DEVELOPMENT OF SEPARABLE ANSATZE FOR THE DESCRIPTION OF MOLECULAR VIBRATIONS

A Thesis
Submitted for the Degree of

DOCTOR OF PHILOSOPHY

By

TAPTA KANCHAN ROY

SCHOOL OF CHEMISTRY
UNIVERSITY OF HYDERABAD
HYDERABAD 500 046
INDIA

October 2010

STATEMENT

I hereby declare that the matter embodied in this thesis is the result of investigations carried out by me in the School of Chemistry, University of Hyderabad, Hyderabad, under the supervision of **Prof. M. Durga Prasad**.

In keeping with the general practice of reporting scientific observations, due acknowledgement has been made wherever the work described is based on the findings of other investigators.

Hyderabad-46 (**Tapta Kanchan Roy**)
October 2010

CERTIFICATE

Certified that the work contained in this thesis entitled "DEVELOPMENT OF SEPARABLE ANSATZE FOR THE DESCRIPTION OF MOLECULAR VIBRATIONS " has been carried out by Mr. **Tapta Kanchan Roy** under my supervision and the same has not been submitted elsewhere for a degree.

Hyderabad-46 (**Prof. M. Durga Prasad**)
October 2010 **Thesis Supervisor**

Dean
School of Chemistry
University of Hyderabad
Hyderabad 500 046
INDIA

ACKNOWLEDGEMENTS

It gives me immense pleasure to express my profound gratitude and deep respect to my research supervisor **Prof. M. Durga Prasad**, for his constant cooperation, encouragement and unparallel guidance throughout my research work. He is a great teacher and a dynamic personality with a unique way to generate simple and interesting research problems. He has been outstandingly helpful to me with his critical and meticulous comments which will help me in all my future endeavors. I will always treasure the care and concern of him towards me.

My sincere respect to Prof. Susanta Mahapatra for his helpful guidance and encouragement. It has been my privilege to work with him in few of my research projects. I would like to thank Dr. Tushar Jana for his help during few of my projects with him. I am indebted to Prof. Anunay Samanta for his help in various fields. I whould also like to thank Prof. S. P. Bhattachariyya who first introduced me to the field of research during my M.Sc. days.

I extend my sincere thanks to the former and present Deans, School of Chemistry, for providing all necessary facilities to carry out my research work. I also thank all the faculty members for their support. I would like to extend my thanks to CMSD for providing all the computational facilities. I also thank all non-teaching staff for their timely help and to all my colleagues in the School of Chemistry for helping and supporting me in various issues.

Financial assistance from ACRHEM, University of Hyderabad and CSIR, New Delhi for providing Research Fellowship are sincerely acknowledged.

I express my heartful thanks to my lab mates Saritha, Kumar, Sridhar and Dinesh for their help and cheerful environment. I thank all the project students in my lab.

I am deeply predicated to all my teachers. My special thanks to Meghla-di, Bidyut-da, Bikash Babu, Kollol-da, Subir Babu, Sanat Babu, Prof. A. K. Sarkar, Dr. S. Dutta, Dr. B. C. Kundu, Dr. A. Nag, Dr. R. Chakrabarti and Dr. R. A.

Singh for their excellent support, teaching and valuable suggestions.

I have had a great number of friends throughout my life and most of them leave wonderful memories. I like to thank all of my school friends for their support. I must thank to my best buddy Prasun whose uncountable help from my childhood provided me enough courage to struggle for existence. Special thanks to Prosenjit (jatha) for his excellent friendship and help. I greatly acknowledge Arindam, Shubhranshu, Prosenjit (pocha), Arnab, Dhritiman, Nishan, Bhaskar, Amit, Soumik, Shankha (pachu), Ranadeep and Rahul for their selfless friendship. I still spend great times with them and never forget 'mather adda'. I must thank Sudeepa, Indrani and Jhuma for their friendship.

I would like to thank all my friends of Presidency College and Banaras Hindu University. Its my pleasure to thank Chatu, Sudip, Pragna, Mondal and Sangita for their support. A special note of thanks to Sonia and Mekhala for their great support in my life. I would also like to express my sincere thanks to their parents, Kaku and Kakima for their support and encouragement.

I would also like to express my sincere thanks to all my dadas and didis with whom I have cherished some wonderful memories in Hyderabad during my Ph.D life. The senior dadas and didis who still matter are Rahul-da, Dinu-da, Binoy-da, Sandy-da, Abhik-da, Sunirban-da, Archan-da, Subhash-da, Manab-da, Saikat-da, Bishu-da, Prasun-da, Moloy-da, Masum-da, Ani-da, Abhijit-da, Prashant-da, Utpal-da, Bipul-da, Pradip-da, Shatabdi-di, Bhaswati-di, Anindita-di, Sriparna-di. I am really fortunate to have great friends like Arindam, Tanmoy, Sandip, Subrata, Susanta, Ghona, Pati and Rumpa. A special thanks to Arindam, with whom I share many wonderful memories from my M.Sc life. I must thank Subrata for many fruitful academic discussions. I am glad to have juniors like Susruta, Rishi, Dinesh, Palash, Tanmoy, Sandip, Meheboob, Anup, Nayan, Raja, Supratim, Satyajit, Biswarup, Suman, Krishnendu, Sanghamitra, Tulika, Paromita, Chandrani, Pramiti, Mousumi, Sutanuka, Monima and many others. I must not forget Joya, Somdatta, Meghna, Gitoshree, Tamali and many more. A special mention of Somnath-da, Boudi and Megh for their warm hospitality in Hyderabad. I am thankful to Murali, Arun, Shiva, Rajagopala, Rajagopal, Nagaprasad, Ranjit, Sanjib, Nabo and many others. I always remember the wonderful memories of Saraswati Pujo, Bengali Freshers and Picnic in the HCU campus as we celebrated those occasions with high passion and lots of enthusiasm. I always enjoyed as a part of the organisers of those events. I would like to thank all of my friends who have taken an active part in those events and cultural programmes.

I thank all my relatives, in particular, Mamoni, Boro Jethu and Boro Jethi for their moral support. My sincere gratitude to my Mejo Jethu for introducing me to the fascinating world of chemistry. I thank all of my uncles, aunties, cousins and nephews. I must thank Asim-da, Rahul-da, Rintu, Pinki and Papai with whom I spent many wonderful times. I value the association of my Didi and Mili-di with whom I grew up. A special thanks to my beloved Bonubhai for her care and affection and to my little niece Hia.

I would like to express my gratitude and admiration to Vasudhara. She is always there to understand me with great friendly support and encouragement. I specially thank her for editing this thesis.

Without my parents' relentless support, love and blessing I would have not reached at this stage of life. My mother, who has been a great source of inspiration for my studies. She has been extremely patient with me and always supported me whenever I have faced difficult situations. I am greatly indebted from the bottom of my heart to my father for his encouragement and mental support. He is also a great friend of mine with whom I love to share many things. I owe everything to them.

Tapta Kanchan Roy

October 2010
University of Hyderabad
Hyderabad 500 046, India

List of Abbreviations

BO	Born-Oppenheimer
B3LYP	Becke's three-parameter hybride functional with Lee-Young-Parr correction
CC	Coupled cluster
CI	Configuration interaction
DFT	Density functional theory
EHO	Effective harmonic osclilator
FVCI	Full vibrational configuration interaction
FGB	Feynman variational princeple to Gibbs-Bogoluibov inequality
GBI	Gibbs-Bogoluibov inequality
GWP	Gaussian wave packet
HO	Harmonic oscillator
HF	Hartree-Fock
HFSCF	Hartree-Fock self-consistent field
IVR	Initial value representation
MBPT	Many body perturbation theory
MP2	Second order Møller-Plesset perturbation theory
MPPT	Møller-Plesset perturbation theory
PES(s)	Potential energy surface(s)
PI	Path intigral
SCF	Self-consistent field
t-EHO	Thermal effective harmonic osclilator
t-SCF	Thermal self-consistent field
VCI	Vibrational configuration interaction
VCCM	Vibrational coupled cluster method
VSCF	Vibrational self-consistent field
TDSE	Time-dependent Schrödinger equation
TISE	Time-independent Schrödinger equation
VOHB	variationally optimize harmonic oscillator basis
VMCSCF	Vibrational multiconfigurational self-consistent field
VSCF	Vibrational self-consistent field
ZPE	Zero-point energy

Contents

Chapter 1

Introduction

1.1 General problem of the solution of Schrödinger and Bloch equations

In quantum mechanics, we deal with wave function ψ, which is the replacement of the trajectory in classical mechanics. It describes the state of a system and is a function of coordinates and time. In 1926, Schrödinger [1] constructed two equations that describe how the quantum state of a physical system changes with coordinates and time. For stationary states, as a special case, ψ does not depend on time and it is the function of only the coordinates. The general form of the time dependent and time independent Schrödinger equations for coordinate x and time t can be written as

$$H\psi(x,t) = i\hbar\frac{d}{dt}\psi(x,t), \tag{1.1a}$$

$$H\psi(x) = E\psi(x). \tag{1.1b}$$

Here H is the Hamiltonian of a system and E is the corresponding state energy. Rewriting the expression for H explicitly in time independent approach, the Schrödinger equation for a particle of mass m and energy E in one dimension is

$$-\frac{\hbar}{2m}\frac{d^2}{dx^2}\psi(x) + V(x)\psi(x) \quad = \quad E\psi(x), \tag{1.2}$$

where the first term is the kinetic energy and $V(x)$ is the potential energy of the particle at point x. This wave mechanical equation of a stationary state is the starting point for most of the quantum mechanical calculations. However, except for a few systems such as hydrogen atom, harmonic oscillator (HO) and particle in a box, it is impossible to find exact solutions to the Schrödinger equation. To deal with such non-exactly solvable problems such as many electron systems or anharmonic vibrations, various mathematical techniques for approximate solutions have been constructed that lead to an approximate but close to exact evaluation of the energy values and wave functions. Perturbation theory and variational methods [2–5] are the two most common examples of such approximation.

In general, the quantum mechanical wave function ψ deals with the pure state of a system in which a maximum of information is available about the system under consideration. There is the other approach of quantum statistical mechanics which includes both the pure and impure (mixed) states of a system i.e. states with less than maximum information. This is represented by density matrix, ρ [6]. The general form of the density matrix is

$$\rho \quad = \quad \sum_i p_i|\psi_i\rangle\langle\psi_i|. \tag{1.3}$$

Here the coefficients p_i are non-negative and $\sum_i p_i = 1$. For canonical ensemble

ρ is defined as

$$\rho \quad = \quad e^{-\beta H}. \tag{1.4}$$

The equation of motion for the density matrix is

$$\dot{\rho} \quad = \quad -H\rho. \tag{1.5}$$

and is known as the Bloch equation.

As it is impossible to find an exact ψ or ρ we need to invoke some approximations. For such approximations, the description of ψ or ρ plays a crucial role. To invoke an approximate ψ or ρ the major problem is twofold, the computational problem and the size-consistency [7] problem. In general the solution of the Schrödinger equation requires the construction of the Hamiltonian matrix in a suitable basis and then its subsequent diagonalization for the eigenvalues. For most of the cases, an approximate but well described wave function requires a large basis set [8]. These basis sets increase exponentially with the number of particles or degrees of freedom. Consequently, the computational time also increases more or less exponentially. The larger the system, the more difficult it is to solve with desired accuracy. Another common problem is the size consistency. Size consistency is a property that guarantees the consistency of the energy behavior when interaction between the involved molecular system is removed. For example, let us assume A and B are two non-interacting systems. Now for a given theory if

$$E(AB) \quad = \quad E(A) + E(B), \tag{1.6}$$

which shows that the energy of the subsystems A and B are additively separable and equal to the energy of the supersystem AB, then the theory is size consistent.

The wave function and density matrix are multiplicatively separable,

$$\psi(AB) = \psi(A).\psi(B), \tag{1.7a}$$

$$\rho(AB) = \rho(A).\rho(B). \tag{1.7b}$$

1.2 The molecular vibrations and the anharmonic effects

Molecular vibrations [9] occur when atoms in a molecule are in periodic motion. The potential energy surface for molecular vibrations is not known. There is no generic functional form of it. Within Born-Oppenheimer approximation, the potential energy surface of molecular vibrations is given by electronic energy at each nuclear geometry. There are several coordinate systems to represent the potential energy surface in terms of the nuclear coordinates. Normally we make a Taylor series expansion for it in terms of the normal coordinates [9]. Normal coordinates are defined as the coordinate systems in which the mass weighted Hessian matrix is diagonal. If x_i are the cartesian displacement coordinates of the atoms in the molecule then the Hessian is

$$\mathcal{H}_{ij} = \left(\frac{\partial^2 E_{el}}{\partial x_i \partial x_j}\right)_{eq}. \tag{1.8}$$

If the mass tensor is M, and

$$(M^{-\frac{1}{2}}\mathcal{H}M^{-\frac{1}{2}})\, C = C\, \Omega^2, \tag{1.9}$$

then C is the coefficient matrix that defines the mass weighted normal coordinates

$$Q_i = \sum_j x_j C_{ji} \sqrt{m_j} \ . \tag{1.10}$$

Normally, the rotational motions are coupled with the vibrational motions. Watson [10] derived a simple form of ro-vibrational Hamiltonian in normal coordinates for general many particle systems where all particles are interacting with each other. In the Watson Hamiltonian the centre of mass momentum and the total angular momentum are conserved quantities. The Watson Hamiltonian in mass weighetd normal coordinates (Q) is

$$\begin{aligned} H &= -\frac{1}{2}\sum_{i=1}^{N} \frac{d^2}{dQ^2} + V(Q) - \frac{\hbar^2}{8}\sum \mu_{\alpha\alpha} \\ &\quad + \frac{1}{2}\sum_{\alpha\beta} (J_\alpha - \pi_\alpha)\mu_{\alpha\beta}(J_\beta - \pi_\beta) \end{aligned} \tag{1.11}$$

Here, the first and the second term are the pure vibrational kinetic energy and potential energy term, respectively. The third term is the so called Watson mass term. The indices α and β represent the x, y and z components of cartesian coordinates. The $\mu_{\alpha\beta}$ are the components of the inverse moment of inertia at a given point on the potential energy surface. J_α and π_α are the α^{th} component of the total and vibrational angular momentum respectively.

The most common model for molecular vibrations is the HO approximation. It is one of the exactly solvable system in quantum mechanics. However, most of the systems in the physical world are not harmonic. The anharmonic vibrational problems are not analytically solvable. Thus, we need to invoke some approximation for them. The most common approximation in the anharmonic regime is to approximate the potential energy (V) up to quartic terms in the mass weighted normal coordinates Q

$$V(x) \quad = \quad \sum_{i} f_{ii}Q_i^2 + \sum_{i\leq j\leq k} f_{ijk}Q_iQ_jQ_k + \sum_{i\leq j\leq k\leq l} f_{ijkl}Q_iQ_jQ_kQ_l \; . \qquad (1.12)$$

The corresponding wave equation for this potential is solved approximately by several theoretical methods. There are several phenomena where HO is not adequate. The vibrational levels of HO is equally spaced and hence the energy difference between two successive levels is constant. On the other hand, for anharmonic oscillator, these levels are not equally spaced and the energy differences between two successive levels generally decrease with the increasing energy. As the partition functions and other thermodynamic properties such as free energy, entropy or equilibrium constants depend upon the vibrational levels [11], the anharmonic terms give better description than HO. Generally, HO modals underestimate the partition function, because, as energy increases, the molecular vibrational energy levels for real systems come closer. So, the partition function at a given temperature for real systems are larger than for the pure harmonic system. To calculate the spectra of a molecule accurately, we need anharmonic expansion. The Fermy resonance induced spectral line splitting for CO_2 for example can not be described by HO approximation. If we invoke a corresponding approximation for the dipole moment, then the transition probabilities to the overtones and combinations are zeroes. If the potential is anharmonic or the dipole is anharmonic then transition probabilities are not zeroes.

1.3 The approximation methods

The number of physical systems which can be solved exactly by quantum mechanics is very few. Except for very simple cases like harmonic oscillator, hydrogen atom or hydrogen molecule cation, quantum chemists face problems in solving many particle problem exactly [12]. Thus, for anharmonic molecular vibrations or many electron problems, the wave equation is of such a nature as to resist accurate solution. This same problem is also present for density matrices. Thus, for physical problems, various methods of approximate solution of the wave equation or density matrix equations have been formulated which lead to more or less accurate evalution of wave functions or density matrix.

1.3.1 Approximations for the wave functions

There are several approximate methods developed and used for the wave functions. We discuss some of them in this section.

1.3.1.1 The perturbation theory

Quantum mechanical perturbation theory (PT) [2–5] is one of the most important approximation method. It is developed for both time dependent and the time independent approach. In time-independent perturbation theory two different approaches exist. Rayleigh-Schrödinger (RS) perturbation theory [13] and Brillouin-Wigner (BW) perturbation theory [14]. The former one is more popular and widely used in quantum mechanics.

Given a physical system with the Hamiltonian H and a related soluble system with the Hamiltonian H_0, eigenvalues $E_n^{(0)}$ and eigenfunctions $\psi_n^{(0)}$

$$H = H^0 + \lambda H_1. \tag{1.13}$$

Here λ is some parameter and the term λH_1 is called a perturbation. So, the Schrödinger equation for the system of interest becomes

$$(H^0 + \lambda H_1)\psi_n = E_n \psi_n. \tag{1.14}$$

We need to relate the unknown eigenvalues and eigenfunctions of the perturbed system to the known eigenvalues and eigenfunctions of the unperturbed system.

We can see from the Eq. (1.13), when $\lambda \rightarrow 0$, the E_n and ψ_n approaches to $E_n^{(0)}$ and $\psi_n^{(0)}$. At $\lambda = 0$, we have exactly the unperturbed system. As λ increases, the perturbation increases and when $\lambda = 1$, the perturbation is fully turned on.

To achieve this, the perturbed wave function and energy are expanded as

$$\psi_n = \psi_n^{(0)} + \lambda\psi_n^{(1)} + \lambda^2\psi_n^{(2)} + ... \tag{1.15a}$$

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + ... \tag{1.15b}$$

The resulting expression for energy is

$$E_n^{RS} = E_n^{(0)} + \langle\psi_n^{(0)}|H_1|\psi_n^{(0)}\rangle + \sum_m \frac{\langle\psi_n^{(0)}|H_1|\psi_m^{(0)}\rangle\langle\psi_m^{(0)}|H_1|\psi_n^{(0)}\rangle}{E_n^{(0)} - E_m^{(0)}} + ... \tag{1.16}$$

in the RS perturbation theory.

The BW perturbation theory uses Eq. (1.15a) but not Eq. (1.15b) leaving E_n as an unknown. It leads to

$$E_n^{BW} = E_n^{(0)} + \langle\psi_n^{(0)}|H_1|\psi_n^{(0)}\rangle + \sum_{m\neq n} \frac{\langle\psi_n^{(0)}|H_1|\psi_m^{(0)}\rangle\langle\psi_m^{(0)}|H_1|\psi_n^{(0)}\rangle}{E_n^{BW} - E_m^{0}} + .. \tag{1.17}$$

The BW formulation has the advantages that the higher order terms are much simpler than their counterparts in RS perturbation theory. A disadvantage of the BW approach is that the perturbed energy appears on both sides. This equation has to be solved iteratively for the solution of the wave function and the energy. A major problem with BW perturbation theory is that it is not size consistent. Even in the RS perturbation theory, individual terms at a given order are not manifestly size consistent. Goldstone derived a form of RS perturbation theory that is manifestly size consistent. It is termed the many body perturbation theory (MBPT) [12]. It is the most commonly used form of perturbation theory for molecular applications along with the Möller-Plasset partitionary theory of the Hamiltonian [15].

1.3.1.2 The variational theory

A variational principle develops general methods for finding functions which minimize or maximize the value of quantities that depends upon those functions. In quantum mechanics variational method [2–5] allows us to calculate an approximate ground state energy of a system without solving the Schrödinger equation explicitly. Given a normalized well behaved wave function $|\phi\rangle$ that satisfies the appropriate boundary conditions, a system with Hamiltonian operator H and lowest energy eigenvalue E_0, the expectation value of the Hamiltonian is an upper bound to the exact ground state energy.

$$\langle\phi|H|\phi\rangle \quad \geq \quad E_0. \tag{1.18}$$

In this equation, the equality holds only when $|\phi\rangle$ is equal to $|\psi\rangle$, the exact ground state wave function for that system. The inequality for the ground state tells us that the energy of an approximate wave function is always an upper bound to the exact ground state energy of the system. Thus, lower the upper bound of energy, better is the approximate wave function. Considering a normalized trial wave function $|\phi\rangle$ which depends on certain parameters, one can vary these parameters until the expectation value reaches a minimum. Consequently, this minimum value is then the variational estimate of the exact ground state energy. It is called Ritz variational principle.

1.3.1.3 The self-consistent field theory

Separability approximation is one of most popular approximation for quantum chemists. It is assumed that each vibrational states ψ is a product separable of single mode wave functions ϕ_i,

$$\psi(Q_1, Q_2.....Q_n) \;=\; \prod_{i}^{n} \phi_i(Q_i). \tag{1.19}$$

This set ϕ_i are the one particle wave function or modals. The best one particle wave function can be found variationally. This leads to the self consistent field approximation [16]. It was first introduced by Hartree and later improved by Fock [17] and Slater [18] for many electron system. Much later, Carney *et al.* [19] and Bowman and co-workers [20] developed the SCF method for the molecular vibrations.

In a typical analytic solution of SCF method the product separable trial wave functions of Eq. (1.19) can be written as

$$\psi_t \;=\; \prod_{k} \phi_k^0(Q_k), \tag{1.20}$$

The Watson Hamiltonian is rewritten as

$$\begin{aligned} H &= \sum_{k} h_k(q_k) + \sum_{k,l} V_2(q_k q_l) + \sum_{k,l,m} V_3(q_k q_l q_m) + ... \\ &= \sum_{k} h_k(q_k) + V \quad . \end{aligned} \tag{1.21}$$

Here V is the anharmonic potential approximate upto desired level such as cubic or quartic etc. The trial energy as

$$\begin{aligned} E_t &= \frac{\langle\psi_t|H|\psi_t\rangle}{\langle\psi_t|\psi_t\rangle} \\ &= \sum_{k} \langle\phi_k^0|h_k|\phi_k^0\rangle + \sum_{k,m} \langle\phi_k^0\phi_m^0|V_2|\phi_m^0\phi_k^0\rangle + ... \end{aligned} \tag{1.22}$$

This equation is to be minimized subject to the constraints of orthonormality

$$\langle \phi_k^\beta | \phi_k^\alpha \rangle = \delta_{\alpha\beta}. \tag{1.23}$$

To incorporate these, one uses the constrained functional

$$E = E_t - \sum_{k,\alpha,\beta} \lambda_{\alpha\beta}^k (\langle \phi_k^\beta | \phi_k^\alpha \rangle - \delta_{\alpha\beta}) \tag{1.24}$$

such that $\lambda_{\alpha\beta}^k$ are to be determined to satisfy the constraints. Now minimizing this functional with respect to ϕ_l^0 and equating to zero we have,

$$h_l \phi_l^0 + \sum_m \langle \phi_m^0 | V_2 | \phi_m^0 \rangle \phi_l^0 + \sum_{k,m} \langle \phi_k^0 \phi_m^0 | V_3 | \psi_m^0 \phi_k^0 \rangle \phi_l^0 + ... - \sum_\beta \lambda_{\alpha\beta}^l \phi_l^\beta = 0. \tag{1.25}$$

Now define the operators f_l such that

$$\langle \phi_l^\alpha | f_l | \phi_l^\beta \rangle = \langle \phi_l^\alpha | h_k | \phi_l^\beta \rangle + \langle \phi_l^\alpha | \Big[\sum_m \langle \phi_m^0 | V_2 | \phi_m^0 \rangle \Big] | \phi_l^\beta \rangle + ... \tag{1.26}$$

From Eq. (1.25) and (1.26), we have

$$f_l \phi_l^0 = \sum_\beta \lambda_{\alpha\beta}^l \phi_l^\beta. \tag{1.27}$$

Now choose ϕ_l^α as eigenfunctions of the f_l

$$f_l \phi_l^\alpha = \epsilon_l^\alpha \phi_l^\alpha. \tag{1.28}$$

This equation satisfies the constraints and the variational equation (1.25).

