Quantum Optics of Laser Cooling of Molecules

Dissertation

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Summary/Abstract of the Thesis

This thesis contains the theoretical developments of quantum optical formalisms and techniques to manipulate the internal quantum states and the center of mass momentum of molecules, with the aim of laser cooling of molecules. Atoms have been successfully laser-cooled to nano-Kelvin temperature using the combinations of kinetic effects of lasers, dissipative mechanism and the formation of ?dark? (non-absorbing) state. For molecules, laser cooling is not regarded as a feasible option compared to non-laser techniques. The complex internal energy levels in molecules precludes the use of existing laser cooling methods to cool molecules. A new scheme is required if molecules were to be laser-cooled. A new scheme is developed theoretically to laser-cool the translational degree of a dilute gas of molecules to temperature below micro-Kelvin using quantum optical techniques. The scheme is based on the repetition of a cycle, composed of three simple concepts: velocity selection, deceleration and irreversible accumulation. It overcomes the long-standing problem: the impossibility of maintaining repeated cycles of optical pumping in molecular levels. No closed pumping cycle nor repeated spontaneous emissions are required. The three concepts are represented by a combination of laser techniques used to shape the momentum distribution of the molecular gas: Raman p-pulse for velocity selection, Stimulated Raman Adiabatic Passage (STIRAP) for deceleration, and a single spontaneous emission for irreversible accumulation. The quantum dynamics of the cooling process is modeled analytically using the density matrix. This enables convenient computations of the transient internal and center of mass (external) entropies. A thorough quantum theory of laser-molecule interactions with quantized center of mass variables is developed. Fundamentals of molecular spectra for diatomics are given. The general master equation with field-dependent dissipation is derived using projection operator approach. It is used to study the effect of dissipation on the momentum spread in spontaneous emissions and the possibility of controlling the decay rate using strong laser fields and multiple pulses. The Fourier transform method is used to solve the momentum spread dynamics. The relationships between quasi-phase space Wigner function, entropy, dissipative Liouvillean, momentum probability distribution are given. The full quantum dynamics of Raman velocity selection and STIRAP processes are analyzed and simulated using the density matrix equations including the effect of center of mass momentum. The optimal conditions for complete population transfers are derived. The time and momentum dependent light force on the molecules during the coherent population transfer is simulated.
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Chapter 1

Introduction

The 1997 and 2001 Nobel prize was given in connection with the ultracold atomic gases [32], [33] shows the scientific importance of this area of research. The ability to confine and manipulate ultracold gas of atoms with extremely low kinetic and temperature down to \( \mu K \) provides new applications [3] which were not possible before. Examples of technological applications of cold atomic gas are high fidelity frequency standards from atomic clock [5], atom interferometers [4] used for navigation in space-probe voyages, atom lithography [164] to produce higher resolution nanostructures, atom lasers [6] used for atom optics [21] and quantum computer technology with trapped qubits. In scientific applications, cold atoms minimizes the Doppler broadening and provides long interaction time for very precise spectroscopic measurements of atomic parameters [7], the studies of collisional dynamics in cold regime, the testing of atomic parity non-conservation and atomic Bose-Einstein condensation (BEC) [12]. New physical effects like Bloch oscillations of cold atoms in accelerating periodic potential has also been observed [10]. This effect is more difficult to be observed in solid crystal because the oscillation damps so fast due to high collision rate of the electrons. All these new possibilities stem from two distinct physical properties of cold atoms: a) reduced Doppler broadening, and b) quantum interference effects arising from the pronounced wave nature of particle due to the longer de Broglie wavelength at low velocity. The interference of matter wave of atoms has been used creatively, to shift the matter wave frequency [19] via Bragg diffraction from periodic light potential [20], and for interferometry [18].

1.1 Outline and History of Laser Cooling of Atoms

The techniques to cool solids have been developed much earlier based on the thermodynamic principles of isothermal magnetization and isentropic demagnetization [25]. This technique enables solids with permanent nuclear magnetic moment to be cooled down to \( \mu K \). The irreversible and dissipative mechanism in the cooling is thermalization, which relies on a large specific heat of the material. However, the cooling principle is inapplicable
to gases because of the low specific heat. The possibility of using electromagnetic fields for cooling of the internal degree of matter was proposed in 1973 by Zeldovich [28]. However, light has never been used to cooled solids until recently [27]. Deflection of atomic beam by light had been known ever since Maxwell derived an expression for the light pressure of radiation. This was observed experimentally with conventional light sources.

Since laser was developed into a practical tool in the 1960s, it was realized that the high intensity and excellent directionality of the laser beam can provide powerful energy and momentum density not available from conventional light sources for manipulating the atomic motion. The classical theory of gradient light force from spatially varying high intensity electromagnetic field was developed early [165]. In 1968, Lethokov [29] found the reduction of the Doppler width of gas in standing light field and suggested atomic trapping with electromagnetic fields. It has been the dream of spectroscopists to eliminate the Doppler effect in gas in order to reduce the broadening of the spectral lines and obtain more precise measurements. The radiation pressure of laser was first used for trapping, acceleration and deflection of particles by Ashkin [168]. In 1975, Hänsch and Schawlow [30] proposed cooling of atomic gas with laser based on Doppler effect. After that, the theory of laser cooling and trapping have been developed by various groups. The first laser cooling experiment was performed using magnesium ions [31]. After Wineland and Itano [167] published the detailed theoretical analysis of laser cooling, there has been burgeoning surge in the interest of laser cooling of atoms. Semiclassical theory of laser cooling and trapping was further developed by Letokhov's group [166]. Stenholm and Javanainen later developed rigorous full quantum theory based on master equation [170]. Up to now, there is an enormous amount of theoretical works and reviews on the Doppler laser cooling and trapping of atoms with laser light by major atom cooling and trapping groups: Tannoudji [32], Chu [34], Phillips [33], Stenholm [38], Metcalf [37]; and special editions [39],[35], [36].

1.2 Cooling Schemes for Atoms

Laser cooling schemes for atoms have relied on closed pumping cycles within a few energy levels by repeated optical excitation followed by spontaneous emissions in the optical regime. Since spontaneous emission is a quantum mechanical process due to the quantized nature of vacuum fields [217], laser cooling is quantum effect. The Doppler cooling relies on the coupling between the internal atom states and the momentum states by laser photon. If the laser frequency is tuned slightly below the atomic transition frequency (red detuned laser), those atoms moving against the laser direction will 'see' a higher photon frequency and thus 'blue- shifted' closer to resonant with the excited level. These atoms are more likely to absorb the red detuned photon than the atoms moving away from the laser direction. The absorption process transfers the photon momentum to the atoms, which become decelerated. In subsequent spontaneous emission, the atom decays to the same ground state and is accompanied by a momentum recoil at random directions. After each
cycle of absorption-spontaneous emission, on average the momentum component along the laser is reduced by the photon momentum. The lowest temperature in Doppler cooling was derived for broad line ($\Gamma \gg \frac{\omega^3}{3c_\text{F}}$) as $T_{\text{min}} \sim \frac{\hbar \Gamma}{k_B}$ in semiclassical regime based on adiabatic elimination which gives the Fokker-Planck equation [38] and for narrow line ($\Gamma \lesssim \hbar k^2/2M$) as $T_{\text{min}} \sim \left(\frac{\hbar k^2}{2MB}\right)$ by Castin [46] using the full quantum Bloch equations. For most atomic transitions, the natural linewidth of the excited state $\Gamma$ is in the order of $10^7 \text{s}^{-1}$ which corresponds to the lowest achievable effective temperature of $10-100 \mu K$. However, this is higher than the observed temperature of cold atoms in 3D laser light (optical molasses) which are simultaneously cooled and trapped by magneto-optical trap (MOT) [305]. This has been explained as due to the additional cooling mechanism, the polarization gradient of the counter-propagating laser beams used for simultaneous trapping and cooling of the atoms [48]. It is also called 'Sisyphus cooling' or sub-Doppler cooling mechanism which works based on the position dependent light shifts through the position dependent polarization. Later, the Sisyphus effect has been extended to cooling in two dimensions [41]. More sophisticated schemes to cool atoms below the recoil (subrecoil) temperature $(\hbar k^2/2Mk_B$ were proposed. One is the velocity selective coherent population trapping (VSCPT) [47] scheme based on the creation of dark state from the superpositions of quantum states around zero velocity. The lasers parameters are controlled such that the atoms with velocity below the recoil velocity $\hbar k/M$ form the dark state and become uncoupled from pumping lasers. It has been shown that polarization gradient cooling works best at off resonance and low laser intensities, whereas the VSCPT is optimized on resonance [49]. Raman cooling [313] is another subrecoil cooling scheme which uses repeated cycles of velocity selection and spontaneous emissions, also lead to subrecoil temperature. Recently, a scheme similar to the Raman cooling was demonstrated. It uses a narrow line of the excited state to achieve lower cooling temperature without causing long cooling time by quenching the excited state to a fast decaying state [50]. White light cooling has also been proposed [43]. Faster cooling rate using isotropic light [44] has also been demonstrated. Cooling schemes which use cavity [53] for dissipation instead of free space spontaneous emission have also been proposed. Laser techniques have evolved to high sophistication that Bose-Einstein condensations (BEC) can be obtained by all optical means [13]. The kinetic energy and the temperature of a gas in the laser standing wave can be reduced by adiabatically reducing the intensity [54]. The principle here is the same as the adiabatic expansion of a gas in thermodynamics where the entropy is unchanged but the temperature is reduced. This technique has been combined with dissipation in a microwave cavity to reduce the both the kinetic energy and entropy [53]. High intensity standing laser fields has also been used to assist cooling. The stimulated emissions process is the dominant cooling mechanism, which can be modelled in dressed state picture [51].

Atoms have been successfully cooled to extremely cold temperature (nanoKelvin) using sophisticated laser pumping schemes described above. The atoms have been trapped in a magneto-optical trap (MOT), dipole light force trap [93], quasi-electrostatic trap [100],
microwave trap [101], magnetic [57] and electrostatic traps [311] to avoid contact with any surface and particle which would heat up the atoms. By trapping, the atoms can be manipulated more easily for many applications. Also, the phase space density of cooled gas can be further increased by evaporative cooling [11], thus leading to the creation of new state of matter, the Bose-Einstein condensations [12]. When the density is sufficiently high, interparticle interactions become significant and the theory should include the many particles effects [142], [143], [144] and quantum statistics of interacting identical particles. Otherwise, single particle theory can be a good approximation.

1.3 Motivations for Cooling Molecules

Ultracold atoms has led to many interesting applications. Techniques for obtaining ultracold molecules would extend the applications to molecules and can also open up new possibilities due to the rich internal structures of molecules and that it is a many-body system. Thus, we are poised at the second generation of extreme cooling: from atomic gas to molecular gas. We shall review on the existing non-laser cooling schemes which can cool molecules down to only mK temperature. Molecules have not been directly cooled to near optical recoil temperature (typically in $\mu K$), as in the case of atoms. Cooling to such a low temperature is possible if there is a reliable laser cooling scheme. So far, there is no reliable laser cooling scheme for molecules and therefore molecules have not been laser cooled. Molecules have additional motional degrees of freedom compared to atoms, namely the vibration and rotation [171]. This creates a more complicated internal (vibrational and rotational) energy levels. The distinct differences in the internal structures between atoms and molecules make the existing laser techniques for creating ultracold atoms inapplicable to cool even the simplest diatomic molecules.

It is the purpose of this thesis to explore new laser schemes to cool molecules. It is hoped that the theoretical schemes developed in this thesis will lead to the creation of ultracold molecules in $\mu K$ temperature regime. With ultracold molecules, the above-mentioned applications become more interesting mainly due to the additional motional degrees of freedom in molecules. It would become possible to study new dynamics and properties of cold atom-molecule [22] and molecule-molecules collisions [23], [24], for metrology (gyroscopes), ultracold chemistry and photochemistry (with ultimate control of chemical reactions)[154], molecule laser (coherent source of molecules) and possible quantum computing, making use of the additional internal degrees of freedom of molecules to create additional entanglements. The physics of laser cooling of molecules provides interesting merge of chemical physics [156] and the control of the internal and external dynamics of molecules with lasers. The use of laser for manipulating molecules has evolved into a very powerful tool. Manipulations of the external motional degrees of molecules using intense laser fields have opened up potentials for next generation nanotechnology with shaped molecular beam [163] and molecular optics [164]. Alignment of molecules with intense lasers has been proposed [158]
and demonstrated for homonuclear molecules [159] and more complex molecules [160]. Techniques for controlling the molecular orientations [157] and to split the molecule apart [161] were also proposed. Thus, the possibilities from the study of laser-molecules interactions is growing. However, the use of lasers to cool molecules remains a challenging possibility.

1.4 Developments in Cooling of Molecules

The existing laser cooling schemes for atoms are based on the concept of a repeated cycle of optical pumping followed by spontaneous emission which transfers the atoms back into a resonant ground state. However, laser cooling of the translational motion of molecules is a formidable challenge due to the difficulty of maintaining such a closed optical pumping cycle. The reason is due to the additional degrees of freedoms from vibration and rotation of the nuclei. Optical spontaneous emissions populate many rovibrational states which are non-resonant with the lasers and this interrupts the cycle. There are several translational laser cooling schemes for molecules which are being proposed theoretically and non-laser cooling schemes which are being developed experimentally. Bohns et al. [59] have proposed a laser cooling scheme that uses multiple-frequency lasers. The disadvantage of this technique is that it requires too many lasers to be practically applicable. Besides, in depth spectroscopic data of the internal structures is required for generating lasers with the right frequencies. Vuletic and Chu [60], and Ritsch [61] independently proposed using optical cavity as a channel for dissipation instead of spontaneous emission, but has not been experimentally demonstrated. So far, there has been no established laser cooling scheme for molecules. An interesting translational cooling scheme which uses interference of the molecular center of mass wavepacket has been proposed [69]. Recently, slow formaldehyde molecules are selected from a distribution of gas using a curved electric quadrupole guide [70].

Currently, there are three main non-laser techniques which are able to produce moderately cold molecules. The first technique is the photoassociation technique [62], which produces cold molecules by associating cold atoms in a magneto-optical trap (MOT) [305] using lasers, via two photon-absorption followed by spontaneous emission. Normally, the cold molecules are nearly as cold as the cold atoms. Since the cold molecules are not in ground rovibrational state, they can be heated up through non-radiative transitions in atom-molecule or molecule-molecule collisions. Thus, only a limited number of the molecules remain cold enough to be optically trapped [98].

The second technique is the buffer gas cooling [64]. It relies on elastic collisions with the colder helium (He) gas as a thermalization mechanism for removal of the molecular external entropy. Calcium monohydrate (CaH) molecule has been demonstrated [65] to thermalize at lower temperature and loaded into a magnetic trap. This method is quite versatile and applicable to essentially any paramagnetic molecules as well as atoms [63], but it requires a small ratio of inelastic collisions rate to elastic collisions. Also, the temperature of the buffer gas is limited to the minimum temperature achievable with dilution
refrigeration. If a large amount of buffer gas can be cooled to much lower temperature, this technique would be highly versatile. It is interesting to note that He atomic gas has been laser cooled to subrecoll temperature [52], but it is a challenge to cool a large amount of He for use as buffer gas.

The third technique uses the time varying electric field (Stark deaccelerator), [67] to decelerate a fast supersonic molecular beam \(^1\) which has a narrow momentum width and internally cold and then trap it using electrostatic fields. It also incorporates the phase space rotation to further reduce the momentum width of the gas [66]. It has been demonstrated with ammonia molecules [68]. This technique uses coherent mechanism for removal of kinetic energy and does not involve any dissipative mechanism. Friedrich [75] has proposed a scheme which uses the centrifugal force from optical dipole trap to decelerate the supersonic molecular beam which has a narrow momentum distribution and internally cool.

Despite the complicated internal states of molecules, there have been proposals for preparing molecules with a single internal state by lasers state selection [80], by static combinations of strong electric and magnetic fields [157]. Laser cooling of the molecular internal degrees of freedoms has also been explored, especially cooling the vibrational motion using optimal pulse control approach [72], [73], [74],[71]. Recently, the creation of molecules in high rotational states [77] has also led to possible rotational cooling [76]. It seems that internal cooling and translational cooling schemes have existed independently. So far, there is no scheme which cools both the internal and translational degrees of molecule simultaneously. If we are able to translationally cool those molecules prepared in a single internal state without causing internal heating, we would have internally and translationally cooled molecules.

1.5 Organization of the Thesis

In this thesis, a theoretical laser cooling scheme for molecules is developed for a dilute molecular gas. Interactions between particles like collisions, dipole-dipole interactions and van der Waals force have been neglected within the timescale of laser-molecules interaction period. The theory is developed within the quantum optics domain using single particle Hamiltonian with emphasis on the effects of having quantized the center of mass spatial and momentum variables. The radiation is treated quantum-mechanically by the creation and annihilation operators. The laser fields are treated classically with e-number as a coherent state of radiation.

