The Transfer Matrix Grid Method for Quantum Partition Functions, Eigenvalues and Eigenfunctions

J. P. Prates Ramalho and F. M. Silva Fernandes
Department of Chemistry and CECUL (INIC), University of Lisbon, Portugal

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A method for the calculation of quantum partition functions, and bound eigenvalues and eigenfunctions of the Hamiltonian operator is presented. The method is based on the discretization of the transfer matrix that relates the Feynman path integral to the conventional operator formulation of quantum mechanics. Its implementation is very simple, only requiring the diagonalization of the discretized transfer matrix.

The method is applied to the harmonic oscillator and Morse potential. The results are in excellent agreement with the exact ones.

Key words: Path integral, Transfer matrix, Eigenvalues, Eigenfunctions.

1. Introduction

In the last years, path integral methods have been used frequently for the calculation of quantum partition functions and ensemble averages.

Molecular dynamics (MD) or, more typically, the Monte Carlo (MC) algorithm of Metropolis [1] have been used for the numerical implementation of those methods. Brownian dynamics also has been used successfully [2, 3] and it appears to give a better convergence rate. Although such techniques are very powerful, they have the disadvantage of requiring the generation of very many configurations in order to obtain accurate results even for systems of low dimensionality. Nevertheless, they seem to be the only viable techniques for systems with many degrees of freedom.

However, for systems with few quantum degrees of freedom, other approaches have been proposed which are very efficient in terms of execution time. The work of Nauenberg et al. [4], based on the renormalization group method for the resolution of the Ising model, and the numerical matrix multiplication method (NMM) of Thirumalai et al. [5], are examples of those approaches.

The use of the transfer matrix to relate the Feynman path integral to the conventional operator formulation of quantum mechanics is well known [6, 7]. The diagonalization of the transfer matrix is equivalent to the diagonalization of a matrix representation of the Hamiltonian – the approach usually used in quantum chemistry to find the energy eigenvalues. In this context, we present a method to deal with systems with only a few quantum degrees of freedom and based on a discretized transfer matrix. The method is much more efficient than the usual MC methods and, in addition to the partition function, it also provides the eigenvalues and eigenfunctions of the Hamiltonian operator. The discretization of configuration space is also fundamental to very recent approaches [8, 9] which produce the eigenvalues and eigenfunctions of the Hamiltonian, but in a different way.

For the sake of simplicity the method is derived for 1-D systems. In particular the method is applied to the harmonic oscillator and Morse potentials. The values of the free energy, internal energy, and the eigenvalues and eigenfunctions are compared with exact ones.

2. The Method

The partition function for a quantum system can be written as

$$Z = \mathrm{Tr}\,[\exp(-\beta \hat{H})]\,, \tag{2.1}$$

where $\hat{H}$ is the Hamiltonian operator and β is the inverse of the absolute temperature multiplied by Boltzmann's constant.

For a single particle of mass m moving in one linear dimension under the influence of a potential $V(x)$ the Hamiltonian operator is

$$\hat{H} = \hat{p}^2/2m + V(\hat{x})\,. \tag{2.2}$$

Reprint requests to Dr. F. M. Silva Fernandes, Departamento de Quimica, Faculdade de Ciencias, Universidade de Lisboa, Rua Ernesto de Vasconcelos, 1700 Lisboa, Portugal.

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Using Trotter's formula [10], it is easy to derive the representation of the partition function as a discretized path integral:

$$Z = \int \mathrm{d}x_1 \int \mathrm{d}x_2 \cdots \int \mathrm{d}x_P \left(\frac{mP}{2\pi\hbar^2\beta}\right)^{p/2} \cdot \exp[-\beta V_{\mathrm{eff}}(x_1, x_2, \ldots, x_P)], \tag{2.3}$$

where

$$V_{\mathrm{eff}}(x_1, x_2, \ldots, x_P) \tag{2.4}$$
$$= \frac{mP}{2\hbar^2\beta^2} \sum_{i=1}^{P} (x_{i+1} - x_i)^2 + \frac{1}{2P} \sum_{i=1}^{P} V(x_i) + V(x_{i+1})$$

with the periodic boundary conditions

$$x_{i+1} = x_1 \quad \text{if} \quad i = P.$$

The effective potential can be visualized as describing a ring of P beads, each one interacting with its neighbours through a harmonic potential and feeling the average potential $[V(x_i) + V(x_{i+1})]/2$ with a strength reduced by $1/P$. When $P \to \infty$, (2.3) can be formally written as a full path integral:

$$Z = \int \mathscr{D}x \exp\left\{-\frac{1}{\hbar} \int_0^{\hbar\beta} \mathrm{d}\tau\, [1/2 m\, \dot{x}(\tau)^2 + V(x(\tau))]\right\}. \tag{2.5}$$

