On Emerging Field of Quantum Chemistry at Finite Temperature

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Abstract

In this article, we present an emerging field of quantum chemistry at finite temperature. We discuss its recent developments on both theoretical and experimental fronts. We describe and analyze several experimental investigations related to the temperature effects on the structure, electronic spectra, or bond rupture forces for molecules. This includes the study of the temperature impact on the pathway shifts for the protein unfolding by atomic force microscopy (AFM), the temperature dependence of the absorption spectra of electrons in solvents, and temperature influence over the intermolecular forces measured by the AFM. On the theoretical side, we review a recent advancement made by the author in the coming fields of quantum chemistry at finite temperature. Starting from Bloch equation, we have derived the sets of hierarchy equations for the reduced density operators in both canonical and grand canonical ensembles. They provide a law according to which the reduced density operators vary in temperature for the identical and interacting many-body particles. By taking the independent particle approximation, we have solved the equation in the case of a grand canonical ensemble, and obtained an eigenequation for the molecular orbitals at finite temperature. The explicit expression for the temperature-dependent Fock operator is also given. They will form a foundation for the study of the molecular electronic structures and their interplay with the finite temperature.
Furthermore, we clarify the physics concerning the temperature effect on the electronic structure or processes of the molecules which is crucial for both theoretical understanding and computational study. Finally, we summarize our discussion and point out the theoretical and computational issues for the future explorations in the fields of quantum chemistry at finite temperature.

**Keywords** Quantum chemistry at finite temperature; temperature dependent; polymers; protein folding; intermolecular forces; solved electrons.

## 1 Introduction

The history for quantum chemistry development is almost synchronous to that of quantum mechanics itself. It begins with Heitler and London’s study of electronic structure of $H_2$ molecule shortly after the establishment of wave mechanics for quantum particles [1]. There are two major types of molecular electronic theories: valence bond approach vs. molecular orbital method with the latter being the popular one for the present investigation. It has gone through the stages from the evaluation of molecular integrals via a semiempirical way to the one by an *ab initio* method. Correlation issue is always a bottleneck for the computational quantum chemistry and is under intensive study for over fifty years. For large molecular systems such as biomolecules and molecular materials, the development of the combined QM/MM approach, pseudopotential method and linear scaling algorithm has significantly advanced our understanding of their structure and dynamics. There are about eight Nobel prize laureates whose researches are related to the molecular electronic structure theory. This not only recognizes the
most eminent scientists who have made the outstanding contributions to the fields of quantum chemistry, but more importantly, it indicates the essential roles the electronic structure theory has been playing in the theoretical chemistry as well as for the whole areas of molecular sciences. Nowadays, quantum chemistry has been becoming a maturing science [2, 3].

Nevertheless, the current fields of quantum chemistry are only part of the story for the molecular electronic structure theory. From the pedagogical points of view, the quantum mechanics based on which the traditional quantum chemistry is built is a special case of more general quantum statistical mechanics [4, 5, 6]. In reality, the experimental observations are performed under the conditions with thermodynamic constraints. Henceforth, there is a need to extend the current areas of quantum chemistry to the realm of, for instance, finite temperature [4, 5, 6].

Indeed, many experimental investigations for various fields and for different systems have already shown the temperature or pressure effects on their microscopic structures [7-30, 49-57, 63, 71-87]. The polymeric molecules are one of the most interesting systems for this sort of studies [7-16]. The experimental measurement on the absorption spectra, photoluminescence (PL), and photoluminescence excitation (PLE), and spectral line narrowing (SLN) for the PPV and its derivatives all show the same trend of the blue shift with the increasing temperature [7, 8, 9]. This attributes to the temperature dependence of their very rich intrinsic structures such as the vibronic coupling [14, 15, 16]. The experimental investigation of the temperature effect on the biomolecules started in the late nineteenth century [17, 18]. Most recently, it has been extended to the study of folding and unfolding of protein
or DNA [19, 20, 21]. In addition to the observed patterns for the unfolding forces with respect to the extension or temperature, it has been proved that the temperature-induced unfolding is another way for the study of mechanisms or pathways of protein folding or unfolding processes [19-23]. The newest related development is on the AFM measurement made by Lo et al. of the intermolecular forces for the biotin-avidin system in the temperature range from 286 to 310K [63]. It has shown that an increase of temperature will almost linearly decrease the strength of the bond rupture force for the individual biotin-avidin pair. The study of temperature effect on the absorption spectra of solvated electron began in the 1950’s and it is still of current interest. A striking effect is that an increasing temperature will cause the positions of their maximal absorption red shift [71-85].