Thus for SCF calculation, one needs to start the calculation from some approximate form of the wave functions and ϕ_l^α Eq. 1.28 is solved. So, we have a set of improved wave functions which are then used to calculate the averaged potential and the computational cycle is performed again. This iteration procedure is continued until the new improved set of wave functions do not differ significantly from the wave function at the start cycle.

1.3.1.4 The configurational interaction method

In quantum mechanics, the best possible calculation that can be done within the choice of basis set is the full configurational interaction method [2–5, 21] which is in principle variational in nature. It considers every possible contribution of complete set of functions. Consequently, full CI with an infinite basis set is an exact solution of the time independent Schrödinger equation. The exact many particle wave function $|\psi_0\rangle$ for any state of a system can be expressed as

$$|\psi_0\rangle = C_0|\phi_0\rangle + \sum_{a,p} C_a^p|\phi_0^p\rangle + \sum_{\substack{a<b,\\ p<q}} C_{ab}^{pq}|\phi_{ab}^{pq}\rangle + \sum_{\substack{a<b<c,\\ p<q<r}} C_{abc}^{pqr}|\phi_{abc}^{pqr}\rangle + ... \quad (1.29)$$

Here, $|\phi_0\rangle$ is hartree product states, a, b etc. are occupied orbitals and p, q etc. are virtual orbitals in the Hartree reference wave function. The second term in the right hand side includes all the possible single particle excitations, the third term includes all possible double excitations, etc. Thus, the infinite set of N-particle Hartree product states are the complete set for the expansion of any N-particle wave function. The exact energies of the ground and excited states of the system are eigenvalues of the Hamiltonian matrix formed from the complete set of $|\phi\rangle$. The general matrix eigenvalue equation for CI is

$$\mathbb{H}c = ce \quad (1.30)$$

where c is the coefficient vector and e is the eigenvalue matrix. $\mathbb{H}_{ij}$ is the Hamiltonian matrices and can be written as

$$\mathbb{H}_{ij} = \langle\phi_i|H|\phi_j\rangle, \quad (1.31)$$

Unfortunately, the solution of the full CI for many particle system can not be implemented in practice. Because, the number of possible configurational functions with the proper symmetry increases rapidly with the increase of number of particles (N) and number of basis functions (B). The number of configurational functions turns out to be roughly proportional to B^N. Consequently, for infinite basis set, these configurations are also infinite which is practically impossible to solve as one can not handle infinite basis sets. Thus, full CI calculation with large basis set are usually carried out only for small molecular systems. For medium sized molecule, Full CI is not possible and we need limited CI where only few configuration functions are considered. Unfortunately, this practically feasible limited CI approach is not always size-consistant. To use limited CI, one must be careful to decide the types of configuration functions that need to be considered and which are likely to make the largest contribution to ψ.

1.3.1.5 The coupled cluster theory

Presently, the coupled cluster method [22, 23] is the most popular *ab initio* approach which is size-consistent but not variational. The CC method introduces the cluster operator T, with the equation,

$$\psi = e^T \phi_0, \tag{1.32}$$

where ψ is the exact ground state many particle wave function and ϕ_0 is the normalized HF wave function. The operator e^T is defined by Taylor series expansion

$$e^T = 1 + T + \frac{T^2}{2!} + \frac{T^3}{3!} + \; ..... \; = \sum_{k=0}^{\infty} \frac{T^k}{k!} \tag{1.33}$$

and the cluster operator T is

$$T = T_1 + T_2 + T_3 + ... + T_n \tag{1.34}$$

where n is the the number of particle in the system. The effect of T on ϕ_0 is to create a linear combination of Staler determinant that includes all the singly, doubly ..... upto n-tuply from ϕ_0 i.e. all possible excitations of particle from occupied to virtual orbitals. Thus $e^T\phi_0$ gives exact ψ like full CI. The one particle (T_1) and two particles (T_2) excitation operators are defined as

$$\begin{aligned} T_1\phi_0 &= \sum_{a,p} t_a^p \phi_a^p, \\ T_2\phi_0 &= \sum_{a,b,p,q} t_{ab}^{pq} \phi_{ab}^{pq}, \end{aligned}$$

where ϕ_a^p and ϕ_{ab}^{pq} are the singly and doubly excited slater determinants and t_a^p and t_{ab}^{pq} are the corresponding single and double excitation amplitude, respectively. Note that, no operator beyond T_n appears as ϕ_0 has all particles in n occupied orbitals. The excitation amplitudes are determined by solving CC equations. Once these amplitudes are found, the wave function ψ in Eq. (1.32) can be calculated. Substituting it in the Schrödinger equation [Eq. (1.1b)] we have

$$He^T|\phi\rangle = Ee^T|\phi_0\rangle. \tag{1.35}$$

Multiplying it by e^{-T} in both side we have,

$$e^{-T}He^T|\phi\rangle = E|\phi_0\rangle, \tag{1.36a}$$

$$\bar{H}|\phi\rangle = E|\phi_0\rangle, \tag{1.36b}$$

where $\bar{H} = e^{-T}He^T$. Now we can write the conditions for the ground state $\langle\phi_0|$ and any other state $\langle\phi_m|$ as

$$\langle\phi_0|\bar{H}|\phi_0\rangle = E, \tag{1.37a}$$

$$\langle\phi_m|\bar{H}|\phi_0\rangle = 0. \tag{1.37b}$$

Depending on the approximation in the cluster operator (T) one can truncate the CC method in different levels of theory, such as coupled cluster doubles (CCD) for $T = T_2$, coupled cluster singles and doubles (CCSD) for $T = T_1 + T_2$ or coupled cluster singles, doubles and triple (CCSDT) for $T = T_1 + T_2 + T_3$ and so on.

1.3.2 Approximations for the density matrices

There are several semiclassical and quantum mechanical methods available for the density matrices. We discuss some of them in this section.

1.3.2.1 Miller's semiclassical approach

Semiclassical approach is an important tool which requires classical trajectories to describe essentially all types of quantum effects in molecular systems. An approximate semiclassical methodology was developed by Miller and co-workers [24, 25] to evaluate the density matrix at finite temperatures. In this approach the density matrix is written as

$$\begin{aligned} e^{-\beta H} &= (2\pi\hbar)^{-1} \int dx_0 \int dp_0 D(x_0, p_0) \times \\ &\quad e^{-S(x_0,p_0)/\hbar} |x_{\hbar\beta}, ip_{\hbar\beta}\rangle \langle x_0, ip_0|, \end{aligned} \tag{1.38}$$

where the $|x_0, p_0\rangle$ is a standard HO coherent state centred at the $(x_0 p_0)$ in the phase space. Its coordinate space representation is

$$|x_0, p_0\rangle = \left(\frac{\gamma}{\pi}\right)^{\frac{1}{4}} exp\Big[-\frac{\gamma}{2}(x - x_0)^2 + \frac{i}{2} p_0 (x - x_0)\Big], \tag{1.39}$$

S is the action along the temperature (imaginary) axis.

$$S(x_0, p_0) = \int_0^{\hbar\beta} \left[\frac{1}{2} m \dot{x}(\tau)^2 + V(x(\tau))\right] d\tau, \tag{1.40}$$

and the prefactor D is given by

$$D(x_0,p_0) \;=\; 2^{-1/2}\left[\hbar\gamma\frac{\partial x_{\hbar\beta}}{\partial p_0}+\frac{1}{\hbar\gamma}\frac{\partial p_{\hbar\beta}}{\partial x_0}-\frac{\partial x_{\hbar\beta}}{\partial x_0}-\frac{\partial p_{\hbar\beta}}{\partial p_0}\right]^{1/2}. \tag{1.41}$$

Miller and cowrkers used this approach to calculate finite temperatute expectation values for a one-dimensional symmetric quartic oscillator and average position of symmetric oscillator.

1.3.2.2 The path integral based approaches

Path integral (PI) approach for quantum mechanics was developed by Feynman [6]. It expresses the propagator matrix elements $\langle x'|exp(-iHt/\hbar)|x\rangle$ as the sum over all paths from x to x' in time t, weighted by a phase factor $exp(iS/\hbar)$ where S is the classical action defined as

$$S \;=\; \int_x^{x'} p\; dx, \tag{1.42}$$

integrated from initial point to a final point. Here p is the momentum and x is the coordinate of a system or particle. Here the path means a sequence of (x_n,t_n) with the fixed endpoints. Each path completely determines the velocity $\dot{x}$ at all times. Feynman himself noted the similarity between the propagator (e^{-iHt}) and the desity operator $(e^{-\beta H})$ and suggested that one might extend the time variable on to the imaginary axis to obtain the density matrix by the PI technology. Improvements of Feynman PI method are mainly of two categories. The formulation of quantum statistical mechanics based on the path centroid density [26–28] and the ring polymer molecular dynamics (RPMD) [29].

In the path centroid density approach the centroid is the imaginary time average of a particular closed Feynman path $x(t)$. Here t is the imaginary time variable, and

$$x_0 \quad = \quad \frac{1}{\hbar\beta}\int_0^{\hbar\beta} dt\ x(t). \tag{1.43}$$

The centroid density is defined as

$$\rho_c(x_c) \quad = \quad \int ....\int \mathcal{D}x(t)\delta(x_c - x_0)exp(-S[x(t)]/\hbar) \tag{1.44}$$

and the quantum partition function is obtained for all possible values of the centroid

$$Z \quad = \quad \int dx_c\ \rho_c(x_c). \tag{1.45}$$

In RPMD, it is recongnized that the quantum mechanical PI partition function and the classical partition function of a fictitious ring-polymer are isomorphous. As a result of this isomorphism, the canonical partition function can be calculated exactly as,

$$Z = Lt_{n\to\alpha}\ Z_n, \tag{1.46}$$

where

$$Z_n \quad = \quad \frac{1}{(2\pi\hbar)^n}\int dp \int dx\ e^{-\beta_n H_n(p,x)}. \tag{1.47}$$

Here, $\beta_n = \beta/n$ and $H_n(p,x)$ is the classical Hamiltonian of a ring polymer.

$$H_n(p,x) \quad = \quad \sum_{j=1}^{n}\frac{p_j^2}{2m} + \frac{m}{2\beta_n^2\hbar^2}\sum_{j=1}^{n}(x_j - x_{j-1})^2 + \sum_{j=1}^{n} V(x_j). \tag{1.48}$$

The thermal averages $\langle A\rangle_\beta$ are calculated anlogously from

$$\langle A\rangle \quad = \quad \frac{1}{Z}Tr.[e^{-\beta H}A] \tag{1.49}$$

which also can be calculated within the isomorphism as $\langle A \rangle = Lt_{n\to\infty}\langle A \rangle_n$, where

$$\langle A \rangle_n = \frac{1}{(2\pi\hbar)^n Z_n}\int dp \int dx \; e^{-\beta_n H_n(p,x)} A_n(x) \tag{1.50}$$

with

$$A_n(x) = \frac{1}{n}\sum_{j=1}^{n} A(x_j). \tag{1.51}$$

1.3.2.3 The Bloch equation based approaches

There is a basic similarity in the mathematical structure of the Bloch equation (Eq. (1.5)) and the time dependent Schrödinger equation (Eq. (1.1a)). A one-to-one mapping is possible between them by replacing the time variable in the wave function of the time dependent Schrödinger equation with the temperature variable into density matrix to reach Bloch equation. Given this mapping, gaussian wave packet (GWP) propagation apporoach that is popular in the time dependent quantum mechanics [30] has been used to solve the Bloch equation. Metiu and co-workers [31], Singer *et al.* [32], Mandelshtam and co-workers [33] and Pollak and co-workers [34] computed the thermal equilibrium density matrices by using the GWP approach. The equilibrium density matrices of quantum many body theory are expressed as a linear superposition of displaced gaussians, and, each gaussian is propagated independently in imaginary time β, starting from the limit $\beta = 0$. In all these cases, the Bloch equation leads to ordinary differential equations for the parameters of the gaussian. In this approach one has to solve Bloch equation as an initial value problem

$$\frac{d}{dt}|x_{n,t}\rangle = -H|x_n^0(t)\rangle; \quad |x^0(t=0)\rangle = |x_n^0\rangle \tag{1.52}$$

using the ansatz

$$|x_n(t)\rangle \;=\; exp\Big[\gamma(t) - \frac{1}{2}\big\{x - x_n(t)\big\}^T G(t)\ \big\{x - x_n(t)\big\}\Big] \tag{1.53}$$

Franstsuzov and Mandelshtam used a variant of the action variational principle to obtain equations of motion for the paramaters in the gaussian. This involves the minimization of the Lagrangian $x_n(t)$ and $G(t)$

$$L \;=\; \left\langle x_n(t)\middle|\frac{d}{dt} + H\middle|x_n(t)\right\rangle. \tag{1.54}$$

From the solutions, the density matrix is reconstructed as

$$\rho \;=\; \sum_n p_n|x_n(t)\rangle\langle x_n(t)| \tag{1.55}$$

with respect to the parameters. The weight factors p_n are determined at $t = 0$, when ρ is equal to the identity matrix. These are not varied as variational parameters.

Metiu and co-workers [31] developed a method using variational GWP to solve the Bloch equation by explicit propagation of the density matrix in imaginary time. They applied it for two different methods, the local harmonic approximation method and minimun error method.

Militzer and Pollock [35] have used McLachlan like variational principle [36] to determine the equations of motion as

$$I(\dot\rho) \;=\; Tr(\dot\rho + H\rho)^2 \tag{1.56}$$

as a functional of $\dot\rho \equiv \partial\rho/\partial\beta$ with fixed ρ. $I(\dot\rho) = 0$, gives the exact density matrix. The variation gives

$$Tr[\delta\dot\rho(\dot\rho + H\rho)] \;=\; 0 \tag{1.57}$$

from which the working equations for the parameters in the ansatz for ρ are derived and applied it for a particle in external field. They too have expanded ρ as a superposition of gaussians (Eq. (1.53)).

The main disadvantage of all these approaches is the specification of the initial conditions. At $\beta = 0$, the density matrix becomes the identity operator. Consequently, one needs a large number of gaussian to represent it. In addition, the width of these gaussian goes to zero asymptotically as $\beta \rightarrow 0$. Representing this conditions are difficult. A few approaches have been taken to overcome this problem, but their implications are poorly understood.

1.3.2.4 The variational approaches

The Feynman variational principle based on the Gibbs-Bogoluibov inequality [6] is a variational approach which gives the upper bound of the exact free energy without calculating the partition function explicitly. If A is the exact Helmholtz free energy of the a system described by the Hamiltonian H, then

$$A \;\leq\; A_0 + \langle H - H_0 \rangle, \tag{1.58}$$

where

$$A \;=\; -\frac{1}{\beta} ln\left[Tr\ exp(-\beta H) \right], \tag{1.59}$$

and A_0 is the Helmholtz free energy corresponding to model system described by H_0. Minimization of the Eq. (1.58) with respect to the parameters in H_0 one gets the corresponding equations for the parameters.

This variational principle was used by Spridonov *et al.* with an effective harmonic oscillator model Hamiltonian to calculate the thermal averages for a coupled oscillators with polynomial anharmonicity in terms of normal coordinates $\{Q\}$. Cao and Voth [37] developed a similar approximation for the calculation of partition functions.

1.3.2.5 Thermal cluster cumulant approach

A nonperturbative cluster-cumulant method for deriving thermal averages of operator in quantum many body system is derived by Mukherjee and co-workers [38]. This approach is similar to theormofield dynamics They introduced a thermal vacuum $|0\rangle_\beta$ and defined a thermal normal ordering of the operators such that the thermal average of the normally ordered operator is zero. Using this definition they prove the associated Wick's theorem. The ket part of the thermal density matrix is posited to be

$$|\beta\rangle \quad = \quad \{exp(S_1 + X_1)\}|0_\beta\rangle, \tag{1.60}$$

where the $\{...\}$ indicates thermally normal ordered product. S and X represent external and closed operator respectively. The partition function is obtained from

$$Z \quad = \quad e^{X_0} \tag{1.61}$$

where X_0 is the C number component of X.

1.3.2.6 Other approaches

In recent years, a few developments using separable ansatz have been reported for the calculation of quantum and statistical properties of molecules. Njegic and Gordon [39] explored the possibilities for the calculations of partition functions by VSCF method with a second order perturbation theory correction. They calculated the anharmonic vibrational frequencies by fundamental excitations from the ground state using VSCF method and second order perturbation theory correction. That excitation energy ν_i is then substituted in the HO partition function equation

$$Z_{vib} \quad = \quad \Pi_{i=1}[1 - exp(\nu_i/k_B T)]^{-1} \tag{1.62}$$

Barone [40] calculated the partition function and the thermodynamic properties with anharmonic correction by a perturbative treatment. He calculated the fundamental frequency as

$$\nu_i \quad = \quad w_i + 2f_i + \frac{1}{2}\sum_{j \neq i} f_{ij} \tag{1.63}$$

and from that thermodynamic properties are calculated. Here f_i and f_{ij} are the anharmonic constants obtained for perturbation theory. The zero point energy (ZPE) is calculated as

$$ZPE \quad = \quad f_0 + \frac{1}{2}\sum_i \Big(w_i + \frac{1}{2}f_{ii} + \sum_{j<i}\frac{1}{2}f_{ij}\Big). \tag{1.64}$$

The expansion for the harmonic partition function is then used

$$Z_{vib} \quad = \quad \frac{e^{-ZPE/KT}}{\Pi_i[1 - exp(\nu_i/k_B T)]} \quad . \tag{1.65}$$

Hensen *et al.* [41] used the VSCF theory to calculate vibrational partition function and the thermal effect of molecular properties. They introduced two different approximations, virtual VSCF (v-VSCF) and state specific VSCF (ss-VSCF). If a given VSCF state is optimized within a given primitive basis set, a complete set of virtual states are also obtained. The eigenvalues associated with such virtual states can be treated as approximate vibrational energies from which the vibrational partition function can be calculated including all possible states within the one-mode basis set.

$$Z_{vib} = \sum_{n} exp\left[\frac{-E_i^{VSCF} + \sum_{m=1}^{M} \Delta\epsilon_n^M}{k_B T}\right] \tag{1.66}$$

Here, E_i^{VSCF} is ground state energy for mode i and $\Delta\epsilon_n^M$ is the excitation energy within the one-mode basis set. This is the virtual VSCF (v-VSCF) method. The state specific VSCF (ss-VSCF) method was constructed as explicit sum over states where each state is optimized in a separate VSCF calculation. They showed that the v-VSCF method is less CPU time demanding than ss-VSCF method. At higher temperatures, the former one is less accurate than the latter. On the other hand, with the increase in temperature the CPU time for the ss-VSCF method increases rapidly.

A few of the early attempts in this area are the finite temperature Green function methods and perturbation theory [42–44], imaginary time convolution method [45, 46] and few others [47–50].

1.4 The goals of the present work

As the foregoing discussions, most of the approaches available for the calculation of the thermal density matrices are semiclassical in nature and not fully quantum mechanical. The few applications that have been made within quantum mechanical frameworks are based on the EHO approximation. The HO approximation suffers from two limitations. The HO density matrix is symmetric around the local minimum of the potential that defines it. Consequently, it can not describe a system governed by a asymptotic potential properly. It moves the centroid towards the softer side of the potential to describe the assymmetry induced by the potential. Second, it can not provide a proper description for systems described by multiple well potentials since the HO density matrix has only one local minimum. It is thus desirable to go beyond the EHO ansatz. This is the primary goal of the present work. We explore the utility of a more general separable ansatz for the vibrational density matrix. We write

$$\rho \;=\; \Pi_k \; \rho_k e^{-\beta E_0}, \tag{1.67}$$

where each ρ_k is the density matrix for one vibrational mode and given by

$$\rho_k \;=\; e^{-\beta h_k}. \tag{1.68}$$

The mathematical framework for such a description is still provided by the Feynman variational principle based on the Gibbs-Bogoluibov inequality (FGB). The resulting equation for the parameters that define various h_k look similar to the quantum mechanical self-consistent field approximation except that the quantum mechanical averages are replaced by the corresponding thermal averages. This part of the work is presented in chapter 2. We then assess the utility of this thermal SCF approach for calculating various thermal averages to asses the reliability of the numerical predictions by these approximations. We compare the SCF results against numerically converged full CI calculation for various thermodynamic properties and thermal averages. We then use it to calculate the equilibrium constants of two model reactions. We also compare the results against EHO to understand the degree of improvement as one moves from EHO to thermal SCF.

The FGB variational principle is specifically tailored to minimize the error in the free energy of the system. Since it involves the trace of the density matrix it is a global property of the density matrix. As a consequence density matrices obtained from the FGB may not describe the probabilities at all points in space with uniform accuracy. There are occasions however, where we need a density matrix in some selected region of space with high accuracy. One example of this type is the density matrix for a potential representing a repulsive barrier near the origin and asymptotically flat. The diagonal part of the density matrix should have a local minima where the potential has a local maxima. A blind application of the FGB principle with the EHO ansatz gives the frequency of the EHO equal to zero instead of a imaginary number corresponding to a parabolic barrier. Thus a different prescription is required to handle systems of this type. We describe the development of a new variation principle in chapter 3, that has the potential to handle such cases. This approach minimizes the mean square difference between the temperature derivatives of the exact and model density matrices similar to the McLachlan type variational principle of time dependent quantum mechanics. We compare the performance of this approach with the FGB results to assess the relative merits of both the approaches in the EHO and SCF framworks.

One of the conclusions that has come up from our numerical studies is that the EHO approximation is quite good and deviates from the SCF approximation very little. This brings up the question, whether the EHO is equally capable of describing individual molecular eigenstates, particularly the highly excited eigenstates. The density matrices contain the excited states with relatively small statistical factors. The individual quantum states, on the other hand, may not be amenable to a description by an EHO potential. To answer this question we study the validity of the EHO approximation for the calculations of the individual molecular states in chapter 4. It turned out that all most all the states upto 2 quanta of energy are very well described by the EHO approximation.

Chapter 2

A Thermal Self-consistent Field Theory for the Calculation of Molecular Vibrational Partition Functions

2.1 Introduction

All thermodynamic properties of molecular systems are derived from the canonical partition functions. The input required for such a calculation is the set of molecular energy levels. The calculation of the energy levels is normally carried out by invoking a series of approximations. In the first step, the Born-Oppenheimer approximation is invoked that separates the electronic and the nuclear motion. Given the large energy difference between different electronic states, only the ground electronic state is considered for further calculations. The potential energy surface associated with this state is used to calculate the ro-vibrational energy levels. For large molecules, the rotational and vibrational degrees of freedom are nearly decoupled, since the Coriolis coupling coefficients depend inversely on the moments of inertia. The rotational partition function is available in the analytical form for the resulting rigid rotor problem. The remaining vibrational problem is often solved in harmonic approximation, where analytical solution to the partition function is available in terms of the normal mode frequencies.

While the harmonic approximation provides a reasonable description of the thermal properties at low temperatures, the anharmonic effects must be included at elevated temperatures. Though the absolute magnitudes of such anharmonic effects are small for at least semi-rigid molecules, they are expected to be significant for energy differences that determine, for example, the equilibrium constants and rate constants. Several approaches have been discussed in literature to incorporate the anharmonic effects in the partition function calculations [25, 31–34, 39–41, 47–52].

