

SELF PRESENTATION

1. First name and surname.

Marcin Buchowiecki

2. Diplomas, academic/artistic degrees – including the titles, places and years of issue and the title of doctoral thesis.

- A. Master engineer of chemical technology, Faculty of Chemical Engineering, Technical University of Szczecin, Szczecin, 2002.
- B. Master of Mathematics, Faculty of Mathematics and Physics, University of Szczecin, Szczecin, 2004.
- C. Ph.D. degree in physics, thesis entitled "Harmonium atom as a tool for testing density matrix functionals" (supervisor prof. J. Cioslowski), Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University in Torun, 2006.

3. Information on employment in scientific/artistic institutions.

- A. from April 2007 - adjunct at The Faculty of Mathematics and Physics of University of Szczecin.
- B. October 2002 - April 2007 - assistant at The Faculty of Mathematics and Physics of University of Szczecin.

4. Indication of achievements pursuant to article 16 item 2 of the act of law dated 14 March 2003, concerning scientific degrees, and scientific titles, and degrees and titles in the domain of arts (Official Journal No. 65, item 595 with amendments)

a) Title of scientific/artistic achievement

“The rate constant, equilibrium constant and isotope effects from the quantum Monte Carlo simulations” (mono-thematic series of 8 scientific publications)

b) (author/authors, title/titles of publications, year, journal)

H1. **M.Buchowiecki** and J.Vanicek *Journal of Chemical Physics* 132 (2010) 194106 Direct evaluation of the temperature dependence of the rate constant based on the quantum instanton approximation (impact factor 2010 = 2.921)

H2. **M.Buchowiecki** *International Journal of Quantum Chemistry* 112 (2012) 1107 Temperature dependence of the rate constant of ionic analogs of $H+H_2 \rightarrow H_2+H$ reaction by quantum instanton method. (impact factor 2012 = 1.306)

H3. **M.Buchowiecki** *Journal of Theoretical and Computational Chemistry* 11 (2012) 143 The rate constant of the $O(^3P) + HCl \rightarrow OH + Cl$ reaction within quantum instanton approximation. (impact factor 2012 = 0.515)

H4. **M.Buchowiecki** *Chemical Physics Letters* 531 (2012) 202 Quantum calculations of the temperature dependence of the rate constant and the equilibrium constant for the $NH_3+H=NH_2+H_2$ reaction. (impact factor 2012 = 2.145)

H5. **M.Buchowiecki** *Journal of Theoretical and Computational Chemistry* 12 (2013) 1350026 TL/PIMC method with the Takahashi-Imada approximation for the equilibrium constant of the $O+HCl=OH+Cl$ reaction. (impact factor 2012 = 0.515)

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- H6. **M.Buchowiecki** and J.Vanicek *Chemical Physics Letters* 588 (2013) 11 Monte Carlo evaluation of the equilibrium isotope effects using the Takahashi-Imada factorization of the Feynman path integral. (impact factor 2012 = 2.145)
- H7. J.Huang, **M.Buchowiecki**, T.Nagy, J.Vanicek, and M.Meuwly *Physical Chemistry Chemical Physics* 16 (2014) 204 Kinetic isotope effect in malonaldehyde from path integral Monte Carlo simulations.
(impact factor 2012 = 3.829)
- H8. **M.Buchowiecki** *Chemical Physics* 431-432 (2014) 1 Path integral Monte Carlo with the Takahashi-Imada approximation for the temperature dependence of the equilibrium constant.
(impact factor 2012 = 1.975)

c) description of the aim of the series of publications, the results, including description of their possible use

General introduction.

The presented publications are devoted to the theoretical chemical kinetics and statistical physics in the context of molecular modeling methods. In the publications known methods are developed and new ones are proposed to calculate rate constants of chemical reactions, equilibrium constants and the respective isotope effects. Methods of calculating these quantities are important part of chemical physics because they are the most basic quantities describing rates, equilibria and isotope effects of chemical reactions. Rate and equilibrium are important in all situations where chemical reactions occurs and knowledge of these constants can be useful in understanding processes in nature and also can be useful in chemical industry.