Introducing discretization of configuration space we obtain

$$Z \cong \Delta x^P \sum_{a_1} \sum_{a_2} \cdots \sum_{a_P} \left(\frac{mP}{2\pi\hbar^2\beta}\right)^{P/2} \cdot \exp[-\beta V_{\mathrm{eff}}(a_1 \Delta x, \ldots, a_P \Delta x)], \tag{2.6}$$

where Δx is a uniform spatial step and the coefficients a_i are integers. The integration limit of the integrals in (2.3) are substituted by $-l/2$ and $l/2$, where l is an integer appropriately chosen according to the problem considered as explained in greater detail at the end of this section.

When discretized, the effective potential, V_{eff}, assumes the form

$$V_{\mathrm{eff}} = \frac{mP}{2\hbar^2\beta^2} \sum_{i=1}^{P} (a_{i+1}\Delta x - a_i \Delta x)^2 + \frac{1}{2P} \sum_{i=1}^{P} [V(a_i \Delta x) + V(a_{i+1} \Delta x)]. \tag{2.7}$$

Introducing the discretized transfer matrix

$$\langle a | \Pi | a' \rangle = \exp\left\{-\beta\left(\frac{mP}{2\hbar^2\beta^2}(a\Delta x - a'\Delta x)^2 + \frac{1}{2P}[V(a\Delta x) + V(a'\Delta x)]\right)\right\} \tag{2.8}$$

one may write the partition function as

$$Z \cong \Delta x^P \left(\frac{mP}{2\pi\hbar^2\beta}\right)^{P/2} \sum_{a_1} \sum_{a_2} \cdots \sum_{a_P} \langle a_1 | \Pi | a_2 \rangle \cdot \langle a_2 | \Pi | a_3 \rangle \ldots \langle a_P | \Pi | a_1 \rangle. \tag{2.9}$$

Considering the unity in the form

$$\sum_{a_i} | a_i \rangle \langle a_i | = 1 \quad (i = 2, \ldots, P) \tag{2.10}$$

we obtain

$$Z \cong \Delta x^P \left(\frac{mP}{2\pi\hbar^2\beta}\right)^{P/2} \sum_{a_1} \langle a_1 | \Pi^P | a_1 \rangle \tag{2.11}$$

or

$$Z \cong \Delta x^P \left(\frac{mP}{2\pi\hbar^2\beta}\right)^{P/2} \operatorname{Tr} \Pi^P. \tag{2.12}$$

Finally

$$Z \cong \Delta x^P \left(\frac{mP}{2\pi\hbar^2\beta}\right)^{P/2} \sum_i \lambda_i^P, \tag{2.13}$$

where λ_i are the eigenvalues of the matrix Π. They are related to the eigenvalues of the operator $\exp(-\beta\hat{H})$ through the equation

$$\exp(-\beta E_i) \cong \Delta x^P \left(\frac{mP}{2\pi\hbar^2\beta}\right)^{P/2} \lambda_i^P. \tag{2.14}$$

The eigenvectors of the matrix Π are also the discretized eigenvectors $\psi(a_i \Delta x)$ of the operator $\exp(-\beta\hat{H})$, apart from a multiplicative factor.

We should emphasize that P, which ensures the convergence, is just a parameter and the execution time does not depend upon it. This is not so in MD and MC methods where an increase in P, always necessary at low temperatures, implies an integration over more variables.

On the other hand, we must ensure that the space interval $(-l/2, l/2)$ is sufficiently large in order to contain the essential features of the wave functions. This can be easily verified by looking at the resulting eigenfunctions and ensuring that their values at the boundaries are very small. The value of Δx must be sufficiently small so that the resolution is acceptable. A partition of the space interval into 100–400 steps is sufficient for the present applications.

For each case under study, the values of P and Δx must be varied in order to check the convergence.