Recent advances in electronic structure theory have made it possible to obtain anharmonic potential energy surfaces upto fourth power of normal mode displacements [53–55]. With this development, several authors have attempted to assess the reliability of using *ab initio* quartic force fields for the calculation of thermal properties [39–41, 51]. Solution of the vibrational Schrödinger equation for the molecular anharmonic vibrational energy levels is a formidable task. It requires the construction and subsequent diagonalization of the Hamiltonian matrix in a suitable basis for its eigenvalues. The size of the basis in such calculations scales exponentially with the number of degrees of freedom. This basis set bottleneck provides the motivation for exploring alternative methods and approximations for the calculation of the vibrational energy levels or the partition function directly. One such method which received considerable attention is the vibrational self consistent field (VSCF) approximation [19, 20]. It has been used successfully for interpreting molecular vibrational spectra [56]. Recently Njegic and Gordon [39] and Hensen and co-workers [41] have used the VSCF approximation to evaluate molecular thermodynamic properties. The primary advantage of this method is that, it scales linearly with the number of degrees of freedom and thus avoids the basis set bottleneck inherent in the vibrational configurational interaction (VCI) method for the calculation of the energy levels. However, the sum over states required for the evaluation of partition function still remains. To avoid that, Hensen *et al.* [41] considered a further approximation, termed the virtual VSCF (v-VSCF), in which the virtual modal energies in a single VSCF calculation are used to estimate the excited state energy levels. Similarly, Njegic and Gordon [39] derived the anharmonicity corrected vibrational frequencies from VSCF calculations and used the harmonic oscillator (HO) expression for the partition function. In this work, we explore an alternative separable ansatz to the thermal density matrix and use the Feynman variational principle [6] based on the Gibbs-Bogoliubov inequality to obtain the working equation for its calculation. The resulting theory resembles the VSCF procedure with the replacement of the quantum mechanical averages with their thermal counterparts. For that reason it is called the thermal self consistent field theory (t-SCF). The computational effort in this approach is similar to a single VSCF calculation at a given temperature. However, no further approximation is invoked in terms of the anharmonic frequencies or the excited modals energies. The formal aspects of the theory are presented in Sec. 2.2.1.

A special case of such t-SCF theory is the effective harmonic oscillator (EHO) theory developed by Spiridonov and co-workers [57] for quartic force fields. Voth and co-workers [37] have developed a similar procedure to handle arbitrary potentials from a different perspective and discussed possible ways to go beyond it. In the EHO approximation, the thermal modals are further approximated to be HO eigenstates. Since thermodynamic properties are dominated by the ground state, and, the higher excited states that are significantly influenced by the anharmonicity contribute little to the thermal density matrix due to the Boltzmann factors, it might be expected that the EHO theory should perform as well as the t-SCF theory. We compare the performance of EHO against the t-SCF results. The essential features of the EHO theory are summarized in Sec. 2.2.2.

Numerical studies using these two approaches are presented in Sec. 2.2, where we compare various thermodynamic properties obtained by those two approximate theories against converged basis set calculation for two model triatomic system H_2O and F_2O. A second set of calculations for the equilibrium constants of a cis-trans isomerization reaction and an isotopic exchange reaction based on several *ab initio* potential energy surfaces are also presented in this section and compared with the available experimental and other theoretical data. The last section summarizes our conclusions.

2.2 Theory

The t-SCF approximation described in this section is based on the mean field theory. In this theory, the complex many body potential in the Hamiltonian is replaced by a sum of single particle potentials. The single particle potential corresponding to each degree of freedom is taken to be the average potential felt by that particle in an ensemble. Such mean field theories have a long history in statistical physics and have been used to describe a variety of phenomena earlier [58]. However, they have not been applied molecular vibrational problem to date.

2.2.1 The thermal SCF theory

The starting point for our derivation of the t-SCF theory is the variational principle based on the Gibbs-Bogoluibov inequality [6, 59],

$$A \leq A_0 + \langle H - H_0 \rangle. \tag{2.1}$$

Here A is the exact Helmholtz free energy of the vibrational system described by the Hamiltonian H,

$$A = -\frac{1}{\beta} ln\Big[Tr\ exp(-\beta H)\Big], \tag{2.2}$$

and A_0 is the Helmholtz free energy corresponding to model system described by H_0, defined similarly. The Watson Hamiltonian [10] for the molecular vibrational system is given by

$$H = \frac{1}{2}\sum_{i=1}^{N} P_i^2 - \frac{\hbar^2}{8}\sum \mu_{\alpha\alpha} + \frac{1}{2}\sum_{\alpha\beta} \mu_{\alpha\beta}\pi_\alpha\pi_\beta + V(Q), \tag{2.3}$$

in mass weighted normal co-ordinate representation. Here, the first term is the kinetic energy (KE) term and the second one is the so called Watson mass term. $\mu_{\alpha\beta}$ are the components of the inverse effective moment of inertia tensor at a given point on the potential energy surface (PES). π_α is the α^{th} component of the vibrational angular momentum and the last term is the potential energy. In the spirit of the independent particle model, we posit the model Hamiltonian H_0 as

$$H_0 = \sum_k h_k, \tag{2.4}$$

where each h_k is an effective single particle Hamiltonian given by

$$h_k = -\frac{1}{2}P_k^2 + U_k(Q_k). \tag{2.5}$$

The coefficients appearing in U_k in Eq. (2.5) are the variational parameters and have to be determined by minimizing the right hand side of the inequality in Eq. (2.1). Thus we require

$$\delta\Big[-\frac{1}{\beta} ln\big\{Tr\ exp\ (-\beta H_0)\big\} + \langle H - H_0\rangle\Big] = 0. \tag{2.6}$$

Thus Eq. (2.1) can be written as

$$A \leq -\frac{1}{\beta} ln(Tr\ e^{-\beta H_0}) + \frac{Tr\ (H-H_0)e^{-\beta H_0}}{Tr\ e^{-\beta H_0}} \tag{2.7}$$

and as $\delta A = 0$ and $\delta H_0 = \sum_k \delta h_k$, we can expand this equation as

$$\begin{aligned} \frac{Tr\ \delta h_k\ e^{-\beta H_0}}{Tr\ e^{-\beta H_0}} - \frac{Tr\ \delta h_k\ e^{-\beta H_0}}{Tr\ e^{-\beta H_0}} + \frac{Tr(H-H_0)(-\beta\delta h_k)e^{-\beta H_0}}{Tr\ e^{-\beta H_0}} & \\ -\frac{Tr(-\beta\delta h_k)e^{-\beta H_0}\ Tr(H-H_0)e^{-\beta H_0}}{Tr\ e^{-\beta H_0}\ \ Tr\ e^{-\beta H_0}} &= 0. \end{aligned} \tag{2.8}$$

Cancelling the common terms we have

$$\frac{Tr(H-H_0)\delta h_k\ e^{-\beta H_0}}{Tr\ e^{-\beta H_0}} - \frac{Tr\ \delta h_k\ e^{-\beta h_k}\ Tr(H-H_0)e^{-\beta H_0}}{Tr\ e^{-\beta h_k}\ \ Tr\ e^{-\beta H_0}} = 0. \tag{2.9}$$

Rearranging this

$$Tr\Big\{e^{-\beta H_0}(H-H_0)\Big[\delta h_k - \frac{Tr\ \delta h_k\ e^{-\beta h_k}}{e^{-\beta h_k}}\Big]\Big\} = 0. \tag{2.10}$$

As the second term in the square bracket is a number, we can rewrite this equation after carrying out the trace on all degrees of freedom l except k

$$\frac{Tr\ \delta h_k h_k\ e^{-\beta h_k}}{Tr\ e^{-\beta h_k}} - \frac{Tr\ \delta h_k\ e^{-\beta h_k} Tr_{l\neq k}\ H\ e^{-\sum_{l\neq k}\beta h_l}}{Tr\ e^{-\beta h_k}}. \tag{2.11}$$

Rewriting this we have

$$Tr\ \delta h_k \Big[h_k - \frac{Tr_{l\neq k}\ H\ e^{-\beta\sum_{l\neq k} h_l}}{Tr_{l\neq k} e^{-\beta\sum_{l\neq k} h_l}}\Big] e^{-\beta h_k} = 0 \tag{2.12}$$

and hence we have

$$h_k = \Big[Tr_{l\neq k}\ H\ exp\ (-\beta \sum_{l\neq k} h_l)\Big] \Big/ \Big[Tr_{l\neq k}\ exp\ (-\beta \sum_{l\neq k} h_l)\Big]. \tag{2.13}$$

This leads to the final result

$$U_k(Q_k) \;=\; \Big[Tr_{l\neq k}\; V\; exp\;(-\beta\sum_{l\neq k} h_l)\Big]\Big/\Big[Tr_{l\neq k}\; exp\;(-\beta\sum_{l\neq k} h_l)\Big]. \tag{2.14}$$

We now specify the approximations used in our studies presented below. Since we expect to use this approach for large molecules, we ignore the Coriolis interaction terms as they depend inversely on the moment of inertia. Second, we approximate the anharmonic PES $V(Q)$ by a quartic force field

$$V(Q) \;=\; \sum_i f_{ii}Q_i^2 + \sum_{i\leq j\leq k} f_{ijk}Q_iQ_jQ_k + \sum_{i\leq j\leq k\leq l} f_{ijkl}Q_iQ_jQ_kQ_l\ . \tag{2.15}$$

This approximation is motivated by the observation that several *ab initio* electronic structure programs, such as the Gaussian 03 suite [60] and GAMESS [61], provide quartic force fields. As a consequence of this approximation, the single particle effective potentials take the form

$$U_k(Q_k) \;=\; u_k^{(1)}\; Q_k + u_k^{(2)}\; Q_k^2 + u_k^{(3)}\; Q_k^3 + u_k^{(4)}\; Q_k^4. \tag{2.16}$$

The working equations for the parameters $u_k^{(n)}$ are obtained from Eq. (2.14).

$$\begin{aligned} u_k^{(1)} \;=\; & \sum_{j<i\neq k} f_{kji}\langle Q_j\rangle_\beta\langle Q_i\rangle_\beta + \sum_{j\neq k} f_{kjj}\langle Q_j^2\rangle_\beta + \sum_{j<i<l\neq k} f_{kjil}\langle Q_j\rangle_\beta\langle Q_i\rangle_\beta\langle Q_l\rangle_\beta \\ & + \sum_{j\neq i\neq k} f_{kjji}\langle Q_j^2\rangle_\beta\langle Q_i\rangle_\beta + \sum_{j\neq k} f_{kjjj}\langle Q_j^3\rangle_\beta, \end{aligned} \tag{2.17}$$

$$u_k^{(2)} = f_{kk} + \sum_{j\neq k} f_{kkj}\langle Q_j\rangle_\beta + \sum_{j\neq k} f_{kkjj}\langle Q_j^2\rangle_\beta + \sum_{j\neq i\neq k} f_{kkji}\langle Q_j\rangle_\beta\langle Q_i\rangle_\beta, \tag{2.18}$$

$$u_k^{(3)} \;=\; f_{kkk} + \sum_{j\neq k} f_{kkkj}\langle Q_j\rangle_\beta, \tag{2.19}$$

$$u_k^{(4)} = f_{kkkk}. \tag{2.20}$$

Here the thermal averages values $\langle Q_l \rangle_\beta$ etc are defined as

$$\langle Q_l^n \rangle_\beta = \frac{Tr\ Q_l^n\ exp\ (-\beta h_l)}{Tr\ exp\ (-\beta h_l)}. \tag{2.21}$$

Note that Eqs. (2.16-2.21) are essentially the quantum mechanical VSCF equation generalized to finite temperature. Once the single particle effective potentials are constructed, the eigenfunctions and eigenvalues of the single particle Hamiltonians h_k are obtained,

$$h_k \phi_n^{(k)} = \varepsilon_n^{(k)} \phi_n^{(k)}. \tag{2.22}$$

The eigenfunctions $\phi_n^{(k)}$ are the thermal analogues of the modals obtained in the VSCF theory. In practice, the thermal modals are expanded in a suitable HO basis

$$\Phi_n^{(k)} = \sum_m \chi_m^{(k)} C_{mn}. \tag{2.23}$$

With this substitution, Eq. (2.23) is converted into a matrix eigenvalue problem, and is solved by the usual numerical procedures.

The thermal modals are then used to construct the thermal density matrices associated with each normal mode.

$$\begin{aligned} \rho_k &= exp(-\beta h_k) \\ &= \sum_n |\phi_n^{(k)}\rangle\ exp(-\beta \varepsilon_n^{(k)})\ \langle \phi_n^{(k)}|. \end{aligned} \tag{2.24}$$

The thermal traces required in Eq. (2.14) are evaluated using these density matrices. Thus the thermal trace in Eq. (2.21) is explicitly given by

$$\langle Q_l^n \rangle \;=\; \Big[\sum_m \langle \phi_m^{(l)} | Q_l^n | \phi_m^{(l)} \rangle \; exp(-\beta \varepsilon_m^{(l)})\Big] \Big/ \Big[\sum_m \; exp(-\beta \varepsilon_m^{(l)})\Big] \tag{2.25}$$

Finally, the overall thermal density matrix and the free energy are given by

$$\rho \;=\; \prod_k \rho_k \; exp\big[-\beta \langle V - V_0 \rangle\big] \tag{2.26}$$

$$A \;=\; -\frac{1}{\beta} ln\big[Tr \; exp(-\beta H_0)\big] + \langle V - V_0 \rangle. \tag{2.27}$$

Thus, the t-SCF procedure consists of the following steps. We start with a set of guess modals and the associated A. We then calculate the new U_k by Eqs. (2.16-2.21) and obtain the associated modals (2.22) and free energy (2.27). The process is iterated until either the free energy or the thermal density matrix is converged.

2.2.2 The thermal EHO theory

We now briefly summarize the EHO theory as developed by Spirinov and co-workers [57] and Voth and co-workers [37]. This is a special case of the t-SCF theory in that the effective potentials defining the single particle Hamiltonians h_k are restricted to quadratic terms.

$$U_k \;=\; \frac{1}{2} w_k (Q_k - Q_k^0)^2 \tag{2.28}$$

Because the single particle Hamiltonians are HO Hamiltonians, the associated single particle thermal density matrices are available in analytical form

$$\begin{aligned}\rho_k(Q,Q') &= \sqrt{\frac{mw_k}{2\pi\hbar sinh(\hbar\beta w_k)}} \quad \times \\ & exp\Bigg[-\frac{mw_k}{2\hbar sinh(\hbar\beta w_k)}\Big[\big(x^2+x'^2\big)cosh(\hbar\beta w_k)-2xx'\Big]\Bigg], \qquad (2.29)\end{aligned}$$

where $x = (Q_k - Q_k^0)$ and $x' = (Q'_k - Q'^0_k)$. The mass (m) is unity in the mass weighted normal co-ordinate representation. From now on we use atomic units in which $\hbar$ is one. The variational parameters in this case are the EHO frequencies w_k and the displacements Q_k^0. Explicit equation for these parameters have been derived earlier [57] for triatomic molecules. More generally for any polyatomic molecule, these are given by

$$\begin{aligned}Q_k^0 &= -\frac{1}{2\ f_{kk}}\Bigg[\sum_{j\leq i} f_{kji}\ g_{kji}\ Q_i^0Q_j^0 + \sum_{j\leq i\leq l} f_{kjil}\ g_{kjil}Q_i^0Q_j^0Q_l^0 + \\ & \sum_j f_{kjj}g_{kj}\frac{1}{2w_jtanh(\beta w_j/2)} + \sum_{j\neq i} f_{kjji}g_{kji}\frac{Q_i^0}{2w_jtanh(\beta w_j/2)}\Bigg], \qquad (2.30)\end{aligned}$$

$$\begin{aligned}w_k^2 &= 2\Bigg[f_{kk} + \sum_j f_{kkj}\ g_{kj}\ Q_j^0 \ + \sum_{j<i} f_{kkji}\ g_{kji}\ Q_j^0Q_i^0 + \\ & f_{kkkk}\frac{3}{w_ktanh(\beta w_k/2)} \ + \ \sum_{j\neq k} f_{kkjj}\ g_{kj}\ \frac{\beta}{2w_jtanh(\beta w_j/2)}\Bigg]. \qquad (2.31)\end{aligned}$$

The factors g_{ij} etc., are the combitorial factors that arise when the terms that are averaged over, are picked out of the product of the operators. Once again, these equations are the thermal generalizations of the Hartree approximation used in the quantum mechanical EHO description of molecular vibrations [62, 63]. The overall thermal density matrix and the free energy still satisfy Eq. (2.26) and Eq. (2.27) respectively.

One limitation of the EHO theory as discussed here is that, it assumes that the effective single particle potentials U_k, have a single minimum. As discussed by Voth and co-workers [37], the approach can be generalized for multiple minima in U_k by writing the density matrix as a superposition of gaussians, each centered around one local minimum. In addition, in the presence of such multiple minima, Eq. (2.31) may breakdown in the high temperature limit, as the barrier region is sampled to the extent that the effective force constant becomes negative. Note that this problem does not arise in the case of t-SCF theory, since the full U_k is utilized in the construction of the thermal modals. The higher order terms in U_k, specifically the quartic term is expected to cover the problems of local negative curvatures and multiple minima, though it would require either a large basis if a single centre expansion is used or a multi centre expansion for a proper description of the modals.

2.3 Numerical studies

Two sets of calculations were carried out to assess the reliability of the t-SCF and EHO approaches for the calculation of thermal properties. In the first step, two small molecules, H_2O and F_2O are studied. For these systems with three degrees of freedom, it is possible to obtain numerically converged values for all thermodynamic properties and thus it provides a rigorous benchmark for the two approximate theories discussed in the previous section. In the second study, the equilibrium constant of a cis-trans isomerization of 1,2-difluroethylene and the isotopic substitution reaction of monohydrated chloride are calculated. We compare the thermodynamic quantities ΔH^0 and ΔS^0 obtained from this calculations against the experimental results to assess the ability of the present day electronic structure calculations to predict experimental results.

2.3.1 Triatomics

We have used the ‘exact’ potential energy surface of Mills and co-workers [64] for water and the surface of Stanton *et al.* [65] for F_2O for our calculations. For benchmarking the t-SCF and EHO results, we have carried out a full vibrational configurational interaction (FVCI) calculation on this surface, and, used the resultant eigenvalues and eigenfunctions to calculate numerically converged thermodynamic properties. We present in Fig. 2.1, ΔA vs. temperature, where

$$\Delta A \quad = \quad [A_{FVCI}(T) - A_{FVCI}(T=0)] - [A_a(T) - A_a(T=0)] \qquad (2.32)$$

for the three approximation schemes t-SCF, EHO and harmonic approximation to the partition function. The upper and lower panels in the figure display the data for the water and F_2O molecule respectively. Here $A(T=0)$ is the zero point energy of the system. The error in the three approaches increases in the sequence t-SCF $<$ EHO $<<$ HO. The t-SCF and EHO approaches are within 5% of the exact results, whereas the harmonic approximation is off by as much as $\sim$20%. Obviously both t-SCF and EHO approximations recover most of the effects of the anharmonic terms in the Hamiltonian on the free energy. The variation of internal energy (ΔU) and entropy (ΔS) against temperature is presented in Fig. 2.2 and Fig. 2.3, respectively. Again the t-SCF approximation is within 5% of the FVCI values. The EHO is close behind it. There is a curious trend noticeable here and in the other systems we have studied. It appears that the two variational theories (t-SCF and EHO) provide lower bounds on the entropy and internal energy such that the Helmholtz free energy itself is bounded from above as required by the variational condition. This would imply that the variational theories provide a tighter bound on U than on the product TS. We are not aware of any proof of this statement however.

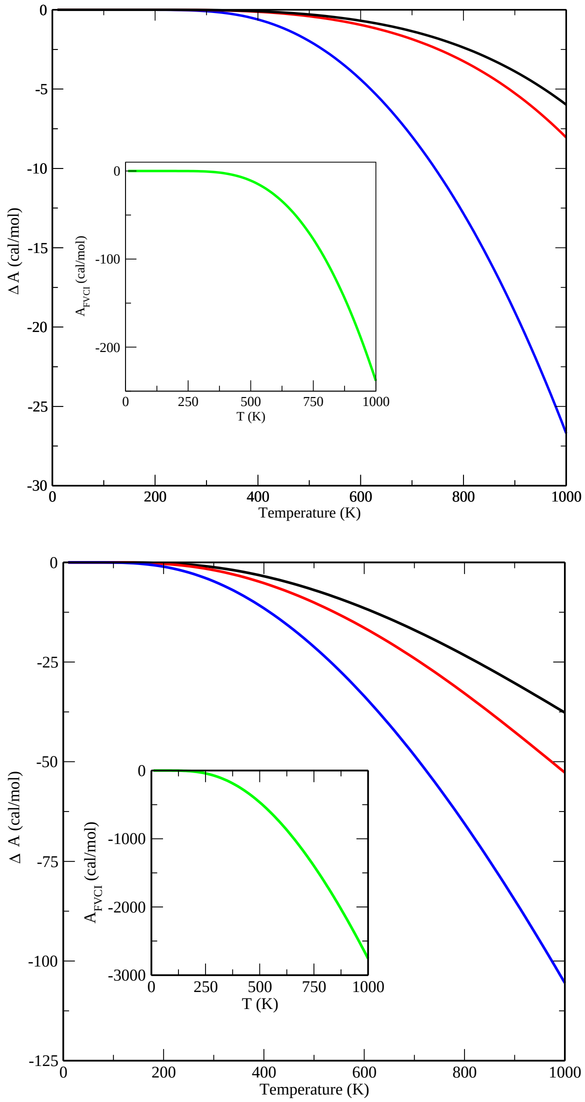

Fig. 2.1. Variation of the error ($\Delta A = [A_{FVCI}(T) - A_{FVCI}(T=0)] - [A_a(T) - A_a(T=0)]$) in the free energy against the temperature for the three approximation methods, t-SCF (black), EHO (red) and HO (blue). Inset is the converged free energy, $A_{FVCI} = A_{FVCI}(T) - A_{FVCI}(T=0)$. Upper and lower panel correspond to H_2O and F_2O respectively.

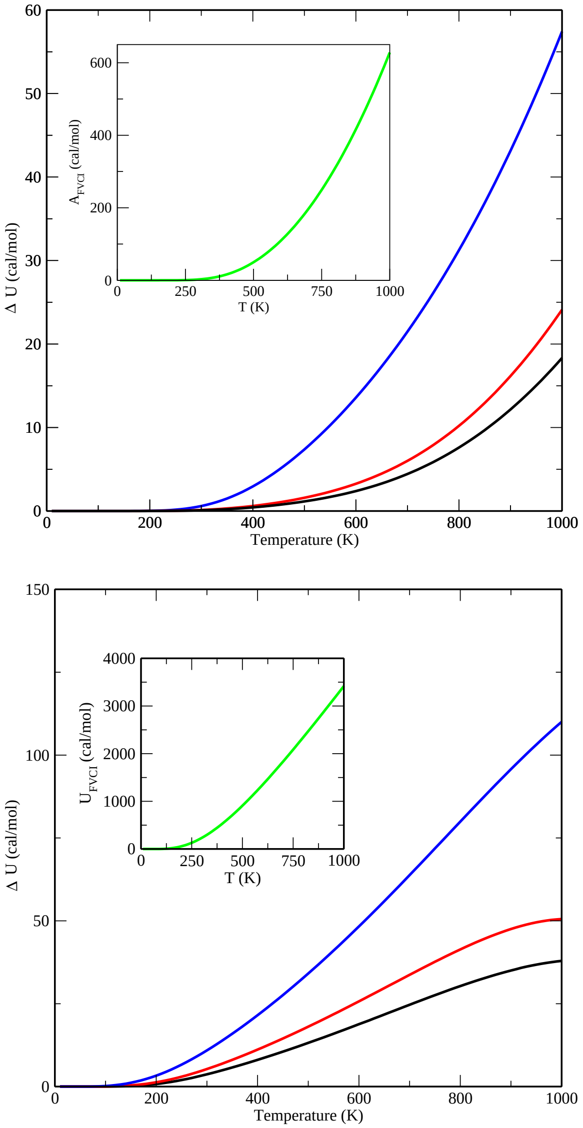

Fig. 2.2. Variation of the error ($\Delta U = [U_{FVCI}(T) - U_{FVCI}(T=0)] - [U_a(T) - U_a(T=0)]$) in the internal energy against the temperature for the three approximation methods, t-SCF (black), EHO (red) and HO (blue). Inset is the converged free energy, $U_{FVCI} = U_{FVCI}(T) - U_{FVCI}(T=0)$. Upper and lower panel correspond to H_2O and F_2O respectively.