The rate constant is a basic quantity characterizing chemical reactions and can be obtained from the classical transition state theory or one of the quantum transition state theories for example quantum instanton theory [1] which is applied here; the rate constant can be also obtained without approximations from the quantum scattering theory. Quantum effects of the atomic nuclei, such as zero point energy or tunneling through energy barrier, influence the rate constant especially at low temperatures and when hydrogen atom takes part in bond breaking or creation in the course of reaction. These effects influence even biochemical reactions at the physiological temperatures [2]. From the above theories kinetic isotope effects (i.e. ratios of the rate constants of the reactions in two isotope versions) can be obtained.

Recently a lot of research is conducted to develop such quantum theories for calculating reaction rate constants and isotope effects [1,3,4,5,6,7,H1,H2,H3,H4,H7].

The equilibrium constants and equilibrium isotope effects (influence of isotopic composition of molecules on equilibrium) were and still are studied much less than equilibrium constants because the standard harmonic approximation with possible corrections [8] is usually in agreement with experiment; the problem of mounting energy barrier between the reacting molecules and the transition state is not present what makes the situation simpler. Anyway, anharmonicity at high temperatures and quantum effects at low temperatures influence equilibrium constant.

Because of the above facts publications on methods of calculating equilibrium constants and equilibrium isotope effects are not so many and such methods also use various approximations [9,10,11,12,13,H4,H5,H6,H8].

The equilibrium constant can be also calculated as the ratio of the rate constants for the reaction in both directions, however this reduces problem to the rate constant calculation and complicates the situation at the same time.

Introduction to the series of publications.

Keynote of the publications series is a quantum treatment of studied systems in a possibly full fashion, that is without approximations (except the indispensable for the computer simulation) or starting from exact expressions for the calculated quantities.

Second, more technical aspect, is minimization of simulation time by the proper energy estimators and more accurate approximation (Takahashi-Imada) what decreases the effective simulation time.

The common point of the presented articles is the application of the Path Integral Monte Carlo (PIMC) method [14]. By application of discretized version of Feynman path integral, PIMC method allows to take into account quantum movement of atomic nuclei in Monte Carlo simulations. Typical in molecular dynamics or Monte Carlo method is to assume classical movements of nuclei on potential energy surface (PES) of a given molecular system. It turns out that taking into account quantum movements of nuclei can be crucial; the especially good example is isotope effect, which is quantum in nature (classical simulations give the same results independently of isotopic composition of molecule [8]).

Work on publication [15] was an incentive to start the research on Monte Carlo methods. The results in this publication were confirmed thanks to search for the potential energy surface minima of particles interacting with the Coulomb potential with the basin-hopping Monte Carlo method.

In the publication mentioned above as well as in publications presented for assessment, Monte Carlo simulations were performed with the use of Fortran code which I have written. There also exists quantum version of molecular dynamics, however PIMC method does not require knowledge of the PES derivatives, which is an advantage.

In the presented publications, PIMC simulations were used for calculations of fundamental properties characterizing chemical reactions, namely the rate constant, the equilibrium constant and isotope effects. Development of such computational methods was an aim of the publications series under consideration.

For the rate constant calculations (exactly – its temperature dependence) and the kinetic isotope effect quantum instanton method [1] was used. This method allowed to estimate properties

characterizing transition state (TS). In this part of research reactive PESs were necessary for the TS simulations. The quantum instanton method starts from the exact expression for the rate constant and naturally takes into account quantum effects that is no corrections (for example for tunneling) are not needed.

For the equilibrium constant (exactly – its temperature dependence) and equilibrium isotope effect, reactive PESs are not needed, because one have to obtain only partition functions ratios for products and reactants and simulations of TS are not needed. The methods applied, because of path integrals, take into account quantum effect of nuclei without corrections (in the framework of Born-Oppenheimer approximation) and use no approximations.