In Chapter 2, we present the non-relativistic quantum electrodynamic theory to describe the radiation-molecule interactions and obtain the Hamiltonians in two versions. The fundamentals of molecular energy levels are derived. This enables us to understand

\(^1\)In the rapid expansion of gas, the Mach number \( M = \bar{v} / v_{\text{sound}} \) increases due to the decrease in the sound velocity. Thus the temperature and pressure are reduced according to \( \frac{T}{T_0} = \left( \frac{\rho}{\rho_0} \right)^{(\gamma - 1)/\gamma} = 1/(1 + \frac{\gamma - 1}{2}M^2) \).
the structure the internal molecular states and the scales of the energy levels. Multipole interactions for diatomic molecules are derived with emphasis given for the electric dipole interaction Hamiltonian along with quantized center of mass momentum state. The selection rules for all possible transitions in optical, infrared and microwave regimes along with parity and symmetry considerations are presented. These will be the guidelines for designing a laser pumping scheme to cool the translational degree of the molecules.

In Chapter 3, we use the projection operator technique to develop the master equation for a molecule interacting with laser field of arbitrary strength and coupled to the free space thermal blackbody radiation at finite temperature in order to study the dissipation of the molecule. We show that dissipation can be controlled by external laser fields. As an example, we use the Schrödinger equation to show how spontaneous emission rate can be controlled by application of multiple 2π-pulses. A general master equation is derived for multilevel system in thermal reservoir by including the center of mass momentum states.

In Chapter 4, the appropriate quantities which may be used to quantify the extend of cooling are elaborated. We obtain analytical relationships between the quasi phase space Wigner function, entropy production rate and probability distribution; all can be computed from the density matrix elements and the master equation. This enables the quantification of the extend of cooling from the quantum dynamics.

In Chapter 5, techniques for coherent control of momentum are studied. We establish general relations for quantities that can be computed in a coherent process, like mean kinetic energy, mean light force and their relations to probability density. Detailed quantum optical theory of the techniques for coherently controlling the momentum of a gas are presented. In particular, we derive optimal operating conditions for efficient Raman velocity selection of the populations and deceleration through STIRAP. A simple technique for reducing the kinetic energy by momentum squeezing is elaborated using Wigner function.

In Chapter 6, we discuss two preliminary laser cooling schemes which are theoretically possible but not feasible in practice. Then, we present a more practical laser cooling scheme for molecules based on the theoretical foundations from previous the chapters. Simulations are based on optimal operational parameters using OH molecule.

Chapter 7 provides a summary and conclusions of this work. Detailed calculations and general formalisms relevant to the proceeding chapters are given in Chapter 8 as Appendices. Two published papers which contain additional results of this thesis are enclosed in the end of the thesis. They are entitled: 1) Laser Cooling of Molecules via Single Spontaneous Emission [1], 2) Momentum Spread of Spontaneously Decaying Cold Gas in Thermal Radiation [2]. The former paper introduces a new laser cooling concept for reducing the center-of-mass entropy. It is designed to apply for molecules as well as atoms. It is based on the repetition of a cycle, composed of three concepts: velocity selection, deceleration and irreversible accumulation. Well-known laser techniques are used to represent these concepts: Raman π-pulse for velocity selection, STIRAP for deceleration, and a single
spontaneous emission for irreversible accumulation. No closed pumping cycle nor repeated spontaneous emissions are required, so the scheme is applicable to cool a molecular gas. The quantum dynamics are analytically modelled using the density matrix. It is shown that during the coherent processes the gas is translationally cooled. The internal states serve as an entropy sink, in addition to spontaneous emission. This scheme provides new possibilities to translationally laser-cool molecules for high precision molecular spectroscopy and interferometry.

The second paper elaborates on the quantum dynamics of the center of mass momentum distribution for the populations of a cold gas with two–level system undergoing spontaneous decay and coupled to a Markovian thermal reservoir at arbitrary temperature. We derive the momentum-convolutionless coupled equations for momentum Fourier transform of the populations which can be easily solved numerically and analytically for a specific internal scheme and for zero temperature cases. The time and momentum evolutions of the populations are obtained by inverse Fourier Transform. The momentum spread and the center of mass entropy across one momentum dimension are computed and compared for different internal schemes, between zero temperature and finite temperature cases and between $\pi$ and $\sigma_{\pm}$ transitions. For initial subrecoil momentum width, the $\sigma_{\pm}$ transition displays a two-peak feature. Our results well describe the momentum spread dynamics of cold gas in thermal radiation at early time and complement the results based on Fokker-Planck equation.
Chapter 2

Molecular Levels and Electromagnetic Interactions

The entire physics of laser cooling and trapping are based on the interactions of molecules and fields: electrostatic, magnetostatic and/or electromagnetic (from radiation and lasers). The center of mass (c.m.) position and momentum of the molecules are the necessary canonical quantized variables. It is important to formulate a correct molecular quantumodynamical theory with the c.m. variable. The theory will not be mathematically simple. However, a systematic and pedagogical formulation would provide useful foundations for further studies of laser manipulations of molecules, dissipative mechanisms in molecules and also understanding of the molecular spectra and internal energy levels which are important for designing a practical laser cooling scheme for molecules.

In this Chapter, we present a systematic and detailed theory for interactions of a molecule with external fields. Starting from the Lagrangian, we outline the derivations of two versions (minimal coupling and the multipolar) of the non-relativistic Hamiltonians. The Power-Zienau-Woolley gauge transformation which leads to multipolar electric and magnetic interactions is outlined. The Hamiltonians can be partitioned into the parts due to: kinetic energy of free particles and Coulomb interactions, electromagnetic radiation, molecule-radiation interactions, static electric and magnetic fields interactions with molecule. Using the minimal coupling Hamiltonian, we show that the co-existence of radiation fields and external static fields creates new additional mixing terms which may lead to squeezed vacuum.

By transformation to molecule-fixed frame, we separate out the molecular center of mass (c.m.) kinetic energy from the internal molecular energy. In long wavelength approximation, the minimal coupling interaction is written in terms of molecular dipole operator. We show that the Röntgen term is obtained from the magnetic multipole interaction term. New expressions for electric dipole, quadrupole and magnetic dipole interactions which depend on molecular center of mass position/momentum and the total molecular charge are obtained. Thus, we obtain the full Hamiltonian of a single molecule interacting
with external fields in the minimal coupling and multipolar versions.

Using the internal molecular Hamiltonian, we show how the electronic, vibrational and rotational energy levels arise and discern between Born-Oppenheimer approximation, Born approximation and adiabatic approximation. The limiting cases of electronic-nuclear couplings are given. We show how the dipole selection rules arise and obtain expression for the dipole matrix elements. Expressions for the dipole transitions frequencies corresponding optical, infrared and microwave molecular spectra are given. For homonuclear diatomics, additional selection rules from parity considerations are elaborated.

2.1 Two Versions of Hamiltonians

There are two versions of the radiation-particle interaction Hamiltonians which are widely used. The "p.A" or minimal coupling version is usually used in quantum electrodynamics while the "d.E" which come from the multipolar version is preferred in quantum optics. We shall adopt both, since they yield the same physical result if properly used as both versions are related by the unitary "Power-Zienau-Woolley" transformation. The multipolar Hamiltonian has several advantages like gauge invariance, does not lead to false precursor signal and gives the correct Lamb shift spectrum [190].

The non-relativistic quantum theory of particle-radiation interactions has been standardized long ago using the minimal coupling formalism [185]. The non relativistic Hamiltonian in minimal coupling regime for a system of particles interacting with electric and magnetic fields can be obtained from the Lagrangian [188], [190], [186],

\[
L = \sum_i \frac{1}{2} m_i \dot{\mathbf{r}}_i^2 + \frac{\varepsilon_0}{2} \int \left\{ \left( \frac{\partial \mathbf{A}}{\partial t} \right)^2 - c^2 (\nabla \times \mathbf{A})^2 \right\} d^3r + \sum_i q_i \mathbf{v}_i \cdot \mathbf{A}(\mathbf{r}_i, t) - \frac{1}{2} \int \rho \phi d^3r \quad (2.1)
\]

where \(q_i, m_i, \mathbf{r}_i, \mathbf{v}_i = \dot{\mathbf{r}}_i\) are the electric charge, mass, position and velocity of the i-th particle, \(\mathbf{A}\) and \(\phi\) are the vector and scalar potentials and \(\rho(\mathbf{r}, t) = \sum q_i \delta(\mathbf{r} - \mathbf{r}_i(t)) = \varepsilon_0 \nabla \cdot \mathbf{E}(\mathbf{r}, t)\) is the charge density. Although the Lagrangian is non-relativistic, it gives the correct covariant Maxwell’s equations, but a non-relativistic Lorentz force equations through the use of the Euler-Lagrange equations \(\frac{d}{dx} \left( \frac{\partial L}{\partial \dot{\mathbf{r}}_i} \right) = \frac{\partial L}{\partial \mathbf{r}_i} \) for particles and \(\frac{d}{dx} \left( \frac{\partial L}{\partial (\partial \mathbf{r}_i/\partial t)} \right) = \frac{\partial L}{\partial \mathbf{A}}\) for fields.

By using the Poisson equation \(\rho = -\varepsilon_0 \nabla^2 \phi\), the Green’s theorem \(\nabla \cdot (\phi \nabla \phi) = \phi \nabla^2 \phi + \nabla \phi \cdot \nabla \phi, \mathbf{E}_i = -\nabla \phi\), and \(\rho(\mathbf{r}, t) = \sum q_i \delta(\mathbf{r} - \mathbf{r}_i(t))\), the last term in Eq. 2.1 can be written in various forms\(^1\)

\[
\frac{1}{2} \int \rho \phi d^3r = -\frac{\varepsilon_0}{2} \int \phi \nabla^2 \phi d^3r = \frac{\varepsilon_0}{2} \int \mathbf{E}_i \cdot 2d^3r = \frac{1}{2\varepsilon_0} \int \mathbf{P} \cdot 2d^3r = \frac{1}{2} \sum q_i \phi(\mathbf{r}_i). \quad (2.2)
\]

\(^1\)We have used \(\mathbf{P}\) for polarization vector and reserved \(\mathbf{P}\) for the center of mass momentum of a molecule.
where the vanishing fields at infinity gives $\int \nabla \cdot (\phi \nabla \phi) d^3r \to 0$ and in the absence of free changes $\rho_f = 0$, we have written $\varepsilon_0 E_i = P_i = -\varepsilon_0 \nabla \phi$.

The second last term in Eq. 2.1 can be written as $\int J \cdot A d^3r$ using the definition $J(r, t) = \sum q_i v_i(t) \delta(r - r_i(t))$. So, the terms corresponding to the particle-field interactions in Eq. 2.1 can either be written in integral form or summation form. However, the summation form is more convenient to facilitate the evaluation of the canonical momenta for the position and fields from the Lagrangian as

$$\mathbf{p}_i = \sum_x \hat{x} \frac{\partial L}{\partial \dot{x}_i} = m_i \mathbf{v}_i + q_i \mathbf{A}(r_i, t) \quad (2.3)$$

$$\Pi(r, t) = \sum_x \hat{x} \frac{\partial L}{\partial \dot{A}_x} = \varepsilon_0 \frac{\partial}{\partial t} \mathbf{A}(r, t) = -\varepsilon_0 \mathbf{E}(r, t) \quad (2.4)$$

$$\Phi(r, t) = \sum_x \frac{\partial L}{\partial \phi_{ex}} = 0 \quad (2.5)$$

The total electric field is $\mathbf{E}(r, t) = \mathbf{E}(r, t) + \mathbf{E}(r, t) - \Pi(r, t)/\varepsilon_0 = \mathbf{E}(r, t) - \mathbf{P}(r, t)/\varepsilon_0 - \Pi(r, t)/\varepsilon_0$. By using $H = \sum_i \mathbf{p}_i \cdot \mathbf{v}_i + \int \Pi(r) \cdot \frac{\partial \mathbf{A}(r)}{\partial t} d^3r - L$ we have the minimal coupling Hamiltonian

$$H = \sum_i \frac{1}{2m_i} \left( \mathbf{p}_i - q_i \mathbf{A}(r_i, t) \right)^2 + \frac{\varepsilon_0}{2} \int \left( \mathbf{E}^2 + c^2 \mathbf{B}^2 \right) d^3r + \frac{1}{2} \sum_i q_i \phi(r_i, t) \quad (2.6)$$

where $\mathbf{E} = -\frac{\partial \mathbf{A}}{\partial t}$ and $\mathbf{B} = \nabla \times \mathbf{A}$. The non-relativistic Hamiltonian Eq. 2.6 is correct up to the second order in $p$ and with the neglect of the self-mass energy $m c^2$. By noting the relativistic Hamiltonian for particle in the field as $H = \sum m_i c^2 \sqrt{1 + \left( \frac{\mathbf{p}_i}{m c} \right)^2}$ we estimate that the next order correction to be of the fourth order $(q \varepsilon)^2 (g \pi \eta)^2$. In the study of kinetic effects of particles below the room temperature, all fourth order and higher terms can well be neglected.

### 2.1.1 Mixing Terms from External and Radiation Fields

The electric field potential can be decomposed into two parts as $\phi(r, t) = \phi_{ex}(r, t) + \phi_{es}(r, t)$, where $\phi_{es}(r, t) = \sum_j \frac{q_j}{4\pi \varepsilon_0 r_{ij}}$ is the "internal" electrostatic interactions of all charged particles in the system and $\phi_{ex}(r, t)$ is the electrostatic potential from 'external' sources. The transverse vector potential can also be decomposed into two parts, $\mathbf{A}(r, t) = \mathbf{A}_{es}(r, t) + \mathbf{A}_{ex}(r, t)$ due to the electromagnetic radiation $\mathbf{A}_{es}(r, t)$ and the external magnetic field via $\nabla \times \mathbf{A}_{ex}(r, t) = \mathbf{B}_{ex}(r, t)$. We can combine the last two terms in Eq. 2.6 into $\frac{\varepsilon_0}{2} \int \left( \mathbf{E}^2 + c^2 \mathbf{B}^2 \right) d^3r$. Thus, we can write the fields as $\mathbf{E} = -\frac{\partial \mathbf{A}_{es}}{\partial t} - \frac{\partial \mathbf{A}_{ex}}{\partial t} - \nabla \phi_{es} - \nabla \phi_{ex}$ and $\mathbf{B} = \mathbf{B}_{es} + \mathbf{B}_{ex}$. Since $\mathbf{A}_{es}$ may have both transverse and longitudinal components, we can write $\mathbf{E}_e = -\frac{\partial \mathbf{A}_{es}}{\partial t} - \frac{\partial \mathbf{A}_{ex}}{\partial t} \mathbf{E}_{ex}$ and $\mathbf{E}_e = -\frac{\partial \mathbf{A}_{es}}{\partial t} - \nabla \phi_{es} - \nabla \phi_{ex}$, with $\mathbf{E}_{ex} = -\frac{\partial \mathbf{A}_{ex}}{\partial t}$.
Thus, we find the total Hamiltonian is $H_{tot} \equiv H + H_X$, can be written as the sum of the standard Hamiltonian $H$, and the mixing-fields Hamiltonian $H_X$, each is expanded as

$$ H = \sum_i \frac{p_i^2}{2m_i} + V_{Coul} + V_{self} + V_{SR} + H_R + V_{els} + V_{mag} + H_{ex} \quad (2.7) $$

$$ H_X = \sum_i \frac{q_i^2 A_{R}(r_i,t) \cdot A_{ex}(r_i,t)}{\epsilon m_i} + \varepsilon_o \int \left\{ \frac{\partial A_{ex}}{\partial t} \cdot \nabla(\phi_{in} + \phi_{ex}) + \nabla\phi_{in} \cdot \nabla\phi_{ex} \right\} d^3r $$

$$ + \varepsilon_o \int \left\{ -E_R \cdot \frac{\partial \mathbf{A}_{ex}}{\partial t} + c^2 B_R \cdot \mathbf{B}_{ex} \right\} d^3r \quad (2.8) $$

where

$$ V_{Coul} = \frac{\varepsilon_o}{2} \int (\nabla \phi_{in})^2 d^3r - V_{self} = \frac{1}{2} \sum_{i,j \neq i} \frac{q_i q_j}{4 \pi \varepsilon_o |\mathbf{r}_i - \mathbf{r}_j|} = \sum_{i,j \neq i} \frac{q_i q_j}{4 \pi \varepsilon_o |\mathbf{r}_i - \mathbf{r}_j|} \quad (2.9) $$

$$ V_{SR} = -\sum_i \frac{q_i}{m_i} p_i \cdot A_{R}(r_i,t) + \sum_i \frac{q_i^2 A_{R}^2(r_i,t)}{2m_i} \quad (2.10) $$

$$ H_R = \frac{\varepsilon_o}{2} \int \left( \frac{\partial A_{R}}{\partial t} \right)^2 + c^2 B_R^2 d^3r \quad (2.11) $$

$$ V_{els} = \frac{\varepsilon_o}{2} \int (\nabla \phi_{ex})^2 d^3r = \sum_i q_i \phi_{ex}(r_i,t) \quad (2.12) $$

$$ V_{mag} = -\sum_i \frac{q_i}{2m_i} (p_i \cdot A_{ex}(r_i,t) + A_{ex}(r_i,t) \cdot p_i) + \frac{1}{2m_i} (q_i A_{ex}(r_i,t))^2 \quad (2.13) $$

$$ H_{ex} = \frac{\varepsilon_o}{2} \int \left( \frac{\partial A_{ex}}{\partial t} \right)^2 + c^2 B_{ex}^2 d^3r \quad (2.14) $$

Equation 2.7 contains the Hamiltonians for the kinetic energy of free particles $\sum_i \frac{p_i^2}{2m_i}$, Coulomb interactions between charged particles $V_{Coul}$ with the self-energy $V_{self}$, the radiation-particles interactions $V_{SR}$, the radiation fields $H_R$. The diverging self interaction energy $V_{self}$ [186] contributes only to the level shift and contact interactions, and is not important in radiation processes involving the change of states. In the presence of external electric or magnetic fields, the remaining terms in Eq. 2.7 give the Stark effect $V_{els}$, the Zeeman effect $V_{mag}$ and the c-number static fields energy $H_{ex}$ which does not affect the radiative process. The static fields interactions $V_{els}$ and $V_{mag}$ lead to splittings of degenerate states and internal energy level shifts which are used for trapped particles[65], [68].