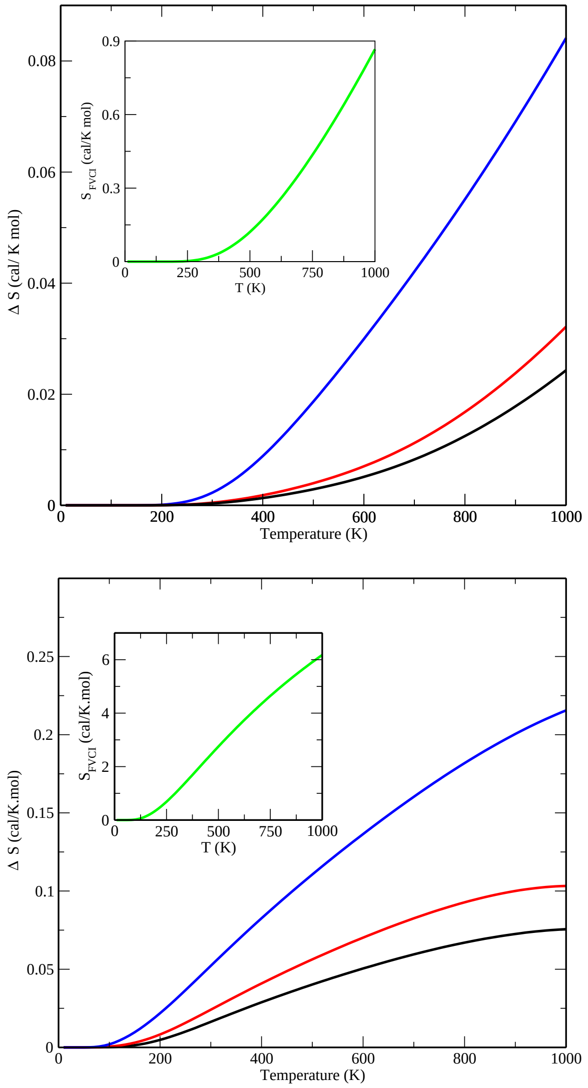

Fig. 2.3. Variation of the error ($\Delta S = [S_{FVCI}(T) - S_{FVCI}(T=0)] - [S_a(T) - S_a(T=0)]$) in the entropy against the temperature for the three approximation methods, t-SCF (black), EHO (red) and HO (blue). Inset is the converged free energy, $S_{FVCI} = S_{FVCI}(T) - S_{FVCI}(T=0)$. Upper and lower panel correspond to H_2O and F_2O respectively.

We next turn to the calculation of expectation values of other physical quantities. In Fig. 2.4 we present $\Delta < Q_1 >=< Q_1 >_{FVCI} - < Q_1 >_a$. Due to symmetry $< Q_1 >_{HO}$ is zero, and hence is not shown here. The variation of $< Q_1 >$ with temperature is very well reproduced by both t-SCF and EHO. The t-SCF is clearly superior to the EHO description over the entire temperature range considered for both the molecules. The expectation values of Q for mode 2 are presented in Fig. 2.5 where the same trend is noticed. The third mode does not belong to totally symmetric representation and hence its expectation values are always zero.

In Fig. 2.6, we present $\Delta < Q_1^2 >$ against temperature. Again the t-SCF results are in good agreement with FVCI and EHO approximation has a slightly higher error. Both these approaches provide a significant improvement over the HO approximation. Similarly, in Fig. 3.7 and Fig. 3.8, we present the $\Delta < Q_2^2 >$ and $\Delta < Q_3^2 >$ against temperature for the second and third mode, respectively. Once again the same agreement are noticed for all the cases.

2.3.2 Equilibrium constants

The calculations presented in this section have two goals. The first of them is to explore the importance of anharmonic effects on the thermodynamic properties of chemical equilibria and the ability of the separable approximations to estimate them quantitatively. The second goal is to investigate the ability of the presently available *ab initio* methods in reproducing the experimental data. We have chosen two simple reactions, the cis-trans isomerization of 1,2-diflouroethylene and isotopic substitution reaction $Cl(H_2O)^- + D_2O \rightleftharpoons Cl(D_2O)^- + H_2O$ for our study.

2.3.2.1 Cis-trans isomerization of 1,2-diflouroethylene

Craig and Entanmenn [66] measured the equilibrium constant for the first reaction in the temperature range of 477 K to 762 K and extracted ΔH^0 and ΔS^0

of the reaction using van't Hoff equation. Currently, several electronic structure programs [60,61] can calculate anharmonic force fields. We have used the Gaussian 03 package [60], where a quartic force field in normal coordinate is generated using Barone's algorithm [53]. We have used two different methods and four different basis sets for the electronic structure calculation.

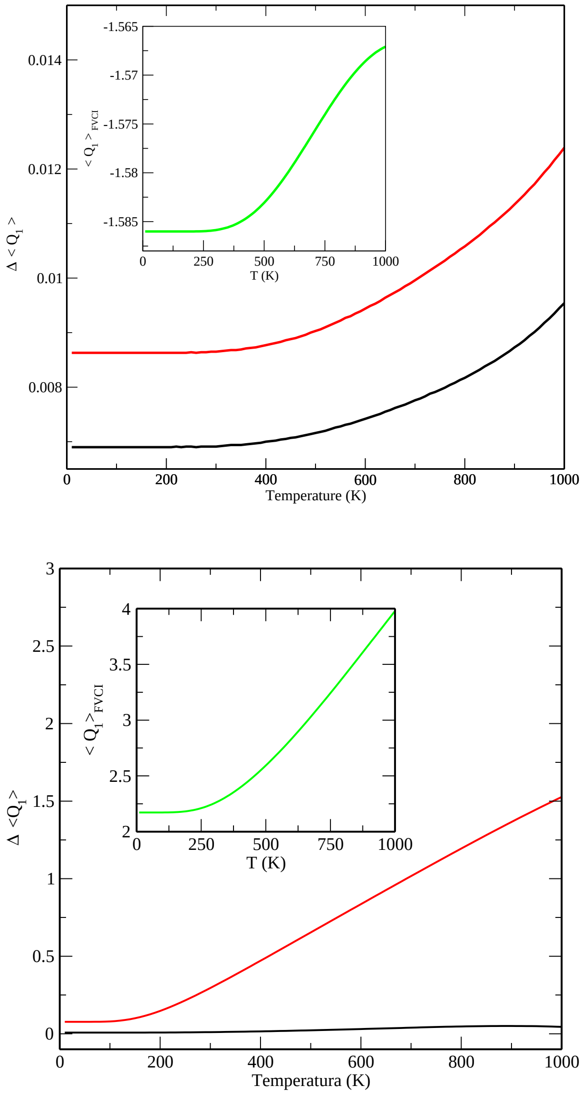

Fig. 2.4. Variation of the error ($\Delta\langle Q_1\rangle = \langle Q_1\rangle_{FVCI} - \Delta\langle Q_1\rangle_a$) in the expectation values of Q for mode 1 against the temperature for the two approximation methods, t-SCF (black) and EHO (red). Inset is the converged expectation value $\langle Q_1\rangle_{FVCI}$ for mode 1. Upper and lower panel correspond to H_2O and F_2O respectively.

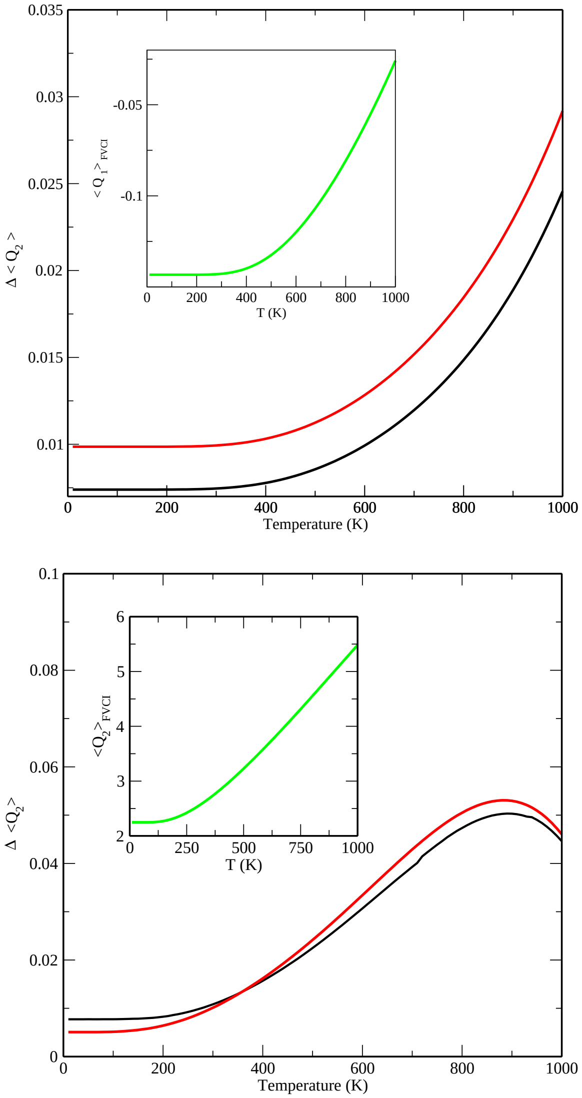

Fig. 2.5. Variation of the error ($\Delta\langle Q_2\rangle = \langle Q_2\rangle_{FVCI} - \Delta\langle Q_2\rangle_a$) in the expectation values of Q for mode 2 against the temperature for the two approximation methods, t-SCF (black) and EHO (red). Inset is the converged expectation value $\langle Q_2\rangle_{FVCI}$ for mode 2. Upper and lower panel correspond to H_2O and F_2O respectively.

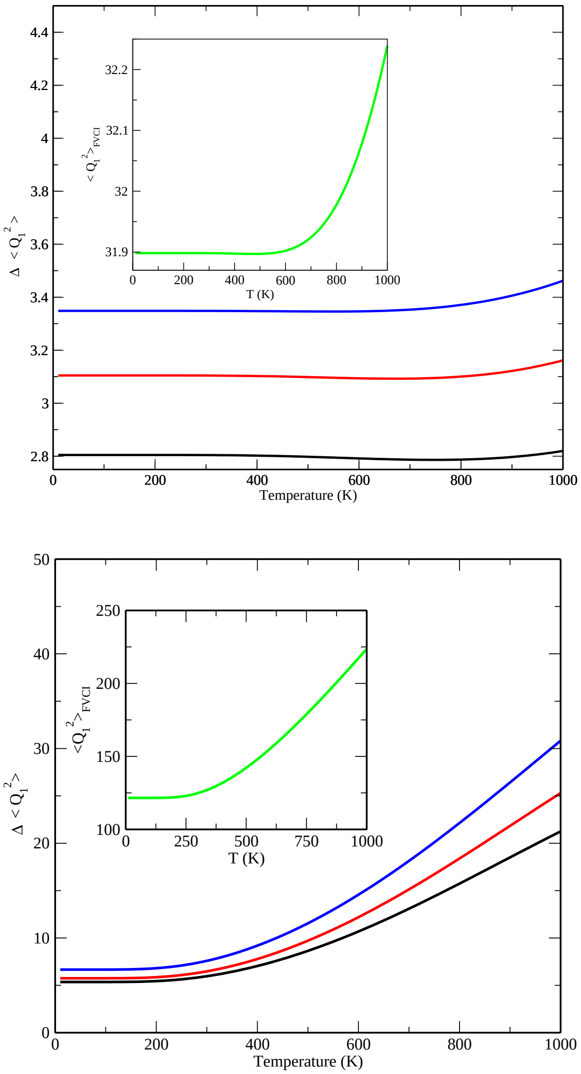

Fig. 2.6. Variation of the error $(\Delta\langle Q_1^2\rangle = \langle Q_1^2\rangle_{FVCI} - \Delta\langle Q_1^2\rangle_a)$ in the expectation values of Q^2 for mode 1 against the temperature for the three approximation methods, t-SCF (black), EHO (red) and HO (blue). Inset is the converged expectation value $\langle Q_1^2\rangle_{FVCI}$ for mode 1. Upper and lower panel correspond to H_2O and F_2O respectively.

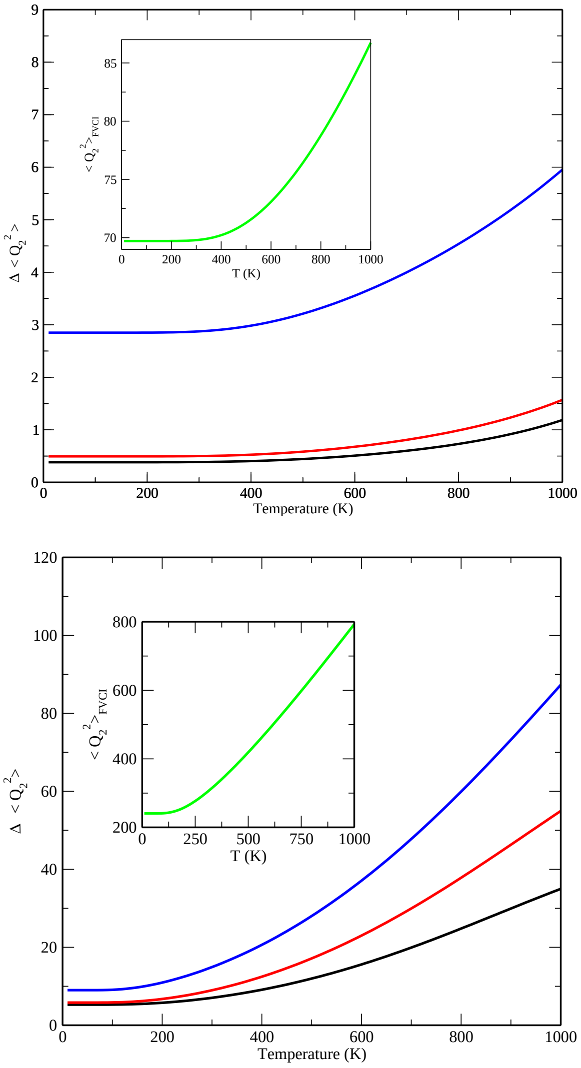

Fig. 2.7. Variation of the error ($\Delta\langle Q_2^2\rangle = \langle Q_2^2\rangle_{FVCI} - \Delta\langle Q_2^2\rangle_a$) in the expectation values of Q^2 for mode 2 against the temperature for the three approximation methods, t-SCF (black), EHO (red) and HO (blue). Inset is the converged expectation value $\langle Q_2^2\rangle_{FVCI}$ for mode 2. Upper and lower panel correspond to H_2O and F_2O respectively.

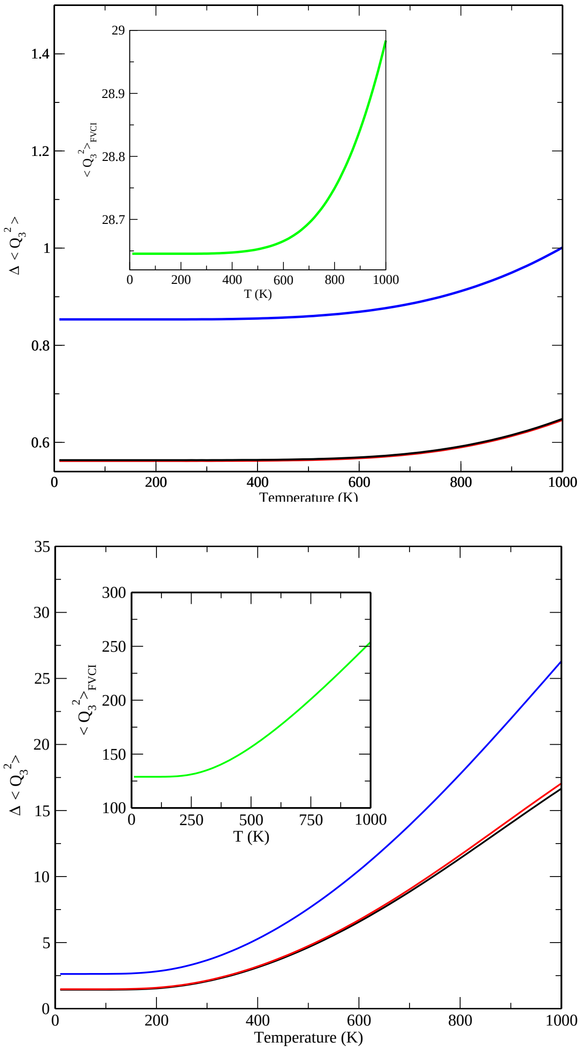

Fig. 2.8. Variation of the error ($\Delta\langle Q_3^2\rangle = \langle Q_3^2\rangle_{FVCI} - \Delta\langle Q_3^2\rangle_a$) in the expectation values of Q for mode 3 against the temperature for the two approximation methods, t-SCF (black) and EHO (red) and HO (blue). Inset is the converged expectation value $\langle Q_2^2\rangle_{FVCI}$ for mode 3. Upper and lower panel correspond to H_2O and F_2O respectively.

Table 2.1: **Enthalpy of isomerization for the cis-trans isomerization of 1,2-difluroethylene (cal/mol). Columns A, B, C and D represent the PES generated with the basis sets 6-31+g*, 6-311++g**, aug-cc-pVDZ and aug-cc-pVTZ respectively**

	B3LYP					MP2			
	A	B	C	D		A	B	C	D
HO	488.3	713.4	852.8	892.2		359.6	802.2	962.8	1135.5
EHO	500.6	723.0	867.0	897.3		369.2	808.2	985.4	1132.8
t-SCF	504.2	726.6	870.5	901.5		372.2	811.3	988.6	1136.8
Exp*					928				

* Ref. [66]

The DFT based methods, Becke three-parameter hybrid (B3) functional along with Lee-Yang-Parr (LYP) [67] correction and the second order Möller-Plesset perturbation theory (MP2) [15] with the aug-cc-pVDZ and aug-cc-pVTZ basis sets of Dunning [68] and 6-31+g* and 6-311++g** of Pople [69] were used. Geometries of the two molecules were optimized tightly and the ultrafine keyword was used in the DFT calculations following the recommendation of Barone [40].

Two sets of t-SCF calculations were made with 8 and 12 basis functions per mode to verify that the t-SCF results are converged with respect to basis set. The results of the 12 basis set calculation are presented here.

The equilibrium constants were calculated from the free energy over the temperature range of 470-760 K corresponding to the experimental conditions and the average enthalpy and entropy of the reaction were extracted using van't Hoff equation. The enthalpy values for the reaction are presented in Table 2.1. As can be seen, the enthalpy values from the DFT based potential energy surfaces underestimate the enthalpy of the reaction. The best result being the t-SCF result on the potential energy surface generated by B3LYP method with aug-cc-pVTZ basis. The error in this case is $\sim 3\%$. The anharmonic effects in this case appear to be small, about 9 cal/mol. The MP2 results are more erratic with the

Table 2.2: **Entropy of isomerization for the cis-trans isomerization of 1,2-difluroethylene (cal/K. mol). Columns A, B, C and D represent the PES generated with the basis sets 6-31+g*, 6-311++g**, aug-cc-pVDZ and aug-cc-pVTZ respectively**

	B3LYP					MP2			
	A	B	C	D		A	B	C	D
HO	0.061	0.103	0.071	0.086		0.022	0.066	0.077	0.085
EHO	0.171	0.206	0.191	0.132		0.193	0.185	0.237	0.188
t-SCF	0.176	0.211	0.195	0.138		0.195	0.188	0.239	0.194
Exp*					0.134				

* Ref. [66]

enthalpy values being underestimated by Pople basis sets and overestimated by the Dunning basis sets. The major source of the error in this case is in the electronic energy by the MP2 method. For example, the electronic energy difference between the two isomers is 1218 cal/mol by the MP2 method with aug-cc-pVTZ basis, while it is 981 cal/mol by the B3LYP method. The vibrational contribution to the ΔH^0 including zero point energy correction is -81 cal/mol and -80 cal/mol by the MP2 and B3LYP methods respectively at the t-SCF level.

The entropy values by the different approaches are presented in the Table 2.2. Unlike the reaction enthalpy, the entropy is completely determined by the ro-vibrational part of the Hamiltonian. Here again we find that the B3LYP generated potential energy surfaces fare better than the MP2 generated surfaces, with the EHO and t-SCF approximation falling within 3% of the experimental value. The entropy values are far more sensitive to the anharmonic effects than the enthalpy. The harmonic approximation to the entropy is off by about 30% from the experimental value. The entropy values on the MP2 generated surfaces have significant errors. While the harmonic approximation gives almost the same number for both the B3LYP and MP2 surfaces, both EHO and t-SCF approximations of the MP2 surfaces overestimate from the reaction entropy by more than 50%.

While the results presented here indicate that the DFT based approach gives thermodynamic properties closer to the experiment for this system, we believe it is more of an accident. There is not adequate computational evidence to suggest that the B3LYP approximation is better than the MP2 at this point and we would not like to put too much weight on this agreement.

2.3.2.2 An isotopic substitution reaction

As a second test, we have calculated equilibrium constant (K_{eq}) for the isotopic substitution reaction of monohydrated chloride ion by t-SCF method and compared the value with experimental and other available theoretical approaches. This involves the calculation of the differences in free energies and thus should be provided some insight into the cancellation of errors in such calculations. For a reaction like

$$Cl(H_2O)^- + D_2O \rightleftharpoons Cl(D_2O)^- + H_2O$$

strong hydrogen bonds between water and anions play a key role in solvation. The interactions are complex in nature due to the presence of soft vibrational modes. Thus, investigation of this system ought to be a good testing ground. The potential energy surfaces are generated by DFT based functional mPW1PW [70] method in conjunction with aug-cc-pVTZ basis set of Dunning [68] and using tight convergence with ultrafine numerical integration grid using Gaussian 03 package [60], similar to Ref. [51]. We have assumed that rotational and vibrational motions are decoupled and calculated the partition functions in this separable approximation. In Table 2.3, we present the equilibrium constant values at 298K by the present method and compare with the PI approach of Truhlar and coworkers [51] in the SCF approximation. As can be seen, all three theoretical values are identical to the second significant figure. This excellent agreement indicates that, the t-SCF method is as reliable as the PI method.

Table 2.3: **The equilibrium constant for the reaction** $Cl(H_2O)^- + D_2O \rightleftharpoons Cl(D_2O)^- + H_2O$ **by different methods at 298K.**

	PI[a]	t-SCF	Exp[b]
K_{eq}	0.945	0.937	0.76

[a] Ref. [51],
[b] Ref. [71].

2.3.3 Computational considerations

We next turn to the scaling of the computational resources needed for t-SCF theory. The CPU timing depends upon two parameters: number of basis functions (B) per mode and number of normal modes (N). The SCF Hamiltonian matrix construction goes as B^2N and matrix diagonalization goes to B^3N. The calculation of $< V - V_0 >$, the first order correction to the free energy which involves four mode summation for quartic terms, goes as $O(N^4)$. As a result, though the SCF calculation is linearly dependent on N, the calculation for free energy or enthalpy goes to $O(N^4)$ which cuts down the run time significantly compared to a full CI calculation. For FVCI, the Hamiltonian matrix calculation and diagonalization is of the order of B^{3N}.

To appreciate the scaling with respect to the number of vibrational modes, we have taken the force field from the Gaussian 03 [60] package using B3LYP method with 6-31G* basis of Pople [69] and calculated the thermodynamic properties A and U for several molecules in the temperature range of 0-1000 K in steps of 10 K. In all the calculations, the harmonic oscillator basis of the EHO was used for the t-SCF calculation with 8 basis functions per mode. The calculations were carried out on a Linux box (Intel 2.2 GHz Core2Duo CPU). Table 2.4 shows the variation of CPU timings with the increasing number of the vibrational degrees of freedom. As mentioned earlier, the $< V - V_0 >$ terms require upto four nested DO loops due to quartic potential, and the CPU timings go upto N^4 for both the

Table 2.4: **CPU timings for the calculation of thermodyamic properties of the vibrational subsystems by the t-SCF method for several molecules (in second).**

Molecule	No. of modes	t-SCF
Water	3	0.06
Formaldehyde	6	0.14
Trans-Diflouroethelene	12	0.46
Cyclobutene	18	1.24
Chlorobenzene	30	4.3
Napthalene	48	17.7
Anthracene	66	70.6
Tetracene	84	326

t-SCF and EHO. As can be seen, the CPU requirements by the t-SCF theory are quite modest.