In recent papers, we have deduced an eigenequation for the molecular orbitals [4, 5]. It is the extension from the usual Hartree – Fock equation at zero temperature to the one at any finite temperature [88, 89]. It opens an avenue for the study of the temperature effects on the electronic structures as well as their interplay with the thermodynamic properties. In the third section, we will present this equation and give the details for its derivation. In the next section, we will show four major types of experiments related to the study of the temperature influences over the microscopic structure of molecular systems. In the final section, we will discuss and analyze our presentations, and point out both theoretical and computational issues for the future investigation.
2 Experimental Development

In this section, we mainly describe the experimental investigations related to the temperature effect on the bonding, structure and electronic spectra of molecules. We choose four kinds of the most recent developments in these fields which are of chemical or biomolecular interests.

2.1 Temperature effects on geometric structure and UV-visible electronic spectra of polymers

The first important systems where the important issues related to the temperature effect on the geometric structure and electronic spectra are the polymeric molecules. Many experimental investigations and some theoretical work already exist in the literature [7-16]. However, how the temperature changes the microscopic structures of the polymers are still not completely understood and there are many unresolved issues in interpreting their electronic spectra. We list here a few very interesting experimental investigations for the purpose of demonstration.

The poly(p-phenylenevinylene)(PPV) is one of the prototype polymeric systems for the study of their various mechanical, electronic, and optical properties. The impact from the temperature on the absorption spectra, photoluminescence (PL), and photoluminescence excitation (PLE) of the PPV have also been investigated both experimentally and theoretically [7, 8, 9]. In an experiment carried out by Yu et al., the absorption spectra are measured for the PPV sample from the temperature 10 to 330K. The details of the experiment are given in their paper [9]. The resulting spectra for the absorption at $T = 80$ and $300K$ are shown in Figure 1 of that paper. We
see that there is a pronounced change in the spectra when increasing the temperature. They also study the PL and PLE spectra for the PPV. The measured PL spectra at two temperatures: 77 and 300K are demonstrated in the Figure 3, and the PLE spectra at those temperatures are depicted in the Figure 4 of the paper [9]. They both show the dramatic changes of the band blue shift when the temperature is increased. Similar studies have also been performed before by the other groups [7, 8]. They observed the similar behaviors.

Another interesting investigation is related to the temperature effect on the spectral line narrowing (SLN) of the poly(2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene)(MEH – PPV) spin-coated from either THF or CB solvents [11]. In the experiment done by Sheridan et al., the SLN is measured together with the absorption and PL as shown in Fig. 1 of their paper. It is found that the same trend of the SLN blue shift is observed as that for the absorption and PL with an increasing temperature. They attribute this to the same reason of the electronic structure modification resulting from the variation of the temperature.

### 2.2 Temperature effects on structure, dynamics, and folding/unfolding of biomolecules

Biomolecules are complex systems, featuring a large molecular size, a heterogeneity of atomic constitutes and a variety of conformations or configurations. Their energy landscape thereby exhibits multiple substates and multiple energy barrier, and varies in size for the barrier heights [24, 25, 26, 27, 28]. The temperature should have a strong effect on their structure and dynamics in-
cluding the folding or unfolding [17-57]. This effect could be either from the fluctuation of thermal motion of molecules or due to the redistribution of electronic charge as we will discuss in the next section.

The experimental observation of the temperature impact on the microscopic structure of biological systems dates back to the very early days. One focus, for example, is on the measurement of the elastic properties of the human red blood cell membrane as a function of temperature [17, 18]. Another related study is about the influence over the thermal structural transition of the young or unfractionated red blood cells due to the involvement of protein spectrin which might modified the spectrin-membrane interaction [29, 30]. Most recently, the atomic force microscopy (AFM) has been used to detect the impact from the variation of the temperature on the spectrin protein unfolding force as well as on the bond rupture force for the biotin-avidin system [19, 20, 21, 63].