The Hamiltonian $H_X$ contains terms of mixed-interactions between particles, radiation, electric and magnetic fields. It should be noted that the terms $\varepsilon_o \int \{ -E_R \cdot \frac{\partial A_{ex}}{\partial t} - E_R \cdot \nabla(\phi_{in} + \phi_{ex}) \} d^3r$ do not exist in Eq. 2.8 because $E_R$ is transverse. We could have used Eq. 2.2 to write $\frac{\varepsilon_o}{2} \int (\nabla \phi)^2 d^3r = \varepsilon_o \int \nabla \phi_{in} \cdot \nabla \phi_{ex} d^3r + V_{Coul} + V_{self} + V_{els}$. The Coulomb (radiation) gauge used on the radiation field, $\nabla \cdot A_{R} = 0$ implies that $p_i \cdot A_{R} = \mathbf{A}_{R} \cdot p_i$ but may not hold the same for $A_{ex}$. Therefore we have written $V_{mag}$ in symmetrized form $\frac{1}{2}(p_i \cdot A_{ex} + A_{ex} \cdot p_i)$ in (Eq. 2.13) which contains the first order and second order Zeem-
man effects. For spatially homogeneous field $A_{ex}(r, t) = \frac{1}{2} B_{ex}(r, t) \times r$ we can write
$V_{mag} = -\frac{1}{2} \sum_i \frac{m_i}{2m_i} (p_i - m_i \times r_i) \cdot B_{ex}(r, t)$.

The Hamiltonians Eqs. 2.7-2.8 can be quantized by introducing the canonical quantization relations for particles $[\hat{\rho}_{ij}, \hat{\rho}_{j'k'}] = \frac{i\hbar}{2} \delta_{ij'j''k''}$ and the radiation fields $[\hat{A}_{Rj}, \hat{\Pi}_{Rk}] = i\hbar \delta_{j'k'} (\hat{r} - \hat{r}')$ where $j, j' \in x, y, z$. The explicit forms of the quantized fields $\hat{A}_{Rj'}(\hat{r})$ and $\hat{\Pi}_{Rj} (\hat{r})$ are given in Appendix I, defined to depend explicitly only on position operator and not on time in the Schrödinger picture. The Heisenberg equation $i\hbar \frac{d}{dt} O = \frac{1}{\hbar} [O, H]$ when applied to the quantized Hamiltonian gives the relations between the quantized fields and particle variables, the Maxwell’s equations, Newton-Lorentz equation and the definitions for charge density, current density, polarization, magnetization, as shown by Healy in Refs. [202],[201].

2.1.2 Power-Zienau-Woolley Transformation

The minimal coupling formalism has the disadvantage that the Green function of the electrodynamic potential in Coulomb gauge leads to the interpretation of instantaneous signal propagation from a source [188], which is against the special theory of relativity which requires that no signal can propagate faster than the speed of light. Besides, the minimal coupling theory does not correctly predict the experimental spectral line shape of the metastable hydrogen as shown by Power and Zienau [190], although it leads to the correct prediction of the Lamb shift [204]. These deficiencies are resolved by the Power-Zienau-Woolley transformation of the minimal coupling Hamiltonian into the multipolar Hamiltonian. It has been performed by unitary transformation [191] or gauge transformation [195]. The multipolar Hamiltonian with center of mass of an aggregate of particles was derived long ago. Later, the gravitational fields was also included [205] with covariant derivations. Here, we give the outline to obtain the multipolar Hamiltonian for diatomic molecules, and compare it with that obtained from minimal coupling version.

The gauge transformation is performed by first adding the term $-\frac{\partial A}{\partial t} \cdot \frac{\partial^2 \mathbf{P}}{\partial t^2} = -\int \mathbf{P}(r, t) \cdot \frac{\partial \mathbf{A}(r, t)}{\partial t} d^3r$ to the old (minimal coupling) Lagrangian $L$, where $S = \int \mathbf{P}(r, t) \cdot \mathbf{A}(r, t) d^3r$ is the transformation gauge and $\mathbf{P}(r, t)$ is the electric polarization, we have the new multipolar Lagrangian

$$L' = \sum_i \frac{m_i v_i^2}{2} + \frac{\varepsilon_0}{2} \int \left( \left( \frac{\partial \mathbf{A}}{\partial t} \right)^2 - c^2 \mathbf{B}^2 \right) d^3 r + \int \left( \mathbf{J} - \frac{\partial \mathbf{P}}{\partial t} \right) \cdot \mathbf{A} d^3 r - \int \mathbf{P} \cdot \frac{\partial \mathbf{A}}{\partial t} d^3 r - \frac{1}{2} \int \rho \phi d^3 r$$

(2.15)

If the transformation is obtained by unitary transformation operator $\hat{T} = \exp\left(\frac{i}{\hbar} \int \hat{\mathbf{A}}(\mathbf{r}) d^3 r \right)$, $\hat{\mathbf{P}}(\mathbf{r})$ and $\hat{\mathbf{A}}(\mathbf{r})$ are Schrödinger operators which are do not depend explicitly on time. Here, the Hamiltonian and the state vector transform as $\hat{H} = \hat{T} \hat{H} \hat{T}^\dagger$ and $|\Xi\rangle' = \hat{T} |\Xi\rangle$ respectively with $i\hbar \frac{d}{dt} \hat{T}^\dagger = 0$. 
From the continuity equation \( \frac{\partial \rho(r,t)}{\partial t} + \nabla \cdot \mathbf{J}(r,t) = 0 \) and \( \rho_P(r,t) = -\nabla \cdot \mathbb{P}(r,t) \), we obtain

\[
\nabla \cdot \{ \mathbf{J}(r,t) - \frac{\partial \mathbb{P}(r,t)}{\partial t} \} = - \frac{\partial \rho(r,t)}{\partial t} + \frac{\partial \rho_P(r,t)}{\partial t} = \frac{\partial \rho_P(r,t)}{\partial t} \tag{2.16}
\]

The current density \( \mathbf{J}(r,t) \) which satisfies the continuity equation \( \nabla \cdot \mathbf{J} + \frac{\partial \rho(r,t)}{\partial t} = 0 \), and the closed expression for the polarization \( \mathbb{P}(r,t) \) which is the sum of all electric multipoles around a common point (origin) \( \mathbf{R}_C \) are defined as

\[
\mathbf{J}(r,t) = \frac{1}{2} \sum_i q_i \delta^3(r-r_i(t)) + \delta^3(r-r_i(t)) \dot{r}_i(t) \tag{2.17}
\]

\[
\mathbb{P}(r,t) = \sum_i q_i (r_i - \mathbf{R}_C) \int_0^1 \delta^3(r - \mathbf{R}_C - u(r_i - \mathbf{R}_C)) du \tag{2.18}
\]

By Fourier transforming \( \mathbf{J}(r,t) \) and \( \mathbb{P}(r,t) \), using the identities \( \mathbf{k} \times (\mathbf{r} \times \mathbf{r}) = (\mathbf{k} \cdot \mathbf{r}) \mathbf{r} - (\mathbf{r} \cdot \mathbf{r}) \mathbf{k} \), \( \int_0^1 u e^{-\mu^2 a} du = \frac{\sin(\mu a)}{\mu a} \) for \( a \geq 0 \), \( \int_0^1 e^{-\mu^2 a} du = \frac{\sinh(\mu a)}{\mu a} \) and \( \nabla \cdot \mathbb{P}(r,t) = \rho(r,t) - \rho_P(r - \mathbf{R}_C) \), with \( \rho_P(r - \mathbf{R}_C) = Q \delta^3(r - \mathbf{R}_C) \), we obtain the general relation in Refs. [193], [205]

\[
\mathbf{J}(r,t) - \frac{\partial \mathbb{P}(r,t)}{\partial t} = \nabla \times \mathbb{M}(r,t) + \nabla \times \frac{1}{2} \left\{ \mathbb{P}(r,t) \times \mathbf{R}_C - \mathbf{R}_C \times \mathbb{P}(r,t) \right\} + \dot{\mathbf{R}}_C (\nabla \cdot \mathbb{P} + \rho(r,t))
\]

where \( \mathbf{J}_{\text{Rö}}(r,t) \) is the Röntgen current and the magnetization \( \mathbb{M}(r,t) \) is defined as

\[
\mathbb{M}(r,t) = \frac{1}{2} \sum_i q_i ((r_i - \mathbf{R}_C) \times (\dot{r}_i - \dot{\mathbf{R}}_C) - (\dot{r}_i - \dot{\mathbf{R}}_C) \times (r_i - \mathbf{R}_C)) \int_0^1 \delta^3(r - \mathbf{R}_C - u(r_i - \mathbf{R}_C)) du
\]

\[
\equiv \frac{1}{2} \sum_i (\mathbf{n}_i(r,t) \times (\dot{r}_i - \dot{\mathbf{R}}_C) - (\dot{r}_i - \dot{\mathbf{R}}_C) \times \mathbf{n}_i(r,t)) \tag{2.20}
\]

with

\[
\mathbf{n}_i(r,t) = q_i (r_i - \mathbf{R}_C) \int_0^1 \delta^3(r - \mathbf{R}_C - u(r_i - \mathbf{R}_C)) du.
\]

\( ^3\)The \( \mathbb{P} \) polarization and \( \mathbb{M} \) magnetization are the sum of electric and magnetic multipoles series referring to a common origin \( \mathbf{R}_C \).

Hence, Eq. 2.19 leads to

\[
\int \mathbf{J} \cdot \frac{\partial \mathbb{P}}{\partial t} d^3r = \int \mathbb{M} \cdot \mathbf{B} d^3r - \int \frac{1}{2} (\mathbb{P} \times \mathbf{B} + \mathbf{B} \times \mathbb{P}) d^3r + Q \dot{\mathbf{R}}_C \cdot \mathbf{A} \tag{2.22}
\]

where we have used the fact that \( \mathbb{P}(r,t) \) and \( \mathbf{B}(r,t) \) commutes but they don’t commute with \( \dot{\mathbf{R}}_C \).

\( ^3\)We note that \( \mathbb{P}(r,t) \neq \sum_i \mathbf{n}_i(r,t) \) due to the additional \( u \) in \( \mathbf{n}_i \).
The first term is the magnetic multipole interaction, second term is the Röntgen interaction, and finally the interaction with total charge at center center of mass position.

The new canonical momenta (with primes) \( p_i', \Pi'(r, t) \) are found as

\[
\begin{align*}
p_i' &= \sum_x \dot{x} \frac{\partial L'}{\partial \dot{x}_i} = m_i \dot{x}_i + O_i \quad (2.23) \\
\Pi'(r, t) &= \sum_x \dot{x} \frac{\partial L'}{\partial \dot{A}_x} = \varepsilon_x \partial_t A(r, t) - P_\perp(r, t) = -D_\perp(r, t) \quad (2.24) \\
\Phi'(r, t) &= \sum_x \dot{\phi} \frac{\partial L'}{\partial \dot{\phi}_x} = 0 \quad (2.25)
\end{align*}
\]

where

\[
O_i = \int B(r, t) \times n_i(r, t) d^3r = q_i (r_i - R_C) \int_0^1 B(R_C + u(r_i - R_C)), t) u du
\]

and we have used \( \int P_\perp(r, t) \frac{\partial A(r, t)}{\partial \phi} d^3r = 0 \) in Coulomb gauge. Here, the total electric field is \( E(r, t) = \{ D_\perp(r, t) + D_\perp(r, t) - P(r, t) \} / \varepsilon_0 = E_j(r, t) - P(r, t) / \varepsilon_0 - \Pi(r, t) / \varepsilon_0 \), with \( P(r, t) \) instead of \( P_\perp(r, t) \) (in minimal coupling) and \( E_j(r, t) = D(r, t) / \varepsilon_0 \). As noted in Ref. [186] (p. 293), the field \( \Pi' \) can be approximated by \( -\varepsilon_0 E_\perp \) when far away from the system of charges since \( P_\perp(r, t) \sim 0 \).

By using Eqs. 2.22, 2.23 and 2.24, we obtain the multipolar Hamiltonian as

\[
H' = \sum_i \left( \frac{p_i'^2}{2m_i} - \frac{1}{\varepsilon_0} \int D_\perp \cdot P d^3r - \int M \cdot B d^3r + \frac{1}{2} \int \left\{ \frac{D_i^2}{\varepsilon_0} + \varepsilon_0 c^2 B_i^2 \right\} d^3r \right)
\]

\[
+ \frac{1}{2} \int \{ P \times B \cdot \dot{R}_C + \dot{R}_C \cdot P \times B \} d^3r - Q \dot{R}_C \cdot A(R_C) + \frac{1}{2\varepsilon_0} \int \| P \| d^3r + \frac{1}{2} \int \rho d^3r
\]

where the first two terms in the second line are respectively the Röntgen term and a moving aggregate of particles with the total charge \( Q \) in the magnetic field. The multipolar Hamiltonian depends on the electric and magnetic fields and the center of mass motional variables. Thus it is non covariant although it is gauge invariant. In contrary, the minimal coupling Hamiltonian depends on the vector potential and scalar potential which are covariant, but does not depend on the center of mass motional variables and can be transformed to different form by gauge.

The respective terms in the first line of Eq. 2.27 (from left) are due to the kinetic energy, diamagnetic interaction, electric polarization, magnetization and the transverse electromagnetic fields (radiation). The last two terms in second line correspond to the self energy with contact interactions and electrostatic interactions. By using Eqs. 2.18 and

4The forms of the Hamiltonians for stationary particle and a moving particle are different.
2.20, the electric and magnetic interaction Hamiltonians can be written as

$$\frac{1}{\varepsilon_0} \int \mathbf{D}_\perp \cdot \mathbf{P}^\perp d^3r = \frac{1}{\varepsilon_0} \sum_i q_i \Delta r_{iC} \cdot \int_0^1 \mathbf{D}_\perp(r - \mathbf{R}_C - u \Delta r_{iC}, t) du$$

$$\int \mathbf{M} \cdot \mathbf{B} d^3r = \sum_i \frac{q_i}{2} \langle \Delta r_{iC} \times \frac{d}{dt}(\Delta r_{iC}) - \frac{d}{dt}(\Delta r_{iC}) \times \Delta r_{iC} \rangle \cdot \int_0^1 \mathbf{B}(r - \mathbf{R}_C - u \Delta r_{iC}, t) u du$$

(2.28)

$$\frac{\partial}{\partial t} \mathbf{r}_{iC} = \frac{\partial}{\partial t} \mathbf{\hat{r}}_{iC} = \mathbf{P}_{iC} = \sum_i ^{\mathbb{N}} q_i \mathbf{r}_{iC}$$

(2.29)

where \(\Delta r_i \equiv r_i - \mathbf{R}_C\) and \(\frac{\partial}{\partial t} (\Delta r_{iC}) = (\mathbf{\hat{r}}_i - \mathbf{\hat{R}}_C)\).

The canonical particle momenta \(\mathbf{p}_i\) and the field momenta \(\mathbf{P}(\mathbf{r}, t)\) (Eqs. 2.23 and 2.24) in the multipolar version are different from that in minimal coupling (Eqs. 2.3 and 2.4). The the transverse electric displacement is interpreted as the electric field of the radiation. Detailed discussions on the their relationships and the transformation of the states have been given by Ref. [200] in dipole approximation, who pointed out that the quantum state must also be transformed when using the (new) multipolar version.