2.4 Conclusions

In this chapter, we have derived the t-SCF method for the calculation of vibrational partition functions and thermal averages of molecular properties. We have also presented numerical results to indicate the accuracy of the method and its scaling with the size of the system. The method posits a separable ansatz for the thermal density matrix. The effective Hamiltonians that define the single particle density matrices are determined by the variational principle emanating from the Gibbs-Bogoluibov inequality. As a consequence, the free energy obtained from t-SCF theory is an upper bound to the exact free energy.

This formal property of the t-SCF theory is of immense practical implications. Experimentally one often measures the differences in the free energies, for example, in the determination of equilibrium constants. Having errors of the same sign in the computed free energies would imply that the errors would cancel at least partially rather than add up when the difference is taken. Since the differences in energies are expected to be small, this cancellation implies that the percentage of error in the differences is also reasonably small.

Since the t-SCF theory is based on a separable ansatz, the computational resources required for its implementation, scale almost linearly with the number of degrees of freedom. Indeed as we noted earlier, except for the calculation for the first order correction to the free energy, all the other steps scale linearly with the number of degrees of freedom. The first order correction term scales as N^4 for a quartic force field. However, it can be brought down to the order of N^2 if the quartic terms in the potential energy surface are restricted to semi-diagonal form, though the validity of this approximation is not known.

We have compared the performance of the t-SCF theory against converged FVCI results for water and F_2O on realistic potential energy surfaces. The t-SCF theory provides thermodynamic state functions and other thermal averages within a maximum error of about 5%.

Given that the t-SCF theory is capable of reproducing thermal averages with reasonable accuracy, we next used it to obtain the thermodynamic properties of two simple reaction with currently available *ab initio* potential energy surfaces. We found that the t-SCF theory can provide quantitative predictions for the thermodynamic state functions associated with the equilibria. Second, B3LYP method with aug-cc-pVTZ quality basis provides a good estimate of ΔH^0 and ΔS^0 of this reaction. On the other hand, the MP2 approximation gave erratic results for both reaction enthalpy and entropy. This result is probably fortuitous and additional studies are required to confirm this trend. The mPW1PW functional has not however provided such a good potential energy surface for the second reaction.

Chapter 3

Development of a New Variational Approach for Thermal Density Matrices

3.1 Introduction

Variational methods have a preeminent position in the calculation of thermal density matrices because of their ability to provide bounds to the free energy of the system [6]. Most of the variational method used to date are based on the Feynman variational principle [6] inherent in the Gibbs-Bogoluibov inequality (FGB) [59]

$$A \;\leq\; A_0 + \langle H - H_0 \rangle. \tag{3.1}$$

From an experimental perspective, one often observes differences in free energy rather than the absolute quantities. Since the error in a calculation using the FGB is always negative, the errors tend to cancel out to some extent when one calculates the differences. This is the main advantage of the FGB. This approach has been used recently by several authors to calculate the density matrices and other properties in the effective harmonic oscillator and self-consistent field approximation based on the independent particle model [37, 57]. Since the free energy is a global property, optimization of it does not always produce the associated density matrix with uniform accuracy over the entire configurational space. This is the essential limitation of the FGB variational principle.

There have been several attempts [31,35] in the recent past to develop methods for the calculation of the density matrix through the Bloch equation,

$$\frac{\partial \rho}{\partial \beta} + H\rho = 0. \tag{3.2}$$

Here β is the inverse temperature $1/k_BT$. The density matrix is represented as superposition of gaussian wave packets (GWP). Frantsuzov *et al.* [31] have invoked the least action variational principle to determine the equations of motion for the parameters of the gaussians. On the other hand, Militzer and Pollock [35] have used McLachlan like variational principle [36] to determine the equations of motion. These approaches require numerical integration of the differential equations inherent in Eq. (3.2) to obtain the parameters of the gaussians from some starting temperature (T), typically $T = \infty$.

The goal of the present work is to develop a McLachlan type variational principle [36] for the thermal density matrix that is free of numerical integration of ordinary diffrential equations for the parameters. In the process, we arrive at a variational principle that is based on the minimization of the error in $\dot{\rho}$ rather than the free energy. By choosing a suitable anzatz for the density matrix, it is possible to derive a variational principle for the density matrix directly without going through the free energy route. Such a variational procedure is discussed in Sec. 3.2. We explore the reliability and the efficiency of the variational principle within the framework of a separable approximation to the density matrix in Sec. 3.3. Sec. 3.4 contains a few concluding remarks.

3.2 The variational principle

3.2.1 Preliminary remarks

We begin our analysis with the quantity,

$$I(\dot{\rho}) = Tr[\dot{\rho} + H\rho]^2, \tag{3.3}$$

as a functional of $\dot{\rho} = \partial\rho/\partial\beta$. When $\dot{\rho}$ satisfies the Bloch equation,

$$\dot{\rho} = -H\rho, \tag{3.4}$$

$I(\dot{\rho}) = 0$. Since I is a positive definite functional, one can minimize it with respect to $\dot{\rho}$ to obtain the best possible solution for ρ. This gives us

$$Tr[\delta\dot{\rho}\ (\dot{\rho} + H\rho)] = 0. \tag{3.5}$$

Upto this extent we have followed the route of the McLachlan variational principle [36]. At this point we posit the ansatz

$$\rho = e^{-\beta H_0}, \tag{3.6}$$

for the density matrix. H_0 is the Hamiltonian of the model system that mimics the original system. The parameters in H_0 are chosen to provide the best possible description. It follows

$$\dot{\rho} = -H_0\ \rho, \tag{3.7}$$

and, to first order,

$$\delta\dot{\rho} = -\delta H_0\ \rho. \tag{3.8}$$

Substituting Eq. (3.7) and (3.8) in to Eq. (3.5) and dividing with $Tr\ \rho\rho$, we arrive at

$$\frac{Tr[\delta H_0\ \rho(H-H_0)\rho]}{Tr\ \rho\rho}=0. \tag{3.9}$$

Eq. (3.9) is the working equation for determining ρ by the present approach. Note that, in the limit $H \rightarrow H_0$, the density matrix would be exact.

Eq. (3.9) is not manifestly hermitian. Consequently, in an approximate calculation, ρ may not turn out to be hermitian. Eq. (3.4) and (3.7) can be written as

$$\dot{\rho}=-\frac{1}{2}(H\rho+\rho H) \tag{3.10}$$

and

$$\dot{\rho}=-\frac{1}{2}(H_0\rho+\rho H_0) \tag{3.11}$$

respectively. Similarly

$$\delta\dot{\rho}=-\frac{1}{2}(\delta H_0\rho+\rho\delta H_0). \tag{3.12}$$

Thus Eq. (3.5) becomes

$$Tr[\delta H_0\rho+\rho\delta H_0][(H-H_0)\rho+\rho(H-H_0)]=0. \tag{3.13}$$

From this we arrive at the symmetric form of Eq. (3.9).

$$\frac{Tr\ \delta H_0[2\rho(H-H_0)\rho+(H-H_0)\rho\rho+\rho\rho(H-H_0)]}{Tr\ \rho\rho}=0. \tag{3.14}$$

Eq. (3.9) and Eq. (3.14) consist of a set of non-linear equations for the parameters appearing in the model Hamiltonian H_0. This equation must be solved iteratively, from a set of guess values for the parameters in H_0. Note that, these equations are algebric equations unlike the differential equations that appear in Ref. [31] and [35].

3.2.2 General separable ansatz for ρ

We now turn to the parametrization of the model Hamiltonian H_0. As essential requirement for defining H_0 is that, it should be possible to construct the associated density matrix easily. One such model Hamiltonian is the independent particle model Hamiltonian.

$$H_0 = \sum_k h_k + E_0, \tag{3.15}$$

where each h_k is an effective single particle Hamiltonian,

$$h_k = T_k + U_k(Q_k). \tag{3.16}$$

Here T_k is the kinetic energy of the k^{th} particle and $U_k(Q_k)$ is the corresponding potential energy term as a function of coordinate Q_k. As a consequence, the density matrix assumes the multiplicatively separable form

$$\rho = \prod_k \rho_k \; exp[-\beta E_0], \tag{3.17}$$

where the effective single particle density matrix ρ_k is defined as

$$\rho_k = exp[-\beta h_k]. \tag{3.18}$$

Given the ansatz for H_0 and ρ, the working Eqs. (3.9) and (3.14) give identical results and yield

$$U_k(Q_k) = \frac{Tr_{l\neq k}\, V\; exp\,(-2\beta \sum_{l\neq k} h_l)}{Tr_{l\neq k}\; exp\,(-2\beta \sum_{l\neq k} h_l)}. \tag{3.19}$$

The algorithm for the calculation of the density matrix consists of the following steps. Starting from an initial set of single particle Hamiltonians and the associated eigenstates for each degree of freedom, one constructs U_k from Eq. (3.19).

Given U_k, one solves the eigenvalue problem,

$$h_k \phi_n^k = \varepsilon_n^k \phi_n^k. \tag{3.20}$$

From these, ρ_k is obtained as,

$$\rho_k(\beta) \;=\; \sum_n |\phi_n^k\rangle \; exp(-\beta\varepsilon_n^k) \; \langle\phi_n^k|. \tag{3.21}$$

The steps are iterated until the density matrix or some other associated property such as free energy converges. Note that the procedure is similar to the thermal self-consistent field theory [72] from FGB variational principle described with previous chapter. The primary difference between the two approaches is the weighing factor used to average the many body interaction in Eq. (3.19). In the present approach the statistical factor is $\rho(2\beta)$ whereas in the FGB approach it is $\rho(\beta)$.

3.2.3 Effective harmonic oscillator

In the last chapter, we have shown how the EHO approximation for thermal ansatz [72] worked well for vibrational systems. In this section we again test the reliability of the EHO approximation by the present method using the ansatz stated for thermal density matrix. As stated earlier, EHO is a special case of the VSCF theory where the effective potentials that define the single particle Hamiltonians h_k are restricted to quadratic terms,

$$U_k \;=\; \frac{1}{2} w_k (Q_k - Q_k^0)^2. \tag{3.22}$$

Here the single particle Hamiltonians are HO Hamiltonians and associated single particle thermal density matrices are available the in analytical form as stated ealier in Eq. (2.29). The variational parameters for this particular case are once again the displacements Q_k^0 and the frequencies w_k. The working equations for our new variational principle are derived using equation Eq. (3.14). The general form of the equation for Q_k^0 and w_k are given by

$$\begin{aligned} Q_k^0 &= -\frac{1}{2\ f_{kk}}\Bigg[\sum_{j\leq i} f_{kji}\ g_{kji}\ Q_i^0 Q_j^0 + \sum_{j\leq i\leq l} f_{kjil}\ g_{kjil} Q_i^0 Q_j^0 Q_l^0 \\ &\quad + \sum_j f_{kjj}\ g_{kj} \frac{1}{2w_j tanh(\beta w_j)} + \sum_{j\neq i} f_{kjji}\ g_{kji} \frac{Q_i^0}{2w_j tanh(\beta w_j)}\Bigg] \end{aligned} \tag{3.23}$$

$$\begin{aligned} w_k^2 &= 2f_{kk} + 2\sum_j f_{kkj}\ g_{kj}\ Q_j^0\ + 2\sum_{j<i} f_{kkji}\ g_{kji}\ Q_j^0 Q_i^0 \\ &\quad + 5 f_{kkkk} \frac{1}{w_k tanh(\beta w_k)}\left[\frac{3-1.2\ tanh^2(\beta w_k)}{3 - tanh^2(\beta w_k)}\right] \\ &\quad + \sum_{j\neq k} f_{kkjj}\ g_{kj}\ \frac{1}{w_j tanh(\beta w_j)} \end{aligned} \tag{3.24}$$

g_{ij} *etc.* are the combitorial factors. Those arise when the averaged over terms are picked out of the product of the operators. The overall optimized thermal density matrix still satisfies Eq. (3.17).

3.3 Numerical studies

To assess the reliability of the new variational principle described above, we have implimented it for calculating thermal properties of a multidimensional anharmonic oscillators representing the vibrations of two polyatomic molecule F_2O and H_2O. The anharmonic potential energy surfaces are taken from the Ref. [64, 65]. It is of the form

$$V(Q) = \sum_i f_{ii} Q_i^2 + \sum_{i\leq j\leq k} f_{ijk} Q_i Q_j Q_k + \sum_{i\leq j\leq k\leq l} f_{ijkl} Q_i Q_j Q_k Q_l\ . \tag{3.25}$$

As a consequence of this, the single particle effective potentials by the separable ansatz corresponding to Eq. 3.19,

$$U_k(Q_k) \;=\; u_k^{(1)}\;Q_k + u_k^{(2)}\;Q_k^2 + u_k^{(3)}\;Q_k^3 + u_k^{(4)}\;Q_k^4. \tag{3.26}$$

The working equations for the parameters $u_k^{(n)}$ obtained from Eq. (3.15) and (3.16) are

$$\begin{aligned} u_k^{(1)} \;=\; & \sum_{j<i\neq k} f_{kji}\langle Q_j\rangle_{2\beta}\langle Q_i\rangle_{2\beta} + \sum_{j\neq k} f_{kjj}\langle Q_j^2\rangle_{2\beta} + \sum_{j<i<l\neq k} f_{kjil}\langle Q_j\rangle_{2\beta}\langle Q_i\rangle_{2\beta}\langle Q_l\rangle_{2\beta} \\ & + \sum_{j\neq i\neq k} f_{kjji}\langle Q_j^2\rangle_{2\beta}\langle Q_i\rangle_{2\beta} + \sum_{j\neq k} f_{kjjj}\langle Q_j^3\rangle_{2\beta}, \end{aligned} \tag{3.27}$$

$$u_k^{(2)} = f_{kk} + \sum_{j\neq k} f_{kkj}\langle Q_j\rangle_{2\beta} + \sum_{j\neq k} f_{kkjj}\langle Q_j^2\rangle_{2\beta} + \sum_{j\neq i\neq k} f_{kkji}\langle Q_j\rangle_{2\beta}\langle Q_i\rangle_{2\beta}, \tag{3.28}$$

$$u_k^{(3)} \;=\; f_{kkk} + \sum_{j\neq k} f_{kkkj}\langle Q_j\rangle_{2\beta}, \tag{3.29}$$

$$u_k^{(4)} \;=\; f_{kkkk}. \tag{3.30}$$

Note that, Eqs. (3.27-3.30) are essentially the quantum mechanical vibrational self-consistent field (VSCF) equation generalized to finite temperature. In these equations, $\langle Q_l^n\rangle_{2\beta}$ are the thermal averages at 2β

$$\langle Q_l^n\rangle_{2\beta} \;=\; \frac{Tr\;Q_l^n\;exp\;(-2\beta h_l)}{Tr\;exp\;(-2\beta h_l)}. \tag{3.31}$$

After constructing the single particle effective potentials, the eigenfunctions and eigenvalues of the single particle Hamiltonians h_k are obtained. The eigenfunctions ϕ_n^k are expanded in a suitable HO basis of the form of

$$\phi_n^k = \sum_m \chi_m^k C_{mn}. \tag{3.32}$$

With this substitution, Eq. (3.20) is converted into a matrix eigenvalue problem which can be solved by the usual numerical methods.

Once the thermal modals ϕ_n^k are obtained, they are used to construct the thermal density matrices associated with each normal mode (Eq. (3.21)), and the thermal traces required in Eq. (3.31) are evaluated using these density matrices. Thus, Eq. (3.31) is explicitly given by

$$\langle Q_l^n \rangle_{2\beta} = \frac{\sum_m \langle \phi_m^l | Q_l^n | \phi_m^l \rangle \; exp(-2\beta \varepsilon_m^l)}{\sum_m \; exp(-2\beta \varepsilon_m^l)}. \tag{3.33}$$

The working equations for the EHO model are presented in Eq. (3.23, 3.24).

3.3.1 Triatomics

To test the accuracy of the present approach, we have carried out converged full vibrational configurational interaction (FVCI) calculation to obtain the numerically converged properties. In the Fig. 3.1, we plot free energy, $A - A(0)$ (where $A(0)$ is the free energy at $T = 0$) of F_2O (upper panel) and H_2O (lower panel) against temperature by the present method (SCF and EHO), FGB (SCF and EHO) and FVCI. As can be seen, the free energy by the present method resembles with FGB to a good extent, and it is difficult to distinguish them throughout the temperature range considered. At very high temperature it gives marginally higher value than the FGB approach. Note that, the FGB approximation specifically minimizes the free energy, whereas the present formalism optimizes the derivatives of the density matrix. The present results are very close behind the FVCI results, and the error is less than 2%-3% even at 1000K. In Fig. 4.2 and 4.3 we present the internal energy $(U - U(0))$ and entropy $(S - S(0))$ against temperature. Again the present approach produces results very similar to the FGB based approach. The error in U and S with respect to the FVCI is less than 3% at 1000K.

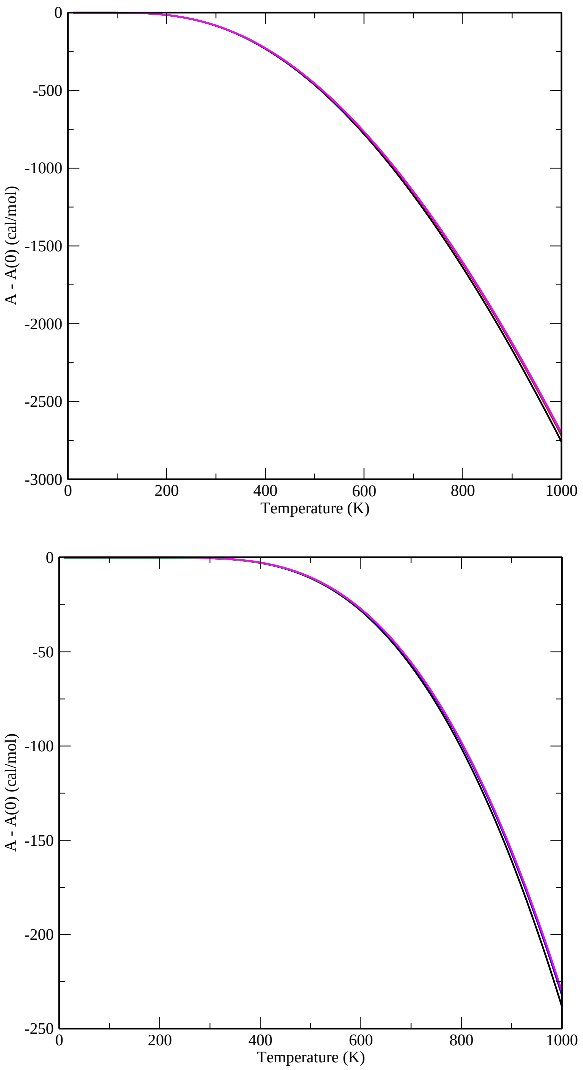

Fig. 4.1. Free energy (A - A(0)) against the temperature (T) by present method (EHO: magenta, SCF: blue), FGB (EHO: green, SCF: red) and FVCI (black). Upper and lower panel correspond to F_2O and H_2O respectively

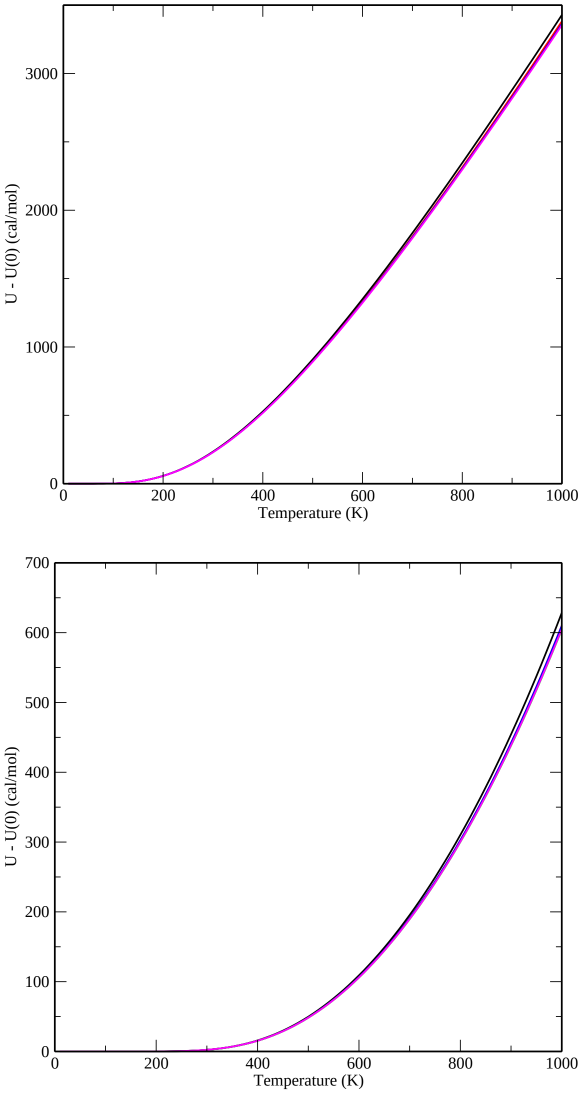

Fig. 4.2. Internal energy (U - U(0)) against the temperature (T) by present method (EHO: magenta, SCF: blue), FGB (EHO: green, SCF: red) and FVCI (black). Upper and lower panel correspond to F_2O and H_2O respectively

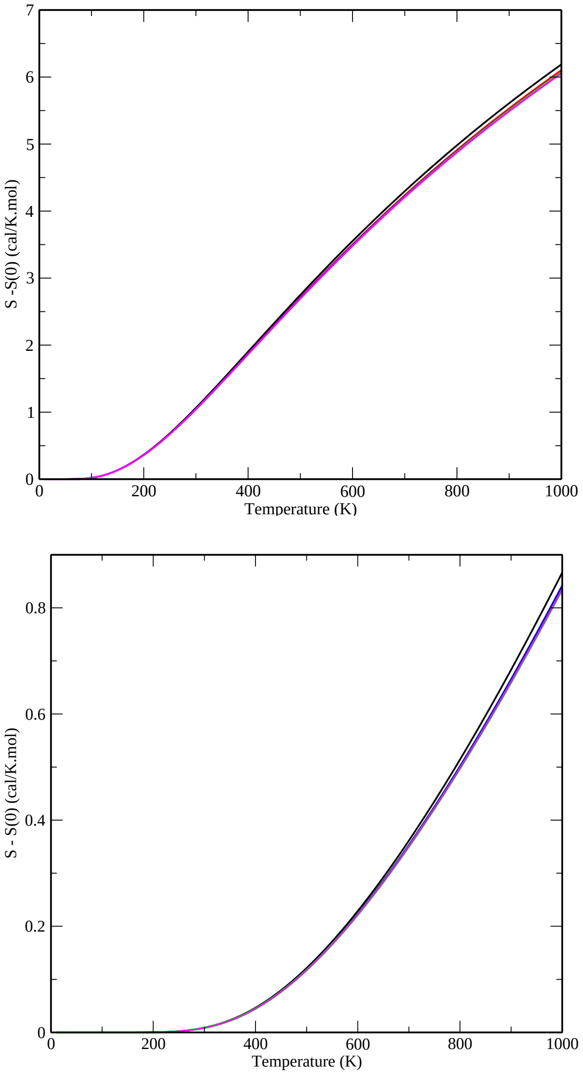

Fig. 4.3. Entropy (S - S(0)) against the temperature (T) by present method (EHO: magenta, SCF: blue), FGB (EHO: green, SCF: red) and FVCI (black). Upper and lower panel correspond to F_2O and H_2O respectively

