bonding of the hydrogen molecule ion becomes properly described.

Hydrogen atom reference energies for different Trotter numbers are shown in Fig 1 where triangles are obtained from infinite nuclear mass and circles are from AQ simulations. Extrapolated ground state values are \(-0.4947(1) \text{ Ha} \) and \(-0.4938(3) \text{ Ha} \) for infinite nuclear mass and AQ simulations, respectively, statistical standard error of mean (SEM) given as uncertainty in parenthesis. We can note that within 2SEM limits proportion of these energies 0.9982 reproduces that of Rydberg constants, \( \hat{R}_1/\hat{R}_\infty = 0.9995 \).

\section*{Spectroscopic constants}

Within the BO approximation of diatomic molecules the corrections to electronic energies due to rovibrational motion of the nuclei can be evaluated from a Dunham
where \( v \) and \( J \) are vibrational and rotational quantum numbers, respectively, and \( B_e, \omega_e, \omega_c x_c \) and \( \alpha_e \) are the spectroscopic constants.

The spectroscopic constants of \( \text{H}_2^+ \) and \( \text{D}_2^+ \) are obtained as introduced in Ref. [52]. In atomic units

\[
B_e = \frac{1}{2I} = \frac{1}{2\mu R^2},
\]

\[
\omega_e = \frac{1}{\mu} \frac{d^2E}{dR^2},
\]

\[
\omega_c x_c = \frac{1}{48\mu} \left( \frac{d^3E/dR^3}{d^2E/dR^2} \right)^2 - 3 \frac{d^4E/dR^4}{d^2E/dR^2}
\]

and

\[
\alpha_e = -\frac{6B_e^2}{\omega_e} \left[ \frac{R d^4E/dR^3}{3 d^2E/dR^2} + 1 \right].
\]

Instead of determining these constants at the equilibrium distance only, as in Ref. [52], we evaluate expectation values from the distribution of nuclei, e.g. for the rotational constant,

\[
B_e = \frac{1}{2I} \int g(R) \frac{1}{R^2} dR,
\]

where the pair correlation function \( g(R) \) is normalized to unity. The other constants, Eqs. (8)–(10), are evaluated similarly.

**Centrifugal distortion**

Effects caused by the centrifugal distortion, arising from rotational motion of the nuclei, on the equilibrium distance can be assessed by inspecting the extremum values of the energy of harmonic oscillator in rotational motion: \( E_J(r) = \frac{1}{2}k(r-r_c)^2 + J(J+1)/2\mu r^2 \). We find an approximate equation

\[
\Delta R = \frac{4B_e}{\mu \omega_e^2 R_c^2} J(J+1),
\]

where \( R_c \) is the equilibrium distance. Eq. (12), however, does not include the anharmonic effects shown in Eq. (6), which evidently increase the bond length.

At finite temperature the rotational energy states should be weighted by the Boltzmann factor, which leads to

\[
\Delta R = \frac{4B_e}{\mu \omega_e^2 R_c^2} \sum_j J(J+1) \frac{\exp(-\beta B_e J(J+1))}{\sum_j \exp(-\beta B_e J(J+1))}.
\]

**RESULTS**

We consider three different cases separately in order to demonstrate the non-adiabatic effects. First, the electronic part only is evaluated as a function of internuclear distance in the spirit of BO approximation. Second, the adiabatic nuclear dynamics is evaluated in the BO potential curve. Finally, \( \text{H}_2^+ \) is treated fully non-adiabatically with the AQ simulation. These allow us to demonstrate the non-adiabatic electron–nuclei coupling by a projection of the AQ dynamics onto the adiabatic approximations. In addition, spectroscopic constants and isotope effects are looked into.

**Adiabatic electron dynamics**

Though the PP, Eq. (5), reproduces the hydrogen atom energy exactly, an error of \(-0.00342 \text{ Ha} \) from the exact value \(-0.10263 \text{ Ha} \) results in binding of another proton to form \( \text{H}_2^+ \). This is demonstrated in Fig. 2 where potential curves of \( \text{H}_2^+ \) from finite difference calculations with \( V_{PP} \) from Eq. (5) and exact \( V(r) = -r^{-1} \) are shown.

Our PIMC energies with increasing Trotter number \( M \) and the extrapolation to \( M = \infty \) using Eq. (3) are shown in the same figure. These indicate clearly that the Trotter number has to be at least 2\(^{13} \) in order to find the
minimum of the potential curve at the nuclear separation $R = 2.0 \ a_0$. The extrapolated values are in good agreement with the potential curve FDPP, and there is almost a perfect match at $R = 2.0 \ a_0$, where the value of the extrapolated dissociation energy is 0.1061(2) Ha.

For larger nuclear separations than 3.5 $a_0$, however, we are not able to reproduce the potential curve with these Trotter numbers: we get too weakly binding molecule. This is assumed to be a consequence of the electronic wave function becoming more delocalized as the internuclear distance increases, and thus the “polymer ring” representing the electron is not capable of sufficient sampling of configuration space. This error should diminish with increasing $M$.