The AFM is a surface imaging technique with an atomic-scale resolution capable of measuring any types of the forces as small as $10^{-18} \text{ N}$. It combines the principle of scanning tunnelling microscopes (STM) and stylus profilometer, and therefore can probe the surfaces of both conducting and nonconducting samples [31, 52]. The imaging on soft materials such as biomolecules with the AFM has been performed beginning in the 1980's [33, 54, 35]. Recently, it has been applied to measure the adhesive forces and energies between the biotin and avidin pair also as we will show in the next subsection [36, 37, 38, 39]. Unlike other experimental techniques, the AFM features a high precision and sensitivity to probe the surface with a molecular resolution, and can be done in physiological environments.
In an AFM investigation of mechanical unfolding of titin protein, for example, the restoring forces all show a sawtooth like pattern with a definite periodicity. It reveals much information about the mechanism of unfolding processes [42, 43]. The observed pattern, in addition to fit a worm-like chain model, has also been verified by the steered molecular dynamics or Monte carlo simulations [44, 45]. Similar study has been extended to other systems [46, 47, 48].

The same kind of experiments has also been performed by varying the temperature. In the experiment carried out by Spider and Discher et al. [21], the spectrin protein is chosen for the AFM study at different temperatures. Thousands of tip-to-surface contacts are performed for a given temperature because of the statistical nature of the AFM measurement. The observed curve for the relation between the unfolding force and extension shows the similar sawtooth pattern for all temperatures. In addition, the tandem repeat unfolding events are more favored at lower temperature as demonstrated in the unfolding length histograms. Most striking is that the unfolding forces show a dramatically nonlinear decreasing relation as the temperature $T$ approaches the transition temperature $T_m$. This is shown in the Figure 3B of paper [21].

Similar behaviors regarding the force-temperature dependence have also been observed via either AFM or optical tweezers for the forced overstretching transition for the individual double-stranded DNA molecules [19, 20, 49, 50].

Some other interesting experiments which illustrate the effect of temperature on the microscopic structure of biomolecules have also been performed
even though the detailed physical origins of the effect (from either the electrons or the molecules) have not been specified. In a circular dichroism (CD) spectra and high resolution NMR study, for instance, it shows that the secondary structure of the Alzheimer β (12-28) peptide is temperature-dependent with an extended left-handed 3_1 helix interconverting with a flexible random coil conformation. Another example is related to the analysis of the temperature-dependent interaction of the protein Ssh10b with DNA which influences the DNA topology. The study from the heteronuclear NMR and site-directed mutagenesis indicates that the Ssh10b exists as a dimer: T form and C form. Their ratio is determined by the Leu^{61} − Pro^{62} peptide bond of the Ssh10b which is sensitive to the temperature.

2.3 Temperature effects on intermolecular forces

The study of the general issues related to the temperature effects on the microscopic structure has been most recently extended to the realm of intermolecular forces. Since the usual intermolecular forces such as hydrogen bond, van der Waals force, ionic bond, and hydrophobic interaction are weak and typically of the order of 0.1 eV or 4.0 kT at the physiological temperature, the variation of temperature will thereby have a very strong influence over the strength of these forces.

The first experimental investigation on the temperature-dependent intermolecular forces is for the biotin-avidin system and by an AFM measurement. The biotin-avidin complex is a prototypical receptor and ligand system with the biotin binding strongly up to four avidin protein.
They have an extremely high binding affinity, and therefore serves as a model system for various experimental investigations. In the experiment carried out in Beebe’s group, the receptor avidin is attached to the AFM tip and linked to the agarose bead functionalized with the biotin. The temperature of the entire AFM apparatus is varied at a range from 286 to 310K. In addition, the loading rate is kept very slow so that the thermal equilibrium for the biotin-avidin pairs is assumed. The forces expected to be determined is the rupture force $F_i$ between the individual biotin-avidin pair which is defined as the maximum restoring force. In actual AFM experiment, however, the total adhesive force between the tip and substrate is measured. It is a sum of finite number $n$ of the interactions between each biotin and avidin pair. To extract the individual and average bond rupture, a statistical method has been developed in Beebe’s group. They assume a Poisson distribution for the number $n$ of the discrete rupture forces or linkages from multiple measurements, and have obtained the single force $F_i$ at different temperatures. The result is shown in the Figure 3 of the paper. We see that the individual rupture force $F_i$ for the biotin-avidin pair is decreased by about five-fold in strength when the temperature is increased from 286 to 310K.