3. Applications

a) Harmonic Oscillator

The Hamiltonian for a one-dimensional harmonic oscillator is

$$\hat{H} = \hat{p}^2/2m + 1/2 m\omega^2 x^2 , \tag{3.1}$$

where ω is the angular frequency. Its simplicity and exact analytical solutions make the harmonic oscillator a typical test example.

We take $m=1, \hbar=1, \omega=1, \beta=5$ and $\Delta\xi = \sqrt{m\omega/\hbar}\,\Delta x = 0.09$.

In Table 1 we present the values of the free energy and internal energy obtained for different values of P and with a matrix of dimension $N=99$. The exact values of A and $\langle U\rangle$, at $P=\infty$, are respectively

$$A = (1/\beta)\ln[2\sinh(1/2\,\beta\hbar\omega)] \tag{3.2}$$

and

$$\langle U\rangle = \hbar\omega/2 + [\hbar\omega\exp(-\beta\hbar\omega)]/[1-\exp(-\beta\hbar\omega)] . \tag{3.3}$$

The convergence is very good and, as we have noted, the execution time does not depend on the value of P. The program takes a few seconds on a Vax 3600.

Table 2 shows the first six eigenvalues, obtained with $P=600$ and two matrices of dimensions 99 and 199. The exact values are given by

$$E_n = \hbar\omega(n+1/2) . \tag{3.4}$$

Figures 1–4 compare the first four eigenfunctions with the exact ones. The overall agreement is excellent.

Once we have obtained the eigenvalues and eigenvectors of the Hamiltonian operator, in a single run, we can calculate the partition function at other temperatures.

b) Morse Potential

The potential [11],

$$V(x) = D_e\{1-\exp[-\alpha(x-x_0)]\}^2 \tag{3.5}$$

has been extensively used to model diatomic molecules. D_e is the equilibrium energy and x_0 is the equilibrium distance.

The Hamiltonian operator is

$$\hat{H}(x) = -\frac{\hbar\, d^2}{2\mu\, dx^2} - D_e\{1-\exp[-\alpha(x-x_0)]\}^2 , \tag{3.6}$$

where μ is the reduced mass.

Table 1. Free energy (A) and internal energy ($\langle U\rangle$) for the harmonic potential for several values of P ($N=99$).

P	A	$\langle U\rangle$
10	0.493510	0.501999
20	0.497337	0.505562
70	0.498540	0.506683
100	0.498595	0.506735
200	0.498635	0.506772
300	0.498643	0.506779
400	0.498646	0.506782
500	0.498647	0.506783
600	0.498648	0.506784
∞	0.498648	0.506784

Table 2. The first eigenvalues of the harmonic oscillator obtained with $P=600$.

n	$N=99$	$N=199$	Exact
0	0.4999998	0.4999998	0.5
1	1.4999971	1.4999969	1.5
2	2.4999987	2.4999939	2.5
3	3.5000463	3.4999909	3.5
4	4.5004301	4.4999879	4.5
5	5.5025903	5.4999850	5.5

Table 3. Morse parameters for HF.

$D_e = 6.125$ eV $= 0.22508$ a.u.
$\alpha = 1.1741\ a_0^{-1}$
$x_0 = 1.7329\ a_0$
$M_H = 1.00797$ a.m.u.
$M_F = 18.9984$ a.m.u.

The exact eigenvalues are

$$E_n = D_e B(n+1/2)[2-B(n+1/2)] \tag{3.7}$$

with

$$B = \hbar^2\beta^2/2\mu D_e . \tag{3.8}$$

We used the parameters for the molecule HF given in Table 3.

The spatial interval was discretized into 199–399 steps, and we have ensured that the 23 eigenfunctions for the bound states of HF were well represented in that interval.

The energy eigenvalues for the 23 bound states of HF are shown in Table 4 and compared with the exact ones [12]. The overall agreement is rather good. If we were only interested in the lower energy levels, the spatial interval should be shortened, and with the same discretization a greater precision should be obtained.

Figures 5–8 compare the eigenfunctions for the levels 3, 10, 15 and 22 of HF with the exact ones. The overall agreement is excellent.

