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 approach. 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 through-
out 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,

$$
<X>_{\beta} = Tr \ X \rho(\beta) = Tr \ \rho(\beta/2)X\rho(\beta/2). \quad (5.1)
$$
If we now define a new operator

$$X_{\beta} = \rho(\beta/2)X\rho(\beta/2)$$  \hspace{1cm} (5.2)

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

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

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

$$Tr(\delta H_0)[2X_{\beta}(H - H_0)X_{\beta} + X_{\alpha}X_{\beta}(H - H_0) + (H - H_0)X_{\beta}X_{\beta}] = 0.$$  \hspace{1cm} (5.4)

Note that this expression is similar to the symmetrized version (Eq. (3.14)) of the working equation for $\rho$. Here, $H_0$ is once again the modal Hamiltonian. Construction of $X_{\beta}$ operator is a trivial exercise. For example, in the separable approximation the ansatz for the coordinate operator $Q_k$ is

$$Q_{k\beta} = \sum_{n,m} |\phi_n^k\rangle\langle\phi_n^k|Q_k|\phi_m^k\rangle\langle\phi_m^k| \exp[-\beta(\varepsilon_n^k + \varepsilon_m^k)/2].$$  \hspace{1cm} (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

$$C(t) = Tr[A(t) \, B(0) \, \rho].$$  \hspace{1cm} (5.6)

It can be written as,

$$C(t) = Tr[A_{\beta}^T(t) \, B_{\beta}(0)],$$  \hspace{1cm} (5.7)
where

\[ A_\beta = A\rho(\beta/2). \]  \hfill (5.8)

\( A_\beta \) and \( B_\beta \) can be obtained independently and propagated in time. However, the working equations for \( A_\beta \) 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 1000\( K \) (100 points) takes about 5 seconds 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.