The electron–nucleus pair correlation function is shown in Fig. 3 and will be discussed below.

### Adiabatic nuclear dynamics

For the quantum dynamics of the nuclei only (QN) we consider both $H_2^+$ and $D_2^+$ to see the isotope effect, too. The FDPP potential curve in Fig. 2 is used, for which convergence with respect to Trotter number is found at $M \geq 2^6$ for both isotopes. Resulting pair correlation functions are shown in Fig. 3.

Average nuclear separation of 2.019(1) $a_0$ for $H_2^+$ and 2.007(2) $a_0$ for the isotope $D_2^+$ is found with $M \geq 2^6$. The full width at half maximum (FWHM) of the pair correlation functions are 0.539(1) $a_0$ and 0.454(1) $a_0$ for these isotopes, respectively.

Difference in the bond length of $H_2^+$ between the adiabatic electron and adiabatic nuclei simulations, i.e. total distortion, is 0.019 $a_0$. Centrifugal contribution to this, the difference between one and three dimensional simulations of the nuclei, is 0.009(1) $a_0$, which unexpectedly is about twice as much as the value 0.0045 $a_0$ evaluated from the approximate Eq. (13). The anharmonic contribution, i.e. difference between total and centrifugal distortions, is 0.010(1) $a_0$. In Ref. [54] it was shown that anharmonic effects in $H_2$ molecule contribute about the same amount to total distortion as centrifugal force, which turns out to be the case here, too.

Difference between the total energies of the previous simulations (3D vs. 1D) is 0.0009383(2) Ha, which is close to $k_B T \approx 0.00095$ Ha as expected due to the presence of the two rotational degrees of freedom in 3D. Difference between the dissociation energies of adiabatic electron and nuclear simulations, i.e. the zero-point vibrational energy, is 0.0064(2) Ha.

A Morse potential [53] fitted to the FDPP potential curve is used in the evaluation of the spectroscopic constants, see Table I. This is justified because the nuclear simulations and analytical Morse wave function [54] calculations coincide. The spectroscopic constants of $H_2^+$ are close to those given in Ref. [52], which have been determined at the equilibrium distance of the nuclei, only. Same procedure is used for the spectroscopic constants of the other isotope. In Table I the same constants evaluated using the AQ instead of BO nuclear pair correlation function are also shown.

### Non-adiabatic “all-quantum” dynamics

For $H_2^+$ the total energy of AQ simulation with the Trotter number $M = 2^{13}$ is $-0.60159(3)$ Ha. The extrapolation procedure yields total energy $-0.59872(3)$ Ha, which is only 0.0016 Ha more binding than the value $-0.5971$ Ha from variational Monte Carlo (VMC) simu-
by weighting the equations by the nuclear pair correlation values of the spectroscopic constants are obtained correction of change in the values, except for
    "AQ spectroscopic constants" should be interpreted mainly as the di-

BO potential energy surface. Thus, the "AQ spectroscopic constants" is
    using the derivatives from a fitted Morse potential, i.e. here.

Density Functional Theory (MCDFT) scheme, not shown one in Ref. [26] computed within the Multicomponent

Table II: \( \text{H}^+ \) energetics (atomic units). First three are BO and the next three are non-adiabatic values.

| Method       | \( E_{\text{tot}} \) | \( D_e \) | \( D_0^0 \) | \( R \) |
|--------------|-------------------|----------|-------------|------|
| HF\(^a\)     | \(-0.6026\)       | 0.1026   | 2.000       |
| VMC\(^b\)    | \(-0.6026\)       | 0.1026   | 2.000       |
| PIMC\(^c\)   | \(-0.6061(2)\)    | 0.1061(2) | 0.997(1)  | 2.0  |
| VMC\(^c\)    | \(-0.5971\)       | 0.0971   | 2.064       |
| MCDFT\(^d\)  | \(-0.581\)        | 0.081    | 2.08        |
| PIMC\(^e\)   | \(-0.59872(3)\)   | 0.09872(3) | 2.075(2) |

\(^a\) Hartree–Fock
\(^b\) VMC, Born–Oppenheimer
\(^c\) VMC, non-adiabatic
\(^d\) MCDFT, non-adiabatic (SAO)
\(^e\) This work

The zero-point energy obtained from simulations is \( D_e - D_0^0 = 0.0074 \) Ha, see Table II. It should be
    pointed out that the error due to the pseudopotential in the AQ total energy is only about half of that found for

the BO total energies.

Difference in dissociation energies of AQ and the 3D QN \( \text{H}_2^+ \) simulations is 0.00097 Ha, which is about \( k_B T \)
    revealing additional electronic energy degrees of freedom in the first. AQ simulation for \( \text{H}_2^+ \) gives for the average

nuclear separation \( R = 2.075(2) a_0 \), which is 0.056 \( a_0 \) larger than that in the QN simulation. The AQ FWHM
    of the nuclear pair correlation function is 0.5785(2) \( a_0 \), which shows a spreading of 0.040 \( a_0 \) compared to the QN

results, see Fig. 3.