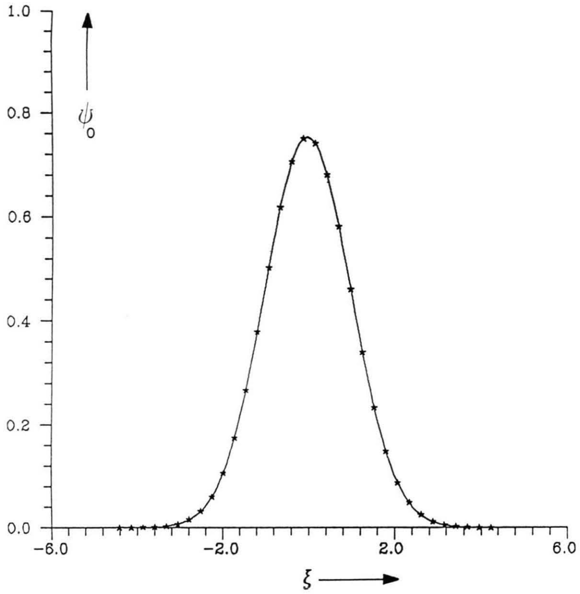

Fig. 1. The exact ground state eigenfunction (solid line), and our results (stars), for the harmonic oscillator.

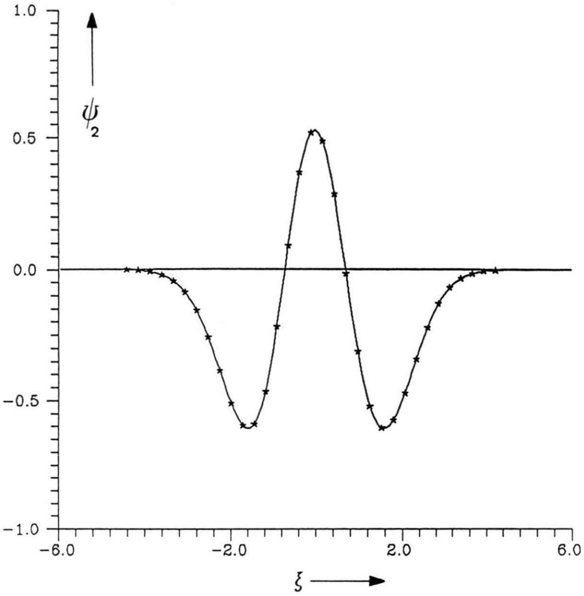

Fig. 3. The exact second excited level eigenfunction (solid line), and our results (stars), for the harmonic oscillator.

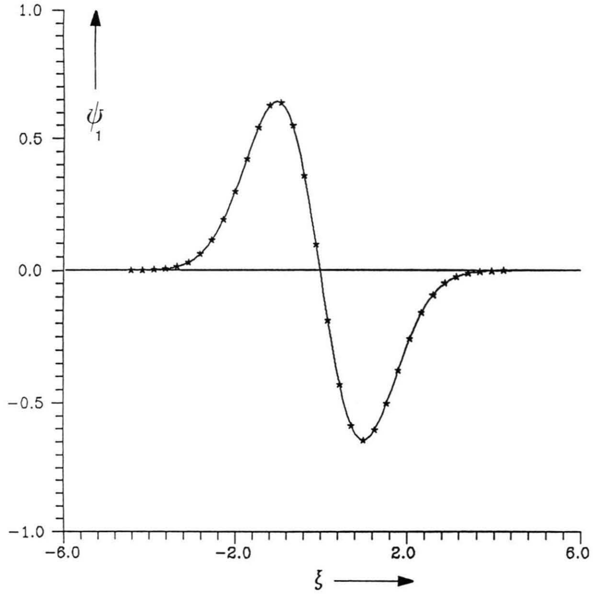

Fig 2. The exact first excited level eigenfunction (solid line), and our results (stars), for the harmonic oscillator.