To interpret the observed temperature impact on the biotin-avidin forces, Beebe’s group has performed a thermodynamic analysis. Based on the simple models and arguments, they have come out an equation that connects the square of the single bond-rupture force $F_i$ to the absolute temperature $T$ as follows,

$$F_i^2 = 2\Delta E^\ddagger k_{bond} - 2k_B T k_{bond} \ln \left( \frac{T_R}{T_D} \right)$$

(1)
where the $k_{bond}$ is the force constant of the individual biotin-avidin pair, and the time $\tau_R$ is the characteristic time needed to break $n$ pairs of those forces. The $E^\dagger$ is the energy required to remove the biotin from avidin’s strongest binding site and the corresponding time is $\tau_D$. More detailed on this analysis can be found in the paper [63]. The relation between the square of the force $F_i$ and temperature $T$ is also plotted as Figure 5 in that paper. Therefore, from the relation (1) and that Figure, the information about the stiffness of the ligand and receptor bond and the critical binding energy, etc. can be obtained. Obviously, what we need at present is a microscopic theory which can account for all these relations and properties.

2.4 Temperature effects on absorption spectra of electrons in solvents

The structure and dynamics of solute in solvent is one of the most important fields in chemistry since most of the chemical reactions occur in solution phases. In the meantime, it is also one of the most challenging fields in theoretical chemistry with many unsettled issues. The variation of temperature in the measurement of absorption spectra of solvated electron in various solvents has proved to be a useful means for the understanding of the solvation processes [71-85].

There are several experimental techniques available for this type of studies with the pulse radiolysis being the most commonly used one. There are also several research groups doing the similar experimental investigations and obtaining the consistent results relating to the temperature effects on the optical absorption spectra of solvated electron in solvents. In a recent
experiment carried out in Katsumura’s group, for example, the pulse radiolysis technique is employed to study the optical absorption spectra of the solvated electron in the ethylene glycol at different temperatures from 290 to 598K at a fixed pressure of 100 atm. In addition to the faster decay of absorptions, it is found that, their maximal positions shift to the red with the increasing temperature as shown in the Figures 1 to 3 of the paper [81]. This is in contrast to the situation for the electronic spectra of the polymers. They also point out the need to quantify the change of the density in the experiment in order to really understand the observed results.

The same type of experiment has been extended to the study of the optical absorption spectra for Ag^0 and Ag^+_2 in water by varying the temperature, and similar results have been obtained [80].

3 Theoretical Development

Having presented four different types of experiments above, we have seen that the temperature effect on the microscopic structure of molecules is a very interesting and sophisticated field. Many more needs to be understood and probed. Even though the experimental study has been for a long time, very limited number of the related theoretical work is available, especially at the first-principle level. In other words, the quantum chemistry at finite temperature is not a well-defined or well-established field [4, 5, 6].

It is true that the influence of temperature on the microscopic structure is a complicated phenomenon. There exists different functioning mechanisms. One consideration is that the variation of the temperature, according to
the Fermi-Dirac statistics, will change the thermal probability distribution of single-particle states for a free electron gas. It is expected that similar situation should occur for an interacting electron system, and therefore its microscopic structure will be correspondingly altered. Another consideration is that, for molecules or solids, the thermal excitation will cause the change of the time scales for the molecular motions. This will most likely bring about the transitions of the electronic states, and therefore lead to the breakdown of the Born-Oppenheimer approximation. Electron-phonon interaction is a fundamental topic in solid state physics and its temperature dependence is well-known. As a result, the temperature could change the strength of the coupling between the electronic and molecular motions. Nevertheless, we tackle the issues in a simpler way. We treat only an interacting identical fermion system, or neglect the coupling of the electronic motion with those of the nucleus in molecules or solids. We expect that some sort of the general conclusions will come out from this study. As a matter of fact, this is also the approach usually adopted in a non-adiabatic molecular dynamics, in which purely solving the eigenequation for the electrons will provide the reference states for the investigation of the coupling motions between the electrons and the nucleus of the molecules.

In the following, we will present a self-consistent equation within the framework of equilibrium statistical mechanics which decides the molecular orbitals at a given temperature.
3.1 Hierarchy Bloch equations for reduced density operators in canonical ensemble

We consider an identical and interacting \(N\)-particle system. In a canonical ensemble, its \(N\)th-order density operator takes the form

\[
D_N = \exp(-\beta H_N),
\]

and satisfies the Bloch equation \[90, 91\]

\[
- \frac{\partial}{\partial \beta} D^N = H_N D^N,
\]

where

\[
H_N = \sum_{i=1}^{N} h(i) + \sum_{i<j}^{N} g(i,j),
\]

is the Hamiltonian for the \(N\) particle system composed of the one-particle operator \(h\) and two-body operator \(g\). The \(\beta\) is the inverse of the product of Boltzmann constant \(k_B\) and absolute temperature \(T\).