In Fig. 4 BO and AQ electron–nucleus pair correlation functions are compared. AQ projection onto the
    BO bond length, \( R = 2.0 a_0 \), and BO results coincide, which indicates that the adiabatic BO approach for the

electron dynamics is sufficient. Thus, it seems that the electron–nuclei coupling effects are more clearly seen in the
    dynamics of the nuclei, see Fig. 3 As one might expect, there is a noticeable difference between the AQ and

the BO electron–nucleus pair correlation functions due to varying bond length, see Fig. 4.

The AQ average nuclear separation is close to the value 2.064 \( a_0 \) obtained by a non-adiabatic VMC simulation
    28. The AQ pair correlation function of the nuclei, see Fig. 3 coincides with the SAO (Scaled Atomic Orbital)

one in Ref. 26, computed within the Multicomponent Density Functional Theory (MCDFT) scheme, not shown here.

All the spectroscopic constants in Table I are defined using the derivatives from a fitted Morse potential, i.e. BO potential energy surface. Thus, the "AQ spectroscopic constants" should be interpreted mainly as the direction of change in the values, except for \( B_e \). The expectation values of the spectroscopic constants are obtained by weighting the equations by the nuclear pair correlation function from the corresponding simulation.

A projection of the AQ simulation to a potential curve of the nuclei is constructed with the help of the known solutions to the Morse potential. Distribution from the Morse wave function is fitted to the pair correlation function of the AQ simulation. The three-body sys-

Figure 4: (Color online) \( \text{H}_2^+ \) electron–nucleus pair correlation functions: AQ (solid, second lowest curve), AQ projection to \( R \approx 2.0 a_0 \) (solid) and BO at \( R = 2.0 a_0 \) (dashed). The latter two almost coincide. Dashed vertical line indicates the size of the pseudopotential core, \( r = 0.6 a_0 \). For comparison corresponding pair correlation functions for hydrogen atom (dotted line) and \( \text{H}_2^+ \) (dotted) obtained by using the analytical ground state wave function of hydrogen atom are also shown.

Figure 5: (Color online) \( \text{H}_2^+ \) potential curves: Morse potential fitted to FDPP (dashed) and the effective Morse potential obtained from the projection of the AQ simulation (solid), see the text for details. Corresponding nuclear pair correlation functions are shown in Fig. 4. The shift in the bond length is 0.036 \( a_0 \).
The spectroscopic constants with the projected potential curve are $B_e = 29.26$ cm$^{-1}$, $\omega_e = 2047.94$ cm$^{-1}$, $\omega_e a_e = 78.12$ cm$^{-1}$ and $\alpha_e = 2.110$ cm$^{-1}$. All this indicates that an effective Morse potential is not capable of describing non-adiabatic effects correctly.

Finally, it may be of interest to see a visualization of the "polymer rings" representing the quantum particles in the PIMC simulation. So, Fig. 6 presents the xy-plane (z-projection) snapshot from AQ simulation with Trotter number 2$^{13}$ for all three particles. "Polymer ring" describing the electron is in the background and those of the nuclei are placed on top.

**CONCLUSIONS**

The three-body quantum system, hydrogen molecule ion (H$_3^+$), is revisited, once again. Path integral Monte Carlo (PIMC) method is used for evaluation of the stationary state quantum dynamics. PIMC offers a finite-temperature approach together with a transparent tool to describe the correlations between the particles involved. We aim at tracing the electron–nuclei coupling effects in the three-body all-quantum (AQ), i.e. non-adiabatic, molecule. This is carried out by comparing the differences in adiabatic Born–Oppenheimer (BO) and AQ simulations, and inspecting the projections from the AQ simulation onto the BO description of the electron-only and nuclear-only subsystems.

The approach turns out to be computationally demanding, but with the chosen pseudopotential for the attractive Coulomb potential and extrapolation to infinite Trotter number the task becomes feasible. By choosing low enough temperature, 300 K, we are able to compare our data to those from zero–Kelvin quantum methods available in literature. Among others we have evaluated spectroscopic constants and molecular deformation, also considering the isotope effects.

With our fully basis set free, trial wave function free and model free approach we are not able to compete in accuracy with the zero–Kelvin benchmark values. However, due to the mixed state density matrix formalism of PIMC we are able to present the most transparent description of the particle–particle correlations.

Total energies from our simulations are more binding in nature compared to the benchmark values, see Table II. This is an expected effect of the pseudopotential in use, see Fig. 2 and FD therein. Quantum dynamics of the system is well described and distinct features of coupling are observed for the nuclei: shift of 0.056 $a_0$ in the equilibrium bond length, increase of 0.040 $a_0$ in the width of the pair correlation function of the nuclei and non-adiabatic correction of about 0.00097 Ha to dissociation energy. Electronic distribution, however, is less influenced by the coupling, see Fig. 4 and therefore, we could say that the adiabatic approximation is better for the electron than for the nuclei.

Projection of the non-adiabatic three-body system with the help of Morse wave functions onto two-body nuclei-only subsystem indicates that Morse potential is not capable of describing non-adiabatic effects correctly, see Fig. 5.

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