

# Quantum Oscillator in a Heat Bath

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**Abstract.** In the present article, we use the density matrix evolution method to study the effect of a model solvent on the vibrational spectrum of a diatomic solute particle. The effect of the solvent is considered as a perturbation on the Hamiltonian of the quantum subsystem consisting of a harmonic oscillator. The bath particles are treated classically. The perturbation potential representing the interaction between the solute and the solvent is represented in a bi-exponential form. This provides an effective way to evaluate the required matrix elements needed to compute the evolution of the density matrix. The model calculations indicate that the repulsive parts of the potential dominate causing blue shifts in the vibrational frequencies.

**Keywords:** Density matrix evolution, vibrational spectrum, quantum harmonic oscillator, bi-exponential perturbation potential, Hellmann-Feynman force, Runge Kutta method, molecular dynamics, bath particles.

## 1 Introduction

A study of the effects of solvents on the electronic and vibrational structure and dynamics of molecules has interested chemists for a long time. In recent years, the effect of solvation dynamics on the dynamical behaviour of molecules has been studied experimentally as well as theoretically. In theoretical approaches, one often separates the small molecular system from the bulk or the solvent and is able to treat the two subsystems using methods most appropriate to represent the physical conditions. It is very common to treat the molecular system quantum mechanically and the solvent classically and suitably treat the interaction between the two [1-5]. Several approaches have been used to address the problem, such as the wave packet propagation method, the Car Parrinello method, the path integral method and the density matrix evolution (DME) method. While each method has its advantages, we use the density matrix evolution method in the present work. Our specific interest is in the effect of the solvent structure on vibrational spectrum of a diatomic oscillator. The red and blue shifts in the spectrum have been of significant interest for quite some time [6, 7]. An effective numerical method to obtain the time dependence of the density matrix has been developed by Berendsen and coworkers [8-10]. The method is outlined in the next section. The results are presented in Section 3 followed by conclusions in section 4.

## 2 The DME Method and the Model Potential

In the DME method, the Liouville-von Neumann equation for the density matrix is numerically solved to obtain the elements of the density matrix as a function of time.

The time-dependent wavefunction of the quantum sub-system is expanded in terms of a suitably chosen orthogonal set of  $M$  basis functions  $\phi_n$ .

$$\Psi(\xi, t) = \sum_{n=1}^M c_n(t) \phi_n(\xi) \quad (1)$$

The coordinates of the quantum subsystem are denoted by  $\xi$  and the time evolution of the system is studied in terms of the time dependent coefficients  $c_n(t)$ . In Equation (1),  $M$  is the number of basis functions of the harmonic oscillator and we have taken the first 5 harmonic oscillator wavefunctions in our study. The elements of the  $M \times M$  hermitian density matrix  $\rho_{nm}$  are defined by

$$\rho_{nm} = c_n c_m^* \quad (2)$$

The diagonal elements of the density matrix give the populations of the levels and the off diagonal elements contain the phase information. The Liouville- von Neumann equation for the density matrix is given by

$$\frac{d\rho}{dt} = \frac{i}{\hbar} (\rho H - H \rho) \quad (3)$$

In the absence of the solvent, the Hamiltonian is  $H^0$ . The presence of the solvent perturbs the system and the perturbed Hamiltonian is given by

$$H = H^0 + H' \quad (4)$$

The unperturbed matrix elements can be evaluated analytically while the perturbed matrix elements have to be evaluated by appropriate expansion of the potential. The effect of the solvent particles on the quantum subsystem is incorporated through  $H'$  in Equation (4). The total matrix element is obtained by summing over all the  $N$  particles of the solvent.

$$H'_{n,m} = \sum_{i=1}^N \langle n | H'_i | m \rangle \quad (5)$$

Here,  $H'_i$  represents the interaction between the  $i$  th classical particle and the quantum subsystem [8-10].

The dynamics of the solvent is governed by the classical equations of motion and the quantum subsystem contributes an additional term to the forces on the solvent particles through the Hellmann-Feynman force [11] term which is given by

$$F_{nm,u} = \langle n | -\frac{\partial H}{\partial u} | m \rangle \quad (6)$$

where  $u$  represents the directions  $x$ ,  $y$  and  $z$  respectively. The total force acting on the classical particle due to the quantum subsystem  $F_u^Q$  is

$$F_u^Q = Tr(\rho F_u) \quad (7)$$

Here,  $Tr$  represents the trace. Similarly, the vibrational energy of the quantum subsystem is given by

$$E^Q = Tr(\rho H) \quad (8)$$

The total force on the classical particle is given by

$$F_u = F_u^Q - \sum_{j \neq i}^N \frac{\partial V_{ij}}{\partial u} \quad (9)$$

For the quantum subsystem, we choose a harmonic oscillator with the potential,

$$V(\xi) = \frac{1}{2} k \xi^2 \quad (10)$$

where  $\xi = x_1 - x_2$ .