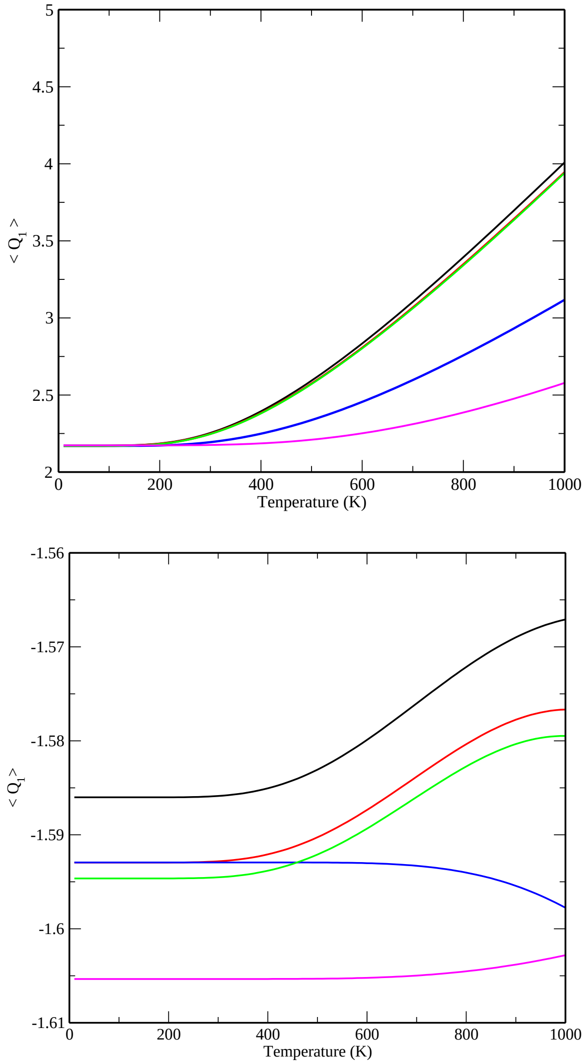

Fig. 4.4. Thermal averagre of Q_1 against the temperature (T) by present method (EHO: magenta, SCF: blue), FGB (EHO: green, SCF: red) and FVCI (black). Upper and lower panel correspond to F_2O and H_2O respectively

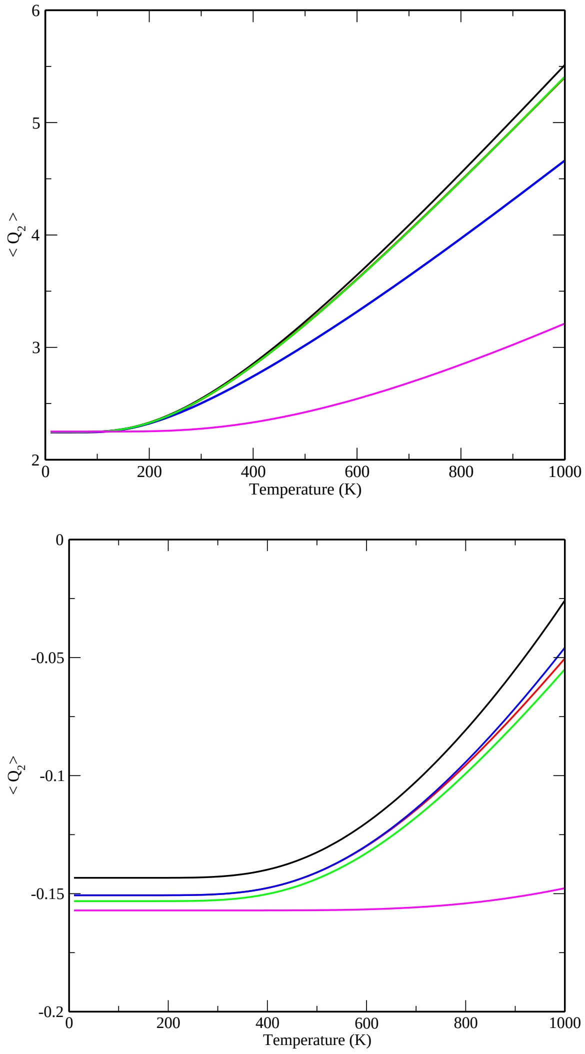

Fig. 4.5. Thermal averagre of Q_2 against the temperature (T) by present method (EHO: magenta, SCF: blue), FGB (EHO: green, SCF: red) and FVCI (black). Upper and lower panel correspond to F_2O and H_2O respectively

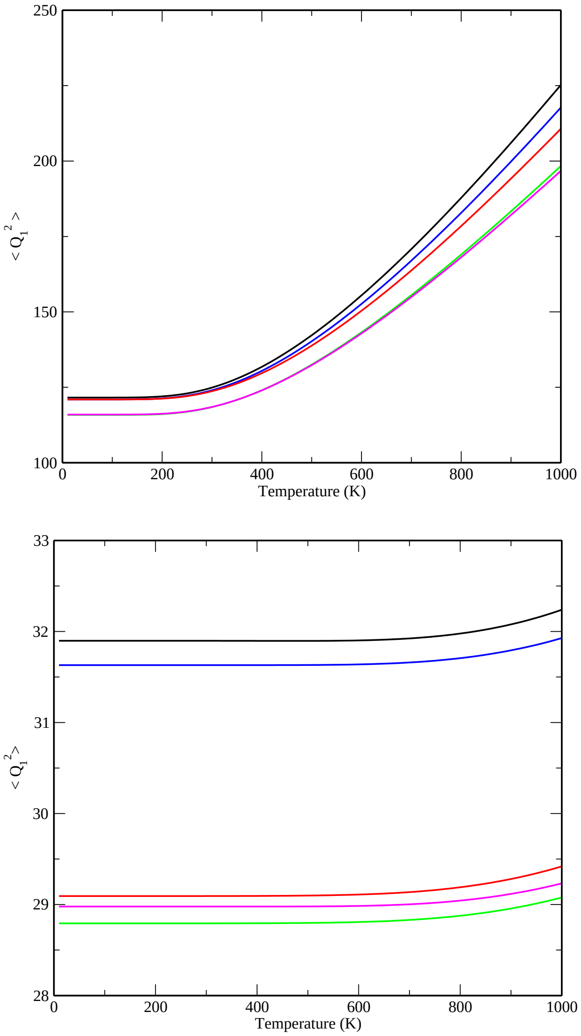

Fig. 4.6. Thermal averagre of Q_1^2 against the temperature (T) by present method (EHO: magenta, SCF: blue), FGB (EHO: green, SCF: red) and FVCI (black). Upper and lower panel correspond to F_2O and H_2O respectively

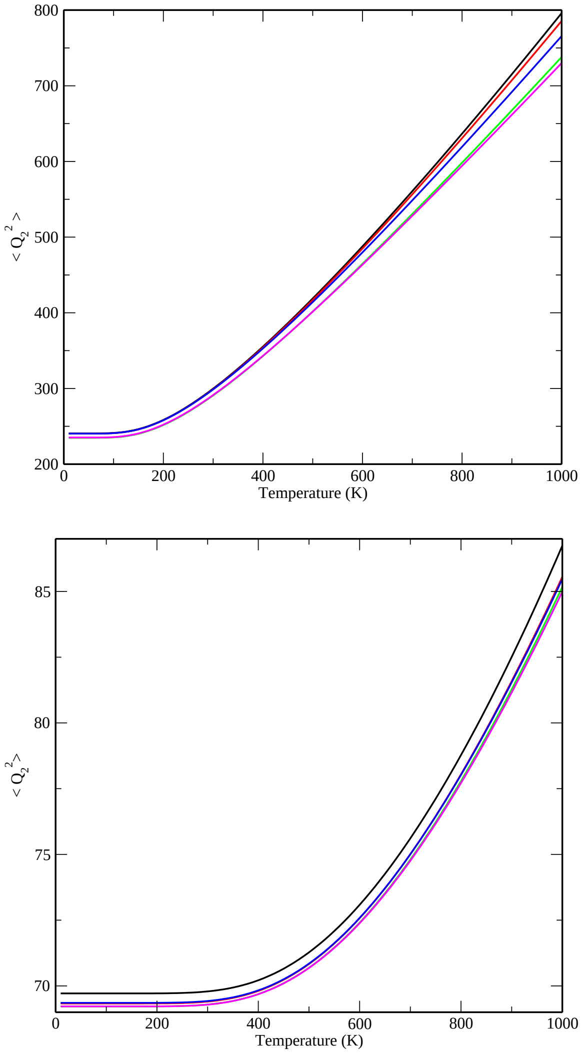

Fig. 4.7. Thermal averagre of Q_2^2 against the temperature (T) by present method (EHO: magenta, SCF: blue), FGB (EHO: green, SCF: red) and FVCI (black). Upper and lower panel correspond to F_2O and H_2O respectively

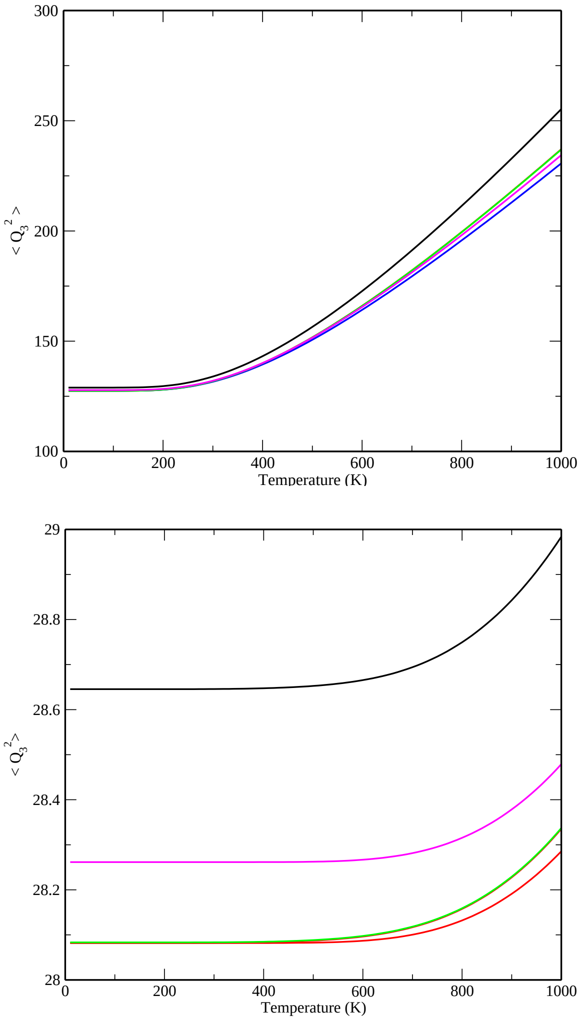

Fig. 4.8. Thermal averagre of Q_3^2 against the temperature (T) by present method (EHO: magenta, SCF: blue), FGB (EHO: green, SCF: red) and FVCI (black). Upper and lower panel correspond to F_2O and H_2O respectively

We next turn to the calculation of the thermal averages of other non thermodynamic quantities. We plot the thermal average of displacement of the first vibrational mode as a function of temperature in Fig. 4.4. The present formalism consistently underestimates the thermal averages $< Q_1 >$. The same trend is noticed for $< Q_2 >$ plotted in Fig. 4.5. In Fig. 4.6, we present $< Q_1^2 >$ against temperature. The agreement with FGB is better in this case. In Fig. 4.7 and Fig. 4.8 $< Q_2^2 >$ and $< Q_3^2 >$ are plotted against temperature, respectively. Once again the thermal avarages of $< Q^2 >$ for mode 2 and 3 give better agreement with FGB. The quality of EHO results by the new variational principle is noticeably bad compared to the SCF results.

3.3.2 Equilibrium constants

We have calculated equilibrium constant (K_{eq}) using the present formalism for the SCF approach for the reaction

$$Cl(H_2O)^- + D_2O \ \ \rightleftharpoons \ \ Cl(D_2O)^- + H_2O$$

by the new variational principle. The equilibrium constant turns out to be 0.934 against the FGB of 0.937. It thus appears that the present approach can estimate the differences in the free energies as well as the FGB aproach.

3.3.3 Computational efficiency

We next explore the computational efficiency of the new approach against the FGB approach. As stated earlier, the new formalism is constructed such a way that it uses a statistical factor of $\rho(2\beta)$ for the calculation of the temperature dependent effective single particle potential, whereas, FGB uses $\rho(\beta)$. Consequently, we expect the calculation based on the new formalism converge rapidly than FGB for each target temperature. One simple parameter that reflects this convergence is the number of SCF iterations for both the methods. In Fig. 3.9, we present the number of iterations at a given temperature for formic acid dimer (FAD). It is a floppy molecule which ought to give good insight for our purpose. The quartic potential energy surface for FAD is calculated by Gaussian 03 package [60] in DFT based B3LYP [67] method with the aug-cc-pVTZ basis set of Dunning [68] using tight convergence and ultrafine numerical integration grids. As can be seen the present formalism takes far fewer number of iterations than FGB and consequently it is significantly faster than FGB. Thus within the acceptable accuracy level this new variational principle can be used for very large molecules and molecules with soft vibrations.

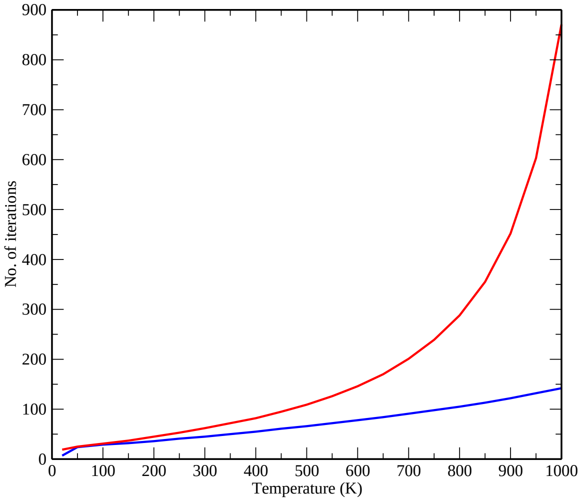

Fig. 3.9. Number of SCF iterations to converge the thermal modals against the temperature (T) for present method (blue) and FGB (red).

3.4 Conclusions

In this paper we have developed a new variational method for the thermal density matrices inspired by the McLachlan variational principle of time dependent quantum mechanics. The approach minimizes the trace of the mean square of the difference between the derivatives of the exact and model density matrices with respect to the parameters in the model Hamiltonian. As a consequence of the minimization of the mean squar error, the effective potentials that determine the thermal modals in the independent particle model for the density matrix are constructed as the thermal averages of the many body potential at 2β. The final density matrix is constructed at β however.

We have tested the validity of the new formalism to calculate the thermodynamic functions and thermal averages of Q and Q^2 and compared it with the well established FGB variational principle on two model systems. All the thermodynamic state functions such as free energy, internal energy and entropy calculated by the present approach gives almost identical results with FGB. The thermal averages of Q and Q^2 consistently underestimated.

Since the present theory is applied on a separable ansatz, the computational resources required for it scales almost linearly with the number of degrees of freedom. We have found that the present approach requires far fewer number of iterations to converge compared to the FGB approach.

Chapter 4

Effective Harmonic Oscillator Description of Anharmonic Molecular Vibrations

4.1 Introduction

The work presented in this chapter grew out of our observation that the effective harmonic oscillator (EHO) approach gives results nearly as good as the SCF approximation. This brought forth the question whether the EHO can describe the individual molecular eigenstates equally well? This question is relevant because the density matrix is dominated by the ground state due to the Boltzman factor. So, the error in the excited state energies and wave functions may not be that important for its calculation. This work was carried out to answer this question. Several methods have been developed to solve the Schrödinger equation for anharmonic molecular vibrations. Prominent among them is the vibrational self consistent field (VSCF) approach [19, 20, 73]. Recently Gerber and co-workers described a procedure to accelerate the correlation corrected VSCF calculations for large molecules [74, 75]. Bowman and co-workers have developed three programs for carrying out such VSCF calculations [76–78]. Most of these earlier works do not incorporate the Coriolis coupling terms in the self consistent field (SCF) procedure. Carter *et al.* [77] and more recently Rauhut [79] discussed the possibilities of including the Coriolis coupling in the SCF procedure itself.

The VSCF approximation is based on a separable ansatz. The N-mode trial wave function is parameterized as

$$\Psi(q_1, q_2.....q_n) \quad = \quad \prod_i \Phi^i_{n_i}(q_i) \tag{4.1}$$

where the one mode wave functions $\Phi^i_{n_i}$ are called modals. In a typical calculation, each of the modal is expanded in a basis as

$$\Phi^i_n = \sum_m \chi^i_m C_{mn} \tag{4.2}$$

The basis functions are usually orthogonal harmonic oscillator (HO) eigenfunctions. These functions are normally centered at the equilibrium point of the potential and the widths of the HO eigenfunction are chosen to match the zeroeth order frequencies of the potential [80, 81].

As a secondary goal, we assess the importance of the Coriolis coupling at the level of SCF procedure itself for non-rotating states.

The VSCF equations in the presence of Coriolis coupling are presented in Section 4.2 and the construction of variationally optimized harmonic oscillator basis (VOHB) is presented in Section 4.3. After a brief discussion of the program in Section 4.4 some illustrative results are presented in Section 4.5. Section 4.6 summarizes our conclusions.

4.2 The VSCF theory including Coriolis coupling

In mass weighted normal coordinate representations, the Watson Hamiltonian [10] for a non-rotating ($J = 0$) molecule is

$$H = \frac{1}{2}\sum_{i=1}^{N} P_i^2 - \frac{\hbar^2}{8}\sum \mu_{\alpha\alpha} + \frac{1}{2}\sum_{\alpha\beta} \mu_{\alpha\beta}\pi_\alpha\pi_\beta + V(Q). \tag{4.3}$$

Here, the first term is the pure vibrational kinetic energy term. The second one is the so called Watson mass term. The indices α and β refer to the x, y and z components of Cartesian coordinates, and $\mu_{\alpha\beta}$ are the components of the inverse effective moment of inertia tensor at a given point on the potential energy surface (PES). π_α is the α^{th} component of the vibrational angular momentum and is given by

$$\pi_\alpha = \sum_{i>j} \xi_{ij}^{\alpha}\left(Q_i P_i - Q_j P_j\right), \tag{4.4}$$

where ξ_{ij}^{α} are the Coriolis coupling constants. Two approximations are made in defining the parameters of the Hamiltonian (4.3) in our calculations. First, the potential is taken to be a quartic polynomial in Q_i,

$$V(Q) = \sum_i f_{ii} Q_i^2 + \sum_{i\le j\le k} f_{ijk} Q_i Q_j Q_k + \sum_{i\le j\le k\le l} f_{ijkl} Q_i Q_j Q_k Q_l\,. \tag{4.5}$$

Second, following the earlier works [80, 82], the moment of inertia is taken to be a constant. As stated earlier, a Hartree product of single-mode wave functions is taken as VSCF variational ansatz. Minimization of the total energy with respect to the modal functions $\Phi_{n_i}^{i}(Q_i)$ of Eq.(4.1) gives the working equations. The general form of these equations for mode i is

$$(h_i^{vscf} - \varepsilon_{n_i}^{(i)})\ \Phi_{n_i}^i(Q_i) = 0\ , \tag{4.6}$$

where the h_i^{vscf} is given by

$$h_i^{vscf} \quad = \quad -\frac{1}{2m_i}\left(\frac{d^2}{dQ_i^2}\right) + \sum_{n\ =\ 1}^{4} u_i^{(n)} Q_i^n + u_0\ . \tag{4.7}$$

Here the effective mass m_i is given by the equation

$$m_i^{-1} = \big[1 + 2\sum_j \zeta_{jiji}\langle Q_j^2\rangle + 2\sum_{j\leq k}\zeta_{jiki}\langle Q_j\rangle\langle Q_k\rangle\big], \tag{4.8}$$

and the ζ matrix is defined as

$$\zeta_{ijkl} = \sum_{\alpha}\ \xi_{ij}^{\alpha}\ I_{\alpha\alpha}^{-1}\ \xi_{kl}^{\alpha}, \tag{4.9}$$

where $I_{\alpha\alpha}$ are the moments of inertia along the principle axes of the molecule and ξ_{ij} are the coupling parameters that define the vibrational angular momentum. Note that the effective mass in Eq.(4.8) appears due to Coriolis coupling. Since the Coriolis coupling term is a product of both position and momentum operators [cf., Eqs.(4.3, 4.4)], its partial averages lead to an effective kinetic energy operator and an additional quadratic potential term to the SCF Hamiltonian. The additional kinetic energy operator manifests itself in the form of an effective mass term in the SCF Hamiltonian. This effective mass goes to unity in the absence of Coriolis coupling. The coefficients $u_i^{(n)}$ are the coefficients of Q_i^n in the SCF potential,

$$u_o = \frac{1}{2}\sum_{i,j}\zeta_{ijji}, \tag{4.10}$$

$$u_i^{(1)} = \sum_{j<k} f_{ijk}\langle Q_j\rangle\langle Q_k\rangle + \sum_j f_{ijj}\langle Q_j^2\rangle + \sum_{j<k<l} f_{ijkl}\langle Q_j\rangle\langle Q_k\rangle\langle Q_l\rangle$$
$$+ \sum_{j\neq k} f_{ijjk}\langle Q_j^2\rangle\langle Q_k\rangle + \sum_j f_{ijjj}\langle Q_j^3\rangle + \sum_{j,k} \zeta_{ijkj}\langle P_j^2\rangle\langle Q_k\rangle, \qquad (4.11)$$

$$u_i^{(2)} = f_{ii} + \sum_{i\neq j} f_{iij}\langle Q_j\rangle + \sum_j f_{iijj}\langle Q_j^2\rangle + \sum_{j<k} f_{iijk}\langle Q_j\rangle\langle Q_k\rangle + \sum_j \zeta_{ijij}\langle P_j^2\rangle, \qquad (4.12)$$

$$u_i^{(3)} = f_{iii} + \sum_j f_{iiij}\langle Q_j\rangle, \qquad (4.13)$$

$$u_i^{(4)} = f_{iiii}. \qquad (4.14)$$

Since the expectation values $\langle Q_i^n\rangle$ and hence the SCF Hamiltonian in Eq.(4.6-4.14), depend on the modal functions Φ_n^i, these equations have to be solved iteratively until self consistency is reached.

4.3 Variationally optimized effective harmonic oscillator approximation

We next turn to the variational formulation of the effective harmonic oscillator (EHO). Note that the EHO approximation is a special case of the VSCF approximation. The ansatz in this case is a harmonic oscillator eigenfunction. As mentioned earlier, the modal wave functions Φ^i are expanded in terms of orthogonal HO eigenfunctions [cf., Eq.(4.2)] and the convergence of Eq.(4.2) depends upon the choice of χ_n^i. Such HO eigenfunctions are characterized by two parameters, the centroid of the function (Q_0) and the width parameter (w) of the functions,

$$\chi_n^i(Q) \quad = h_n \left[\sqrt{mw}\ (Q - Q^0)\right]\ exp\big[mw(Q-Q^0)^2/2\big]. \tag{4.15}$$

It is possible to adjust these two parameters such that the expansion of Φ_n^i is significantly dominated by the single function χ_n^i. One way of achieving this is to determine χ_n^i variationally. To this end we posit a trial wave function for the N-mode system as in Eq.(4.1), but write Φ_n^i as

$$\Phi_n^i \quad = \quad \chi_n^i. \tag{4.16}$$

The working equation for Q_i^0 and w_i are obtained by minimizing the resulting expectation value of the Hamiltonian with respect to Q_i^0 and w_i. The resulting equation for Q_i^0 is

$$\begin{aligned} Q_i^0 \quad = \quad & -\frac{1}{2\ f_{ii}}\Bigg[\sum_j f_{ijj}\ g_{ij}\ (2n_j+1)/2w_j + \sum_{j\neq k} f_{ijjk}\ g_{ijk}\ (2n_j+1)\ Q_k^0/2w_j \\ & + \sum_{i<k} f_{ijk}\ g_{ijk}\ Q_k^0 Q_j^0 + \sum_{j\neq k\neq l} f_{ijkl}\ g_{ijkl} Q_k^0 Q_j^0 Q_l^0 \\ & + \sum_{ijk} \zeta_{ijkj}\ (2n_j+1)\ Q_k^0\ w_j\Bigg], \end{aligned} \tag{4.17}$$

and the equation for the corresponding frequency is

$$\begin{aligned} m_i w_i \quad = \quad & 2^{\frac{1}{2}} \Bigg[f_{ii} + \sum_j f_{iij}\ g_{ij}\ Q_j^0 \ + \ \sum_{j<k} f_{ijjk}\ g_{ijk}\ Q_j^0 Q_k^0 i \\ & + f_{iiii}\ g_{ijk} \frac{(6n_i^2 + 6n_i + 3)}{(2n_i + 1)\ m_i w_i} \ + \ \sum_{j \neq i} f_{iijj}\ g_{ij}\ \frac{(2n_j + 1)}{m_j w_j} \\ & + \frac{1}{2} \sum_j \zeta_{ijij}\ (2n_j + 1)\ \frac{(m_j^2 w_j^2 - m_i^2 w_i^2)}{m_j w_j} \\ & - \sum_{jiki} \zeta_{jiki}\ Q_j^0 Q_k^0\ (m_i w_i)^2 \Bigg]^{\frac{1}{2}}, \end{aligned} \tag{4.18}$$

where

$$m_i^{-1} \quad = \quad 1 + 2 \sum_{jiki} \zeta_{jiki}\ Q_j^0 Q_k^0 + \sum_{ijij} \zeta_{ijij}\ \frac{(2n_j + 1)}{m_j w_j}\ . \tag{4.19}$$

Here n_i is the occupation number of the i^{th} mode and g_{ij} etc. are the combinatorial factors associated with the expansion of the potential around Q_i^0 as before. These equations are the generalization of the Hartree approximation used by several earlier authors to describe the ground state of an anharmonic oscillator [62, 83, 84] to arbitrary states. Once Q_i^0 and w_i are determined, the eigenfunctions of the effective harmonic oscillator (EHO) become the approximate eigenfunctions for the corresponding state.

$$h_i^{EHO} = -\frac{1}{2m_i} \frac{d^2}{dQ_i^2} + \frac{1}{2} m_i w_i^2 (Q_i - Q_i^0)^2, \tag{4.20}$$

The state energy is given by the expectation value of the Hamiltonian for one of the target states. Since the EHO approximation is a special case of the VSCF approximation, in that it constrains the modal functions to be HO eigenfunctions, the EHO energy for the ground state would always be higher than the VSCF ground states. However, this may not hold always due to variational collapse [85].

