# A FAST FOURIER TRANSFORM METHOD FOR CALCULATING THE EQUILIBRIUM DENSITY MATRIX

Bo HELLSING, Abraham NITZAN [1] and Horia METIU

*Department of Chemistry, University of California, Santa Barbara, CA 93106, USA*

Received 5 October 1985; in final form 5 December 1985

We calculate the low-temperature quantum density matrix by integrating numerically the Bloch equation. The initial condition is the classical high-temperature value of the density matrix. The integration method uses short "time" propagators computed by a fast Fourier transform method.

## 1. Introduction

There are many problems in physical chemistry whose solution depends on knowing the equilibrium properties of systems in which a few quantum degrees of freedom interact with a large number of classical ones. The computation of such quantities begins by generating the positions of the classical particles (i.e. the "classical configuration") and using them to calculate the potential energy for the quantum degrees of freedom. This defines the Hamiltonian for the quantum subsystem and permits the computation of its density matrix, which can be used to calculate expectation values of various quantum variables. Observable quantities are generated by averaging the expectation values of various operators over all possible classical configurations. To obtain correct average properties we must calculate the quantum density matrix for a very large number of classical configurations, and therefore we need extremely efficient algorithms for the quantum part of the calculation. This has stimulated work [1–13] in which computational efficiency is a major concern.

In this article we present a method for the calculation of density matrix which is extremely efficient when applied to localized systems with low dimensionality.

[1] Permanent address: Chemistry Department, Tel Aviv University, Tel Aviv, Israel.

## 2. The method

The starting point is the observation that the equation [14]

$$\partial\rho(x,x';\beta)/\partial\beta = -H(x)\,\rho(x,x';\beta)\,, \tag{1}$$

for the coordinate representation $\rho(x,x';\beta)$ of the density matrix is a diffusion equation in which $\beta = 1/k_\beta T$ plays the role of time. Since at high temperatures we have [14]

$$\rho(x',x;\beta) = (m/2\pi\hbar^2\beta)^{1/2}\exp[-\tfrac{1}{2}\beta V(x')] \times \exp[-(m/2\hbar^2\beta)(x-x')^2]\exp[-\tfrac{1}{2}\beta V(x)]\,, \tag{2}$$

we can calculate $\rho(x',x;\beta)$ by integrating eq. (1) from a small initial value of $\beta$ (i.e. high temperature) to the desired $\beta$ value. Eq. (2) provides the initial condition for the integration.

The calculation is based on the iteration scheme

$$\rho(x'',x;\beta+\epsilon) = G(x'',x';\epsilon)\,\rho(x',x;\beta)\,, \tag{3}$$

where $G(x'',x';\epsilon)$ is a short-time propagator. Throughout this article repeated indices, coordinates or momenta are summed (or integrated) over.

To obtain an expression for $G$ we take $\epsilon$ small enough to permit the approximation

$$G(x'',x';\epsilon) = \langle x''|\exp(-\epsilon H)|x'\rangle \approx \langle x''|\exp(-\epsilon K)\exp(-\epsilon V)|x'\rangle\,. \tag{4}$$

0 009-2614/86/$ 03.50 

Here $K$ and $V$ are the kinetic and the potential energy operators, respectively, and $H = K + V$. The formal conditions defining what is meant by a sufficiently small $\epsilon$ are known, but are not practically useful. We prefer to test whether $\epsilon$ is small enough by repeating the calculation with smaller $\epsilon$ and showing that the results are unchanged.

By combining the eqs. (3) and (4) and using simple basis sets manipulations we can write

$$\rho(x'',x';\beta+\epsilon) \approx \langle x''|k\rangle \exp(-\epsilon\hbar^2k^2/2m) \times \langle k|x'\rangle \exp[-\epsilon V(x')]\,\rho(x',x;\beta). \quad (5)$$

To calculate $\rho(x'',x';\beta+\epsilon)$ from this equation we must perform two integrals: one, over $x'$, gives the Fourier transform $f(k)$ of $\exp[-\epsilon V(x')]\,\rho(x',x;\beta)$; the other, over $k$, is the inverse Fourier transform of $\exp(-\hbar^2k^2\epsilon/2m^2)f(k)$. The key to making this calculation very efficient is the use of a fast Fourier transform (FFT) routine to calculate these integrals.

