Chapter 1

Introduction

1.1 General problem of the solution of Schrödinger and Bloch equations

In quantum mechanics, we deal with wave function $\psi$, 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, $\psi$ 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

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

$$H\psi(x) = E\psi(x). \quad (1.1b)$$
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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

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

(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 $\psi$ 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, $\rho$ [6]. The general form of the density matrix is

$$\rho = \sum_i p_i |\psi_i\rangle\langle\psi_i|.$$ 

(1.3)

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

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

The equation of motion for the density matrix is

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

and is known as the Bloch equation.

As it is impossible to find an exact $\psi$ or $\rho$ we need to invoke some approximations. For such approximations, the description of $\psi$ or $\rho$ plays a crucial role. To invoke an approximate $\psi$ or $\rho$ 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

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

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,

\[ \psi(AB) = \psi(A)\psi(B), \]  
\[ \rho(AB) = \rho(A)\rho(B). \]  

**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

\[ \mathcal{H}_{ij} = \left( \left. \frac{\partial^2 E_{el}}{\partial x_i \partial x_j} \right|_{eq} \right). \]  

If the mass tensor is \( M \), and

\[ (M^{-\frac{1}{2}}\mathcal{H}M^{-\frac{1}{2}}) C = C \Omega^2, \]
then $C$ is the coefficient matrix that defines the mass weighted normal coordinates

$$Q_i = \sum_j x_j C_{ji} \sqrt{m_j}.$$  \hspace{1cm} (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 weighted normal coordinates ($Q$) is

$$H = -\frac{1}{2} \sum_{i=1}^{N} \frac{d^2}{dQ^2} + V(Q) - \frac{\hbar^2}{8} \sum \mu_{\alpha\alpha}$$

$$+ \frac{1}{2} \sum_{\alpha\beta} (J_\alpha - \pi_\alpha) \mu_{\alpha\beta} (J_\beta - \pi_\beta) \hspace{1cm} (1.11)$$

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 $\alpha$ and $\beta$ 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. $J_\alpha$ and $\pi_\alpha$ are the $\alpha^{th}$ 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 $Q$

\[
V(x) = \sum_i f_{ii} Q_i^2 + \sum_{i \leq j \leq k} f_{ijk} Q_i Q_j Q_k + \sum_{i \leq j \leq k \leq l} f_{ijkl} Q_i Q_j Q_k Q_l. \quad (1.12)
\]

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 Fermi 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 evaluation 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 $\lambda$ is some parameter and the term $\lambda H_1$ 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.
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We can see from the Eq. (1.13), when $\lambda \to 0$, the $E_n$ and $\psi_n$ approaches to $E_n^{(0)}$ and $\psi_n^{(0)}$. At $\lambda = 0$, we have exactly the unperturbed system. As $\lambda$ 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

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

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

The resulting expression for energy is

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

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

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

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-Plesset 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 depend 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 \(|\psi\rangle\) 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.

\[
\langle \phi | H | \phi \rangle \geq E_0.
\] (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 \(\psi\) is a product separable of
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single mode wave functions $\phi_i$,

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

(1.19)

This set $\phi_i$ 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

$$
\psi_t = \prod_{k} \phi_0^k(Q_k),
$$

(1.20)

The Watson Hamiltonian is rewritten as

$$
H = \sum_{k} h_k(q_k) + \sum_{k,l} V_2(q_k q_l) + \sum_{k,l,m} V_3(q_k q_l q_m) + ...
$$

$$
= \sum_{k} h_k(q_k) + V.
$$

(1.21)

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

$$
E_t = \frac{\langle \psi_t | H | \psi_t \rangle}{\langle \psi_t | \psi_t \rangle}
$$

$$
= \sum_{k} \langle \phi_0^k | h_k | \phi_0^k \rangle + \sum_{k,m} \langle \phi_0^k \phi_0^m | V_2 | \phi_0^m \phi_0^k \rangle + ....
$$

(1.22)
This equation is to be minimized subject to the constraints of orthonormality

\[ \langle \phi^\beta_k | \phi_k^\alpha \rangle = \delta_{\alpha\beta}. \] (1.23)