Since the Hamiltonian (4) can be written as a reduced two-body operator form, the second-order reduced density operator suffices to describe its \(N\) (\(\geq 2\)) particle quantum states. A \(p\)th-order reduced density operator is generally defined by \[92, 93\]

\[
D^p = L^p_N(D^N),
\]

where \(L^p_N\) is the contraction operator acting on an \(N\)th-order tensor in the \(N\)-particle Hilbert space \(V^N\). The trace of the \(D^p\) gives the partition function,

\[
Tr(D^p) = Z(\beta, V, N).
\]

Rewrite the Hamiltonian in a form

\[
H_N = H^p_1 + \sum_{j=p+1}^{N} h(i) + \sum_{i=1}^{p} \sum_{j=p+1}^{N} g(i,j) + \sum_{i<j \geq p+1}^{N} g(i,j),
\]
where
\[ H_p^1 = \sum_{i=1}^{p} h(i) + \sum_{i<j}^{p} g(i, j), \] (8)
and apply the contraction operator \( L^p_N \) on both sides of the Eq. (3), we develop an equation that the \( p \)th-order density operator satisfies \[ -\frac{\partial}{\partial \beta} D^p = \left[ H^1_p D^p + (N - p)L^p_{p+1} \left[ h(p+1)D^{p+1} \right] + (N - p)L^p_{p+1} \left[ \sum_{i=p}^{p} g(i, p+1)D^{p+1} \right] + \right] \]
\[ + \left( \frac{N - p}{2} \right) L^p_{p+2} \left[ g(p+1, p+2)D^{p+2} \right]. \] (9)
It provides a law according to which the reduced density operators vary in terms of the change of temperature.

**3.2 Hierarchy Bloch equations for reduced density operators in grand canonical ensemble**

The above scheme for deducing the equations for the reduced operators can be readily extended to the case of a grand canonical ensemble, which is a more general one with a fluctuating particle number \( N \). In this ensemble, the density operator is defined in the entire Fock space
\[ F = \sum_{N=0}^{\infty} \oplus V^N, \]
and is written as the direct sum of the density operators \( D_G(N) \) associated with the \( N \)-particle Hilbert space \( V^N \),
\[ D_G = \sum_{N=0}^{\infty} \oplus D_G(N), \] (10)
where
\[ D_G(N) = \exp[-\beta(H - \mu N)], \]
\[ = \exp(-\beta \bar{H}), \] (11)
and
\[ \hat{H} = H - \mu N, \]  
(12)
is called the grand Hamiltonian on \( V^N \). The form of the Hamiltonian \( H \) has been given by Eq. (4) and the \( \mu \) is the chemical potential. The corresponding \( p \)th-order reduced density operator is therefore defined as
\[ D^p_G = \sum_{N=p}^{\infty} \oplus \binom{N}{p} L_N^p[D_G(N)], \]  
(13)
with the trace given by
\[ Tr(D^p_G) = \left\langle \binom{N}{p} \right\rangle D^0_G, \]  
(14)
and
\[ D^0_G = \Xi(\beta, \mu, V). \]  
(15)
The \( \Xi(\beta, \mu, V) \) is the grand partition function.

In a similar manner, we can also derive the hierarchy equations that the reduced density operators in the grand canonical ensemble obey
\[ -\frac{\partial}{\partial \beta} D^p = \tilde{H}^p D^p + (p + 1)L_{p+1}^p \left[ \tilde{h}(p + 1)D^{p+1} \right] + (p + 1)L_{p+1}^p \left[ \sum_{i=1}^{p} g(i, p + 1)D^{p+1} \right] + \]  
\[ + \left( \frac{p + 2}{2} \right) L_{p+2}^p \left[ g(p + 1, p + 2)D^{p+2} \right], \]  
(16)
where
\[ \tilde{H}^p = \sum_{i=1}^{p} \tilde{h}(i) + \sum_{i<j}^{p} g(i, j), \]  
(17)
and
\[ \tilde{h}(i) = h(i) - \mu. \]  
(18)
It gives us a law with which the reduced density operators in the grand canonical ensemble vary in temperature.
The Eqs. (9) and (16) define a set of hierarchy equations that establish the relation among the reduced density operators $D^p$, $D^{p+1}$, and $D^{p+2}$. They can be solved either in an exact scheme or by an approximate method. The previous study of $N$ electrons with an independent particle approximation to the Schrödinger equation for their pure states has lead to the Hartree − Fock equation for the molecular orbitals [94-100]. We thereby expect that the same approximate scheme to the reduced Bloch equations (9) or (16), which hold for more general mixed states, will yield more generic eigenequations than the usual Hartree − Fock equation for the molecular orbitals.