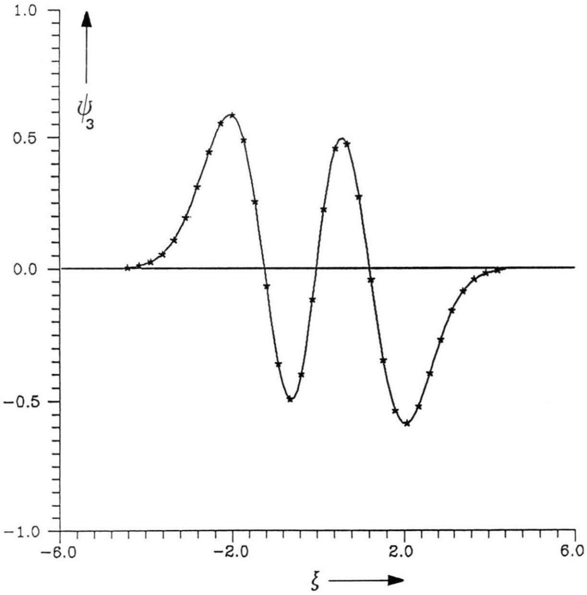

Fig. 4. The exact third excited level eigenfunction (solid line), and our results (stars), for the harmonic oscillator.

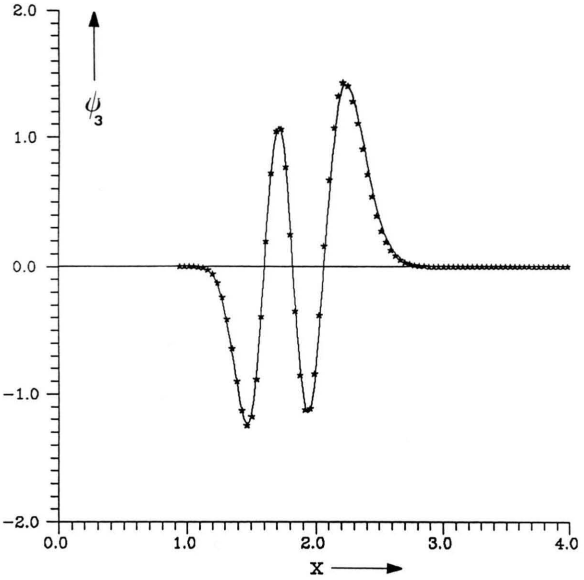

Fig. 5. The exact $v=3$ level eigenfunction (solid line), and our results (stars), for the Morse potential.

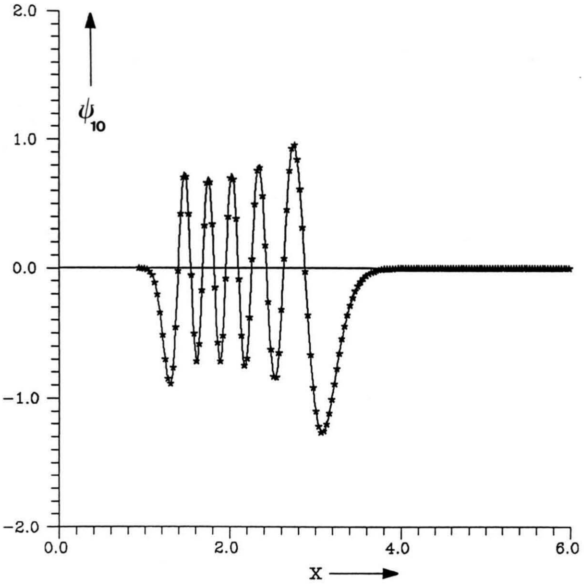

Fig. 6. The exact $v=10$ level eigenfunction (solid line), and our results (stars), for the Morse potential.

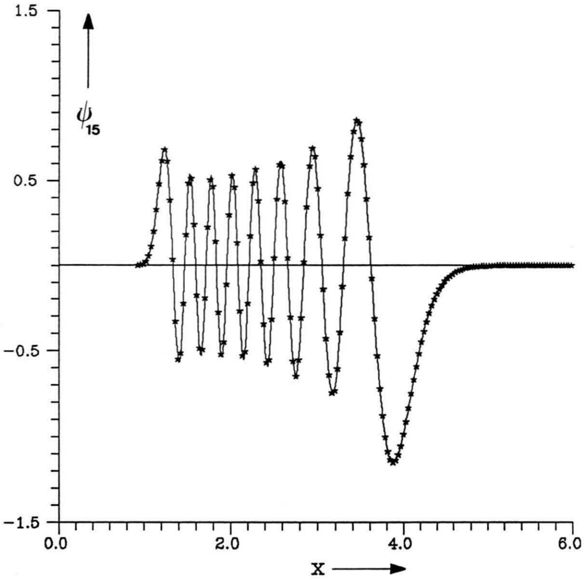

Fig. 7. The exact $v=15$ level eigenfunction (solid line), and our results (stars), for the Morse potential.