### 2.2 Intermolecular Interactions in Many-Molecule Hamiltonians

For a system composed of many molecule \(\xi\), and each molecule contains aggregate of charges labelled as \(\alpha(\xi)\), the second last term of Eq. 2.27 can be written as

$$\frac{1}{2 \varepsilon_0} \int \mathbf{P}_{\perp}^2 d^3r = \frac{1}{2 \varepsilon_0} \sum_\xi \int \mathbf{P}_{\perp}^2 d^3r + \frac{1}{2 \varepsilon_0} \sum_\xi \sum_\xi (\xi \neq \xi) \int \mathbf{P}_{\perp} \cdot \mathbf{P}_{\perp}^\perp d^3r.$$  

(2.30)

The last term of Eq. 2.27 and 2.6 is decomposed as

$$\frac{1}{2} \int \rho d^3r = \frac{1}{2} \sum \xi \sum \alpha(\xi) \sum \xi' \sum \alpha'(\xi') \frac{q_\alpha(\xi) q_\alpha'(\xi')}{4 \pi \varepsilon_0 |r_\alpha(\xi) - r_\alpha'(\xi')|} = \sum_\xi \sum_\xi (\xi \neq \xi') V^\xi_{\xi''} + \sum_\xi V^\xi_{\xi''}$$

(2.31)

where

$$V^\xi_{\xi''} = \frac{1}{2} \sum_\alpha(\xi) \alpha(\xi') \frac{q_\alpha(\xi) q_\alpha'(\xi')}{(4 \pi \varepsilon_0 |r_\alpha(\xi) - r_\alpha'(\xi')|)}$$

(2.32)

is the \textit{intra-Coulombic interaction} of charged particles in molecule- \(\xi\) and molecule-\(\xi'\) while

$$V^\xi_{\xi''} = \frac{1}{2} \sum_\alpha(\xi) \alpha(\xi') \frac{q_\alpha(\xi) q_\alpha'(\xi')}{(4 \pi \varepsilon_0 |r_\alpha(\xi) - r_\alpha'(\xi)|)}$$

(2.33)

is the \textit{inter-Coulombic interaction} of charged within the same molecule- \(\xi\). To the order of dipole-dipole interaction, \(V^\xi_{\xi''} \approx \{ \mathbf{d}_\xi \cdot \mathbf{d}_{\xi'} - 3(\mathbf{d}_\xi \cdot \mathbf{\hat{r}}_{\xi} \xi)(\mathbf{d}_{\xi'} \cdot \mathbf{\hat{r}}_{\xi' \xi'})/|\mathbf{r}_{\xi \xi'}|^3\}. \text{ From } \mathbf{P}_{\perp} = \ldots
\[-\varepsilon_0 \nabla \phi_\xi(r) \text{ and } \phi_\xi(r) = \sum_{\alpha(\xi)} q_{\alpha(\xi)}/(4\pi \varepsilon_0 |r - r_{\alpha(\xi)}|), \text{ we find} \]

\[
\sum_{\xi} \sum_{\xi'(\neq \xi)} \int \mathbf{P}_\xi \cdot \mathbf{P}_{\xi'} d^3r = V^\xi_{\text{Coul}}. \tag{2.34}
\]

The sum of the last two terms of Eq. 2.27 is \[\frac{1}{2\varepsilon_0} \int \{ \mathbf{P}_\perp^2 + \mathbf{P}_\parallel^2 \} d^3r = \frac{1}{\varepsilon_0} \sum_{\xi} \int \mathbf{P}_\perp^2 d^3r + \frac{1}{2\varepsilon_0} \sum_{\xi} \sum_{\xi' \neq \xi} \int \mathbf{P}_\xi \cdot \mathbf{P}_{\xi'} d^3r + \sum_{\xi} V_{\text{Coul}}^\xi \]

Thus, we can write the many-molecule minimal coupling Hamiltonian as

\[
H = \sum_{\xi} \sum_{\alpha(\xi)} \left( \frac{(D_{\alpha(\xi)} - q_{\alpha(\xi)} A_{(r\alpha(\xi), l)})^2}{2m_{\alpha(\xi)}} \right) + \frac{\varepsilon_0}{2} \int (E^\parallel_1 + \mathbf{c}^2 \mathbf{B}^2) d^3r + \sum_{\xi} \sum_{\xi'(\neq \xi)} V_{\text{Coul}}^\xi + \sum_{\xi} V_{\text{Coul}}^\xi \tag{2.35}
\]

and the many-molecule multipolar Hamiltonian as

\[
H' = \sum_{\xi, \alpha(\xi)} \left( \frac{(P_{\alpha(\xi)}^2 + C_{\alpha(\xi)}^2)}{2m_{\alpha(\xi)}} \right) - \int \mathbf{D}_\perp \cdot \mathbf{E} d^3r - \int \mathbf{M} \cdot \mathbf{B} d^3r + \frac{1}{2} \int \{ \frac{\mathbf{D}_\parallel^2}{\varepsilon_0} + \varepsilon_0 \mathbf{c}^2 \mathbf{B}^2 \} d^3r \]

\[
+ \frac{1}{2\varepsilon_0} \sum_{\xi} \int \mathbf{P}_{\parallel}^2 d^3r + \frac{1}{2\varepsilon_0} \sum_{\xi} \sum_{\xi' \neq \xi} \int \mathbf{P}_\xi \cdot \mathbf{P}_{\xi'} d^3r + \sum_{\xi} V_{\text{Coul}}^\xi \tag{2.36}
\]

The inter-Coulombic interactions \( V_{\text{Coul}}^{\xi, \xi'} \) which give the dipole-dipole interactions and van der Waals force in minimal coupling case, does not exist in the multipolar case. The first term in the second line of Eq. 2.36 does not arise unless the fields are quantized \[\text{[199]}\] and it is important for the self-energy and mass renormalization of the system. It has been included along with the dipole interaction Hamiltonian \[\text{[9]}\] to obtain the correct Lamb shift as predicted by Bethe \[\text{[204]}\] using the minimal coupling version. The corresponding second term is approximately zero unless the molecules overlap and the last term is clearly the intra-Coulombic interactions within the respective molecules.

### 2.3 Single Diatomic Molecular Hamiltonian

If we are dealing with the gas which contains admixture of molecules in the ground electronic state and excited electronic state separated at frequency \( \omega_o \), the cooperative effects through dipole-dipole interactions would be significant if the intermolecular distance \( r \) is sufficiently small such that \( \omega_o r/c \lesssim 10 \) \[\text{[134]}\], \[\text{[142]}\], \[\text{[144]}\]. The van der Waals interaction potential energy between two particles at short distance is proportional to \( 1/r^6 \) and is modified by Casimir and Polder to \( 1/r^7 \) at larger distance due to retardation effect \[\text{[217]}\]. The interaction potential energy near conducting wall is proportional to \( 1/r^4 \). These interactions are essentially short range and can be neglected if we assume a sufficiently dilute
gas of molecules such that \( r > 10/k_0 \sim 10^{-6} \) \( m \) for \( k_0 \sim 10^7 \) \( m^{-1} \) in optical regime. This corresponds to density of lower than about \( 10^{13} \) molecules/cm\(^3\).

Thus, we are concerned with the quantum electrodynamics of a single molecule composed of bounded nuclei and electrons in the presence of electromagnetic, electric and/or magnetic fields. In minimal coupling version, the intermolecular interactions \( \sum \sum V_{\text{Coul}}^{\xi} \) are negligible. The single molecule can be decomposed into: the interaction free Hamiltonian of molecular system \( H_S \), transverse electromagnetic radiation \( H_R \), system-radiation interaction \( V_{SR} \), system-magnetic field (Zeeman) interaction \( V_{\text{mag}} \) and system-electric field (Stark) interaction \( V_{\text{els}} \).

\[
H = H_S + H_R + V_{SR} + V_{\text{mag}} + V_{\text{els}} \tag{2.37}
\]

### 2.3.1 Coordinates Transformation and Center of Mass Variables

In the study of kinetic effects of radiation on a gas of molecules, the center of mass momentum and position are important variables that should be quantized. By coordinate transformation, we can obtain the terms which depend on the center of mass variables for the both versions of the Hamiltonians. First, we have to perform the coordinates transformation from *space-fixed frame* \( \{r_n, r_e\} \) to a new set of coordinates \( \{R_n, R_e, R\}^6 \) in *molecule-fixed frame* (in capital letters), where \( R = \frac{1}{M} \sum \sum M_n r_n + m \sum r_e \) is the molecular center of mass(c.m.) position with \( M = \sum M_n + Nm \) the molecular mass, \( R_n = r_n - r_e \) the nuclear coordinate relative to \( r_e \) a central nuclear position, \( R_e = r_e - R_N \) the electron coordinate relative to nuclear center of mass position with \( R_N = \frac{1}{M_n} \sum \sum M_n r_n \) the nuclear center of mass position. For diatomic molecules, the new coordinates become

\[
R_n = r_n - r_1 \tag{2.39}
\]

\[
R_e = r_e - \left( \frac{M_1 r_1 + M_2 r_2}{M_1 + M_2} \right) \tag{2.40}
\]

with the inverse relations

\( ^6 \)The \( R_C \) defined previously for a general center position now refers to the molecular center of mass \( R \).
\[ r_1 = \frac{M}{M_1 + M_2} R - \frac{m}{M_1 + M_2} \sum_{c}^{N} r_{c} - \frac{M_2}{M_1 + M_2} R_n \]  

(2.41)

\[ r_2 = \frac{M}{M_1 + M_2} R - \frac{m}{M_1 + M_2} \sum_{c}^{N} r_{c} + \frac{M_1}{M_1 + M_2} R_n \]  

(2.42)

\[ r_c = R + \frac{M}{M_1 + M_2} R - \frac{m}{M_1 + M_2} \sum_{c}^{N} r_{c} \]  

(2.43)

Equations 2.43-2.42 are not in closed form. By summing over all electron coordinates in Eq. 2.43, we obtain

\[ \sum_{c}^{N} r_{c} = \frac{M_1 + M_2}{M} \sum_{c}^{N} R_{c} + N R. \]  

(2.44)

In order to obtain closed expressions for the old variables in terms of new variables, we eliminate \( \sum_{c}^{N} r_{c} \) in Eqs. 2.43-2.42 using Eq. 2.44, which finally gives

\[ r_1 = R - \frac{M_2}{M_1 + M_2} R_n - \frac{m}{M} \sum_{c}^{N} R_{c} \]  

(2.45)

\[ r_2 = R + \frac{M_1}{M_1 + M_2} R_n - \frac{m}{M} \sum_{c}^{N} R_{c} \]  

(2.46)

\[ r_c = R + R_c - \frac{m}{M} \sum_{c}^{N} R_{c} \]  

(2.47)

By using the chain rule \( \frac{\partial X}{\partial x_{i}} = \frac{\partial X}{\partial x} + \sum_{c}^{N} \frac{\partial X_{c}}{\partial x_{c}} + \frac{\partial X_{n}}{\partial x} \frac{\partial X_{n}}{\partial x} \), where \( i \in e, 1, 2 \) and \( \frac{\partial X}{\partial x_{i}} = \frac{M_1}{M} \frac{\partial X}{\partial x_{1}}, \frac{\partial X_{c}}{\partial x_{c}} = \delta_{c,1}, \frac{\partial X_{n}}{\partial x_{n}} = \frac{M_1}{M_1 + M_2}, \frac{\partial X_{n}}{\partial x} = 0, \frac{\partial X_{n}}{\partial x} = -1, \frac{\partial X_{c}}{\partial x_{c}} = 1 \), we write the old (space fixed) dels \( \nabla_1, \nabla_2, \nabla_c \) in terms of the new (molecule fixed) dels \( \nabla, \nabla_{R_n}, \nabla_{R_c} \) (subscript 'nr' stands for 'nuclear relative'). These also give the relationships between the old particle momenta \( p_{1,2,e} = -i\hbar \nabla_{1,2,e} \) and the new ones \( p_{n,e} = -i\hbar \nabla_{R_n,R_c} \) and \( \mathbf{P} = -i\hbar \nabla_{\mathbf{R}} \) as

\[ \nabla_1 = \frac{M_1}{M} \nabla - \nabla_{R_n} - \frac{M_1}{M + M_2} \sum_{c}^{N} \nabla_{R_{c}} \Leftrightarrow p_1 = \frac{M_1}{M} \mathbf{P} - \mathbf{P}_n - \frac{M_1}{M_1 + M_2} \sum_{c}^{N} \mathbf{P}_{c}. \]  

(2.48)
where it can be verified that the sum of all particles momenta is the center of mass momentum of the molecule, \( \mathbf{p}_1 + \mathbf{p}_2 + \sum_i^N \mathbf{p}_i = \mathbf{P} \). From Eq. 2.23, we find

\[
\mathbf{P} = \sum_i m_i \mathbf{r}_i + \sum_i \mathbf{O}_i \text{ with } \sum_i m_i \mathbf{r}_i = M \mathbf{\hat{R}}. \tag{2.49}
\]

Hence, Eq. 2.49 (with \( \mathbf{R}_C \to \mathbf{R} \) and \( \mathbf{\hat{R}}_C \to \mathbf{\hat{R}} \)) and Eq. 2.23 enable the expressions for magnetization \( \mathbf{M}(r, t) \) to be rewritten in terms of canonical momenta \( \mathbf{p}_i' \)

\[
\mathbf{M}(r, t) = \mathbf{M}(r, t) - \sum_i \frac{1}{2} \{ \mathbf{n}_i(r, t) \times \mathbf{O}_i - \frac{\mathbf{O}_i}{m_i} \times \mathbf{n}_i(r, t) \}
+ \frac{1}{2M} \{ \sum_i \mathbf{n}_i(r, t) \times \sum_i \mathbf{O}_i - \sum_i \mathbf{O}_i \times \sum_i \mathbf{n}_i(r, t) \}
\]

\[
\mathbf{M}(r, t) = \sum_i \frac{1}{2} \{ \mathbf{n}_i(r, t) \times \left( \frac{\mathbf{p}_i'}{m_i} \right) \left( \frac{\mathbf{P}}{M} \right) - \left( \frac{\mathbf{p}_i'}{m_i} \right) \left( \frac{\mathbf{P}}{M} \right) \times \mathbf{n}_i(r, t) \} \tag{2.51}
\]

Hence, we obtain the relation

\[
\int \mathbf{M}(r, t) \cdot \mathbf{B}(r, t) d^3r = \int \mathbf{M}(r, t) \cdot \mathbf{B}(r, t) d^3r - \sum_i \frac{\mathbf{O}_i^2}{m_i} + \frac{1}{M} \left( \sum_i \mathbf{O}_i \right)^2 \tag{2.52}
\]

We should also replace \( \mathbf{\hat{R}} \) in the last two terms of Eq. 2.27 using Eq. 2.49. Finally, the multipolar Hamiltonian including the moving center of mass can be rewritten in terms of canonical quantized variables using Eq. 2.27

\[
H' = \sum_i \frac{(\mathbf{p}_i^2 + \mathbf{O}_i^2)}{2m_i} - \frac{1}{M} \left( \sum_i \mathbf{O}_i \right)^2 + \frac{1}{\varepsilon_o} \int \mathbf{P} \cdot \mathbf{P} d^3r - \int \mathbf{M} \cdot \mathbf{B} d^3r
+ \frac{1}{2} \int \left\{ \mathbf{P} \cdot \mathbf{P} + \varepsilon_o c^2 \mathbf{B}^2 \right\} d^3r + \frac{1}{2\varepsilon_o} \int \mathbf{P}_\perp \cdot \mathbf{P}_\perp + \frac{1}{2} \int \rho d^3r
+ \frac{1}{2M} \int \{ \mathbf{P} \times \mathbf{B} \cdot \mathbf{P} + \mathbf{P} \cdot \mathbf{P} \times \mathbf{B} \} d^3r
- \frac{1}{2M} \int \{ \mathbf{P} \times \mathbf{B} \sum_i \mathbf{O}_i + \sum_i \mathbf{O}_i \cdot \mathbf{P} \times \mathbf{B} \} d^3r
- \frac{Q}{M} \mathbf{P} \cdot \mathbf{A}(\mathbf{R}_C) \tag{2.53}
\]

The third line is the Röntgen term. The term \( \sum_i \mathbf{O}_i \) in the fourth line is in the order of \( qr\mathbf{B} \) and corresponds to velocity of \( 1\text{mms}^{-1} \) for a static field around 1 Tesla, and thus can be neglected for ordinary laser fields. For neutral molecules, the last line vanishes. Equation 2.53 is similar to that of Ref. [236], written in different forms.
2.3.2 Commutation Relations in New Molecular Frame

The quantizations of all the charged particles in the molecule give \([r_{c,q}, p_{c,q}] = [r_{1,q}, p_{1,q}] = [r_{2,q}, p_{2,q}] = i\hbar \delta_{qq}\), other commutators vanish. From Eqs. 2.45-2.47, and 2.48, we have

\[
[r_{c,q}, p_{c,q}] = (1 - \frac{m}{M})[R_{c,q}, P_{c,q}] + \frac{m}{M}[R_q, P_q] = i\hbar
\]

\[
[r_{1,q}, p_{1,q}] = \frac{M_1}{M}[R_{1,q}, P_{1,q}] + \frac{M_2}{M}[R_{n,q}, P_{n,q}] + \frac{m}{M} \frac{M_1}{M_1 + M_2} \sum_{e'} [R_{e',q}, P_{e',q}] = i\hbar (2.55)
\]

\[
[r_{2,q}, p_{2,q}] = \frac{M_2}{M}[R_{2,q}, P_{2,q}] + \frac{M_1}{M}[R_{n,q}, P_{n,q}] + \frac{m}{M} \frac{M_2}{M_1 + M_2} \sum_{e'} [R_{e',q}, P_{e',q}] = i\hbar (2.56)
\]

Equations 2.54-2.56 can be written in matrix form,

\[
\left(\begin{array}{c}
\frac{M_1}{M} \\
\frac{M_2}{M} \\
\frac{N m}{M}
\end{array}\right)
\left(\begin{array}{c}
\frac{M_1}{M_1 + M_2} \\
\frac{M_2}{M_1 + M_2} \\
0
\end{array}\right)
\left(\begin{array}{c}
[R_{c,q}, P_{c,q}] \\
[R_{n,q}, P_{n,q}] \\
\sum_{e'} [R_{e',q}, P_{e',q}]
\end{array}\right)
= \left(\begin{array}{c}
1 \\
1 \\
N
\end{array}\right) i\hbar
\]

(2.57)

and solved exactly for the commutation relations of the center of mass variables, electronic and nuclear variables in molecular frame

\[
[R_{c,q}, P_{c,q}] = i\hbar \quad (2.58)
\]

\[
[R_{n,q}, P_{n,q}] = i\hbar \quad (2.59)
\]

\[
\sum_{e'} [R_{e',q}, P_{e',q}] = N i\hbar \quad (2.60)
\]

Equation 2.58 is the result that will be used to establish further quantum operator algebras between the molecular center of mass position and momentum in Appendix III.