We consider the case of a grand canonical ensemble. When $p = 1$, Eq. (16) reads

$$\frac{\partial}{\partial \beta} D^1 = H_1 D^1 + \frac{Tr(\hbar D^1)}{D^0} D^1 - \frac{1}{D^0} D^1 \hbar D^1 + 2L_2^{1} [g(1,2)D^2] + 3L_3^{1} [g(2,3)D^3].$$

(19)

Under the orbital approximation, the above second-order and third-order reduced density operators for the electrons can be written as

$$D^3 = D^1 \wedge D^1 \wedge D^1 / (D^0)^2$$

(20)

and

$$D^2 = D^1 \wedge D^1 / D^0.$$  

(21)

These are the special situations for the statement that a $p$th-order reduced density matrix can be expressed as a $p$-fold Grassmann product of its first-order reduced density matrices. With these approximations, the last two
terms of Eq. (19) can be evaluated in a straightforward way as follows

\[ 2L_2^1 \left[ g(1, 2)D^2 \right] = (J - K)D^1, \quad (22) \]

and

\[ 3L_3^1 \left[ g(2, 3)D^3 \right] = \frac{\text{Tr}(gD^2)}{D^0} - \frac{1}{D^0}D^1(J - K)D^1, \quad (23) \]

where

\[ J = \text{Tr}_2 \left[ g \cdot D^1(2; 2) \right] / D^0, \quad (24) \]

and

\[ K = \text{Tr}_2 \left[ g \cdot (2, 3) \cdot D^1(2; 2) \right] / D^0, \quad (25) \]

are called the *Coulomb* and exchange operators, respectively. With the \((2, 3)\) being the exchange between the particle 2 and 3, the action of the \(K\) on the reduced density operator is

\[ K \cdot D^1(3; 3) = \text{Tr}_2 \left[ g \cdot (2, 3) \cdot D^1(2; 2) \right] / D^0 \cdot D^1(3; 3) = \text{Tr}_2 \left[ g \cdot D^1(3; 2) \cdot D^1(2; 3) \right] / D^0. \quad (26) \]

Substitution of Eqs. (22) and (23) into Eq. (19) yields the *Bloch* equation for the first-order reduced density matrix of \(N\) interacting electrons under orbital approximation,

\[ -\frac{\partial}{\partial \beta}D^1 = (F - \mu)D^1 + \left( \frac{\text{Tr}\tilde{h}D^1}{D^0} + \frac{\text{Tr}D^2}{D^0} \right)D^1 = \frac{1}{D^0}D^1(F - \mu)D^1, \quad (27) \]

where

\[ F = h + J - K, \quad (28) \]

is called the *Fock* operator at finite temperature. Redefine the normalized first-order reduced density operator

\[ \rho^1 = D^1 / D^0, \quad (29) \]
we can simplify above equation into

$$-\frac{\partial}{\partial \beta} \rho^1 = (F - \mu)\rho^1 - \rho^1(F - \mu)\rho^1.$$  \hspace{1cm} (30)

Furthermore, from Eq. (30) and its conjugate, we get

$$F \rho^1 - \rho^1 F = 0,$$  \hspace{1cm} (31)

which means that the Fock operator $F$ and the first-order reduced density matrix $\rho^1$ commute. They are also Hermitian, and therefore have common eigenvectors $\{|\phi_i\rangle\}$. These vectors are determined by the following eigen equation for the Fock operator,

$$F |\phi_i\rangle = \epsilon_i |\phi_i\rangle.$$  \hspace{1cm} (32)