I would like to stress three publications. Method of calculating temperature dependence of the rate constant presented in [H1] was proposed by the authors and the errors were discussed in a detailed way. Method of calculating temperature dependence of the equilibrium constant presented in [H4] was proposed by the author and assessed by the Editor of Chemical Physics Letters as an important contribution to the field. Publication presenting the known method of calculating the equilibrium isotope effect augmented with the method of speeding up the PIMC simulations [H6] was published in Chemical Physics Letters as Editor's Choice.

PIMC method [14].

The PIMC method is based on the discretized version of Feynman path integral for the trace of Boltzmann operator, i.e. the partition function. This representation of the molecular partition function allows in turn to represent thermodynamical equilibrium quantities of the molecule.

Discretized representation of the partition function has the Trotter number as a parameter, which in the limit of infinity gives exact partition function. Important part of the PIMC simulation is to determine Trotter number value needed to converge given physical quantity in the considered temperature. At low temperatures molecular systems shows stronger quantum effects than at high temperatures, moreover light atoms – especially hydrogen – also make system more quantum, so that such simulations need high Trotter number. All reactions considered here involved hydrogen atom or its isotopes.

The PIMC simulations sample the configuration space according to appropriate weight – in case of the TS, apart from the PES dependent Boltzmann distribution, one have to take into account additional potential which keeps the system in the TS geometry. Monte Carlo method, similarly to the molecular dynamics, does not allows to calculate the partition function itself but the ratio of

the partition functions – this fact is used in all the publications discussed here.

In the PIMC method the effective potential appears, which consists of the potential part (which stems from the PES of the system) and kinetic part, which depends on positions of so called *beads* (their number is equal to the Trotter number) and on masses of atoms. The shape of the effective potential means that in the PIMC simulation each atom is represented by so called *chain*, i.e. a group of beads (in each group interactions are harmonic). Masses of atoms in kinetic part of potential energy allows isotope effects to be simulated, which is impossible in classical simulations.

The MC sampling of beads positions can be classical with the step which has to be determined for a given PES or can be made more effective by staging algorithm (multi-element moves of free particle type where the step is determined by the algorithm). Classical positions of atoms on PES are performed with moves of all chains (without changing the relative beads positions).

Estimators of a given quantity have to be derived from the discretized partition function. For the TS, constraining potential has to be taken into account in derivation of the estimators. In presented publications, estimators of the energy and the appropriate derivative of free energy (specified later) were applied, for all that quantities three types of estimators can be used – thermodynamical, virial and centroid virial. The centroid virial estimator is preferred due to fact that its statistical error do not increase with the Trotter number. For the TS, two other quantities were used (specified later).

Typical high-temperature decomposition of the Boltzmann operator trace (primitive approximation) may require at low temperatures the Trotter number of hundreds. This can be avoided by the Takahashi-Imada decomposition [16] which is more accurate and allows to speed up the simulations decreasing the Trotter number. For the Takahashi-Imada approximation derivatives of PES are needed and should be calculated analytically and called in the code with PES; numerical calculation of the derivatives does not allow to speed up the code. Application of the Takahashi-Imada approximation changes the effective potential and the estimators, which have to be properly derived in this case.

I have implemented all the elements described above in the Fortran code for PIMC simulations. In order to simulate given system code has to be augmented by the PES of that system. All research described here was performed by exploiting this code and extending it with new elements.

Rate constant and kinetic isotope effect.

In order to include quantum effects for the rate constant and kinetic isotope effect, the quantum instanton method (QI) [1] was used. The QI method is one of the quantum transition state theories and was used in publications [H1,H2,H3,H4,H7].

The QI method exploits representation of the rate constant as the symmetrized flux-flux correlation function. The QI approximation allows to calculate the ratio of rate constants in different temperatures $k(T)/k(T_0)$ (in the respective publications this ratio is calculated with respect to the same temperature T_0 and resulting T-dependence is called the temperature dependence of the rate constant) [H1,H2,H3,H4] or the ratio of rate constants pertaining to different isotope masses at the given temperature that is the kinetic isotope effect [H7].