To incorporate these, one uses the constrained functional

\[ E = E_t - \sum_{k,\alpha,\beta} \lambda^k_{\alpha\beta} (\langle \phi^\beta_k | \phi_k^\alpha \rangle - \delta_{\alpha\beta}) \] (1.24)

such that \( \lambda^k_{\alpha\beta} \) are to be determined to satisfy the constraints. Now minimizing this functional with respect to \( \phi^0_i \) and equating to zero we have,

\[ h_i \phi^0_i + \sum_m \langle \phi^0_m | V_2 | \phi^0_m \rangle \phi^0_i + \sum_{k,m} \langle \phi^0_k \phi^0_m | V_3 | \psi^0_m \phi^0_k \rangle \phi^0_i + \ldots - \sum_{\beta} \lambda^l_{\alpha\beta} \phi^\beta_l = 0. \] (1.25)

Now define the operators \( f_i \) such that

\[ \langle \phi^\alpha_i | f_i | \phi^\beta_i \rangle = \langle \phi^\alpha_i | h_k | \phi^\beta_i \rangle + \langle \phi^\alpha_i | \left[ \sum_m \langle \phi^0_m | V_2 | \phi^0_m \rangle \right] | \phi^\beta_i \rangle + \ldots \] (1.26)

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

\[ f_i \phi^0_i = \sum_{\beta} \lambda^l_{\alpha\beta} \phi^\beta_l. \] (1.27)

Now choose \( \phi^\alpha_i \) as eigenfunctions of the \( f_i \)

\[ f_i \phi^\alpha_i = \epsilon^\alpha_i \phi^\alpha_i. \] (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 \( \phi^\alpha_i \) 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

\[
|\psi_0\rangle = C_0|\phi_0\rangle + \sum_{a,p} C_p^a|\phi_p^a\rangle + \sum_{a<b,\atop p<q} C_{pq}^{ab}|\phi_{pq}^{ab}\rangle + \sum_{a<b<c,\atop p<q<r} C_{pqr}^{abc}|\phi_{pqr}^{abc}\rangle + ... \ (1.29)
\]

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

\[
\mathbf{H} \mathbf{c} = \mathbf{e} \mathbf{c} \quad (1.30)
\]

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

\[
\mathbf{H}_{ij} = \langle \phi_i | H | \phi_j \rangle, \quad (1.31)
\]
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 $\psi$.

### 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,

$$\psi = e^T \phi_0,$$

where $\psi$ is the exact ground state many particle wave function and $\phi_0$ is the normalized HF wave function. The operator $e^T$ is defined by Taylor series expansion

$$e^T = 1 + T + \frac{T^2}{2!} + \frac{T^3}{3!} + \ldots = \sum_{k=0}^{\infty} \frac{T^k}{k!}$$

and the cluster operator $T$ is

$$T = T_1 + T_2 + T_3 + \ldots + T_n$$
where $n$ is the number of particle in the system. The effect of $T$ on $\phi_0$ is to create a linear combination of Staler determinant that includes all the singly, doubly ... up to $n$-tuply from $\phi_0$ i.e. all possible excitations of particle from occupied to virtual orbitals. Thus $e^T \phi_0$ gives exact $\psi$ like full CI. The one particle ($T_1$) and two particles ($T_2$) excitation operators are defined as

$$T_1 \phi_0 = \sum_{a,p} t^p_a \phi^p_a,$$

$$T_2 \phi_0 = \sum_{a,b,p,q} t^{pq}_{ab} \phi^{pq}_{ab},$$

where $\phi^p_a$ and $\phi^{pq}_{ab}$ are the singly and doubly excited slater determinants and $t^p_a$ and $t^{pq}_{ab}$ are the corresponding single and double excitation amplitude, respectively. Note that, no operator beyond $T_n$ appears as $\phi_0$ has all particles in $n$ occupied orbitals. The excitation amplitudes are determined by solving CC equations. Once these amplitudes are found, the wave function $\psi$ in Eq. (1.32) can be calculated. Substituting it in the Schrödinger equation [Eq. (1.1b)] we have

$$He^T |\phi\rangle = Ee^T |\phi_0\rangle. \quad (1.35)$$

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

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

$$\tilde{H}|\phi\rangle = E|\phi_0\rangle, \quad (1.36b)$$

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

$$\langle \phi_0 | \tilde{H} |\phi_0\rangle = E, \quad (1.37a)$$

$$\langle \phi_m | \tilde{H} |\phi_0\rangle = 0. \quad (1.37b)$$
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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

\[
e^{-\beta H} = \left(2\pi \hbar\right)^{-1} \int dx_0 \int dp_0 D(x_0, p_0) \times e^{-S(x_0, p_0)/\hbar} |x_0, p_0\rangle \langle x_0, i p_0|
\]

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

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

\( \gamma = \hbar / (2\beta) \).