2.3.3 Minimal Coupling Molecular Hamiltonian

We treat the n-th nuclei as point source with mass \(M_n \approx A_n a.m.u\) and charge \(Z_n\) at position \(r_n\) with momentum \(p_n\), while the e-th electron with mass \(m\) and charge \(-q\) at position \(r_e\) with momentum \(p_e\). If we neglect the cross fields terms (Eq. 2.8), the terms
in the standard minimal coupling Hamiltonian Eq. 2.7 can be written as

$$H_S = \sum_n \frac{P_n^2}{2M_n} + \sum_e \frac{P_e^2}{2m} + \frac{1}{4\pi\varepsilon_0} \left\{ \sum_{n \neq n'} \frac{Z_n Z_{n'} q^2}{r_n - r_{n'}} + \sum_e \frac{q^2}{|r_e - r_n|} - \sum_{n,e} \frac{2Z_n q^2}{r_e - r_n} \right\}$$

$$H_R = \frac{\varepsilon_0}{2} \int (E_0^2(r) + c^2B_0^2(r))d^3r$$

$$V_{SR} = \sum_n \left\{ \frac{Z_n q^2 \mathbf{p}_n \cdot \mathbf{A}_R(r_n)}{M_n} + \frac{Z_n q^2 \mathbf{A}_R^2(r_n)}{2M_n} \right\} + \sum_n \left\{ \frac{q^2 A_n^2(r_e)}{m} \right\}$$

$$V_{\text{cls}} = \sum_n \frac{Z_n q \phi_{ex}(r_n, t)}{m} \cdot \mathbf{A}_R(r_n)$$

where we have neglected the self energy $V_{\text{self}}$ term which is only important for the purpose of mass renormalization and Lamb shift calculations. The static magnetic field interaction $V_{\text{mag}}$ is identical to $V_{SR}$ except with the replacements of $\mathbf{A}_R$ by $\mathbf{A}_{ex}$ and $\mathbf{p}_e \cdot \mathbf{A}_R(r_a)$ by the symmetrized form $\frac{1}{2} \{ \mathbf{p}_e \cdot \mathbf{A}_{ex}(r_a) + \mathbf{A}_{ex}(r_a) \cdot \mathbf{p}_e \}$ since the transversality condition for radiation vector potential may not be satisfied for external field $\mathbf{A}_{ex}$.

### 2.3.4 Multipolar Molecular Hamiltonian

Similarly, the multipolar Hamiltonian Eq. 2.53 for a single molecules is written in primes, $H' = H'_S + H'_R + V'_{SR} + V'_{\text{mag}} + V'_{\text{cls}}$

$$H'_S = \sum_n \frac{P_n^2}{2M_n} + \sum_e \frac{P_e^2}{2m} + V_{\text{Coul}} + V_{\text{self}} + \frac{1}{2\varepsilon_0} \int P_e^2 d^3r$$

$$H'_R = \frac{1}{2} \int \left\{ \frac{\mathbf{H}^2}{\varepsilon_0} + \varepsilon_0 c^2 \mathbf{B}^2 \right\} d^3r$$

$$V'_{SR(E)} = \frac{q}{\varepsilon_0} \sum_e \Delta r_e \cdot \int_0^1 D_\perp (R + u\Delta r_e) du - \frac{q}{\varepsilon_0} \sum_n Z_n \Delta r_n \cdot \int_0^1 D_\perp (R + u\Delta r_n) du$$

$$V'_{SR(M)} = \int_0^1 \sum_e \frac{q}{2} \left\{ \frac{v_e^2}{m} \mathbf{P}_e - \frac{v_e^2}{M} \mathbf{P} \right\} \cdot \Delta r_e \cdot \mathbf{B}_R (R + u\Delta r_e) du$$

$$V'_{\text{cls}} = \sum_n \frac{Z_n q \phi_{ex}(r_n, t)}{m} \cdot \mathbf{A}_R (R + u\Delta r_n)$$

where $\Delta r_e \triangleq r_e - R$, $\Delta r_n \triangleq r_n - \mathbf{R}$ and we have used Eq. 2.28 and Eq. 2.51 to obtain Eqs. 2.67 and 2.68 respectively. The expression for $V'_{\text{mag}}$ is the same as $V'_{SR(M)}$ except with the replacement of the radiation magnetic field $\mathbf{B}_R$ by external magnetic field $\mathbf{B}_{ex}$. It gives the Zeeman effect in external magnetic field.

The multipolar particle system Hamiltonian Eq. 2.65 has an extra term from the transverse polarization $\frac{1}{2\varepsilon_0} \int P_e^2 d^3r$ which contributes only to the self energies and does not contribute to the interactions with external fields. The particle-radiation interaction $V'_{SR}$
is now composed of the interactions with the electric $V_{SR(E)}''$ and magnetic $V_{SR(M)}''$ fields components of the radiation. The Zeeman interaction $V_{mag}'$ comes from the expansion of the magnetic interaction term $\int \mathcal{M}(\mathbf{r}) \cdot \mathbf{B}(\mathbf{r}) d\mathbf{r}$ while the Stark effect is due to $V_{ela}'$.

The above Hamiltonians are non-relativistic. The Dirac equation would provide extra leading terms due to relativistic effects. The first term is $H_{so} = -\sum_i \frac{2}{m_i} \mathbf{S}_i \cdot \mathbf{B}_{in}(\mathbf{r}_i)$ the interaction between the electronic spin and the internal magnetic field generated by the orbiting electrons and the second is the Darwin term $H_D = \sum_i \frac{\mu_i}{2m_i} \nabla^2 \phi_i$.

2.3.5 Field-Free Molecular Hamiltonian

By using Eqs. 2.48, the kinetic energy (first two terms) in Eqs. 2.65 and 2.61 can be rewritten in molecule fixed frame as

$$K = \frac{\hbar^2}{2M} \nabla^2 - \frac{\hbar^2}{2\mu} \nabla^2_{\mathbf{r}_e} - \left\{ \frac{\hbar^2}{2m_{\mathbf{r}_e}} \sum_{\mathbf{r}_e} \nabla_{\mathbf{r}_e}^2 + \frac{\hbar^2}{2(M_1 + M_2)} \sum_{\mathbf{r}_e} \nabla_{\mathbf{r}_e} \cdot \sum_{\mathbf{r}_e} \nabla_{\mathbf{r}_e} \right\} \tag{2.70}$$

$$\equiv H_{cm}(\mathbf{R}) + K_{nuc}(\mathbf{R}_n) + K_{el}(\mathbf{R}_e)$$

where $\frac{1}{\mu} = \frac{1}{M_1} + \frac{1}{M_2}$ is the reduced mass. Equation 2.70 is slightly different from that of Refs. [184] and [183] who have used the center point between the two nuclei as $\mathbf{R}$. The first term $H_{cm}(\mathbf{R})$ is the center of mass translational kinetic energy which is referred as the external degree of freedom.

By replacing the old coordinates $\mathbf{r}_e \in \mathbf{r}_e, \mathbf{r}_1, \mathbf{r}_2$ with the new ones in the molecular frame by using Eqs. 2.41-2.43, we the Coulomb interactions 2.9 in new coordinates for nuclei-nuclei repulsions, electron-electron repulsions and nuclei-electron attractions as in Ref. [180]

$$V_{Coul}(\mathbf{r}_e, \mathbf{r}_n) = \frac{Z_1 Z_2 q^2}{4\pi \varepsilon_0 |\mathbf{R}_n|} + \sum_c \left\{ \sum_{c' \neq c} \frac{q^2}{4\pi \varepsilon_0 |\mathbf{r}_c - \mathbf{R}_c|} - \frac{q^2}{2\pi \varepsilon_0} \left( \frac{Z_1}{|\mathbf{R}_e + \frac{M_e R_e}{M_1 + M_2}|} + \frac{Z_2}{|\mathbf{R}_e - \frac{M_e R_e}{M_1 + M_2}|} \right) \right\} \tag{2.71}$$

Thus, the field-free molecular system Hamiltonian is partitioned into the kinetic energy and the internal energy $H_S = H_{cm} + H_I$ where $H_I = K_{nuc}(\mathbf{R}_n) + K_{el}(\mathbf{R}_e) + V_{Coul}$ for the minimal coupling version (from Eq. 2.61), and $H'_{S} = H'_{cm} + H'_I + \frac{1}{2 \varepsilon_0} \int \mathcal{M}^2 d^3r$ for the multipolar version (from 2.61).

2.3.6 Electric Dipole Interaction from Minimal Coupling Version

The vector potentials in Eqs. 2.63 can also be written in terms of new position variables $\mathbf{A}_R(\mathbf{r}_a) = \mathbf{A}_R(\mathbf{R} + \mathbf{r}_a)$ using Eqs. 2.45-2.47 and expanded around $\mathbf{R}$ for $\mathbf{r}_a \in \mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_e$. The relative magnitude of the $A_R^2$ "seagull" term in Eq. 2.63 to the p.A term is $\mathbf{q} A/p$, which is negligible for weak field. Hence, in the long-wavelength approximation,
only the zeroth order term in $R_n, R_e$ is retained and the molecule-radiation interaction in minimal coupling becomes

$$V_{SR(E1)} = \{-\frac{Q}{M}P + qV_{eff}\} \cdot A_R(R) \tag{2.72}$$

$$v_{eff} = \left(\frac{Z_1}{M_1} - \frac{Z_2}{M_2}\right)P_n + \left(\frac{Z_1 + Z_2}{M_1 + M_2} + \frac{1}{m}\right)\sum_{e}^{N} P_e \tag{2.73}$$

where $Q = q(Z_1 + Z_2 - N)$ is the total charge and we have defined the effective velocity $v_{eff}$. The first and the second terms of Eq. 2.73 correspond to the transitions involving the rotational-vibrational states and the electronic states respectively.

By using $[\dot{x}_i, f(p_{ix})] = i\hbar \frac{\partial f}{\partial p_{ix}}$ with the free internal Hamiltonian

$$H_I = \sum_{q}^{N} \frac{P_{nq}^2}{2m} + \frac{1}{2m} \sum_{q}^{N} \sum_{c}^{p} P_{eq}^2 + \frac{1}{2(M_1 + M_2)} \sum_{q}^{N} \sum_{c, c'}^{p} P_{eq} P_{c' q} + V_{out} \equiv \sum_{\alpha} E_\alpha |\alpha\rangle \langle \alpha| \tag{2.74}$$

where $\alpha \equiv \Lambda, \Sigma, \Omega, \nu, J, M$ is the internal molecular state (for example), we have

$$[R_n, H_I] = \frac{i\hbar}{\mu} P_n \tag{2.75}$$

$$[R_e, H_I] = \frac{i\hbar}{m} P_e + \frac{i\hbar}{(M_1 + M_2)} \sum_{c'}^{N} P_{c'} \tag{2.76}$$

where $H_I$ is the Hamiltonian of the internal degrees of molecule.

Now, we shall make Eq. 2.76 into a closed form. A summation of the electronic momenta in Eq. 2.76 gives $\sum_{e}^{N} [R_e, H_I] = i\hbar \left(\frac{1}{m} + \frac{N}{(M_1 + M_2)}\right) \sum_{e'}^{N} P_{e'}$, which is used with Eq. 2.75 to rewrite Eq. 2.73 as

$$v_{eff} = \frac{1}{i\hbar} \left(\frac{Z_1 M_2 - Z_2 M_1}{M_1 + M_2}\right) [R_n, H_I] + \left(\frac{Z_1 + Z_2 - N}{M} + 1\right) \sum_{e}^{N} [R_e, H_I] \tag{2.77}$$

Thus, for neutral molecule, Eq. 2.72 can be written in terms of the dipole operator as

$$V_{SR(E1)} = -\frac{1}{i\hbar} \sum_{\alpha} \{E_\alpha \hat{d} |\alpha\rangle \langle \alpha| - E_\alpha |\alpha\rangle \langle \alpha| \hat{d}\} \cdot \sum_{k, \lambda} \sqrt{\frac{\hbar}{2\varepsilon_\omega \omega_{k\lambda} V}} (\hat{\varepsilon}_{k\lambda} \hat{a}_{k\lambda} e^{ik \cdot R} + \hat{\varepsilon}_{k\lambda}^* \hat{a}_{k\lambda}^\dagger e^{-ik \cdot R}) \tag{2.78}$$

where $E_\alpha$ is the eigenenergy of $H_I$ and the electric dipole operator is defined as

$$\hat{d} \doteq -\frac{(Z_1 M_2 - Z_2 M_1)}{M_1 + M_2} q R_n - q \sum_{e} R_e \tag{2.79}$$
Thus, we have obtained the dipole approximation Hamiltonian in minimal coupling version from the zeroth order field expansion around $R$. Higher order expansions would lead to magnetic interactions and higher multipoles interactions. The zeroth order 'seagull' term gives terms in second order of radiation absorption/emission

$$V_{SR(2)} = \left\{ \frac{Z_1^2}{M_1} + \frac{Z_2^2}{M_2} + \sum_{\epsilon} \frac{1}{m} \left( \sum_{\kappa: \lambda:} \frac{1}{2} \sum_{\kappa': \lambda':} \frac{\hbar}{2\varepsilon_0 \sqrt{\omega_{\kappa: \lambda:} \omega_{\kappa': \lambda':}}} \times \right) \right. $$

\[ \left. \epsilon_{\kappa: \lambda:/} \cdot \hat{\epsilon}_{\kappa': \lambda':} \hat{\epsilon}_{\kappa: \lambda:/} \hat{\epsilon}_{\kappa': \lambda':} \right\} d\Gamma(\hat{R}) \]

\[ \epsilon_{\kappa: \lambda:/} \cdot \hat{\epsilon}_{\kappa': \lambda':} \hat{\epsilon}_{\kappa: \lambda:/} \hat{\epsilon}_{\kappa': \lambda':} \]

2.3.7 Electric- and Magnetic-Multipole Interactions from Multipolar Version

The expansion of $\mathbf{D}_{\parallel}(\mathbf{R}+u\Delta\mathbf{r}_x)$ in the small parameters $u(\mathbf{r}_x-\mathbf{R})$ compared to $\mathbf{R}$ gives

$$\int_0^1 \mathbf{D}_{\parallel}(\mathbf{R}+u\Delta\mathbf{r}_x)du = \{1 + \frac{1}{2}(\Delta\mathbf{r}_x \cdot \nabla \mathbf{r}_x) + \frac{1}{6}(\Delta\mathbf{r}_x \cdot \nabla \mathbf{r}_x)^2 \} \mathbf{D}_{\parallel}(\mathbf{R}),$$

with $x = 1, 2, \epsilon$. The zeroth and first order terms of Eq. 2.67 give the electric dipole $V_{SR(E1)}^\prime$ and electric quadrupole $V_{SR(E2)}^\prime$ molecule-radiation interactions respectively,

$$V_{SR(E1)}^\prime = -\frac{1}{\varepsilon_0} \mathbf{\hat{d}} \cdot \mathbf{D}_{\parallel}(\mathbf{R}) + \frac{1}{\varepsilon_0} \mathbf{R}_e \cdot \mathbf{D}_{\parallel}(\mathbf{R})$$

(2.80)

$$V_{SR(E2)}^\prime = \frac{q}{2\varepsilon_0} \left( \sum_e \mathbf{R}_e \cdot (\mathbf{R}_e \cdot \nabla) - \frac{\mathbf{R}_m \cdot (\mathbf{R}_m \cdot \nabla)}{(M_1 + M_2)} \right) \mathbf{D}_{\parallel}(\mathbf{R})$$

$$+ \frac{1}{2\varepsilon_0} \frac{m}{M} \left( \sum_e \sum_e \mathbf{R}_e \cdot (\mathbf{\hat{d}} \cdot \nabla) - \frac{\mathbf{R}_m \cdot (\mathbf{\hat{d}} \cdot \nabla)}{M} \right) \mathbf{D}_{\parallel}(\mathbf{R})$$