The expressions for the aforementioned rate constants ratios consist of the following factors:

1. the ratio of the partition functions of the reacting molecules,
2. the ratio of the symmetrized delta-delta correlation functions (i.e. the quantity describing the TS, which takes into account constraining potential to keep the TS geometry),
3. the ratio of the correlation functions characterizing the TS (for both temperatures or masses),
4. the specific type of energy variance (for both temperatures or masses).

The factors 3. and 4. characterizing the TS can be calculated as the average values of the expressions which can be calculated by the PIMC simulation. I have implemented these factors in the PIMC code and they are PES dependent.

The factors 1. and 2. are calculated by the thermodynamical integration method [17]. In case of the temperature dependence of the rate constant the energy of the reacting molecules (for the quantity 1.) or the energy of the TS (for the quantity 2.) is integrated with respect to the inverse temperature. In case of the kinetic isotope effect, the free energy of the reacting molecules (for the quantity 1.) or the free energy of the TS (for the quantity 2.) is integrated with respect to the parameter controlling isotope mass, where the linear dependence of the mass from the parameter is assumed (the parameter belongs to the [0,1] interval).

Publication [H1].

In the publication [H1] authors propose and analyze in a detailed way the method of calculating temperature dependence of the rate constant for the Eckart potential, which is the one-dimensional model for the reaction with a potential barrier, and for the real reaction $H_2+H \rightarrow H+H_2$ (the simplest

hydrogen exchange reaction). Calculating not the rate constant itself but the ratio of the rate constants results in higher effectiveness of the method because a tedious umbrella sampling procedure is not used. Both reactions were studied in the 200K-1500K temperature range; for 200K, required Trotter numbers were 96 for the Eckart barrier and 160 for the H_2+H reaction. The resulting effective dimension of the simulations (the number of Cartesian coordinates) for H_2+H is even $3*3*160=1440$, not $3*3=9$ as in the classical simulations.

The calculations for the TS energy were performed with three groups of estimators (group of thermodynamical estimators, group of virial estimators, group of centroid virial estimators) which results from different ways of taking into account potential constraining TS. The estimators of the TS energy and the energy of the reacting molecules were analyzed for its statistical errors (quantities from simulations are not independent, so that the block averaging method [18] was used to estimate the errors). It is known that virial estimators have errors independent of the Trotter number, the same behavior was shown for the TS simulations (i.e. with constraining potential).

An interesting observation for the TS simulations is the fact that the stronger constraint is applied for the TS, the higher is the statistical error of calculated energy. On the other side, the constraining potential have to be strong enough to keep the system in the TS geometry, so the constraining potential have to reconcile this two opposite effects. As a result, the centroid virial estimator does not have to be optimal for the TS as for the unconstrained simulations. Analysis of the estimators behavior is important for the simulations because the choice of the optimal estimator (with the lowest statistical error) allows to minimize time of simulation needed to achieve the given error.

The temperature dependence of the rate constant, as could be expected, is non-Arrhenius. Quantum effects of the nuclei cause significant deviation from linear Arrhenius plot at the low temperatures.

The presented method, thanks to calculating the rate constant ratios, increases accuracy of the QI method because of the systematic errors cancellation – relative errors with respect to the exact quantum mechanical value are smaller and do not exceed 10% in any of the situations considered in the publication even if the deviation from the linear Arrhenius law is very high.

In publications [H2,H3,H4] this method was used for the other simple chemical reactions.

Publication [H2].

The method of [H1] was applied to calculate the temperature dependence for the rate constants of ionic analogs of the previous reaction: $\text{H}_2 + \text{H}^- \rightarrow \text{H}^- + \text{H}_2$ i $\text{H}_2 + \text{H}^+ \rightarrow \text{H}^+ + \text{H}_2$. The anionic version has the temperature dependence of the rate constant (in the range of 200K-1500K) similar to the neutral case because their PESs are similar – the additional electron is at some distance from the rest of the system and its influence on the reaction is limited, in particular the barrier height is similar. The cationic version is significantly different and has a high energy barrier and strong deviation from linear Arrhenius law below 1000K.