The first-order reduced density operator is correspondingly expressed as

$$\rho^1 = \sum_i \omega(\beta, \mu, \epsilon_i) |\phi_i\rangle \langle \phi_i|,$$  \hspace{1cm} (33)

where $\omega(\beta, \mu, \epsilon_i)$ is the thermal probability that the orbital is found to be in the state $\{|\phi_i\rangle\}$ at finite temperature $T$. Substituting Eq. (33) into Eq. (30), we can obtain the equation this thermal probability $\omega(\beta, \mu, \epsilon_i)$ satisfies,

$$-\frac{\partial}{\partial \beta} \omega(\beta, \mu, \epsilon_i) = (\epsilon_i - \mu)\omega(\beta, \mu, \epsilon_i) - (\epsilon_i - \mu)\omega^2(\beta, \mu, \epsilon_i).$$  \hspace{1cm} (34)

Its solution has the same usual form of the Fermi–Dirac statistics for the free electron gas as follows,

$$\omega(\beta, \mu, \epsilon_i) = \frac{1}{1 + e^{\beta(\epsilon_i - \mu)}},$$  \hspace{1cm} (35)

with the energy levels $\{\epsilon_i\}$ determined by Eq. (32).
4 Discussion, Summary and Outlook

In this paper, we have presented a description of both experimental and theoretical developments related to the temperature impact on the microscopic structure and processes for the molecules.

In the theoretical part of this paper, we have depicted the sets of hierarchy Bloch equations for the reduced statistical density operators in both a canonical and a grand canonical ensembles for the identical fermion system with two-body interaction. We have solved the equations in the latter case under a single-orbital approximation and obtained an eigen-equation for the single-particle states. It is the extension of usual commonly used Hartree–Fock equation at the absolute zero temperature to the situation at any finite temperature. The average occupation number formula for each single-particle state is also obtained, which has the same analytical form as that for the free electron gas with the single-particle state energy determined by the Hartree–Fock equation at finite temperature (32).

From Eqs. (24), (25) and (28), we see that the Coulomb operator $J$, the exchange operator $K$, and therefore the Fock operator $F$ are both the coherent and the incoherent superpositions of single-particle states. They are all temperature-dependent through an incoherent superposition factor, the Fermi–Dirac distribution, $\omega(\beta, \mu, \epsilon_i)$. Therefore, the mean force or the force field, and the corresponding microscopic structure are temperature-dependent.

We have expounded the physics relating to the temperature effects on the electronic structure or processes of the molecules. This is very critical for our understanding and studying the temperature influence over the molecular
structure. From this analysis, for example, we could see that the temperature should have a stronger effect on the molecular transition states and therefore their chemical reactivity. Starting from Eqs. (9) or (16), it will be a very significant work to establish a corresponding multireference theory for the molecular orbitals at finite temperature [96, 101, 102].

On the experimental sides, we have exposed four major fields of investigations of chemical or biomolecular interests, which show the temperature impact on their structures, spectra, or bond rupture forces.

The complete determination of the geometric structure and electronic spectra of the polymeric molecules is a very difficult task. As has been stated in papers [15, 16], there are many different components contributing to the change of the spectra. At present, we focus on the study of the effect from the temperature. We have demonstrated that it can alter both the shapes and positions of the absorption and other spectra for the PPV and its derivatives. As has been analyzed, the increase of the temperature will cause the excitation of the vibrational, rotational and liberal motions which might also lead to the electronic transition. The Huang – Rhys parameter has been introduced to describe the strength of the coupling between the electronic ground- and excited-state geometries. Furthermore, it has been found that this factor is an increasing function of the temperature [7, 8, 9]. Obviously, a more detailed study of the electronic structure, excitation and spectroscopic signature at the first-principle level which includes the temperature-dependent force field is expected.

The temperature has proved to be a big player in both experimental and theoretical study of the structure and dynamics of biomolecules including
their folding or unfolding. At a first glance, the energy gap between the HOMO and LUMO for the biomolecules should be small or comparable to the Boltzmann thermal energy $k_B T$ because of their very large molecular size. Therefore a change of the temperature should have a strong influence over their electronic states, and consequently, the energy landscape and the related dynamics including the folding or unfolding, etc. The experimental investigation with the AFM and other techniques of the temperature effect on the shift of their unfolding pathways might have verified this sort of thermal deformation of potential energy landscape [19, 20, 21]. This is in contrast to the tilt and deformation of energy landscape of biomolecules including their transition states resulting from the applied mechanical forces [39].