(2.81)

The last term of Eq. 2.80 and the second line of Eq. 2.81 are $\frac{m}{M}$ smaller and can usually be neglected. The first line in Eq. 2.81 can be rewritten as

$$V_{SR(E2)}^\prime = -\frac{1}{\varepsilon_0} \sum_{ij} \left( \sum_e \frac{\partial}{\partial X_e} + \frac{\partial}{\partial X_e} \right) D_{\parallel}(\mathbf{R}, t)$$

(2.82)

where $i, j = x, y, z$ and the electric dipole operator $\mathbf{\hat{d}}$ is defined in Eq. 2.79 and the quadrupole operators for electronic and nuclear components are defined as

$$\hat{Q}_{ij}^e = -\frac{1}{2} qX_{ei}X_{ej} \quad \text{and} \quad \hat{Q}_{ij}^n = \frac{1}{2} \frac{M_1^2Z_1 + M_2^2Z_2}{(M_1 + M_2)^2} \mathbf{q} \cdot \mathbf{X}_n \cdot \mathbf{X}_n.$$

(2.83)

For neutral molecule, $Q = 0$. For homonuclear molecules, $Z_1M_2 - Z_2M_1 = 0$ and the radiative processes are purely due to the electronic dipole moment, with no rotational nor vibrational transitions.
Similarly, the expansion of $\mathbf{B}_R(\mathbf{R} + u \Delta \mathbf{r}_x)$ in Eq. 2.68 gives $\int_0^1 \mathbf{B}_R(\mathbf{R} + u \Delta \mathbf{r}_x) du = \left\{ \frac{1}{2} + \frac{1}{3} \Delta \mathbf{r}_x \cdot \nabla + \frac{1}{5} (\Delta \mathbf{r}_x \cdot \nabla)^2 + \frac{1}{30} (\Delta \mathbf{r}_x \cdot \nabla)^3 \right\} \mathbf{B}_R(\mathbf{R})$, with $x \in 1, 2, e$. Thus, the zeroth order expansion of $\mathbf{B}_R$ in Eq. 2.68 gives $V'_{SR(M1)}$ the magnetic dipole interactions.

$$V'_{SR(M1)} = \sum_e \frac{q_e}{2m_e} \{ \mathbf{R}_e \times \mathbf{P}_e - \mathbf{P}_e \times \mathbf{R}_e \} \cdot \mathbf{B}_R(\mathbf{R})$$

$$-\frac{q_e}{2} \left( \frac{Z_1 M_2}{M_1} + \frac{Z_2 M_1}{M_2} \right) \frac{1}{M_1 + M_2} \{ \mathbf{R}_n \times \mathbf{P}_n - \mathbf{P}_n \times \mathbf{R}_n \} \cdot \mathbf{B}_R(\mathbf{R})$$

$$+ \frac{q_e}{2} \left( \frac{Z_2 M_1 - Z_1 M_2}{(M_1 + M_2)^2} \right) \{ \hat{\mathbf{d}} \times \sum_e \mathbf{P}_e - \sum_e \mathbf{P}_e \times \hat{\mathbf{d}} \} \cdot \mathbf{B}_R(\mathbf{R})$$

(2.84)

The center of mass momentum do not appear in the multipolar expansions, but has been separated out in the Röntgen interaction. The first order expansion of the polarization in the Röntgen term $V'_{R5} = \frac{1}{2M} \int \{ -\mathbf{B} \cdot \mathbf{d} \mathbf{P} + \mathbf{P} \cdot \mathbf{d} \mathbf{B} \} d^3r$ gives

$$V'_{R5}(1) = -\frac{1}{2M} \left\{ \mathbf{B}(\mathbf{R}) \cdot \hat{\mathbf{d}} \times \mathbf{P} - \mathbf{P} \times \hat{\mathbf{d}} \cdot \mathbf{B}(\mathbf{R}) \right\}$$

(2.85)

which is used in the dipole interaction Hamiltonian in Appendix I. The $V'_{SR(E1)} : V'_{SR(E2)} : V'_{SR(M1)} : \sum_i \frac{c^2}{2m_i}$ have relative magnitudes: $1 : \alpha_B / \lambda : v/c : dE/Mc^2$. For optical wavelength and beyond the electric quadrupole interaction is negligible, and for non relativistic particles the magnetic dipole term is neglected. Thus, it is a good approximation to keep only the electric dipole interaction term $V'_{SR(E1)}$.

In dipole approximation, the total Hamiltonian of Eq. 2.53 reduces to

$$H(t) = H_{cm} + H_I + H_R + V_{SR(E1)}$$

(2.86)

where

$$H_I = K_{mc}(\mathbf{R}_n) + K_{el}(\mathbf{R}_e) + V_{Coul}(\mathbf{R}_e, \mathbf{R}_n)$$

(2.87)

The Hamiltonian Eq. 2.86 acts in the Hilbert space which contains three classes of quantum states: the external center of mass momentum $|\mathbf{P}\rangle$, the internal molecular state represented by $|\alpha\rangle$ and the radiation Fock state $|n_{\lambda\alpha}\rangle$; with the kinetic energy $H_{cm}$, the internal molecular energy $H_I$ and the radiation energy $H_R$. The three degrees of freedom are mutually coupled through the electric dipole interaction Hamiltonian $V_{SR(E1)}$.

### 2.4 Molecular Energy Levels

The total free Hamiltonian (excluding interaction with external fields) can be written as
\[ i \hbar \frac{\partial \Psi_o}{\partial t} = \{ K_{\text{em}}(R) + K_{\text{nuc}}(R_n) + K_{\text{el}}(R_e) + V_{\text{Coupl}}(R_n, R_e) \} \Psi_o = E_o \Psi_o \]  

(2.88)

where \( E_o \) and \( \Psi_o \) are the total eigenenergy and wavefunction of a free molecule. The total wavefunction can be written as the product of the center of mass wavefunction \( \Psi_I \) and the internal wavefunction \( \Psi_I \) since they are completely separable, \( \Psi_o = \Psi_{\text{cm}} \Psi_I \).

\[ \{ K_{\text{nuc}}(R_n) + K_{\text{el}}(R_e) + V_{\text{Coupl}}(R_n, R_e) \} \Psi_I(R_n, R_e) = E_I \Psi_I(R_n, R_e) \]  

(2.89)

The nuclear and electronic degrees are coupled via \( V_{\text{Coupl}} \) and therefore it is strictly not possible to further separate the internal wavefunction into the nuclear and electronic part. However, from Eq. 2.70 we see that the leading term of \( K_{\text{el}} \) is \( M/m \) times much larger than \( K_{\text{nuc}} \). Thus, \( K_{\text{nuc}} \) can be treated as a perturbation and we can approximately write the electronic eigenvalue equation

\[ \{ K_{\text{el}}(R_e) + V_{\text{Coupl}}(R_n, R_e) \} \Psi^m_m(R_n, R_e) = E_m(R_n) \Psi^m_m(R_n, R_e) \]  

(2.90)

where \( \Psi^m_m \) depends explicitly on the electronic coordinates \( R_e \) but depends parametrically on the nuclear coordinates \( R_n \). This is the clamped-nuclei model where the nuclei assume a fixed value of \( R_n \) while Eq. 2.90 is solved for the electronic potential energy curve \( E_m(R_n) \) and wavefunction \( \Psi^m_m(R_n, R_e) \) for a fixed nuclear spacing \( R_n \). By varying \( R_n \), we can solve for the electronic energy curves (which depend on \( |R_n| \) for diatomic molecules) and surfaces (which depend on a few internuclear distances \( \{|R_n|\} \) for polyatomic molecules) for all electronic states.

The term symbol used in spectroscopy of molecules is characterized by the electronic states as given by

\[ ^{2S+1}A^+/-_{\Lambda^+/-\Sigma^+/-, u/g} \]  

(2.91)

where \( \Lambda = |M_L|, -L \leq M_L \leq L \) is the electronic orbital angular momentum along internuclear axis, \(-S \leq \Sigma \leq S \) is the electronic spin angular momentum along internuclear axis and \( \Omega = |\Lambda + \Sigma| \) is the resultant electronic angular momentum along internuclear axis.

The left superscript \( 2S + 1 \) is the multiplicity (e.g., singlet for \( S = 0 \), doublet for \( S = \frac{1}{2} \)) or the number of possible \( \Lambda + \Sigma \) which may take negative values corresponding to different energies splitted by spin-orbit coupling. For example, if \( \Lambda = 1, S = 1 \), there are three possible terms \( ^3\Pi_0, ^3\Pi_1 \) and \( ^3\Pi_2 \). The right superscript denotes \(+/-\) parity of the electronic spatial wavefunction upon reflection through the plane containing the two nuclei. For \( \Lambda = 0 \), the states \( \Sigma^+ \) and \( \Sigma^- \) have different energies. But the states \( \Lambda = 1, 2, 3, 4, \ldots \) (designated by symbols \( \Pi, \Delta, \Phi, \Gamma, \ldots \) respectively) are doubly degenerate. The degeneracy is lifted by the \( \Lambda \) type doubling due to strong coupling between electronic orbital angular momentum and the rotational angular momentum. For molecules with
center of symmetry like homonuclear molecules, the nuclei are indistinguishable and the
effect of interchanging the nuclei produces two possible electronic states, g (gerade) and u
(ungerade) for even and odd parities respectively.

Following Born’s method [179], we expand the total molecular wavefunction in
terms of the complete set of eigenfunctions \( \{ \Psi_m^e(R_n, R_c) \} \) as \( \Psi_f (R_n, R_c) = \sum m \Psi_m^e(R_n, R_c) \)
and replacing it into Eq. 2.89 gives \( \{ \Psi_m^e K_{nuc} \Psi_m^e + \Psi_m^e K_{el} \Psi_m^e + V_{Coul} \Psi_m^e \} = E_I \sum m \Psi_m^e \). Then, by using Eq. 2.90 and \( \int \Psi_m^e \Psi_m^e d^3 R_c = \delta_{mm'} \) we obtain the equation for the nuclear wavefunction similar to Ref. [181]

\[
\{ K_{nuc}(R_n) + E_m(R_n) - E_I \} \Psi_m^e = \sum m \left\{ \frac{\hbar^2}{\mu} \int \Psi_m^e \nabla_{R_n} \Psi_m^e d^3 R_c \cdot \nabla_{R_n} - \int \Psi_m^e K_{nuc} \Psi_m^e d^3 R_c \right\} \Psi_m^e
\]

(2.92)
The nuclear wavefunction \( \Psi_m^e(R_n) \) which incorporates ro-vibrational motion of nuclei, depends only on the nuclear coordinates. The two integrals correspond to the change in the electronic wavefunction as the result of the change in the nuclear coordinates (nuclear motion).

In the Born-Oppenheimer approximation, the nuclear motion is assumed to be
much slower than the electron such that the electronic configurations are essentially unchanged by the nuclear motion. This corresponds to keeping only one term \( \Psi(R_n, R_c) \approx \Psi_0^a(R_n) \Psi_0^a(R_n, R_c) \) and neglecting the integral terms with \( \frac{\hbar^2}{2\mu} \Psi_m^e \nabla_{R_n} \Psi_m^e + 2 \frac{\hbar^2}{2\mu} \Psi_m^e \cdot \nabla_{R_n} \Psi_m^e \), giving \( \{ \Psi_m^e K_{nuc} \Psi_m^e + \Psi_m^e K_{el} \Psi_m^e + V_{Coul} \Psi_m^e \} = E_I \Psi_m^e \). In adiabatic approximation, only the diagonal terms \( (m = m') \) are kept and contribute to the effective electronic potential for the electronic state \( |a \rangle \) with the eigenfunction \( \Psi_a \), as

\[
V_a (R_n) = E_a(R_n) + \int \Psi_a^e K_{nuc} \Psi_a^e d^3 R_c
\]

(2.93)

By writing \( K_{nuc}(R_n) = -\frac{\hbar^2}{2\mu} \nabla_{R_n} \theta, \phi = -\frac{\hbar^2}{2\mu} \left( \frac{1}{R_n} \frac{\partial}{\partial R_n} (R_n^2 \frac{\partial \theta}{\partial R_n}) - \frac{1}{R_n} \frac{\partial}{\partial R_n} (R_n^2 \frac{\partial \phi}{\partial R_n}) \right) \), Eq. 2.92 becomes

\[
\{-\frac{\hbar^2}{2\mu \partial_{R_n}^2} \frac{\partial}{\partial R_n} (R_n^2 \frac{\partial}{\partial R_n}) + \frac{\hbar^2}{2\mu \partial_{R_n}^2} \nabla^2 (\theta, \phi) + V_a(R_n) \} \Psi_a^e(R_n, \theta, \phi) = E_I \Psi_a^e(R_n, \theta, \phi)
\]

(2.94)

The rotational angular momentum eigenvalue equation is \( N^2 \Theta_{ar} = N(N + 1) \Theta_{ar} \) with \( \Theta_{ar}(\theta, \phi) = \sqrt{\frac{2J+1}{4\pi} \frac{(2-J)^2 M^2 + J(M-J)^2}{J(J+1)}} e^{iM\phi} P_J^M(\cos \theta) \) as the spherical harmonics. The coupling between the rotational and electronic angular momentum yields \( J(J+1) = N(N+1) + \Omega^2 \) for Hund’s case-a and \( K(K+1) = N(N+1) + \Lambda^2 \) for Hund’s case-b.

For symmetric top, \( \Theta_{ar} \) depends on the third Euler angle \( \chi \) as

\[
\Theta_{ar}(\theta, \phi, \chi) = N_J K M e^{i \phi} e^{i \chi (J-M)} (\sin \frac{\theta}{2})^{K-M}(\cos \frac{\theta}{2})^{K+M} F_{a,b,c}(\sin^2 \frac{\theta}{2})
\]

(2.95)
where $F_{a,b,c}$ is the hypergeometric function, while $N_{JKM}$ is normalization factor (full expression is given in Ref. [174], p.280)

By using the ansatz $\Psi^a(R_n, \theta, \phi) \doteq X_{av}(R_n) \Theta_{av}(\theta, \phi)$, Eq. 2.92 yields vibrational eigenvalue equation

\[
-\frac{\hbar^2}{2\mu} \left( \frac{\partial^2}{R_n^2 \partial R_n^2} + \frac{\partial^2}{\partial R_n} \right) (J+1) - \Omega^2 \right) X_{av} + V_a(R_n) X_{av} = E_{I} X_{av} \tag{2.96}
\]

For bound electronic states, the potential curve $V_a(R_n)$ has a minimum at the equilibrium internuclear distance $R_o$ and can be approximately represented by the Morse function $V_a(R_n) = D_e(1 - e^{-a(R_n-R_o)})^2$. For small vibrational displacement $R_n - R_o = q$, the potential can be expanded around the equilibrium position $R_o$ (obtained from $\frac{\partial V_a}{\partial q} |_{R_o} = 0$) as $V_a(R_n) \approx V_a(R_o) + \frac{1}{2} V_a^{(2)} q^2 + \ldots$, where $V_a^{(s)} = \frac{\partial^s V_a}{\partial q^s} |_{R_o}$, depends on the electronic bonding between nuclei. By replacing $X_{av}(R_n) \doteq R_n X_{av}(R_n)$ and expansion $\frac{1}{R_n} \approx \frac{1}{R_o} - \frac{2q}{R_o^2} + \frac{3q^2}{R_o^4} - \ldots$, Eq. 2.96 can be written as

\[
\left\{ -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial q^2} + \sum_{s=0}^{\infty} q^s((-1)^s a_s + \frac{1}{s!} V_a^{(s)}) \right\} X_{av} = E_{av} X_{av} \tag{2.97}
\]

where $a_s = \frac{(s+1)B_{e,J}(J+1)}{R_o^2}$, $B_{e,J} = \frac{\hbar}{2\mu R_o^2} V_a^{(1)} = \frac{\partial V_a}{\partial q} |_{R_o} = 0$ and we have used $E_{I} = E_{av} + E_{av} + V_a(R_n)$ with $E_{av} \doteq \hbar B_{e,J}(J+1) - \Omega^2$. The terms $a_s q^s < 2\hbar B_{e,J}(J+1)$ (since $q^s < 1$) are typically smaller than the harmonic oscillator potential energy $\frac{1}{2} V_a^{(2)} q^2$ where $V_a^{(2)} = \mu \omega_0^2 \doteq k_a$.

Thus, we can treat $a_1 q$ and all higher order terms than $\frac{1}{2} V_a^{(2)} q^2$ as perturbations. In the first order perturbation, the odd orders in $q$ vanish by symmetry consideration. Instead of treating $a_1 q^2$ as perturbation, we can include it as the effective harmonic oscillator force constant $k_a,J = \mu + 2\frac{3B_{e,J}(J+1)}{R_o^2}$. Thus, Eq. 2.97 reduces to the harmonic oscillator problem

\[
\left\{ -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial q^2} + \frac{1}{2} k_a,J q^2 \right\} X_{av} = E_{av} X_{av} \tag{2.97}
\]

which includes the rotational-vibrational coupling, with the eigenvalue

\[
E_{av}^0 = \hbar \sqrt{\frac{k_a,J}{\mu} + 2\frac{3B_{e,J}(J+1)}{\mu R_o^2}} (v + \frac{1}{2}) \approx \hbar \omega_v (v + \frac{1}{2}) + \hbar \frac{6B_{e,J}(J+1)}{\omega_v} (v + \frac{1}{2}) \tag{2.98}
\]

The second term gives the lowest order rotational-vibrational coupling energy. The anharmonic energy come purely from $\frac{1}{4!} V_a^{(4)} q^4$ and higher order terms while the centrifugal correction and higher order rotational-vibrational coupling come from the perturbations and higher order expansion of Eq. 2.98.