The oscillator is kept fixed on the  $x$  axis with the two particles of the oscillator located at  $x_1$  and  $x_2$  respectively and is surrounded by an atomic solvent wherein the particles interact via a Lennard-Jones (LJ) potential.

$$V(r) = 4 \varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right] \quad (11)$$

The interaction between the solvent particles and the atoms constituting the oscillator are represented by a bi-exponential function

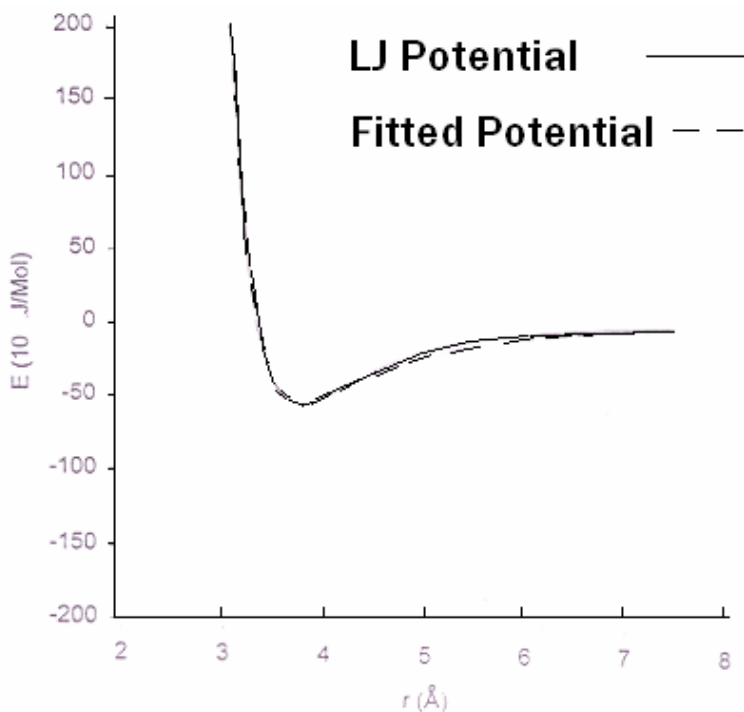
$$V(r) = A e^{-br} + C e^{-dr} \quad (12)$$

The values of  $A$ ,  $b$ ,  $C$  and  $d$  and the graph of the above two potentials are given below. This is necessary because, if we use the LJ potential in Equation (6), the matrix elements will diverge since the integration in Equation (6) includes the small values of  $r$  as  $r$  goes to zero. The matrix elements for the force in Equation (6) are obtained by expanding the perturbation potential  $V(r)$  in terms of the vibrational coordinate  $\xi$  and the coefficients which depend on the distance between the location of the oscillator atoms and the solvent particles [8-10]. The integrations of the equations of motion for the density matrix are done by using the fourth order Runge Kutta method [12].

### 3 Results and Discussion

We treat the quantum subsystem as a diatomic oscillator oscillating with the frequency of  $\text{Cl}_2$ . The two chlorine atoms are placed on the  $x$ -axis of a periodic box of length  $16 \text{ \AA}$  containing solvent particles interacting with an LJ potential with  $\sigma = 3.4 \text{ \AA}$  and  $\varepsilon / k = 120 \text{ K}$ . The Cl atoms and the solvent particles also interact with a similar

potential, except that this potential is expressed in the form of Eq. (12) with the parameters  $A = 1.8025 \times 10^{10}$  J/mol,  $b = 5.0081$  Å,  $C = -25875.225$  J/mol and  $d = 0.8513$  Å which preserve the important features of the LJ potential given in (11).



**Fig. 1.** The Lennard-Jones potential and the fitted bi-exponential function

**Table 1.** The frequencies of diatomic  $\text{Cl}_2$  at various solvent densities. The reduced density is  $\rho\sigma^3$  is shown in the first row. The oscillator frequencies at two solvent temperatures are shown below the corresponding densities.