In the anionic case, the part of the chain for multi-element moves in staging algorithm had to be smaller in order to increase acceptance which very small otherwise. The maximal Trotter number used, as in the neutral case, was 160. The energies of the reacting molecules were calculated with centroid virial estimator and the TS energies with thermodynamical estimator (according to the analysis in [H1]). It was also noted that the specific energy variance in the QI theory (factor 4.) has the poorest convergence with the Trotter number and the statistical error of that quantity is the highest from all four factors.

In the cationic case, for temperatures lower than 400K the energy barrier is too high for reaction to proceed, so that the results are not shown.

The considered reactions were not investigated for the rate constants before by any method. The simulations were performed on the fixed PESs hence the possible reaction channels with charge transfer were not considered.

Publication [H3].

In this publication the temperature dependence of the rate constant of the $\text{O}(^3\text{P}) + \text{HCl} \rightarrow \text{OH} + \text{Cl}$ reaction was calculated in the 200K-700K temperature range. This reaction is important in atmospheric chemistry and combustion processes.

Because of the atomic masses (heavy-light-heavy) the recrossing to the reactants can happen. The QI approximation, as the other transition state theories, do not take into account recrossing effect, however it is important only at high temperatures and can be neglected in the temperature range considered here.

In the computations and for determination of the simulation parameters, the conclusions about sampling, estimators, and statistical errors from the previous publications was taken into account. Here, the thermodynamic estimator was used for both reagents and TS to limit the number of the potential

energy calls (computation of the potential energy is the main cost of the simulation). It can be noticed again that the specific energy variance is the most difficult quantity to converge in the QI theory.

For the reaction under consideration, deviations from the linear Arrhenius law were observed and the results were compared with the ICVT (improved canonical variational theory) method with semi-classical tunneling and with the quantum-mechanical results of the scattering theory. It was concluded that the QI theory corrects the ICVT results but it's not identical with the exact quantum-mechanical values (which are identical with the experimental data).

Publication [H4].

In this publication the temperature dependence of the rate constant of the $\text{NH}_3 + \text{H} = \text{NH}_2 + \text{H}_2$ reaction was calculated. The reaction involves 5 atoms (not 3 like in the previous reactions) and possess more complicated PES. The calculations were performed for the 200K-1000K temperature range for the forward reaction ($\text{NH}_3 + \text{H} \rightarrow \text{NH}_2 + \text{H}_2$) and for the reverse reaction ($\text{NH}_3 + \text{H} \leftarrow \text{NH}_2 + \text{H}_2$) and again in both cases non-Arrhenius behavior is present at the low temperatures.

The results of the QI method are compared with the other quantum method – TDWP (time dependent wave packet) and additionally with the CVT (canonical variational theory) method with tunneling correction. Interesting is the fact that from the three mentioned methods the QI theory gives the best agreement with the experiment. For the forward reaction, the QI method agree with the CVT method (which has better agreement with experiment). For the reverse reaction, the QI method agree with the TDWP method (which has better agreement with experiment in this case).

Again it was confirmed that the main sources of errors in the QI method are the quantities describing the TS.

Publication [H7].

The kinetic isotope effect of the intra-molecular proton transfer in malonaldehyde was calculated with the QI method (centroid virial estimator was used for the free energy derivatives) for the 250K-1000K temperature range.

The simulations were performed on a fully dimensional and validated PES of malonaldehyde based on the molecular mechanics with proton transfer (MMPT) and the MP2/6-311++G(d,p) level of theory. The molecule consists of 9 atoms so it relatively big for quantum dynamics methods.

Similarly to the temperature dependence of the rate constant, avoiding calculations of the rate constants allows to simplify and speed up the simulations. In 300K, the value of the kinetic isotope effect was 5.2 ± 0.4 ; in the previous studies, by a variety of methods, values of 1.54-5.10 and 6.49-11.41

were reported.

Detailed analysis shows that kinetic isotope effect varies considerably with temperature and its low-temperature behavior is dominated by the fact that the free energy derivative increases faster for the reagents than for the TS. It is noted that specific energy variance introduces the most of statistical error.