Algorithms that solve partial differential equations by using FFT have been proposed previously in a different context. Fleck, Morris and Feit [15] solved Maxwell's equations for the propagation of laser in atmosphere; Feit and Fleck [16], and Kossloff and Cerjan [17] applied it to the time-dependent Schrödinger equation; Petschek and Metiu [18] used it to solve the time-dependent Ginzburg–Landau equation. While the detailed implementation by various authors has slight differences, all of them used FFT to compute the partial derivatives with respect to the spatial variables.

## 3. Numerical results

To illustrate the accuracy, the efficiency and the stability of the method we present calculations for a proton in a double well and in a Morse potential. In fig. 1 we show the probability

$$P(x) = \rho(x,x;\beta)/\int dx\,\rho(x,x;\beta) \quad (6)$$

that the particle is located at $x$. The double well is the same as the one used by Thirumalai, Bruskin and Berne [3] and is plotted together with $P(x)$. The initial temperature is $T_i$ = 4000 K and the final one is $T_f$ = 200 K. The grid needed for performing the fast Fourier transform is placed between $x = 0$ and $x = 2\pi$

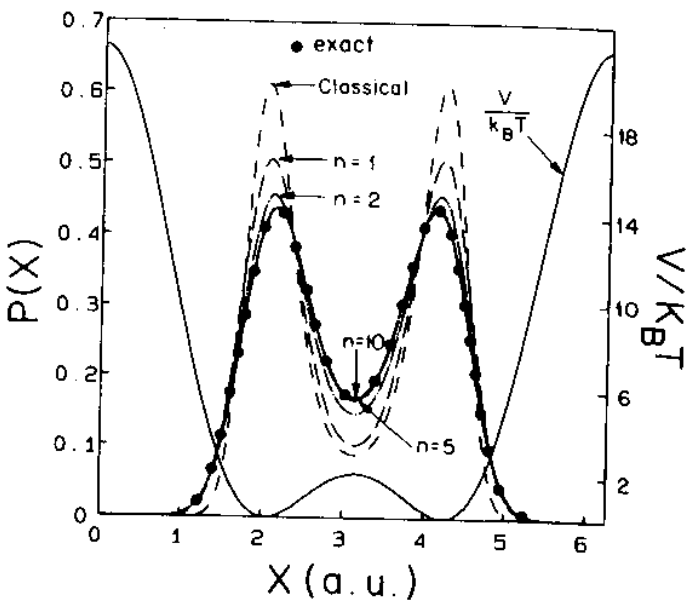


Fig. 1. The normalized probability distribution, $P(x)$, for a proton in the double well potential used in ref. [3]. $P(x)$ calculated using the present method, is given for different number of propagation steps, $n$, from the initial high temperature, $T_f$ = 4000 K to the final temperature, $T_f$ = 200 K, with the time step $\epsilon = (\beta_f - \beta_i)/n$. The classical (solid line) and exact [3] (solid circles) results are also shown.

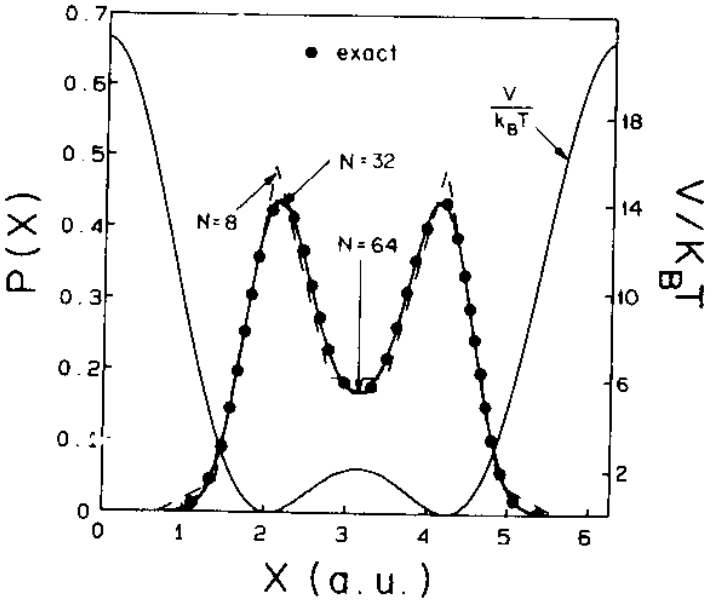


Fig. 2. The probability distribution, $P(x)$, for the same system as in fig. 1. $P(x)$, calculated using the FFT method, is given for different numbers $N$ of grid points. We use 10 time steps, from $T_i$ = 4000 K to $T_f$ = 200 K. The potential (solid line) and the exact result [3] (solid circles) are also shown.