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

\[
S(x_0, p_0) = \int_0^{\hbar \beta} \left[ \frac{1}{2} m \dot{x}^2 + V(x) \right] d\tau,
\]
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and the prefactor $D$ is given by

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

Miller and coworkers used this approach to calculate finite temperature 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

$$S = \int_x^{x'} p \, dx, \quad (1.42)$$

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 density 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

\[ x_0 = \frac{1}{\hbar \beta} \int_0^{h\beta} dt \, x(t). \] (1.43)

The centroid density is defined as

\[ \rho_c(x_c) = \int \ldots \int Dx(t) \delta(x_c - x_0) \exp(-S[x(t)]/\hbar) \] (1.44)

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

\[ Z = \int dx_c \rho_c(x_c). \] (1.45)

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

\[ Z = Lt_{n \rightarrow \alpha} Z_n, \] (1.46)

where

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

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

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

The thermal averages \( \langle A \rangle_\beta \) are calculated analogously from

\[ \langle A \rangle = \frac{1}{Z} Tr[e^{-\beta H} A] \] (1.49)
which also can be calculated within the isomorphism as $\langle A \rangle = Lt_{n \to \infty} \langle A \rangle_n$, where

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

with

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

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 approach 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 $\beta$, 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

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

(1.52)
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using the ansatz

\[ |x_n(t)\rangle = \exp\left[\gamma(t) - \frac{1}{2}\{x - x_n(t)\}^T G(t) \{x - x_n(t)\}\right] \]  \hspace{1cm} (1.53)

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

\[ L = \langle x_n(t) \left| \frac{d}{dt} + H \right| x_n(t) \rangle. \]  \hspace{1cm} (1.54)

From the solutions, the density matrix is reconstructed as

\[ \rho = \sum_n p_n |x_n(t)\rangle \langle x_n(t)| \]  \hspace{1cm} (1.55)

with respect to the parameters. The weight factors \(p_n\) are determined at \(t = 0\), when \(\rho\) 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 minimum error method.

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

\[ I(\dot{\rho}) = Tr(\dot{\rho} + H\rho)^2 \]  \hspace{1cm} (1.56)

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

\[ Tr[\delta \dot{\rho}(\dot{\rho} + H\rho)] = 0 \]  \hspace{1cm} (1.57)
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from which the working equations for the parameters in the ansatz for $\rho$ are derived and applied it for a particle in external field. They too have expanded $\rho$ 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 $\beta \to 0$. 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-Bogoliubov 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

$$A \leq A_0 + \langle H - H_0 \rangle,$$

(1.58)

where

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

(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 Spidonov 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
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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

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

(1.60)

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

$$Z = e^{X_0}$$

(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 $\nu_i$ is then substituted in the HO partition
function equation

\[ Z_{\text{vib}} = \Pi_{i=1} \left[ 1 - \exp(\nu_i/k_B T) \right]^{-1} \]  \hspace{1cm} (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

\[ \nu_i = w_i + 2f_i + \frac{1}{2} \sum_{j \neq i} f_{ij} \]  \hspace{1cm} (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

\[ ZPE = f_0 + \frac{1}{2} \sum_i \left( w_i + \frac{1}{2} f_{ii} + \sum_{j<i} \frac{1}{2} f_{ij} \right) \]  \hspace{1cm} (1.64)

The expansion for the harmonic partition function is then used

\[ Z_{\text{vib}} = \frac{e^{-ZPE/kT}}{\Pi_i [1 - \exp(\nu_i/k_B T)]} \]  \hspace{1cm} (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.
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within the one-mode basis set.

\[ Z_{\text{vib}} = \sum_{n} \exp \left[ \frac{-E_{i}^{\text{VSCF}} + \sum_{m=1}^{M} \Delta \epsilon_{n}^{M}}{k_{B}T} \right] \]  

(1.66)

Here, \( E_{i}^{\text{VSCF}} \) 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 asymmetry 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

$$\rho = \Pi_k \rho_k e^{-\beta E_0},$$  \hspace{1cm} (1.67)

where each $\rho_k$ is the density matrix for one vibrational mode and given by

$$\rho_k = e^{-\beta h_k}.$$  \hspace{1cm} (1.68)

The mathematical framework for such a description is still provided by the Feynman variational principle based on the Gibbs-Bogoliubov 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 assess 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
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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 frameworks.

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.