Reduced Density $\rho\sigma^3$	0.154	0.308	0.616	0.770	0.925
Frequencies ( $\text{cm}^{-1}$ ) $\text{Cl}_2$ (500K)	559.0	559.5	560.5	561.5	562.5
Frequencies ( $\text{cm}^{-1}$ ) $\text{Cl}_2$ (1000K)	559.0	560.5	561.5	563.5	565.5

The expectation value of  $\xi$  is calculated at each time step and its Fourier transform of this expectation value is obtained to obtain the vibrational frequency in the solvent. The production runs extend up to 100 ps with a time step of 0.1fs. We also compute the solute solvent and the solvent solvent radial distribution functions, but these are not reported here as our main interest is in the frequency shifts of the diatomic. The frequencies at various densities of the solvent are given in Table 1. Higher solvent temperatures are chosen so that during the simulations, different elements of the density matrix get significantly populated. At room temperature, the populations of all the elements of the density matrix except  $\rho_{00}$  and  $\rho_{11}$  do not develop significant populations [13, 14].

## 4 Conclusions

We have calculated in the present article the vibrational frequencies of a diatomic in the presence of a model solvent at various densities. The method used herein implies an implicit separation between the vibrational motion of the oscillator and the translational motion of the solvent. The model LJ potential between the solvent and the atoms of the oscillator was written as a sum of two exponentials so that the matrix elements required to evaluate the time evolution could be easily computed. We observe that in our simulations at various solvent densities, there is a predominant blue shift in the oscillator frequencies. As has been observed by several earlier investigators, the major components that contribute to the frequency shifts are the attractive and repulsive parts of the potential, the solvent density and the changes in the equilibrium bond length of the oscillator as a function of solvent density. In earlier calculations [6, 7], red shifts have been observed at low densities of the solvent. At higher densities, there was a blue shift in the spectrum. We observe that when the potential well is made deeper by increasing the well depth, there are red shifts in the spectrum in the low density regions. When the frequency of the oscillator was increased (to represent molecules such as  $N_2$ ), the solvent effects on the oscillator frequency are larger. Red shifts also appear at lower solvent densities. We think that it should be possible to obtain the full density dependence of the vibrational spectrum without using a model potential in which the equilibrium bond length of the quantum oscillator is density dependent [6]. Work is in progress in this direction.

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## References

1. Kapral, R.: Progress in the Theory of Mixed Quantum-Classical Dynamics. *Ann. Rev. Phys. Chem.* 57, 129–157 (2006)
2. Berne, B.J., Thirumalai, D.: On the Simulation of quantum systems by Path Integral Methods. *Ann. Rev. Phys. Chem.* 37, 401–424 (1986)
3. Beck, M.H., Jäckle, A., Worth, G., Meyer, H.-D.: The Multiconfiguration Time-Dependent Hartree (MCTDH) Method: a Highly Efficient Algorithm for Propagating Wavepackets. *Physics Reports* 324, 1–145 (2000)

4. Car, R., Parrinello, M.: Unified Approach for Molecular Dynamics and Density-Functional Theory. *Phys. Rev. Lett.* 55, 2471–2474 (1985)
5. Selloni, A., Carnevali, P., Car, R., Parrinello, M.: Localization, Hopping and Diffusion of Electrons in Molten Salts. *Phys. Rev. Lett.* 59, 823–827 (1987)
6. Herman, M.F., Berne, B.J.: Monte Carlo Simulation of Solvent Effects on Vibrational and Electronic Spectra. *J. Chem. Phys.* 78, 4103–4125 (1983)
7. de Souza, L.E.S., Guerin, C.B.E., Ben-Amotz, B., Szleifer, I.: Statistical mechanics of solvent induced forces and vibrational frequency shifts. Low density expansions and Monte Carlo simulations. *J. Chem. Phys.* 99, 9954–9961 (1993)
8. Berendsen, J.H.C., Mavri, J.: Quantum Simulation of Reaction Dynamics by Density Matrix Evolution. *J. Phys. Chem.* 97, 13464–13468 (1993)
9. Mavri, J., Berendsen, J.H.C.: Dynamical Simulation of a Quantum Harmonic Oscillator in a Noble Gas by Density Matrix Evolution. *Phys. Rev. E.* 50, 198–204 (1994)
10. Mavri, J., Berendsen, J.H.C.: Calculation of the Proton Transfer Rate Using Density Matrix Evolution and Molecular Dynamics Simulations: Inclusion of the Proton Excited States. *J. Phys. Chem.* 99, 12711–12717 (1995)
11. Feynman, R.: Forces in Molecules. *Phys. Rev.* 56, 340–343 (1939)
12. Kreyszig, E.: *Advanced Engineering Mathematics*, 9th edn. John Wiley and Sons, Chichester (2005)
13. Pramodh, V.: *Ab initio MD applied to chemical systems*. M. Sc. Thesis, Department of Chemistry, I.I.T. Bombay (1997)
14. Pandey, P. K.: *Density Matrix Evolution Study for Diatomics*. M. Sc. Thesis, Department of Chemistry, I.I.T. Bombay (1999)