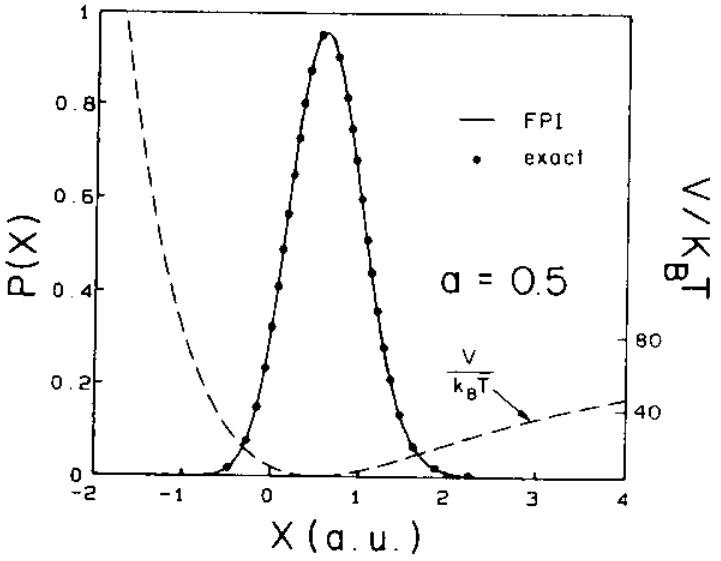


Fig. 3. The probability distribution, $P(x)$, for a proton in a Morse potential, $V(x) = D\{\exp[-2a(x - x_0)] - 2 \times \exp[-a(x - x_0)]\}$, with the parameters $D = 0.01$ au, $x_0 = 0.5$ au and $a = 0.5$ au. The results obtained with the present method (solid line) are compared to the exact result (solid circles). The grid on the $x$-axis is located between $x = -2$ au and $x = 4$ au and has 32 points and the number of time steps $n$ is 20.

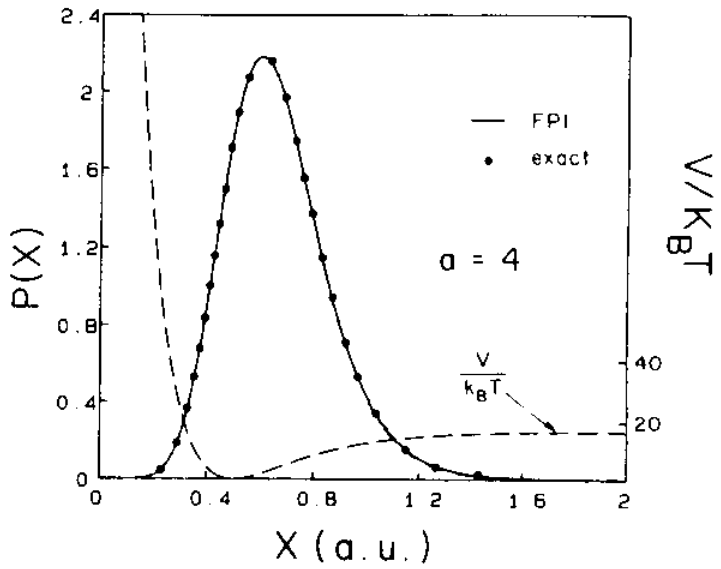


Fig. 4. The same as fig. 3, but $a = 4$ au. The grid on the $x$-axis is located between $x = 0$ and $x = 2$ au and has 32 points. The number of time steps $n$ is 200.

au and has 64 points. The "time" step is defined by $\epsilon = (\beta_f - \beta_i)/n$, where $n$ is an integer and $\beta_\alpha = 1/k_B T_\alpha$, $\alpha$ = i,f. For $n > 5$ our results are identical to the exact results of Thirumalai et al. [3].

In fig. 2 we show the same calculation carried out with grids having different point densities. If we use 8 grid points the method cannot reproduce the regions of high curvature, but it gives exact results for $N = 32$ and $N = 64$.