The expression for the kinetic isotope effect can be divided into the part which is approximately independent of temperature and the part with linear Arrhenius behavior.

Comparison with the classical transition state theory and periodic orbit theory suggest that the kinetic isotope effect is dominated by the zero point energy and tunneling plays a minor role.

Equilibrium constant and equilibrium isotope effect.

In order to calculate the temperature dependence of the equilibrium constant (the ratio of the equilibrium constants for two temperatures $K(T)/K(T_0)$; definition analogous to the rate constant [H4] and equilibrium isotope effect (the ratio of the equilibrium constant of the reaction with the lighter isotope to the constant for the heavier isotope) [9] thermodynamic definition of the equilibrium constant is used, that is the ratio of the partition function of products to the partition function of reactants. As for the rate constant, the ratios of the equilibrium constants can be expressed as the ratios of the partition functions of the molecules involved in the reaction under consideration, which in turn can be calculated with the thermodynamic integration (of energy with respect to inverse temperature for the temperature dependence of the equilibrium constant and free energy derivative with respect to the mass controlling parameter for the equilibrium isotope effect). For the calculations of the equilibrium constants any quantities describing the TS are not needed, so the simulation length (number of Monte Carlo steps) in the publications described below is smaller even by the factor of hundreds than for the QI theory simulations described above.

For calculations of the equilibrium constant and equilibrium isotope effect the Takahashi-Imada approximation was applied, this approximation was not applied in the context of equilibrium constant yet and, like other similar approximations, is still used rarely [19,20,21,22,H5,H6,H8]. The Takahashi-Imada approximation was almost not used for the quantities characterizing chemical reactions (except of isotope effect in [22] but the method used there, in opposition to the one used by author of the publication series, is less straightforward – it uses classical trajectories and some kind of perturbation) but for example to heat capacity of atomic and molecular clusters [20] or the effect of isotope substitution for the structure of the system [21].

Publication [H4].

Apart from the QI calculations described before, a method of calculating the temperature dependence of the equilibrium constant is proposed. This method is fully quantum in nature and do not use any corrections for the quantum effects and is based on the thermodynamic integration (TI) and calculating energies needed with the PIMC simulations (so that the TI/PIMC abbreviation is used).

The temperature dependence of the equilibrium constant of $\text{NH}_3 + \text{H} = \text{NH}_2 + \text{H}_2$ was calculated with the TI/PIMC method in the temperature range 200K-1000K and compared with the equilibrium constant calculated as the forward and reverse QI rate constants ratio; this comparison is especially useful because both methods give the same values (the QI factors pertaining to the TS cancel in the ratios). Additionally, the results were compared with the CVT and TDWP methods and the values based on the JANAF database. The values from the TI/PIMC method were the closest to the quantum TDWP method.

By comparing the TI/PIMC and QI methods, it can be determined how much faster is the simulation with thermodynamic definition compared to the use of the ratio of the rate constants, if the same statistical error is to be achieved – for the reaction under consideration, the TI/PIMC method is 3520-27600 times faster. This speedup is the consequence of the fact that thermodynamic definition does not require any simulations involving the TS. Thanks to the lack of the TS quantities the following choice can be made: the statistical error can be smaller or the same error can be achieved in shorter simulation, what gives the speedup mention above.

Publication [H5].

The TI/PIMC method was used to calculate the temperature dependence of the equilibrium constant of the $\text{O}(^3\text{P}) + \text{HCl} \rightarrow \text{OH} + \text{Cl}$ reaction in the temperature range 200K-700K. The primitive approximation is compared with the Takahashi-Imada approximation which allowed to decrease the Trotter number 3.5-4.1 times. In the primitive approximation the Trotter numbers were 98 for 200K and 28 for 700K, in the Takahashi-Imada approximation the Trotter numbers were 24 for 200K and 8 for 700K. The Takahashi-Imada approximation implementation do not change significantly the existing code – the correcting factor has to be added to the potential energy and taken into account in derivation of the estimators. For the reactive PES used here the analytical derivatives were not available and had to be calculated numerically, as a result the decrease in simulation time is not shown. Numerical derivatives introduce additional statistical error in the Takahashi-Imada simulations. Despite the above fact, this method has advantage of the smaller Trotter number what makes sampling easier – this can be

beneficial in big systems.