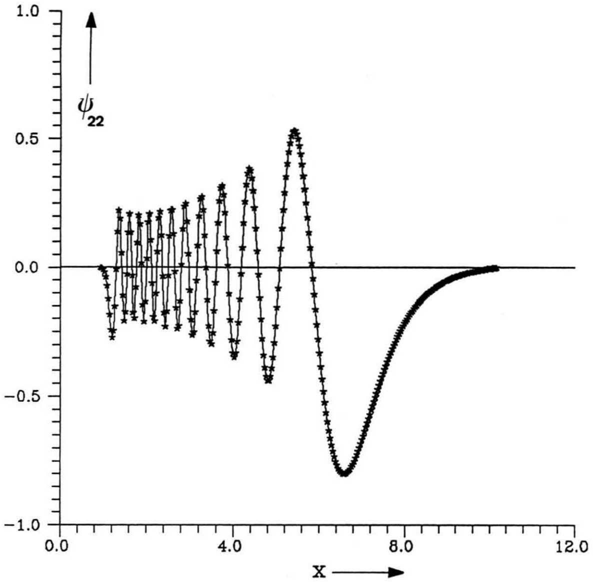

Fig. 8. The exact $v=22$ level eigenfunction (solid line), and our results (stars), for the Morse potential.

Table 4. Comparison of the eigenvalues obtained for the Morse potential with the exact analytic ones.

Quantum no.	$P=100$ $N=199$ $\Delta x=0.046$	$P=205$ $N=299$ $\Delta x=0.031$	$P=330$ $N=399$ $\Delta x=0.023$	Exact results
0	0.0093293	0.0093304	0.0093306	0.0093307
1	0.0273960	0.0273987	0.0273993	0.0273996
2	0.0446728	0.0446771	0.0446780	0.0446785
3	0.0611599	0.0611655	0.0611667	0.0611673
4	0.0768571	0.0768639	0.0768653	0.0768661
5	0.0917645	0.0917724	0.0917739	0.0917748
6	0.1058821	0.1058908	0.1058925	0.1058935
7	0.1192099	0.1192193	0.1192211	0.1192221
8	0.1317478	0.1317577	0.1317596	0.1317607
9	0.1434959	0.1435062	0.1435081	0.1435093
10	0.1544542	0.1544646	0.1544666	0.1544677
11	0.1646226	0.1646331	0.1646351	0.1646362
12	0.1740012	0.1740115	0.1740135	0.1740146
13	0.1825899	0.1826000	0.1826019	0.1826029
14	0.1903887	0.1903984	0.1904002	0.1904011
15	0.1973977	0.1974068	0.1974085	0.1974094
16	0.2036168	0.2036252	0.2036268	0.2036276
17	0.2090460	0.2090536	0.2090550	0.2090557
18	0.2136853	0.2136920	0.2136932	0.2136938
19	0.2175347	0.2175403	0.2175413	0.2175418
20	0.2205942	0.2205986	0.2205994	0.2205998
21	0.2228637	0.2228669	0.2228675	0.2228678
22	0.2243434	0.2243452	0.2243456	0.2243457

5. Conclusions

The transfer matrix grid method (TMG) allows the calculation of the quantum partition function at a given temperature. Since it diagonalizes the density operator it also simultaneously provides the eigenvalues and eigenfunctions of the Hamiltonian operator. The examples show the applicability of the method and the accuracy of the results.

We should emphasize that the implementation of the method is very simple. It only requires a diagonalization routine, and the setup of the matrix is trivial since each matrix element is a simple exponential term. In addition the execution times are very short.

A shortcoming of the method, when its generalization to many dimensions is considered, is the high order of the matrices which must be diagonalized. However, the method seems to be well suited to treat systems consisting of few quantum degrees of freedom coupled to a classical solvent. Combining the TMG method with the Monte Carlo method, one can simulate a system in which the vibrations are treated as quantum degrees of freedom and all other degrees of freedom are treated classically, in a perspective similar to that of Berne and Herman [13, 14]. Apart from thermodynamic properties and distribution functions, we can calculate the eigenvalues and eigenfunctions of the quantum sub-system. Therefore we can have access to spectroscopic properties as well as to the effect of the solvent on the vibrational levels (including the higher ones). Work is in progress and we intend to present the results in a future communication [15].

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