The probability $P(x)$ for the Morse potential $V(x) = D\{\exp[-2a(x - x_0)] - 2\exp[-a(x - x_0)]\}$, with $D = 0.01$ au, $x_0 = 0.5$ au and $a = 0.5$ au for $T = 50$ K is shown in fig. 3. Exact results are obtained by placing 32 grid points between $x = -2$ au and $x = 4$ au. The smallest number of steps giving exact results is $n = 20$. The Morse well used for this calculation has 12 bound states and the energy difference between the ground and the first excited state is $\epsilon_2 - \epsilon_1 = 9.6\ k_\beta T$. The results of the same calculation was performed in fig. 4, except that we used $a = 4$ au to make the potential highly anharmonic, and consequently, the number of steps has to be larger, $n = 200$. The number of grid points is 32. This potential has only two bound states in the well and $\epsilon_1 - \epsilon_0 = 8.1\ k_B T$.

By using the fact that at low temperature (i.e. high $\beta$) we have

$$\ln \int dx \rho(x,x;\beta) \approx \epsilon - \beta^{-1} \exp[-\beta(\epsilon_1 - \epsilon_0)] , \quad (7)$$

we can use the high-$\beta$ points to calculate, by least-squares fitting, $\epsilon_0$ and $\epsilon_1 - \epsilon_0$. The results are shown in table 1.

## 4. Comments

Some of the advantages of this method are ap-

Table 1
The ground-state energy, $\epsilon_0$ and the vibrational frequency, $\hbar\omega = \epsilon_1 - \epsilon_0$, for a proton in a Morse potential, extracted from eq. (6) by least-squares fitting in a low-temperature interval. The potential parameters are $D = 0.01$ au, $x_0 = 0.5$ au and $a = 0.5 \pm 0.05$. The two $a$ values correspond to 10% frequency shifts as compared to the frequency for $a = 0.5$ au. All quantities are in atomic units

| $\alpha$ | $\epsilon_0$ | $\epsilon_0$ (exact) | $\hbar\omega$ | $\hbar\omega$ (exact) |
|---|---|---|---|---|
| 0.45 | −0.00928 | −0.00927 | 0.00136 | 0.00137 |
| 0.55 | −0.00913 | −0.00911 | 0.00165 | 0.00165 |

parent without numerical tests. The heart of the calculation is the evaluation of an exponential operator at each time step. All methods for doing this are equivalent to the diagonalization of the operator appearing at the exponent. The efficiency of the procedure presented here comes from the use of FFT to diagonalize the kinetic energy operator. Since FFT is a discrete algorithm [19] we need to define a coordinate grid $\{x_1, x_2, \ldots\}$ having $N$ points. The grid must span the set of values of $x$ for which the function is non-zero. It must also provide enough points to describe well all the wiggles of the function; for this the distance between two nearest points on the grid must be less than the smallest length scale over which the function changes. Obviously, smooth and localized functions require a small value of $N$. Once $N$ is chosen the use of FFT to diagonalize $\exp(-\epsilon K)$ requires $2N \ln N$ operations [19]. The customary diagonalization methods need $M^2$ operations, where $M$ is the number of eigenvectors required for a faithful spectral representation of the operator at the exponent. Since this operation is carried out once for each time step the FFT method can save considerable computer time especially if $N$ is smaller or comparable to $M$.

Increased efficiency is further achieved if the grid is unchanged throughout the computations so that the arrays $\exp[-\epsilon V(x_\alpha)]$ and $\exp(-\hbar^2 k_\alpha^2 \epsilon/2m)$, $\alpha = 1,2,\ldots,N$, are computed only once. This is the reason why the FFT method is faster than the MEM method [12] proposed previously by us. The MEM has fewer operations per time step, but it must recompute at each time step the potential and its first and second derivatives at the new location of the center of the Gaussian.

We have found that the method has excellent stability with respect to both the number of points in the grid and the number of time steps. If the number of points on the grid is too small the method is unable to reproduce the density matrix in those regions where it has a large curvature; it will however reproduce correctly the general features of the function, giving a smoothed out version of it. This global stability is not generally present in local methods, such as finite difference calculations, where the errors are sometimes amplified when the lattice is too sparse.

The stability with respect to the time step is also understandable. We use small values of the time step $\epsilon$ to ensure that the term $\epsilon^2[K,V]$, which is neglected in eq. (4), is smaller than $K$ and $V$. Qualitatively speaking we expect the commutator $[K,V]$ to be small for a nearly classical particle such as a proton, and we do not expect to need a very small $\epsilon$ to satisfy the above requirement. If we err on the side of too large an $\epsilon$ than we are assuming a more semi-classical behavior than the system truly has. This will give a density matrix between the exact one and the classical value (see fig. 1); this is not likely to generate instabilities in the propagation scheme.