4.4 Description of program

The VSCF-VOHB program is based on the theory presented above. The program requires the quartic force field in the mass weighted normal coordinates as input. It first reads the number of vibrational modes, the number of irreducible representations in molecular symmetry group and a row matrix containing the number of normal coordinates belonging to a given irreducible representation in sequence. Symmetry is used to determining the non-zero elements of the potential energy function, and is used upto the level of the largest abelian point group, D_{2h}. The program then reads the details of the force field. The unique set of non-zero f-coefficients that define the quartic force field in Eq.(4.5) are read. These are stored in an one dimensional array. The program next reads the Coriolis coupling constants ξ_{ij}^{α} followed by the number of basis functions to be used in the SCF calculation for each mode and the quantum numbers of the target state.

After initializing the data, it does the EHO calculation described in the last section and determines the parameters Q_i^0 and w_i. It then shifts the origin of the coordinate system to Q_i^0 and recalculates the potential and Coriolis coupling parameters with respect to this new origin. This step is required to simplify the calculation of the matrix elements of the various operators that appear in the Hamiltonian. These matrix elements are evaluated analytically on the fly as and when required. The coefficient matrix of the modal functions is initialized to identity matrix and the SCF procedure is started. The expectation values of various operators that contribute to the effective single particle potential are constructed. In the next step, the SCF Hamiltonians are calculated in the EHO basis. These are then diagonalized to obtain the modals and the associated single particle energies. The process is iterated until the zeroeth order SCF energy is converged within a preset tolerance. At this point the first order correction to energy is calculated to obtain the final SCF energy.

4.5 Results and discussions

We have used VSCF-VOHB program to calculate the vibrational energy levels of formaldehyde. The potential energy surface and Coriolis coupling parameter were taken from Ref. [80]. The first point we discuss is the improvement in quality of the EHO eigenfunctions. Specially the expectation values of $\langle Q_i \rangle$ and $\langle Q_i^2 \rangle$ for the reference EHO states and the final SCF states are very close. Within the EHO approximation, the expectation value of the displacements are just Q_i^0. We plot $\langle Q \rangle_{SCF}$ vs. Q_i^0 for the three totally symmetric normal modes for all the states containing up to 2 quanta of energy in Fig. 4.1. As can be seen, the agreement between Q_i^0 and $\langle Q \rangle_{SCF}$ is excellent. The largest deviation is less than 1%.

The expectation value of $(Q - \langle Q \rangle)^2$ in the EHO approximation is given by $(n + \frac{1}{2})/mw$. We plot $\langle\ (Q - \langle Q \rangle)^2\ \rangle_{SCF}$ against the corresponding value in the EHO approximation in Fig. 4.2a and 4.2b, for all the six modes. The largest deviation is around 4% for the 1_2 state. Since the zeroeth order function itself represents the expectation value of Q very well, we expect the SCF function to converge rapidly in this basis.

We next look at the overlap between the EHO eigenstates and the corresponding SCF states. This is plotted as the function of the SCF state energy in Fig. 4.3. As can be seen, the reference wave function has an overlap of almost 1 in most of the cases. The maximum deviation occurs for the 1_2 state which has an overlap of about 0.9.

Given that the first two moments of the EHO states and the corresponding SCF states are almost identical and the overlap of the two functions is close to 1, it may be expected that the EHO energy would be close to the SCF energy. This data is presented in Fig. 4.4. As can be seen, the SCF energy correlates almost linearly with the EHO energy with a slope of almost 1.0.

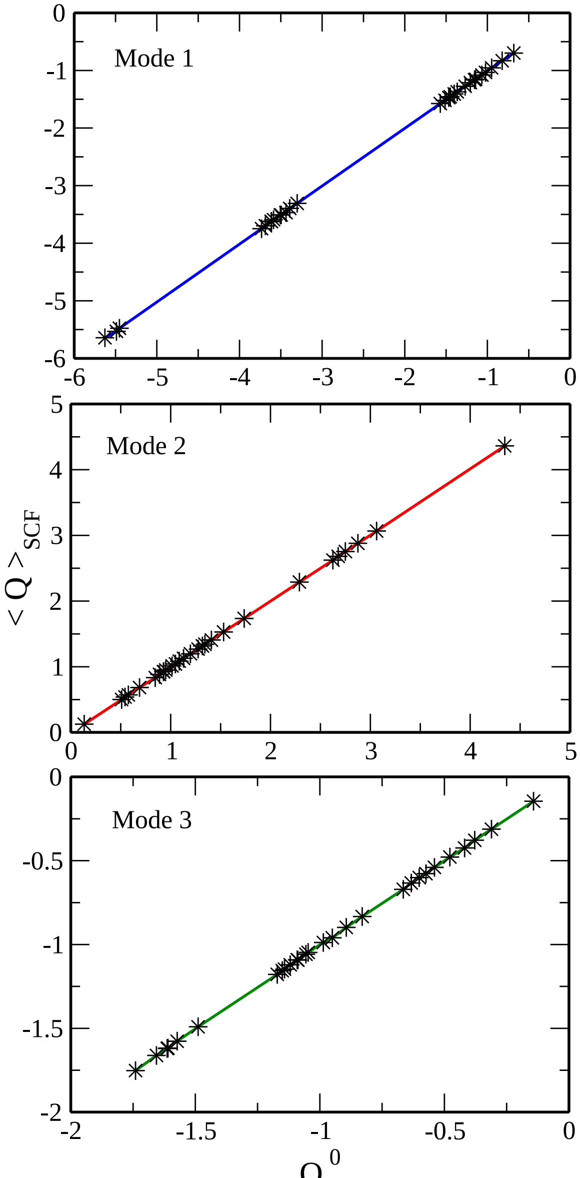

Fig. 4.1. $\langle Q \rangle_{SCF}$ **vs.** Q^0 **(in a.u.) of the three totally symmetric modes for formaldehyde.**

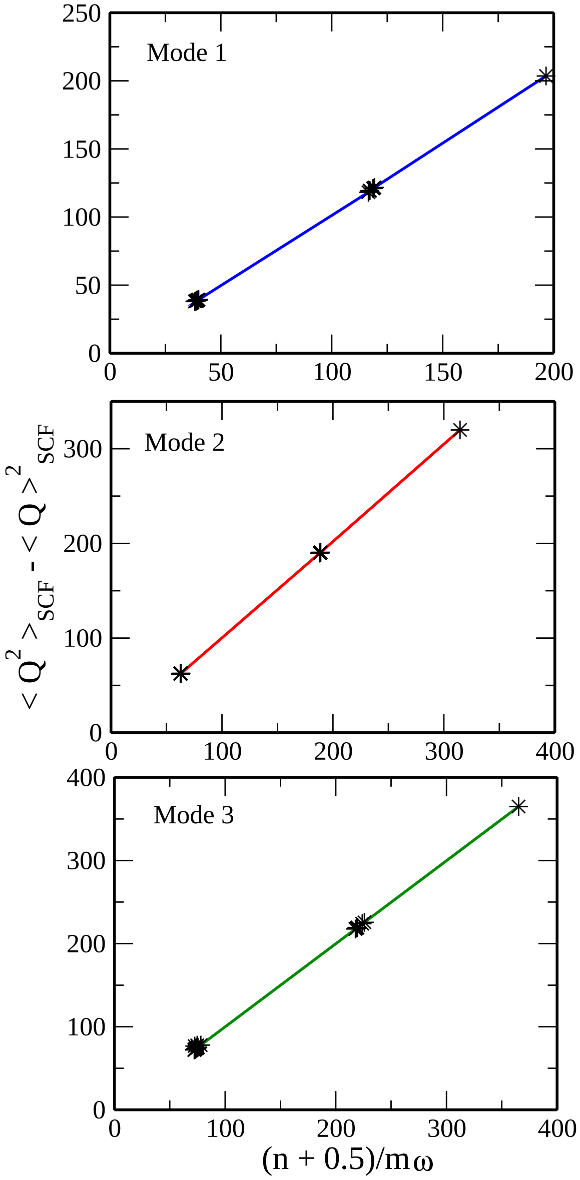

Fig. 4.2a. $(<Q^2>_{SCF} - <Q>_{SCF}^2)$ **vs. (n + 0.5)/mω (in a.u.) for the first three modes of formaldehyde.**

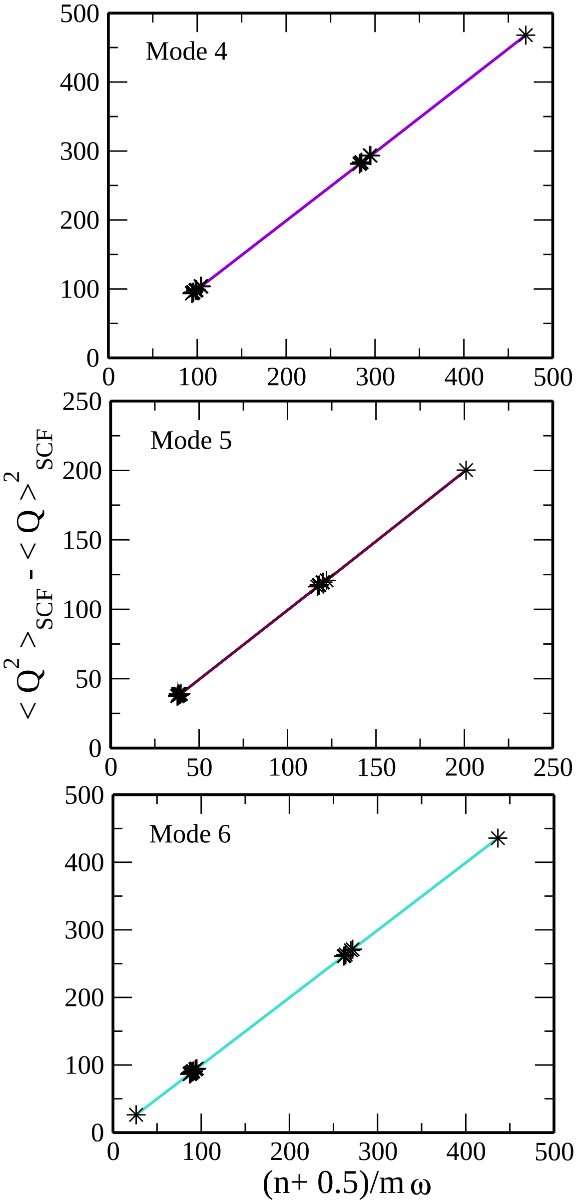

Fig. 4.2b. $(< Q^2 >_{SCF} - < Q >_{SCF}^2)$ **vs. (n + 0.5)/m**ω **(in a.u.) for the last three modes of formaldehyde.**

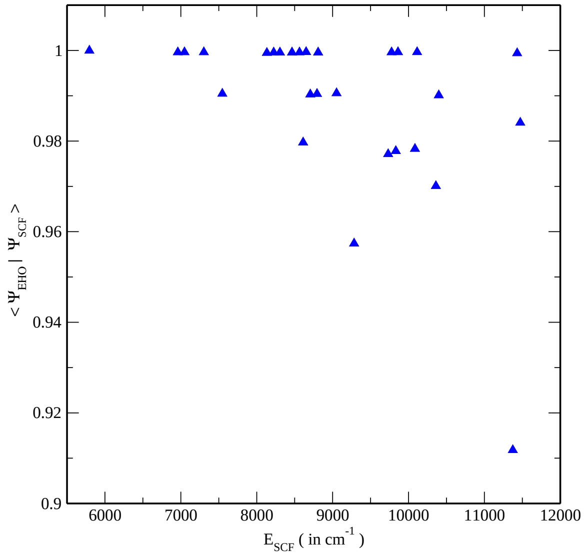

Fig. 4.3. Overlap of the reference EHO eigenfunction with the SCF function.

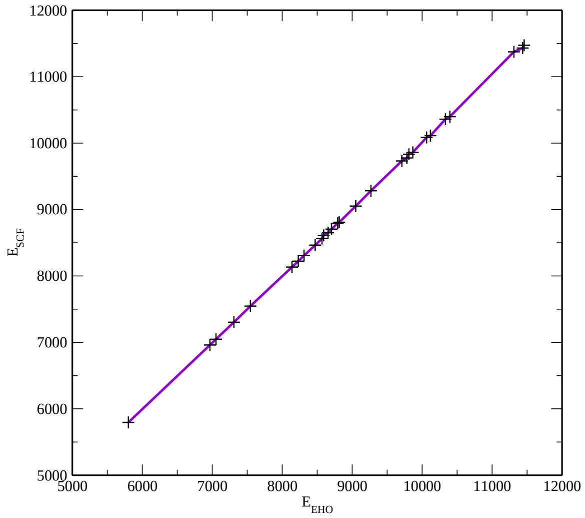

Fig. 4.4. Plot of E_{SCF} *vs.* E_{EHO} in cm^{-1}.

Indeed, it appears that the VSCF modals are essentially the variationally optimized EHO eigenfunctions. The data presented above indicates that the EHO eigenfunctions resemble the SCF modals both in the energy domain and in the coordinate space to a significant extent. Given this close resemblance between the two sets of function, we expect that the VOHB would provide a good basis for post SCF calculations such as VCI and VCCM as well as the VSCF calculations. This would be particularly convenient because the anharmonic matrix elements are available in analytical form for the HO basis, and most of them are zeroes. Such is not the case with the VSCF basis. So, one might expect a faster code in the EHO basis for the post SCF calculations.

We next turn to our secondary goal, the relative importance of Coriolis coupling. For large molecules, this term is insignificant because it is inversely proportional to the moment of inertia. For small molecules, however, it could be significant. We have tested the importance of Coriolis coupling for two molecules, formaldehyde and ketene. Both of them are semirigid, asymmetric rotors with C_{2V} point group. Ketene has softer modes than formaldehyde.

In Table 4.1, we present the energies of the ground state, several fundamental and overtone states of formaldehyde. It is seen that, modes 4 (CH_2 wag) and 5 ($C-H$ asym. str.) are significantly effected by Coriolis coupling. In the last column we present the converged CI values of Ramanowski and Bowman [80] and compare our VSCF and EHO values with it. As can be seen, the contribution of Coriolis coupling to the SCF energy is of the same order of magnitude as the correlation energy, typically of the order of a few tens of wave numbers. The relative sign of the two terms, however, is random. Interestingly, the Coriolis interaction values of the EHO is very close to the VSCF values irrespective of the states. Thus, the EHO approximation is able to capture the effect of the Coriolis coupling more or less fully for formaldehyde.

Ketene suffers from more severe perturbation than formaldehyde due to relatively low lying vibrational states. As the overtone and combination bands of those low lying states are scattered all over the mid-infrared region, it is expected that ketene should have considerable Coriolis interactions (and also Fermi interaction). In Table 4.2, we present the ground state, several fundamentals and overtones of ketene and the magnitude of Coriolis coupling of the corresponding

Table 4.1: **SCF and EHO energies with and without Coriolis coupling (in cm^{-1}) for H_2CO.**

State	E_{cor}^{SCF}	$E_{cor}^{SCF} - E_{no-cor}^{SCF}$	E_{cor}^{EHO}	$E_{cor}^{EHO} - E_{no-cor}^{EHO}$	$^{*}E_{cor}^{CI}$
gs	5795.3	-1.0	5800.6	-1.1	5777.2
1_1	8611.5	0.9	8592.0	0.9	8558.2
2_1	7546.8	0.0	7545.2	-0.1	7524.5
3_1	7303.5	0.6	7309.1	0.5	7277.5
4_1	6960.8	13.0	6966.6	12.9	6937.8
5_1	8650.6	10.6	8655.8	10.6	8635.0
6_1	7047.8	3.3	7053.5	3.1	7022.9
$1_1 2_1$	10360.4	1.9	10333.4	2.0	10306.7
$1_1 3_1$	10085.1	2.5	10064.4	2.5	10048.2
$1_1 4_1$	9732.2	16.1	9710.4	16.1	9692.0
$1_1 5_1$	11472.9	13.1	11458.1	13.3	11366.8
$1_1 6_1$	9832.4	7.4	9811.3	7.5	9783.7
$2_1 3_1$	9051.8	1.6	9050.6	1.6	9017.3
$2_1 4_1$	8705.6	15.2	8704.4	15.1	8676.5
$2_1 5_1$	10398.5	12.4	10396.3	12.3	10362.2
$2_1 6_1$	8794.6	4.3	8793.4	4.3	8780.5
$3_1 4_1$	8464.9	15.6	8470.9	15.4	8432.6
$3_1 5_1$	10113.3	14.1	10118.6	14.1	10128.6
$3_1 6_1$	8563.1	4.7	8569.0	4.6	8478.3
$4_1 5_1$	9776.9	44.4	9782.4	44.3	9777.5
$4_1 6_1$	8223.4	22.3	8207.3	22.3	8193.0
1_2	11374.4	3.3	11311.7	3.1	11274.9
2_2	9283.0	1.0	9268.7	-0.4	9256.2
3_2	8809.1	2.1	8814.9	2.0	8774.8
4_2	8134.0	26.9	8140.1	26.7	8092.3
5_2	11431.5	22.8	11436.0	23.2	11476.6
6_2	8306.1	7.1	8312.1	7.1	8266.4

*Ref. [80]

states for both of the VSCF and EHO methods. The potential energy surface of ketene has taken from Ref. [86]. It is seen that the ν_5 (CH_2 wag), ν_6 ($C = C = O$ linear bend), ν_7 ($C - H$ asym. str.) are greatly affected by Coriolis coupling. The interaction values are doubled with each quantum of excitation, such as, each of the 5_2, 6_2 and 7_2 states are almost double in magnitude than 5_1, 6_1 and 7_1 states. So, for some particular modes, the Coriolis interaction is important to predict the ro-vibrational phenomenon more accurately. Another important point is that the EHO approximation describes the Coriolis coupling interaction as good as VSCF for all the cases. We also compare our results with VCCM (6 boson) [63] to compare the magnitute of Coriolis energy with the correlation energy. It is seen that all of them are comparable.

Coriolis operator is a complicated operator and consequently, inclusion of Coriolis terms is not easy to implement in the purely vibrational Hamiltonian. If it is large, one should consider it and if it is weak, then it can be dropped. If one considers only up to VSCF (or EHO) level to describe the vibrational states, then inclusion of Coriolis coupling is desirable specially for higher excited states of small soft molecules. If the Coriolis interactions are not enough important to be included in the single particle Hamiltonian at the SCF level, one should avoid it. So, for rigid and large molecules one may not consider it. To investigate the importance of the Coriolis coupling for post SCF calculations, one should consider the magnitude of the Coriolis energy with the correlation energies.

If the Coriolis and correlation energies are comparable, then for post VSCF calculations, such as VCCM and VCI, one can skip the inclusion of the Coriolis terms in the VSCF level itself. Thus, it can be clubbed during the correlation energy calculations. If the Coriolis force is very weak compared to the correlation energies then one can treat it even beyond the correlation energy calculations. In such situations, after the correlation energy calculations without Coriolis coupling, one can include it by using perturbation theory. Thus, more studies on this aspect are desirable and consequently, it is difficult to pass a general judgment on

Table 4.2: **SCF and EHO energies with and without Coriolis coupling (in cm^{-1}) for ketene.**

State	E_{cor}^{SCF}	$E_{cor}^{SCF} - E_{no-cor}^{SCF}$	E_{cor}^{EHO}	$E_{cor}^{EHO} - E_{no-cor}^{EHO}$	E_{cor}^{VCCM}
gs	6874.3	5.2	6879.4	5.2	6871
1_1	9949.3	6.8	9930.7	6.8	9998
2_1	9033.1	6.8	9036.2	6.7	9030
3_1	8276.7	5.9	8282.0	5.8	8264
4_1	8008.0	5.4	8012.1	5.3	8004
5_1	7495.1	21.8	7501.4	21.6	7476
6_1	7425.7	21.3	7431.6	21.0	7407
7_1	10027.4	26.5	10032.2	26.2	10060
8_1	7872.2	11.4	7877.6	11.1	7853
9_1	7341.4	13.2	7347.3	13.1	7323
$1_1 2_1$	12106.5	8.4	12085.7	8.3	11156
$1_1 3_1$	1320.6	7.3	11300.4	7.3	11383
$1_1 4_1$	11078.0	6.9	11058.1	6.9	11121
$1_1 5_1$	10538.5	23.7	10518.2	23.5	10625
$1_1 6_1$	10473.5	23.3	10453.5	23.0	10541
$1_1 7_1$	13105.6	30.2	13090.9	29.9	13065
$1_1 8_1$	10923.3	13.6	10903.2	13.5	10977
$1_1 9_1$	10397.7	15.3	10377.7	15.2	10465
$2_1 3_1$	10434.1	7.4	10437.3	7.3	10417
$2_1 4_1$	10165.5	6.9	10167.6	6.9	10150
$2_1 5_1$	9649.8	23.8	9654.0	23.5	9631
$2_1 6_1$	9574.1	23.8	9577.9	23.5	9557
$2_1 7_1$	12185.9	28.3	12188.7	28.0	12210
$2_1 8_1$	10026.0	13.2	10029.3	13.1	10003
$2_1 9_1$	9492.8	15.7	9496.6	15.6	9475
1_2	12972.0	8.9	12911.5	8.9	13045
2_2	11170.8	8.3	11170.0	7.5	11174
3_2	9677.4	6.6	9682.7	6.3	9661
4_2	9137.6	5.6	9139.5	5.4	9124
5_2	8133.6	38.8	8139.0	37.8	8085
6_2	8005.8	36.4	8011.0	36.0	7951
7_2	13103.1	50.8	13107.2	50.2	13218
8_2	8869.7	17.7	8875.2	17.5	8836
9_2	7822.3	20.0	7827.8	20.8	7771
$5_1 6_1 7_1$	11230.9	89.8	11236.8	88.8	11087
$5_2 6_2 7_2$	15556.2	223.6	15558.2	220.6	–

*Ref. [86]

whether the Coriolis coupling should be included at the SCF level at this stage.

4.6 Conclusions

In this chapter we have explored the effective harmonic oscillator approximation for anharmonic molecular vibrations. The EHO approximation posits a separable ansatz as a special case of the VSCF approximation where it constrains the modal functions as HO eigenfunctions. Mathematically, the trial wave function of EHO for the N-mode system is not expanded as a typical HO basis like VSCF calculation, but we write Φ_n^i as χ_n^i. Such HO eigenfunctions are characterized by two parameters, the centroid (Q^0) and the width (ω) of the functions. Minimization of the expectation value with respect to the parameters gives the variationally optimized harmonic oscillator basis functions. The state energy can be calculated by the expectation value of the Hamiltonian using that optimized basis. We have shown that the expectation values for both the approaches are very similar and the overlap between the two eigenstates is excellent. Consequently, they are significantly close in the energy domain. Additionally, we have investigated the importance of the Coriolis coupling both for the EHO and VSCF level. It is found that for floppy and small molecules, it should be considered at the VSCF level. We also found that for formaldehyde and ketene, the Coriolis energy and the correlation energy are in the same order of magnitude irrespective of the sign, though more extensive investigation is needed in this context. Thus to answer the question pased at the begining of this chapter, it appears that the EHO can describe individual vibrational eigenstates as well as it can describe the thermal density matrix, i.e., comparable to the SCF approximation.