The results of the TI/PIMC method are compared with the approximations of the equilibrium constants based on the zero point energies difference and the energies difference from PIMC simulation in 700K. The results based on the zero point energies are significantly different from all other methods (except the highest temperatures), the energies in 700K based results approximate the TI/PIMC results well, giving possibility of calculating the temperature dependence of the rate constant from the simulation in one temperature and decreasing manifold the simulation time.

Publication [H6].

The equilibrium isotope effect is calculated for the $H_2+D=H+HD$ and $H_2+D_2=2HD$ reactions with the primitive approximation (with Trotter number from 30 to 160) and Takahashi-Imada approximation (with Trotter number from 8 to 48) in the temperature range 200K-1000K.

The results are calculated for both thermodynamic and centroid virial estimators (for the free energy derivative) with the primitive and Takahashi-Imada approximations. The errors behavior in the Takahashi-Imada approximation is the same as in the primitive approximation, so that independence of error of centroid virial estimator from the Trotter number can be exploited to speed up the simulations. The speedups are given with respect to the least favorable case of the primitive approximation with the thermodynamic estimator – the highest speedup for the Takahashi-Imada approximation with the centroid virial estimator is from more than 100 times to more than 2000 times.

The results are compared with the harmonic approximation which, after Teller-Redlich rule is applied, is the function of the normal modes frequencies for the given isotopic composition of the molecules. The harmonic approximations were also calculated for the high-temperature ($T \rightarrow \infty$) and low-temperature ($T \rightarrow 0$) limits. The harmonic approximations are based on the numerically calculated frequencies on the PES used for simulations. The harmonic approximation can give results very close to the PIMC simulations, if the error cancellation happens (the second reaction) or give different results if the errors do not cancel (the first reaction, especially at low temperatures). Note that both reactions are very simple and harmonic approximation can be worse in case of other reactions, especially at low temperatures and if the system is strongly anharmonic or loosely bounded.

For the second reaction ($H_2+D_2=2HD$) the results were successfully compared with experimental data.

Publication [H8].

The TI/PIMC method for the temperature dependence of the equilibrium constant proposed in [H4] was applied to the $\text{NH}_3+\text{HD}=\text{NH}_2\text{D}+\text{H}_2$ reaction in the 200K-1000K temperature range. Moreover, to simulate changes in the normal modes' frequencies for substituent effect, the equilibrium constants ratios were calculated for the reaction $\text{NH}_2\text{X}+\text{HD}=\text{NHXD}+\text{H}_2$ where X is the hydrogen-like atom with mass $1,2m_{\text{H}}$ or $0,8m_{\text{H}}$. In case of the isotope exchange the equilibrium constant is equal to the isotope effect and the harmonic approximation dependent only on the normal modes' frequencies, as in [H6], could be used.

Here, both PESs (for H_2 and NH_3) had analytical derivatives, what allowed to show not only decrease in the Trotter number in Takahashi-Imada approximation (like in publication [H5]) but actual decrease in simulation time. The simulations on H_2 PES had parameters like in [H6] and on NH_3 PES the Trotter number was from 6 to 32 in the Takahashi-Imada approximation. When the simulations with centroid virial estimator are compared, simulation time was decreased by a factor of 4, what is consistent with results in [H6]. On the example of hydrogen molecule, it was observed that the convergence with respect to the Trotter number of energy (used here) and free energy estimators is the same.

The TI/PIMC values for the $\text{NH}_3+\text{HD}=\text{NH}_2\text{D}+\text{H}_2$ reaction are compared with the harmonic approximation which yields too high values in the considered temperature range. Additionally, the results with the corrections to the harmonic approximation (approximately reflecting experimental data) are similar to the TI/PIMC results.