### 2.5 Electronic-Nuclear Couplings

The electronic angular momentum $L$, spin momentum $S$, rotational angular momentum $N$ and nuclear spin angular momentum $I$, are not independent but can interact
with each other with the strength depending on the molecules. The strengths of couplings between different degrees of freedoms give rise to fine splitting in energy levels. For diatomic molecules, the limiting cases of electronic-rotational couplings are described by the five Hund’s coupling cases a) to e). We briefly describe the major two cases: a) and b).

**Hund’s case-a** For a small diatomic molecule with small internuclear distance (along the nuclear-axis), the internuclear force is usually stronger than the spin-orbit coupling between the \( S \) and \( L \). As the molecule tumbles, the electrons follow. The spin \( S \) and orbital \( L \) angular momenta of the electrons precess independently around the \( z \)-axis and are not conserved. But their projections along the axis are conserved, giving the good quantum numbers \( \Lambda \) and \( \Sigma \). The rotational angular momentum \( N \) is perpendicular to nuclear-axis and couples to \( \Omega \) to form the total angular momentum

\[
\mathbf{J} = \mathbf{N} + \mathbf{\Omega}
\]

\[
N(N+1) = J(J+1) - \Omega^2
\]

where \( 0 \leq \Omega \leq J \). For each \( (\Lambda, \Sigma) \), the number of \( \Omega \) is \( 2S+1 \). However, the states with \( +\Omega \) and \( -\Omega \) are doubly degenerate.

Thus, the state vector for case-a is \( |\Lambda, \Sigma, \Omega, \nu, J, M\rangle \), written in good quantum numbers of the electronic orbital state \( \Lambda \), electronic spin \( \Sigma \), vibrational \( \nu \), total angular momentum \( J \), projection of the angular momentum on space fixed quantization axis \( M \) and other quantum numbers like nuclear spin. The total internal eigenenergy in the absence of external fields from electronic-vibrational-rotational degrees can be written in conventional spectroscopy symbols

\[
E_{\Lambda, \Sigma, \nu, J, \Omega}/\hbar c = T_e(\Lambda, \Sigma) + \{\omega_e(v + \frac{1}{2}) - \omega_c(x) + (v + \frac{1}{2})^2\}
\]

\[
+ B_v\{J(J+1) - \Omega^2\} - D_v\{J(J+1) - \Omega^2\}^2 + A\Omega^2
\]

(2.100)

where \( B_v \equiv B_c - \alpha(v + \frac{1}{2}) \) and \( D_v \equiv D_c + \beta(v + \frac{1}{2}) \), \( B_c \equiv \frac{\hbar}{8\pi c I_c} \) with \( I_c \) \( \equiv \frac{\mu R_c^2}{\hbar^2} \) the moment inertia which depends on electronic state, \( \alpha \equiv \frac{6\omega_e x_c \omega_c^2}{\omega_e^2} - \frac{6\omega_c^2}{\omega_e} \) (Ref. [173]) is the vibration-rotational coupling constant with \( \omega_e x_c \) the anharmonic coupling, \( D_c \equiv \frac{4\omega_c^3}{\omega_e} \) is the centrifugal distortion constant. The coefficients \( A \) is the spin-orbit coupling constant. The corresponding wavefunction is

\[
\Psi_I(\mathbf{R}_n, \mathbf{R}_c) = \langle \mathbf{R}_n, \mathbf{R}_c|\Lambda, \Sigma, \nu, J, M, \alpha\rangle = \Psi_{\Lambda, \Sigma, \Omega}(\mathbf{R}_n, \mathbf{R}_c) X_{\Lambda, \Sigma, \Omega, \nu}(\mathbf{R}_n) \Theta_{J, M}(\theta, \phi).
\]

(2.101)

The rotational Hamiltonian for symmetric top is similar to that of Hund’s case-a in diatomics, \( H_r = \frac{K}{2}(\frac{I_\alpha^2}{I_\alpha} + \frac{N^2}{I_\alpha}) = \hbar c B_v\{J(J+1) - \Omega^2\} + \hbar c A K^2 \) where \( 0 \leq K \leq J \) is the component of the total angular momentum along molecular symmetry axis. The dipole selection rules here are \( \Delta K = 0 \) and \( \Delta J = \pm 1 \).
**Hund’s case-b** On the other hand, when the electronic spin-orbit coupling is weaker than the coupling of electronic angular momentum to rotation, the spin angular momentum in space fixed frame is a good quantum number. Only the electronic angular momentum (and not spin) couples with the rotation to form $K$

\[
K = N + \Lambda \\
N(N + 1) = K(K + 1) - \Lambda^2
\]  

(2.102)

where $K \geq \Lambda$. Then, the $K$ adds up vectorially with the spin $S$ to form the total angular momentum as

\[
J = K + S
\]

(2.103)

where $|K - S| \leq J \leq K + S$ and $-J \leq M \leq J$. The independent quantum numbers form the state vector as $|\Lambda, S, K, v, J, M\rangle$. Here, the projection of the angular momentum along the nuclear axis in molecular frame is $K$ instead of $\Lambda$ (in case-a). For each $K$, there are $(2S + 1)$ possible values of $J$. So, there are $(2S + 1)$ levels for each $N$ or $K$.

The coupling between rotation and electronic orbital angular momentum leads to the \textit{\Lambda-type doubling} in the states $\Lambda \neq 0$ of Cases a and b, where each $J$ level is splitted into two. The splitting is in the order of rotational level separations (a few cm$^{-1}$) and increases with $J$ but decreases with $\Omega$.

### 2.6 Electric Dipole Matrix Elements and Selection Rules

The dipole moment operator for a molecule in space fixed coordinate is with center of mass $\hat{R}$ is $\hat{d}(\hat{r}_e, \hat{r}_n) = \sum_e q_e \hat{r}_e + \sum_n q_n \hat{r}_n$. In molecule fixed frame, the dipole moment can be partitioned into the electronic part $\hat{d}_e$ and the nuclear part $\hat{d}_n$,

\[
\hat{d}(\hat{R}_n, \hat{R}_e) = -q \sum_e R_e + \frac{M_1 Z_2 - M_2 Z_1}{M_1 + M_2} q R_n \equiv \hat{d}_e(\hat{R}_e) + \hat{d}_n(\hat{R}_n)
\]

(2.104)

The second term on the right-hand-side gives the rotational-vibrational dipole selection rules. For homonuclear molecules, $M_1 = M_2$ and $Q_2 = Q_1$, so there is no rotational-vibrational transition. Although the dipole operator is in molecule-fixed frame, it is not in the rotating frame of the molecules.

For rotating molecules, it is convenient to express the dipole operator in terms of the angles defined relative to a rotating frame of the molecules. This is accomplished by three consecutive rotations in \textit{Euler angles} $(\theta, \phi, \chi)$: a) rotation of $\theta$ around $Z$-axis \footnote{Cartesian coordinates in space(laboratory)-fixed axis $F \in X, Y, Z$ and molecule(body)-fixed axis $g \in x, y, z$.} 

b) rotation of $\phi$ around $y_1$ axis of the first new frame, c) rotation of $\chi$ around the $z_2$ axis (or
$z$ axis) of the second new frame. This is represented by the unitary transformation operator $\Phi$ [175]

\[
\Phi^{-1} = \begin{pmatrix}
\Phi_{xx} & \Phi_{xy} & \Phi_{xz} \\
\Phi_{yx} & \Phi_{yy} & \Phi_{yz} \\
\Phi_{zx} & \Phi_{zy} & \Phi_{zz}
\end{pmatrix}
\]

\[
= \begin{pmatrix}
\cos \theta \cos \phi \cos \chi - \sin \phi \sin \chi & \cos \theta \sin \phi \cos \chi + \cos \phi \sin \chi & -\sin \theta \cos \phi \\
-\cos \theta \sin \phi \sin \chi - \sin \phi \cos \chi & -\cos \theta \sin \phi \sin \chi + \cos \phi \cos \chi & \sin \theta \sin \phi \\
\sin \theta \cos \phi & \sin \theta \sin \phi & \cos \theta
\end{pmatrix}
\]

with $\Phi_F = \Phi^{-1}_F$ due to $\Phi\Phi^{-1} = I$.

Generally, the product of the dipole operator and the field polarization unit vector

\[
\hat{\mathbf{e}} \equiv \sum_{q=0,\pm 1} \hat{e}_q \hat{e}_q + \hat{e}_0 \hat{e}_0 \pm \frac{1}{\sqrt{2}}(\hat{x} \pm \hat{y})
\]
can be written as

\[
\hat{\mathbf{d}} \cdot \hat{\mathbf{e}} = \sum_{q=-1,-0,1} \epsilon_q \hat{d}_q = \epsilon_0 \hat{d}_0 + \epsilon_+ \hat{d}_+ + \epsilon_- \hat{d}_- = \sum_{F=\Xi,\gamma,\zeta} \epsilon_F \hat{d}_F
\]

where $\hat{d}_\pm = \hat{d}_x \pm i \hat{d}_y$. The transformation of the dipole operator to rotating frame is $\hat{\mathbf{d}}' = \Phi^{-1} \hat{\mathbf{d}}$ or $\hat{\mathbf{d}} = \Phi \hat{\mathbf{d}}'$, with the component

\[
\hat{d}_F = \hat{\mathbf{d}} \cdot \hat{e}_F = \sum_{g=x,y,z} \Phi_{Fg} \hat{d}_g
\]

So, Eq. 2.106 can be written as

\[
\hat{\mathbf{d}} \cdot \hat{\mathbf{e}} = \sum_{g=x,y,z} \{ \epsilon_\Xi \Phi_{\Xi g} + \epsilon_+ (\Phi_{\Xi g} + i \Phi_{\gamma g}) + \epsilon_- (\Phi_{\Xi g} - i \Phi_{\gamma g}) \} \hat{d}_g
\]

where $\epsilon_+ + \epsilon_- = \epsilon_\Xi$ and $i(\epsilon_- - \epsilon_+) = \epsilon_\gamma$. The electronic and nuclear dipole moments can be written respectively as

\[
\hat{d}_{eF} = \sum_{g=x,y,z} \Phi_{Fg} \hat{d}_{e,g} \equiv -q \sum_e \mathbf{R}_e \cdot \hat{\mathbf{e}}_F
\]

\[
\hat{d}_{nF} = \sum_{g=x,y,z} \Phi_{Fg} \hat{d}_{n,g} \equiv \frac{M_1 Z_2 - M_2 Z_1}{M_1 + M_2} q \mathbf{R}_n \cdot \hat{\mathbf{e}}_F
\]

where $\Phi_{Fg}$ depends on the of the Euler angles in molecule fixed frame.

The dipole matrix elements of the $F$-component for transition between the eigenstates $|a\rangle$ and $|b\rangle$ is

\[
d_{F,ba} = \langle b| \mathbf{d} \cdot \mathbf{e}_F |a\rangle = \int \int \Psi^*_b \hat{d}_F(\hat{\mathbf{R}}, \hat{\mathbf{R}}) \Psi_a d\tau_c d\tau_n
\]

\[
= \int \Psi^*_b (\int \Psi^*_a \hat{d}_F \Psi^c d\tau_c) \Psi^a d\tau_n + \int \Psi^*_b \Psi^c d\tau_c \int \Psi^*_b \hat{d}_{nF} \Psi^a d\tau_n
\]
where we have used the Born-Oppenheimer (adiabatic) approximation ansatz
\[ \Psi(R_e, R_n) \approx \Psi^e(R_n, R_e) \Psi^n(R_n). \] 

(2.112)

2.6.1 Electronic-Vibrational-Rotational Transitions

The electronic-vibrational-rotational transition involves different electronic states which are orthogonal, so the second term of Eq. 2.111 vanishes due to orthogonality \( \int \Psi^e_v \Psi^e_o dR_e = 0 \). We assume that the coupling between vibration and rotation is weak, so the nuclear wavefunction \( \Psi^n(R_n) \) can be separated into vibrational and rotational wavefunctions as \( \Psi^n(R_n) = \Psi_v(R_n) \Psi_J,K,M(\theta_n, \phi_n, \chi_n) \) and the total wavefunction is written as

\[ \Psi(\mathbf{r}, R_n) = \Psi(\mathbf{r}, R_n) \Psi_J,K,M(\theta_n, \phi_n) \] 

(2.113)

Then, Eq. 2.111 gives the electronic-vibrational-rotational transition matrix elements

\[ d_{FJ,M} = \sum_{g=x,y,z} \int \Psi^e_v(R_n) \mu_{g,\alpha'\alpha}(R_n) \Psi_v(R_n) R^2 dR_n \int \Psi^e_J(\theta_n, \phi_n) \Psi_{J,K,M}(\theta_n, \phi_n) d\Omega_n \]

(2.114)

where \( d\Omega_n \equiv \sin \theta_n d\theta_n d\phi_n \) and

\[ \mu_{g,\alpha'\alpha}(R_n) = \int \Psi^e(\mathbf{r}, R_n) \hat{d}_{g,\alpha}(\mathbf{r}) \Psi(\mathbf{r}, R_n) d\mathbf{r} \] 

(2.115)

is the electronic dipole moment which gives the electronic selection rules and depends parametrically on the nuclear coordinates, specifically the internuclear distance \( R_n = |R_2 - R_1| \). Equation 2.115 gives the following electronic dipole selection rules.

For **Hund’s case-a**, we have \( \alpha \equiv \Lambda, \Sigma, \Omega \) and

\[ \Delta \Lambda = 0, \pm 1 \]
\[ \Delta \Sigma = 0 \]
\[ \Delta \Omega = 0, \pm 1 \] 

(2.116)

For \( \Lambda = 0 \leftrightarrow 0 \), there are parity considerations which give additional rules \( \Sigma^+ \leftrightarrow \Sigma^+, \Sigma^- \leftrightarrow \Sigma^- \). For \( \Omega = 0 \leftrightarrow 0 \), such as \( 1\Sigma \leftrightarrow 1\Sigma \), there is no Q branch \( \Delta J \neq 0 \) and the selection rules becomes \( \Delta J = \pm 1 \) (P and R branches).

For **Hund’s case-b**, we have \( \alpha \equiv \Lambda, S, K [172] \)

\[ \Delta \Lambda = 0, \pm 1 \]
\[ \Delta S = 0 \]
\[ \Delta K = 0, \pm 1 \text{ with } \Delta K \neq 0 \text{ for } \Sigma \leftrightarrow \Sigma \] 

(2.117)
We can expand the dipole moment $\mu_{g,\alpha'\alpha}(R_n)$ around the equilibrium distance $R_o$ (centroid of potential curve) $\mu_{g,\alpha'\alpha}(R_n) = \mu_{g,\alpha'\alpha}(R_o) + (R_n - R_o) \frac{\partial \mu_{g,\alpha'\alpha}}{\partial R_n}|_{R_n = R_o} + \ldots$ and the first integral in Eq. 2.114 gives

$$\mu_{g,\alpha'\alpha}(R_o) \int \Psi^*_\nu(R_n) \Psi_v(R_n) R_n^2 dR_n + \frac{\partial \mu_{g,\alpha'\alpha}}{\partial R_n}|_{R_n = R_o} \int \Psi^*_\nu(R_n) (R_n - R_o) \Psi_v(R_n) R_n^2 dR_n + \ldots$$

(2.118)

The first term in Eq. 2.118 corresponds to the electronic-vibrational transitions which gives the Franck-Condon principle [171]. The overlap integral $\int \Psi^*_\nu(R_n) \Psi_v(R_n) R_n^2 dR_n = \sqrt{FCF_{\alpha\nu}}$ is the square root of the Franck-Condon factor. It is not zero because the different vibrational wavefunctions from different electronic states are generally not orthogonal. In the case of heteronuclear or non-symmetric molecules, $\frac{\partial \mu_{g,\alpha'\alpha}}{\partial R_n}|_{R_n \neq 0}$ gives the first order correction to electronic dipole moment. The Franck-condon factor is normalized $\sum_v FCF_{\alpha\nu} = 1 = \sum_v |\langle \nu'_a | \nu_\alpha \rangle|^2$.