Unfolding proteins by temperature is not just one of the classical experimental techniques for the study of the structure, dynamics and energetics of the biomolecules. It has also been employed, for example, in the molecular dynamic simulation to study the structure of transition states of CI2 in water at two different temperatures: 298 $K$ and 498 $K$ [22]. The later high temperature is required in order to destabilize the native state for monitoring the unfolding as done in the real experiments. In another recent molecular dynamics simulation [23], Karplus’s group has compared the temperature-induced unfolding with the force-stretching unfolding for two $\beta$-sandwich proteins and two $\alpha$-helical proteins. They have found that there are the significant differences in the unfolding pathways for two approaches. Nevertheless, in order to get more reliable results, temperature-dependent force fields need to be developed and included in the molecular dynamics simulations. This is also the case in the theoretical investigation of protein folding since
an accurate simulation of protein folding pathways requires better stochastic or temperature-dependent potentials which have become the bottleneck in structure prediction \cite{24, 25, 26, 27, 28}. From structural points of view, the variation of temperature leads to the change of the mean force or the energy landscape, and therefore provides a vast variety of possibilities, for instance, in the protein design and engineering.

The intermolecular forces are ubiquitous in nature. They are also extremely important for the biological systems and for the existence of life. The intermolecular forces have the specificity which are responsible for the molecular recognition between receptor and ligand, antibody and antigen, and complementary strands of DNA, and therefore for the regulation of complex organization of life \cite{103}. For these reasons, the experiment carried out in Beebe’s group has an immediate significance. It has demonstrated that the temperature can be an important factor for changing the specificity of the intermolecular forces and therefore the function of life \cite{63}. Nevertheless, how the charge redistribution occurs due to the variation of the temperature has not been interpreted, and a microscopic theory for quantifying the temperature influence on the intermolecular forces is still lacking. Since the delicate study of the intermolecular forces provides the insight into complex mechanisms of ligand-receptor binding and unbinding processes or pathways, a paramount future research is to establish the links between the intermolecular forces and the temperature within the quantum many-body theory.

The theoretical study of the temperature effects on the optical absorption spectra of solvated electron is still in very early stage and few published works are available \cite{82, 83, 84, 85}. One of the earliest studies by Jortner
used a cavity model to simulate the solvated electron where the electron is confined to the cavity surrounded by the dielectric continuum solvent [S2]. However, his study is not of fully microscopic in nature since he assumed a temperature dependence of phenomenological dielectric constants which were also obtained from the available experimental data. In addition, the model used is too simplified and, for instance, it neglects the intrinsic structure of the solvent molecules. There are a few recent investigations on the temperature effects on the absorption spectra of solvated electrons. They all cannot catch the full features of the experimental observations. One reason is that the physical nature for the process is not totally understood which might leads to incorrect models used for the simulation. The other is to utilize the crude models which might have omitted some important physical effects. For example, in an analysis by Brodsky and Tsarevsky [S3], they have concluded a temperature-dependence relation for the spectra which is, however, in contradiction with the experimental findings at high temperature. The quantum path-integral molecular dynamics simulation cannot produce those temperature-dependence relations observed in the experiments [S4]. In a recent quantum-classical molecular-dynamics study by Nicolas et al, even though the temperature-dependent features of optical absorption spectra for the solvated electron in water have been recovered [S5], however, they claim that the red shifts of absorption spectra with increasing temperature observed in both experiments and calculation are due to the density effect instead of temperature. This might cast the doubt of usefulness of our current theoretical work in this area. However, after examining their work, we observe that they actually have not included any temperature effect on the electron in
their theoretical model. This effect might be either from the Fermi – Dirac distribution for individual electrons or due to the electronic excitation caused by the thermal excitation of the solvent, as we have discussed in paper [4]. Obviously, much finer theoretical work or more experimental investigations in this area are expected to resolve this dispute.

In addition to the systems discussed above, there are other types which also show the temperature impact on their microscopic structures. Either theoretical or experimental work have been done or are in progress. Examples include the study of the temperature dependence of the Coulomb gap and the density of states for the Coulomb glass, the experimental investigation of the temperature effects on the band-edge transition of ZnCdBeSe, and the theoretical description of the influence from the temperature on the polaron band narrowing in the oligo-acene crystals [104, 105, 106].

To sum up, the quantum chemistry at finite temperature is a new and exciting field. With the combination of the techniques from current quantum chemistry with those developed in statistical or solid state physics, it will provide us with a myriad number of opportunities for the exploration.

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