Chapter 5

Concluding Remarks

The primary goal of this present thesis was to develop fully quantum mechanical approximations to the thermal density matrix of anharmonic molecular vibrations. To this end we chose to study the limits of numerical accuracy of a separable ansatz to the thermal density matrix based on the independent particle model. Our first attempt in this direction was to invoke the Feynman variational principle based on the Gibbs-Bogoluibov inequality (FGB) to derive the working equations to determine the parameters in the effective single particle Hamiltonians that are used to construct the density matrix. The resulting equations resemble the quantum mechanical vibrational self-consistent (VSCF) theory. The only difference is that, the effective single particle potentials are generated as the partial thermal averages of the full many body potential rather than as partial quantum mechanical averages. The method is capable of yielding quite accurate results for thermodynamic state functions and other thermal averages. We have also compared the well known effective harmonic oscillator (EHO) approximation against the thermal self consistent field (t-SCF) approximation. Since, the EHO approximation is a more restricted approximation, we expected it to perform worse than the SCF appraoch. While this is true, surprisingly the EHO performs quite well in its own right.

Motivated by desire to improve the quality of the density matrix throughout the configurational space, we have developed a new variational principle. In this approach the mean square difference between the temperature derivatives of the exact and model density matrices is minimized. This is reminiscent of the McLachlan variational principle from time dependent quantum mechanics. We have used this variational principle in conjunction with a separable model Hamiltonian and EHO Hamiltonian. The performance of this variational principle is comparable to the FGB as far as thermodynamic state functions are concerned. However, the thermal averages of coordinate operator are systematically underestimated by this approach irrespective of whether one uses the separable ansatz or the EHO ansatz. This implies that the new variational principle leads to a more compact probability distribution (the diagonal part of the density matrix) that is centered closer to the local minima of the potential energy surface. One curious feature of this variational principle is that the partial thermal average of the many body potential to generate the temperature dependent effective single particle potentials is done at half of the target temperature. The density matrices are more compact at lower temperatures. This could be the reason why the thermal averages of the coordinate operator are underestimated by this approach. The EHO in particular seems to be susceptible in this regards. Thermodynamic state functions are much less sensitive to this and are well reproduced. The method is computationally very fast and appears to be a good alternative to the FGB approach.

While we were concerned only with the construction of the density matrices, the methodology of chapter 3 can be extended to calculate the thermal averages of arbitrary operators without constructing the density matrix explicitly. For example, if X is an arbitrary operator, its thermal average is given by,

$$\begin{aligned} < X >_\beta &= Tr\ X\rho(\beta) \\ &= Tr\ \rho(\beta/2)X\rho(\beta/2). \end{aligned} \tag{5.1}$$

If we now define a new operator

$$X_\beta = \rho(\beta/2) X \rho(\beta/2) \tag{5.2}$$

then the thermal average is just $Tr\ X_\beta$. The operator X_β satisfies the equation of motion,

$$\frac{dX_\beta}{d\beta} = \frac{1}{2}(HX_\beta + X_\beta H). \tag{5.3}$$

Manipulating the Eq.(5.3) just as we did for the density matrix in chapter 3 we arrive at

$$\frac{Tr(\delta H_0)\left[2X_\beta(H-H_0)X_\beta + X_\beta X_\beta(H-H_0) + (H-H_0)X_\beta X_\beta\right]}{Tr\ X_\beta X_\beta} = 0. \tag{5.4}$$

Note that this expression is similar to the symmetrized version (Eq. (3.14)) of the working equation for ρ. Here, H_0 is once again the modal Hamiltonian. Construction of X_β operator is a trivial excercise. For example, in the separable approximation the ansatz for the coordinate operator Q_k is

$$Q_{k\beta} = \sum_{n,m} |\phi_n^k\rangle\langle\phi_n^k|Q_k|\phi_m^k\rangle\langle\phi_m^k|\ exp[-\beta(\varepsilon_n^k + \varepsilon_m^k)/2]. \tag{5.5}$$

The virtue of this approach is that the density matrix is adopted to minimize the error in the thermal average of Q_k. A similar approach can be developed for the calculation of correlation functions. Consider the two time correlation function

$$C(t) = Tr[A(t)\ B(0)\ \rho]. \tag{5.6}$$

It can be written as,

$$C(t) = Tr[A_\beta^\dagger(t)\ B_\beta(0)], \tag{5.7}$$

where

$$A_\beta = A\rho(\beta/2). \tag{5.8}$$

A_β and B_β can be obtained independently and propagated in time. However, the working equations for A_β as defined here would not be symmetric, since, this operator is not hermitian.

In summary these two studies indicate that the separable approximation provide a fast and reliable approximation for the construction of the thermal density matrices. Since, this calculation scales almost linearly to the degrees of freedom, they can be extended to large systems easily. The computational requirements for such calculations in terms of the memory and CPU time is quite modest. For example, a calculation on ketene over the temperature range 0 to $1000K$ (100 points) takes about 5 seceonds on single core linux box. Our studies showed that the EHO approximation is quite close to the general separable approximation as far as density matrices are concerned. This raises the obvious question as to whether an EHO approximation can compare favourably against a VSCF calculation, particularly for the excited states where the anharmonic terms are expected to be more influencial. This was the subject of our study in the previous chapter. We found that this is indeed true and the EHO wave functions resemble the VSCF wave functions to a significant degree. Indeed the overlap between EHO wave function and the corresponding VSCF wave function is typically of the order of 0.95. Among all the states we have studied the overlap falls to 0.9 only in one case. This close resemblance of the EHO eigenstates raises the possibility of using them as the basis functions for more accurate calculations. Most of the CI calculations are carried out either in a HO basis centered origin of the normal coordinates or in terms of the virtual modals determined from a VSCF calculations on the ground state. One needs a large basis for a former type of calculations. A small basis might be sufficient for the second type of calculation.

However, the matrix elements for various operators are no longer available in analytical forms. The EHO basis might provide a better alternative of these two approaches, since, the matrix elements are available in analytical form and the wave functions themselves resemble the SCF modals to a very good extent.

Bibliography

[1] E. Schrödinger, Ann. Physik, **79**, 361, 478; **80**, 437; **81**, 109 (1926).

[2] I. N. Levine, *Quantum Mechanics, Fouth Edition*, Prentice Hall private Lmt. New Delhi (2001).

[3] A. Messiah and G. M. Temmer, *Quantum Mechanics, Vol. I*, North-Holland Publishing Comp. London (1974).

[4] H. Eyring, J. Walter and G. E. Kimball, *Quantum Chemistry*, John Wiley and Sons, Inc. London.

[5] A. Szabo and N. S. Ostlund, *Moderam Quantum Chemistry*, McGraw-Hill Publishing Comp. New Delhi (1982).

[6] R. P. Feynman, *Statistical Mechanics*, W. A. Benjamin, INC, Reading, Massachusetts, (1974).

[7] W. H. Hehre, L. Radom, P. V. Schleyer and J. A. Pople, *Ab Initio Molecular Orbital Theory*, John Wiley & Sons. New Work (1986).

[8] C. J. Cramer, *Essentials of Computational Chemistry* Chichester: John Wiley and Sons, Ltd. (2002); F. Jensen, *Introduction to Computational Chemistry*, Chichester, England: John Wiley and Sons. (1999).

[9] E. B. Wilson Jr., J. C. Decius and P. C. Cross, *Molecular Vibrations*, McGraw-Hill Book Company, New York (1955).

[10] J. K. G. Watson, Mol. Phys. **15**, 479 (1968).

[11] D. A. McQuaririe, *Statistical Mechanics*, Viva Books Private Limited, Kolkata (2003).

[12] A. L. Fetter and J. D. Walecka, *Quantum Theory of Many Particle System*, McGraw-Hill Publishing Comp. New York (1971); N. H. March, W. H. Young and S. Sampanthan, *Many-Body Problem in Quantum Mechancs*, Cambridge University Press (1976).

[13] J. W. S. Rayleigh, *Theory of Sound*, 2nd edition Vol. I, Macmillan, London (1894); E. Schrdinger, Annalen der Physik, Vierte Folge, Band 80, p. 437 (1926).

[14] L. Brillouin, J. Physique **7**, 373 (1932); E. P. Wigner Math. Naturw. Anz. Ungar. Akad. Wiss. **53**, 475 (1935).

[15] C. Möller and M. S. Plesset, Phys. Rev. **46**, 618 (1934).

[16] D. R. Hartree, Proc. Cambridge Phil. Soc. **24**, 89 (1928).

[17] V. Z. Fock, Z. Phys. **61**, 126, (1930).

[18] J. C. Slater, Phys. Rev. **36**, 57 (1930).

[19] G. C. Carney, L. L. Sprandel and W. C. Kern, Adv. Chem. Phys. **27**, 305 (1978).

[20] J. M. Bowman, J. Phys. Chem. **68**, 608 (1978); J. M. Bowman, Acc. Chem. Res. **19**, 202 (1986).

[21] D. C. Sherrill, H. F. Schaefer III, *The Configuration Interaction Method: Advances in Highly Correlated Approaches* in Lwdin, Per-Olov; Advances in Quantum Chemistry, Vol 34, San Diego: Academic Press (1999); A. C. Hurley, *Electron Correlation in Small Molecules*, Academic Press, London,

1977; S. Wilson, *Electron Correlation in Molecules*, Clarendon Press, Oxford, 1984; K. Raghavachari, J. B. Anderson, Phys. Chem. **100**, 12960 (1996).

[22] F. Coester, Nucl Phys. **7**, 421 (1958); F. Coester and H. G. Kümmel Nucl Phys. **17**, 477 (1960), J. Cizek, J. Chem. Phys. **45**, 4256 (1966); J. Paldus, J. Cizek and I. Shavitt, Phys. Rev A **5**, 50 (1972), O. Sinanuglu, Proc. Roy. Soc. A. **260**, 379 (1961); O. Sinanuglu, J. Chem. Phys. **36**, 207 (1962).

[23] R. J. Bartlett, J. Phys. Chem. **93**, 1697 (1989), R. J. Bartlett and G. D. Purvis, Int. J. Quantum Chem. **14**, 561 (1980); J. A. Pople, R. Krishnan, H. B. Schegel and J. S. Binkley, Int. J. Quantum Chem. **14**, 545 (1978); D. Mukherjee and S. Pal, Adv. Quantum Chem. **20**, 291 (1989).

[24] N. Makri and W. H. Miller, J. Chem. Phys. **116**, 9207 (2002).

[25] Y. Zhao and W. H. Miller, J. Chem. Phys. **117**, 9605 (2002).

[26] J. Cao and G. A. Voth, J. Chem. Phys. **100**, 5093 (1993).

[27] K. R. Glaesemann and L. E. Fried, J. Chem. Phys. **118**, 1596 (2003); K. R. Glaesemann and L. E. Fried, J. Chem. Phys. **123**, 034103 (2005).

[28] R. Q. Topper, G. J. Tawa and D. G. Truhlar, J. Chem. Phys. **97**, 3668 (1992); R. Q. Topper and D. G. Truhlar, J. Chem. Phys. **97**, 3647 (1992); S. L. Mielke and D. G. Truhlar, J. Chem. Phys. **115**, 652 (1992).

[29] I. R. Craig and D. E. Manolopoulos, J. Phys. Chem. **122**, 084106 (2005); I. R. Craig and D. E. Manolopoulos, J. Phys. Chem. **123**, 034102 (2005).

[30] E. J. Heller, J. Chem. Phys. **62**, 1544 (1975); E. J. Heller, J. Chem. Phys. **64**, 1544 (1976).

[31] B. Hellsing, S. I. Sawada and H. Metiu, Chem. Phys. Lett. **122**, 303 (1985).

[32] K. Singer and W. Smith, Mol. Phys. **57**, 761 (1986).

[33] P. Frantsuzov, A. Neumaier and V. A. Mandelshtam, Chem. Phys, Lett. **381**, 117 (2003); P. A. Frantsuzov and V. A. Mandelshtam, J. Chem. Phys. **121**, 9247 (2006).

[34] J. Shao and E. Pollak, J. Chem. Phys. **125**, 133502 (2004).

[35] B. Militzer and E. L. Pollock, Phys. Rev. E **61**, 3470 (2000).

[36] A. D. McLachlan, Mol. Phys. **8**, 39 (1964).

[37] J. Cao and G. A. Voth, J. Chem. Phys. **102**, 3337 (1994).

[38] G. Sanyal, S. H. Mandal and D. Mukherjee, Chem. Phys. Lett. **192**, 55 (1992); G. Sanyal, S. H. Mandal, S. Guha and D. Mukherjee, Phys. Rev. E **48**, 3373 (1993)

[39] B. Njegic and M. H. Gordon, J. Chem. Phys. **125**, 224102 (2006).

[40] V. Barone, J. Chem. Phys. **120**, 3059 (2004).

[41] M. B. Hensen, O. Chirstiansen, D. Toffoli and J. Kongsted, J. Chem. Phys. **128**, 174106 (2008).

[42] G. Parisi, *Statistical field theory* (Addison-Wesley, Reading, 1988); J. W. Negele and H. Orland,*Quantum many particle systems* (Addison-Wesley, Reading, 1988).

[43] T. Matsubara, Prog. Theoret. Phys. **14**, 351 (1955).

[44] K. P. Kadanoff and G. Baym, *Quantum statistical mechanics* (Benjamin, New York, 1962).

[45] H. Mori, Prog. Theoret. Phycs. **33**, 423 (1965).

[46] I. Prigogine and R. Balescu, Physica **25** 281, 302 (1965); P. Esibois, Physica **27**, 541 (1961).

[47] R. M. Feyman and H. Kleinert, Phys. Rev. A **34**, 5080 (1986); B. Palmieri and D. Ronis; Phys. Rev. E **73**, 061105 (2000).

[48] H. J. Korsch, J. Phys. A **12**, 1521 (1979).

[49] M. Messina, G. K. Schenter and C. Garret, J. Chem. Phys. **103**, 8303 (1993).

[50] J. M. Rickman and R. LeSar, Annu. Rev. Mater. Res. **32**, 195 (2002).

[51] S. L. Miekle and D. G. Truhlar, J. Phys. Chem. A **113**, 8717 (2009).

[52] D. G. Truhlar and A. D. Isaacson, J. Chem. Phys. **94**, 357 (1991); A. D. Isaacson and D. G. Truhlar, J. Chem. Phys. **75**, 4090 (1981); A. D. Isaacson and X. Zhang, Theor. Chim. Acta **74**, 493 (1988); A. D. Isaacson and S. C. Hung, J. Chem. Phys. **101**, 3928 (1994); A. D. Isaacson, J. Chem. Phys. **108**, 9978 (1998); A. Chakrabarty, D. G. Truhlar, J. M. Bowman and S. Carter, J. Chem. Phys. **121**, 2071 (2004).

[53] V. Barone, J. Chem. Phys. **122**, 014108 (2005).

[54] K. Yagi, K. Hirao, T. Taketsugu, M. W. Schmidt and M. S. Gordon, J. Chem. Phys. **121**, 1383 (2004).

[55] D. Toffoli, J. Kongsted and O. Christiansen, J. Chem. Phys. **125**, 124108 (2006).

[56] G. M. Chaban, J. O. Jung, and R. B. Gerber, J. Chem. Phys. **111** , 1823 (1999); J. O. Jung and R. B. Gerber, J. Chem. Phys. **105**, 10332 (1996); L. S. Noris, M. A. Ratner, A. E. Roitberg and R. B. Gerber, J. Chem. Phys. **105**, 11261 (1996); N. Matsunaga, G. M. Chaban and R. B. Gerber, J. Chem. Phys. **117**, 3541 (2002).

[57] K. V. Ermakov, B. S. Butayev and V. P. Spirinov, Chem. Phys. Lett. **144**, 497 (1988); V. P. Spirinov, V. S. Lyutsarev and B. S. Butayev, Chem. Phys. Lett. **110**, 32 (1984).

[58] D. Chandler, *Introduction to Modern Statistical Mechanics* (Oxford University Press, Oxford, 1987); D. C. Mattis, *Statistical Mechanics Made Simple* (World Scintific, Singapore, 2003); S. K. Ma, *Statistical Mechanics* (World Scintific, Singapore, 1985); L. D. Landau and E. M. Lifshitz, *Statistical Physics*, Vol 5 (Pergamon Press, New York, 1980).

[59] A. Isihara, J. Phys. A **1**, 539 (1968).

[60] M. J. Frisch et. al., Gaussian 03, Revision E.01, Gaussian, Inc., Wallingford CT, 2004.

[61] M. W. Schmidt et al, J. Comput. Chem. **14**, 1347 (1993); C. E. Dykstra, G. Frenking, K. S. Kim and G. E. Scuseria, *Theory and Applications of Computational Chemistry: the First Forty Years* ed (Elsevier, Amsterdam, 2005).

[62] V. Nagalakshmi, V. Lakshminarayana, G. Sumitra and M. Durga Prasad, Chem. Phys. Lett., **217**, 279(1994).

[63] S. Banik and M. Dugra Prasad, J Chem Phys, **129**, 134111 (2008).

[64] A. G. Csaszar and I. M. Mills, Spectrochemica Acta Part A **53**, 1101 (1997).

[65] J. Breidung, W. Thiel, J. Gauss and J. F. Stanton, J. Chem. Phys. **110**, 3687 (1998)

[66] N. C. Craig and E. A. Entenmann, J. Am. Chem. Soc. **83**, 3047 (1961).

[67] A. D. Becke, J. Chem. Phys. **98**, 5648 (1993); C. Lee, W. Yang and R. G. Parr, Phys. Rev. B **37**, 785 (1988).

[68] T. H. Dunning Jr., J. Chem. Phys. **90**, 1007 (1989).

[69] R. Ditchfield, W. J. Hehre and J. A. Pople, J. Chem. Phys. **54**, 724 (1971); W. J. Hehre, R. Ditchfield and J. A. Pople, J. Chem. Phys. **56**, 2257 (1972);

R. Krishnan, J. S. Binkley, R. Seeger and J. A. Pople, J. Chem. Phys. **72**, 650 (1980).

[70] C. Adamo and V. Barone, J. Chem. Phys. **108**, 664 (1998).

[71] J. W. Larson and T. B. McMahon, J. Am. Chem. Soc. **110**, 1087 (1988).

[72] T. K. Roy and M. Durga Prasad, J. Chem. Phys. **131**, 114102 (2009).

[73] F. Culot and J. Levine, Theor. Chem. Acta. **89** 227 (1994); S. Heisbetz and G. Rauhut, J. Phys. Chem. **132**, 129102 (2010); K. Drukker and S. Hammes-Schiffer, J. Chem. Phys. **107**, 363 (1997); S. P. Webb and S. Hammes-Schiffer, J. Chem. Phys. **113**, 5214 (2000).

[74] L. Pele, B. Brauner and R. B. Gerber, Theor. Chem. Acc. **117**, 69 (2007).

[75] A. Roitberg, R. B. Gerber and M. A. Ratner, Science, **268**, 1318 (1995)

[76] H. Ramanowski and M. J. Bowman, POLYMODE (QCPE 496), QCPE Bull. **5**, 64 (1985).

[77] S. Carter, J. M. Bowman and N. C. Handy, Theor. Chem. Acta. **100**, 191 (1998).

[78] D. A. Jelski, R. H. Hally and J. M. Bowman, J. Comp. chem. **17**, 1645 (1996).

[79] G. Rauhut, J. Phys. Chem. **121**, 9313 (2004).

[80] H. Romanowski and J. M. Bowman, J. Chem. Phys. **82**, 4155 (1984).

[81] H. Romanowski and J. M. Bowman, Chem. Phys. Lett. **110**, 235 (1984).

[82] E. L. Sibert III, J. Chem. Phys. **88**, 4378 (1988); E. L. Sibert III, J. Chem. Phys., **90**, 2672 (1989).

[83] R. F. Bishop and M. F. Flynn, Phys. Rev.A **38**, 2211 (1988).

[84] C. S. Hsue and J. L. Chern, Phys Rev. D **29**, 643 (1984).

[85] S. T. Epstein, *Variational method in quantum chemistry*. New York: Academic Pressi (1974).

[86] A. L. L. East, W. D. Allen and S. J. Klippenstein, J. Chem. Phys. **102**, 8506 (1994).

List of Publications

1. “Effective harmonic oscillator description of anharmonic molecular vibrations ”,
   Tapta Kanchan Roy and M. Durga Prasad, J. Chem. Sci. **121**, 805 (2009).

2. “A thermal self-consistent field theory for the calculation of molecular vibrational partition functions ”,
   Tapta Kanchan Roy and M. Durga Prasad, J. Chem. Phys. **131**, 114102 (2009).

3. “Development of a new variational approach for thermal density matries ”,
   Tapta Kanchan Roy and M. Durga Prasad, (submitted)

4. “Conformational preferences of mono-substituted cyclohydronitrogens: A theoretical study ”,
   Tapta Kanchan Roy, Susanta Ghanta, Tanmoy Mondal, Banda Saritha, S. Mahapatra and M. Durga Prasad, Theochem, **822**, 145 (2007).

5. “On some stategies to design new high energy density molecules ”,
   T. Mondal, B. Saritha, S. Ghanta, **T. K. Roy**, S. Mahapatra and M. Durga Prasad Theochem, **897**, 42 (2009).

6. “Terminal functionalized hydroxyl-terminated: An energytic binder for propellant ”,
   R. Murali Shankar, **Tapta Kanchan Roy** and Tushar Jana, J. Appl. Poly. Sc. **114**, 732 (2009).

7. “Functionalization of the Terminal Carbon Atoms of the Hydroxyl Terminated Polybutadiene by Polyazido Nitrogen Rich Molecules ”,
   R. Murali Shankar, **Tapta Kanchan Roy** and Tushar Jana, Bulletin of Materials Science, (in press).

Posters/Paper/Oral Presentations in Symposia

1. Oral presentation : "5th Singapore India Collaborative and Cooperative Chemistry Symposium ", an international symposium organized by School of Chemistry, University of Hyderabad in 2009, titled- "Variational approaches to thermodynamic quantities ".

2. Oral presentation : "7th Annual In-house Symposium organized by School of Chemistry, ChemFest 2010 ", titled- "Effective Hamonic Oscillator Description of Anharmonic Vibrations ".

3. Poster presentation : "A thermal self-consistent field theory for the calculation of molecular vibrational partition function ": in "Recent Advances in Many Body Theory, Shankarpur, 2010 "; organized by Indian Association of the Cultivation of Science and Raman Centre for Atomic Molecular and Optical Science, Kolkata, India.

4. Poster presentation : "Calculation of thermodynamic quantities of molecules using effective harmonic oscillator and vibrational self-consistent field method": "Theoretical Chemistry Symposium 2009 ", organized by Indian Institute of Science, Bangalore, India.

5. Poster presentation : "4th, 5th, 6th and 7th Annual In-house Symposium of School of Chemistry, ChemFest 2007, 2008, 2009, 2010, organized by School of Chemistry, University of Hyderabad, Hyderabad, India, 2007, 2008, 2009 and 2010.

6. Poster presentation : "School of numerical quantum many body methods in physics and chemistry ", organized by JNCASR, Bangalore, 2007.

7. Attended : HPC Workshop for FIST Institutes conducted during February, 2007 with CDAC at CMSD, University of Hyderabad.

8. Attended : lecture series on “Simulations in Biology and Soft Matter ”November-December 2007 conducted by CMSD at University of Hyderabad.
9. Attended : HPC workshop on Tutorial “Tools for Scientific Computing”on October, 2008, conducted by CMSD at University of Hyderabad.
10. Attended : “NVIDIA TESLA Supercomputing Workshop”on July 2009 conducted by CMSD at University of Hyderabad.