The results of the present method for the equilibrium constant ratios are compared with the method for the equilibrium isotope effect used in [H6], what showed agreement of both methods; it is worth noting that the method of calculating the equilibrium isotope effect posses much less statistical error cumulation.

The TI/PIMC values for both versions of $\text{NH}_2\text{X}+\text{HD}=\text{NHXD}+\text{H}_2$ compared with the harmonic approximation show that smaller mass of atom X causes more difference of these methods, this could be expected especially at low temperatures.

Summary.

The presented research, done mostly on my own, allowed to extend knowledge about calculating basic quantities characterizing chemical reactions and about PIMC simulations of molecular systems.

A new methods of calculating the rate constant ratios and the equilibrium constant ratios in different temperatures were proposed. These methods and the methods for isotope effects, exploiting analogous methodology, were applied to some chemical reactions involving from 3 to 9 atoms. Noteworthy is the fact that the applied methods for equilibrium quantities (equilibrium isotope effect and proposed by the author method for the temperature dependence of the equilibrium constant) do not use approximations and naturally take into account quantum effects.

Important point was to show the speedup of the simulations by the choice of optimal estimators, which allow to minimize statistical error and application (in new situations) of the Takahashi-Imada approximation, which is still used not too often in simulations.

The results of this research were compared with other methods and were in agreement with them or better and were in accordance with experiment when such data were available. For some reactions results were unique and than impossible to compare.

Publications [H2]-[H8] are from years 2012-2014 so they do not have too many citations. However, publications [H1] and [H4] were already cited by the leading researchers in the filed of quantum instanton theory [23,24,25,26]. The publication [H1] was cited in the context of astrochemistry [27].

The discussed methods can be developed in the direction of larger systems (usually not studied completely by the quantum dynamics methods) or application to the cases where the quantum effects are very strong. I plan to continue this research in a very low temperature regime, which occurs in astrochemistry – the quantum effects are then very strong and the decrease in the Trotter number by the Takahashi-Imada method (or other similar approximations) can be very useful. Currently I am preparing an application for a grant to the National Science Centre for such research.

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5. Description of the other scientific/artistic achievements.

5.a. Before Ph.D.

My other research was in the fields of density matrix functional theory and harmonium atom under the supervision of prof. J. Cioslowski.

In publications J. Chem. Phys. 119 (2003) 6443 i J. Chem. Phys. 119 (2003) 11570 a new density matrix functionals were proposed, these functionals depend only on coulomb and exchange integrals – one is based on geminals (orbitals for two electrons) which is exact for two-electron singlet systems in ground state; second is for the closed-shell 4-electron systems that takes into account dispersion interactions.

The publications that followed the above (J. Chem. Phys. 122 (2005) 084102, J. Chem. Phys. 123 (2005) 234102, J. Chem. Phys. 125 (2006) 064105) were devoted to the two-electron harmonium atom i.e. the model of atom with harmonic interactions nucleus-electron. Due to the constant in the Hamiltonian correlation of the system can be changed continuously. The expressions for the occupation numbers of natural orbitals and approximations of orbitals themselves were derived. For strong correlation regime natural orbitals and their occupation numbers (which forms geometric series) were obtained. The calculated occupancies are in agreement with the results of numerical calculations.

5b. After Ph.D.

I have continued the previous research in publication [15] which was an incentive to start the research on Monte Carlo methods and molecular modeling. In this publication analytical expressions for the equilibrium geometries, respective energies and force constants were derived for clusters of 3 to 8 particles interacting with Coulomb potential. The results in this publication were confirmed by the search for the potential energy surface minima of particles interacting with the Coulomb potential with the basin-hopping Monte Carlo method. This research was important because Coulomb clusters are studied much less than Lennard-Jones clusters.

Presently I plan to study influence of radiation on tissues for radiotherapy in cooperation with Pomeranian Medical University in Szczecin. Calculations of radiation doses on different tissues will be done with MCNP5 (General Monte Carlo N-Particle Code) code. I have become interested in such research after training in nuclear energy for the Polish program of nuclear energy at National Institute of Nuclear Sciences and Techniques in France.