Another satisfying feature of the present method is that all the operators used to construct the total propagator are exponential and thus remain unitary even if $\epsilon$ is too large. This is not the case in those methods [16] which use $\exp(-\epsilon H) \approx 1 - \epsilon H$.

We emphasize that for problems of high dimensionality $d$ the computational effort goes up as $(2N \ln N)^d$ per time step. This will put the present method at a disadvantage with respect to the Monte Carlo and Gaussian wave packet methods. Furthermore, problems where the density matrix has multiple length scales of very different magnitude will require large values for $N$ and will lower the efficiency of the method.

## Acknowledgement

This work was supported in part by the Office of Naval Research and the National Science Foundation (NSF CHE82-06130).

## References

[1] J.A. Barker, J. Chem. Phys. 70 (1979) 2914.
[2] D. Chandler and P.G. Wolynes, J. Chem. Phys. 74 (1981) 4074;
K.S. Schweitzer, R.M. Stratt, D. Chandler and P.G. Wolynes, J. Chem. Phys. 75 (1981) 1347;
D. Chandler, J. Phys. Chem. 88 (1984) 3400.
[3] D. Thirumalai, E.J. Bruskin and B.J. Berne, J. Chem. Phys. 79 (1983) 5063.
[4] J.D. Doll and D.L. Freeman, J. Chem. Phys. 80 (1984) 2239;
D.L. Freeman and J.D. Doll, J. Chem. Phys. 80 (1984) 5709.
[5] D. Chandler, Y. Singh and D.M. Richardson, J. Chem. Phys. 81 (1984) 1975;
A.L. Nichols III, D. Chandler, Y. Singh and D.M. Richardson, J. Chem. Phys. 81 (1984) 5109.

[6] B. DeRaedt, M. Sprik and M.L. Klein, J. Chem. Phys. 80 (1984) 5719.
[7] M. Parinelo and A. Rahman, J. Chem. Phys. 80 (1984) 860;
U. Landman, D. Scharf and J. Jortner, Phys. Rev. Letters 54 (1985) 1860.
[8] R.A. Kuharski and P.J. Rossky, Chem. Phys. Letters 103 (1984) 357.
[9] D. Thirumalai, R.W. Hall and B.J. Berne, J. Chem. Phys. 81 (1984) 2523.
[10] D.J. Scalapino, R.L. Sugar and W.D. Toussaint, Phys. Rev. B29 (1984) 5253;
R. Blakenbecker, D.J. Scalapino and R.L. Sugar, Phys. Rev. D24 (1981) 2278;
D.J. Scalapino and R.L. Sugar, Phys. Rev. B24 (1981) 4295;
J.E. Hirsch and D.J. Scalapino, Phys. Today 36 (1983) 44.
[11] M. Creutz and B. Freedman, Ann. Phys. NY 132 (1981) 427;
M. Creutz , Phys. Rev. D21 (1980) 2308;
M. Creutz, L. Jacobs and C. Rebbi, Phys. Rev. Letters 42 (1979) 1390; Phys. Rev. D20 (1979) 1915;
M. Creutz, Phys. Rev. Letters 43 (1979) 533;
D. Zwanziger, Phys. Rev. Letters 50 (1983) 1886.
[12] W.H. Miller, J. Chem. Phys. 55 (1971) 3146; 58 (1973) 1664;
S.M. Hornstein and W.H. Miller, Chem. Phys. Letters 13 (1972) 398.
[13] B. Hellsing, S.-I. Sawada and H. Metiu, Chem. Phys. Letters 122 (1985) 303.
[14] R.P. Feynman, Statistical mechanics (Benjamin, Reading, 1972) p.72.
[15] J.A. Fleck Jr., J.R. Morris and M.D. Feit, Appl. Phys. 10 (1976) 129.
[16] M.D. Feit and J.A. Fleck Jr., J. Chem. Phys. 78 (1983) 301; 80 (1984) 2578;
M.D. Feit, J.A. Fleck Jr. and A. Steiger, J. Comput. Phys. 47 (1982) 412.
[17] D. Kosloff and R. Kosloff, J. Comput. Phys. 52 (1983) 35;
R. Kosloff and D. Kosloff, J. Chem. Phys. 78 (1983) 1823;
R. Kosloff and C. Cerjan, J. Chem. Phys. 81 (1984) 3722.
[18] R. Petschek and H. Metiu, J. Chem. Phys. 79 (1983) 3443.
[19] E.O. Brigham, The fast Fourier transform (Prentice Hall, Englewood Cliffs, 1974).