The second integral in Eq. 2.114 can be decomposed as

$$\int \Psi^*_{J',K',M'}(\theta_n, \phi_n, \chi_n) \Phi_{Fg} \Psi_{J,K,M}(\theta_n, \phi_n, \chi_n) d\Phi_n = \langle J' | \Phi_{Fg} | J \rangle \langle J' M' | \Phi_{Fg} | J M \rangle \langle J' K' | \Phi_{Fg} | J K \rangle$$

(2.119)

where $|\langle J' K' | \Phi_{Fg} | J K \rangle|^2$ is called the Hönig-London factor; $M$ is the magnetic quantum number from the projection of the angular momentum onto quantization axis in laboratory frame while $K$ from the projection in molecular frame. Equation 2.119 gives the total angular momentum selection rules

$$\Delta J = 0, \pm 1 \text{ or } |J - J'| \leq 1 \leq J + J' \text{ and } J = 0 \leftrightarrow 0$$

(2.120)

$$\Delta J 
eq 0 \text{ if } \Sigma \leftrightarrow \Sigma$$

(2.121)

In the presence of external fields, we have the magnetic quantum number selection rules:

$$\Delta M_J = 0, \pm 1, \ M_J = 0 \leftrightarrow 0 \text{ for } \Delta J = 0$$

(2.122)

Effectively, the transition matrix element Eq. 2.114 can be written as

$$d_{Fg,\nu} = \sum_{g,\alpha'\alpha} \mu_{g,\alpha'\alpha}(R_o) \sqrt{FCF_{\alpha\nu}} \langle J' | \Phi_{Fg} | J \rangle \langle J' M' | \Phi_{Fg} | J M \rangle \langle J' K' | \Phi_{Fg} | J K \rangle$$

(2.123)

### 2.6.2 Vibrational-Rotational Transitions

For transition within the same electronic state, $d_{Fg,\nu}(R_n) = \int \Psi^*_\nu \hat{d}_F \Psi_\nu d\tau_e = 0$ since the dipole operator $\hat{d}_F = -q \sum_e \mathbf{R}_e$ is an odd function of position. The transition
matrix element is due to the second term, entirely due to nuclear part since \( \int \Psi^* b (R_v, R_n) \Psi_a (R_v, R_n) d\tau_c = 1 \)

\[
d_{F,ba} = \int \Psi^* b (R_v, R_n) \dot{\Psi}^*_a (R_v, R_n) d\tau_n = \int \Psi^*_b (R_v, R_n) \dot{\Psi}^*_a (R_v, R_n) d\tau_n \\
= \frac{M_1 Z_2 - M_2 Z_1}{M_1 + M_2} \int \Psi^* \beta \phi (R_v) R_v \Psi_{\alpha \phi} (R_v) dR_v \\
\int \Psi^\prime \beta J M \phi (\theta_n, \phi_n) \Phi_{nF} \Psi_{\alpha J M \Omega} (\theta_n, \phi_n) d\Omega
\]

\[
= \frac{M_1 Z_2 - M_2 Z_1}{M_1 + M_2} \langle \psi | R_n | \psi' \rangle \langle J \Omega M | \Phi_{nF} | J' \Omega' M' \rangle (2.124)
\]

where \( R_n, \epsilon_F = R_n, \Phi_{nF} \).

For homonuclear diatomic, \( M_1 Z_2 - M_2 Z_1 = 0 \) and there is no vibrational transition nor rotational transition. By writing \( R_n = R_o + s \), Eq. 2.124 becomes

\[
d_{F,ba} = \frac{M_1 Z_2 - M_2 Z_1}{M_1 + M_2} \langle R_o | \langle \psi | \psi' \rangle + \langle \psi | (R_n - R_o) | \psi' \rangle + ... \rangle \langle J \Omega M | \Phi_{nF} | J' \Omega' M' \rangle (2.125)
\]

The first term of Eq. 2.125 corresponds to the pure rotational transitions where \( \psi = \psi' \),

\[
d_{F,ba} = \frac{M_1 Z_2 - M_2 Z_1}{M_1 + M_2} q R_o \langle J \Omega M | \Phi_{nF} | J' \Omega' M' \rangle (2.126)
\]

The second term gives the infrared rovibrational transitions for harmonic oscillator with the selection rules \( \Delta \psi = \pm 1 \),

\[
d_{F,ba} = \frac{M_1 Z_2 - M_2 Z_1}{M_1 + M_2} q \langle \psi | (R_n - R_o) | \psi' \rangle \langle J \Omega M | \Phi_{nF} | J' \Omega' M' \rangle (2.127)
\]

For rigid molecules, \( R_n = R_o \) and there is no vibrational transition.

### 2.6.3 Transition Energies

The transition scale and nature of the transition energies/frequencies are important for applying a laser pumping schemes on molecules. From Eq. 2.100, we can obtain the optical, infrared and microwave transition frequencies for case \( \Omega = 0 \). The electronic transition frequency \( \Delta T_e \) is in the order of \( 10^{15} \text{s}^{-1} \) (or \( 10^{6} \text{cm}^{-1} \) in wavenumber). These transitions involve different electronic states \( |a\rangle \) and \( |b\rangle \), we have the additional Q branch besides the P and R branches, but all in the optical frequencies. The coefficients \( \omega_e, B_v \) and \( D_v \) depend on the electronic state and the vibrational state. The Q branch which occurs only between different electronic states gives \( (a \rightarrow b, \psi' \rightarrow \psi, J' \rightarrow J) \)

\[
\Delta E_{\alpha \psi, \beta \psi'}^{a \psi, b \psi'} / \hbar = \Delta T_{\alpha \psi, \beta \psi'} + \omega_e \left( \psi' + \frac{1}{2} \right) - \omega_e \left( \psi + \frac{1}{2} \right) - \omega_e \left( \psi' + \frac{1}{2} \right)^2 + \omega_e \left( \psi + \frac{1}{2} \right)^2 \\
+ \left( B' \psi - B \psi \right) J (J + 1) - \left( D' \psi - D \psi \right) J^2 (J + 1)^2 (2.128)
\]

The electronic transitions for P branch give \( (a \rightarrow b, \psi' \rightarrow \psi, J' = J - 1 \rightarrow J) \)
\[ \Delta E^{v',J-1}_{b,v,J}/\hbar c = \Delta T_{e,a\to b} + \omega_e'(v' + \frac{1}{2}) - \omega_e(v + \frac{1}{2}) - \omega_e x_e'(v' + \frac{1}{2})^2 + \omega_e x_e(v + \frac{1}{2})^2 + B_e(J-1)J - B_e J(J+1) - D_e'(J-1)^2J^2 + D_v J^2(J+1)^2 \]  

(2.129)

The electronic transitions for R branch give \((a \to b, v' \to v, J' = J + 1 \to J)\)

\[ \Delta E^{v,J+1}_{b,v,J}/\hbar c = \Delta T_{e,a\to b} + \omega_e'(v' + \frac{1}{2}) - \omega_e(v + \frac{1}{2}) - \omega_e x_e'(v' + \frac{1}{2})^2 + \omega_e x_e(v + \frac{1}{2})^2 + B'_e(J+1)(J+2) - D'_e(J+1)^2(J+2)^2 - B_e J(J+1) + D_v J(J+1)^2 \]  

(2.130)

For pure vibrational transitions from higher energy level \((v', J'-primed) (v' = v + 1 \to v, J' \to J)\)

\[ \Delta E^{v+1,J}_{v,J}/\hbar c = \omega_e(1 - x_e) - \omega_e x_e(2v + 1) - \alpha_e J(J+1) \]  

(2.131)

The R branch infrared spectra at frequency range \(10^{13} - 10^{14} s^{-1}\) corresponds to the rovibrational transitions \((v' = v + 1 \to v, J' = J + 1 \to J)\)

\[ \Delta E^{v+1,J+1}_{v,J}/\hbar c = \omega_e(1 - 2x_e) - \omega_e x_e 2v + 2B_e (J+1) - \alpha_e (J+1)(2v + 3) \]  

(2.132)

The P branch infrared spectra corresponds to the rovibrational transitions \((v' = v + 1 \to v, J' = J - 1 \to J)\)

\[ \Delta E^{v+1,J-1}_{v,J}/\hbar c = \omega_e(1 - 2x_e) - \omega_e x_e 2v - 2B_e J - \alpha_e J(2v - 2) \]  

(2.133)

We can combine Eqs. 2.132 and 2.133 as

\[ \Delta E^{v+1,J\pm 1}_{v,J}/\hbar c = \omega_e - \omega_e x_e 2(v + 1) - 2B_e x - \alpha_e x(x - 2v - 2) \]

where \(x = J\) for P-branch and \(x = -(J + 1)\) for R-branch.

Finally, the microwave spectra at frequency range \(10^{10} - 10^{11} s^{-1}\) is due to the pure rotational transitions, \((v' \to v, J' = J + 1 \to J)\)

\[ \Delta E^{v,J+1}_{v,J}/\hbar c = 2B_e(J+1) - \alpha_e 2(J+1)(v + \frac{1}{2}) \]  

(2.134)

The anharmonicity constant \(\omega_e x_e\) is typically slightly larger than a rotational separation \(B_e \sim 10 cm^{-1}\).
2.7 Parity Selection Rules

There are additional selection rules from the symmetry considerations of the wavefunctions with respect to inversion, reflection and rotation. A dipole transition is allow when \( \int \Psi_b^* \mathbf{d} \Psi_a d\tau \neq 0 \). Since \( \mathbf{d} \) is an odd function of space \( \mathbf{d}(\{\mathbf{R}_c\}, \{\mathbf{R}_n\}) = -\mathbf{d}(\{-\mathbf{R}_c\}, \{-\mathbf{R}_n\}) \), \( \Psi_a \) must have different parity from \( \Psi_b \) so that \( \Psi_b^* \mathbf{d} \Psi_a \) is an even function. The total wavefunction can be decomposed as due to the electronic motion \( \Psi_e \), electronic spin \( \chi_e \), the nuclear spin \( \chi_{nuc} \), the vibrational motion \( \Psi_{vib} \) and the rotational motion \( \Psi_{rot} \).

\[
\Psi = \Psi_e \Psi_{vib} \Psi_{rot} \chi_e \chi_{nuc}
\]  
(2.135)

The vibrational wavefunction is dependent on internuclear distance only \( R_n \), therefore it is an even function. For harmonic oscillator, \( \Psi_{vib} \rightarrow \frac{1}{\sqrt{\Omega_n}} H_n(R_n) \) while the rotational wavefunction is \( \Upsilon_n \).

The total wavefunction can be classified as positive or negative upon inversion through the origin of the molecular fixed frame, as \( \Psi_{\pm}(\{\mathbf{R}_c\}, \{\mathbf{R}_n\}) = \pm \Psi(\{-\mathbf{R}_c\}, \{-\mathbf{R}_n\}) \).

Clearly, the dipole allowed transitions are between different parities.

\[
\Psi_+ \leftrightarrow \Psi_-
\]  
(2.136)

a) Inversion of electronic coordinates at origin  Molecules composed of identical atoms (symmetrical molecule) may have different isotopes. The identical electron of the two atoms can form two possible electronic wavefunctions. They are classified by inversion of electronic coordinates: **gerade** if \( \Psi_{s(g)}(\{\mathbf{R}_c\}) = \Psi_{s(g)}(\{-\mathbf{R}_c\}) \) and **ungerade** if \( \Psi_{s(g)}(\{\mathbf{R}_c\}) = -\Psi_{s(g)}(\{-\mathbf{R}_c\}) \). Since the dipole operator is an odd function, the allowed electronic transitions between electronic states of different parities

\[
g \leftrightarrow u \]
(2.137)

The electronic ground states are usually distinguished between \( \Sigma_u \) and \( \Sigma_g \).

b) Interchange of nuclei coordinates in homonuclear molecule  For homonuclear diatomic molecules, the interchange of nuclear coordinates affects the different components of the total wavefunctions \( \Psi = \Psi_e \Psi_{vib} \Psi_{rot}(\theta, \phi) \chi_e \chi_{nuc}(g/o) \) in different ways.

The electronic wavefunction can be classified as positive (+) or negative (−) upon interchange of the nuclei: \( \bar{P}_{32} \Psi_e(\mathbf{R}_i, \mathbf{R}_j) = \pm \Psi_e(\mathbf{R}_i, \mathbf{R}_j) \) where \( \bar{P}_{32} \) is the operator which interchanges the nuclei with the property \( \bar{P}_{32}^2 = 1 \). As such, the ground electronic state can further be distinguished as: \( \Sigma^+_u \) and \( \Sigma^+_g \) which correspond to even wave functions, and \( \Sigma^-_u \) and \( \Sigma^-_g \) which correspond to odd wave functions.
The electronic spin function is always symmetric since it is independent of nuclear coordinate \( \hat{P}_{12}\chi_e(\vec{r}_j) = \chi_e(\vec{r}_j) \). The vibrational wavefunction depends on the internuclear distance and is therefore always symmetric \( \hat{P}_{12}\Psi_{\text{vib}}(r) = \Psi_{\text{vib}}(r) \). The parity of the rotational wavefunction (spherical harmonics) depends on \( J \) as \( \hat{P}_{12}\Psi_{\text{rot}}(\theta, \phi) = \Psi_{\text{rot}}(\theta, \phi, -\chi) = (-1)^J\Psi_{\text{rot}}(\theta, \phi, \chi) \); even rotational levels for \( J = 0, 2, 4, \ldots \) and odd rotational levels for \( J = 1, 3, 5, \ldots \).

Finally, the interchange operation gives either a symmetric \( \hat{P}_{12}\chi_{\text{nuc}}^s(1, 2) = \chi_{\text{nuc}}^s(2, 1) \) or antisymmetric \( \hat{P}_{12}\chi_{\text{nuc}}^a(1, 2) = -\chi_{\text{nuc}}^a(2, 1) \) nuclear wavefunctions. The nuclei with nuclear spin angular momentum \( I \) has \( 2I + 1 \) components. So, there are \( (2I + 1)^2 \) possible nuclear spin states \( \chi_{\text{nuc}} \), which can be classified into two classes:

- \( (2I + 1)(I + 1) \) symmetric states: \( (2I + 1) \) state of the form \( \chi_{\text{nuc}(s)} = \chi_i(1)\chi_i(2) \) \( (i = 1, \ldots, 2I + 1) \) plus \( (2I + 1)I \) states of the form \( \chi_{\text{nuc}(s)} = \frac{1}{\sqrt{2}}(\chi_i(1)\chi_j(2) + \chi_i(2)\chi_j(1)) \);
- \( (2I + 1)I \) are antisymmetric of the form \( \chi_{\text{nuc}(a)} = \frac{1}{\sqrt{2}}(\chi_i(1)\chi_j(2) - \chi_i(2)\chi_j(1)) \).

Thus, the total wavefunction \( \Psi \) for homonuclear molecules can be written as

\[
\Psi = \Psi_{\text{e}(g)}^\pm \Psi_{\text{vib}}(-1)^J\Psi_{\text{rot}}(\theta, \phi)\chi_e\chi_{\text{nuc}(p/o)} \quad (2.138)
\]

For bosonic molecules (\( I=\text{integer} \)) and fermionic molecules (\( I=\text{half-integer} \)), the total wavefunctions are symmetric and antisymmetric respectively. From Eq. 2.138, the even electronic states \( \Psi_{\text{e}(g)}^\pm, \Psi_{\text{e}(s)}^\pm \) with:

a) even rotational levels and symmetric \( \chi_{\text{nuc}(s)} \) or odd rotational levels and antisymmetric \( \chi_{\text{nuc}(a)} \) give symmetric wavefunctions \( \Psi_s \) for integral spin molecules,

b) even rotational levels and antisymmetric \( \chi_{\text{nuc}(a)} \) or odd rotational levels and symmetric \( \chi_{\text{nuc}(s)} \) give asymmetric wavefunctions \( \Psi_a \) for half-integral spin molecules.

On the other hand, the odd electronic states \( \Psi_{\text{e}(a)}^+, \Psi_{\text{e}(a)}^- \) with:

c) odd rotational levels and symmetric \( \chi_{\text{nuc}(s)} \) or even rotational levels and antisymmetric \( \chi_{\text{nuc}(a)} \) give symmetric wavefunctions \( \Psi_s \) for integral spin molecules,

d) odd rotational levels and antisymmetric \( \chi_{\text{nuc}(a)} \) even rotational levels and symmetric \( \chi_{\text{nuc}(s)} \) give asymmetric wavefunctions \( \Psi_a \) for half-integral spin molecules.

However, the dipole moment is unaffected by the interchange of nuclei, \( \hat{d}_n(\vec{R}_1', \vec{R}_2') = \hat{d}_n(\vec{R}_2', \vec{R}_1') \). This is true also for higher multipole moments. Therefore, the allowed transitions are between the total wavefunction of the same parities

\[
s \leftrightarrow s \text{ or } a \leftrightarrow a \quad (2.139)
\]

In fact this selection rule is general and applies to any type of transitions, radiative or non-radiative.
2.8 Static Electric Field-Stark Shift

The Stark effect can be used to shift the internal energy levels as large as $1k_B$ (in unit of J) and has been used for spatial trapping of particles with spatially dependent electric field. Here, we outline the expressions for the first and second order Stark shift energies. By using the expansion $\phi_{ex}(r_e, t) = \phi_{ex}(R, t) + (r_e - R) \cdot \nabla \phi_{ex} + \{(r_e - R) \cdot \nabla\}^2 \phi_{ex} + ...$ on Eqs. 2.69, 2.64 we have

$$V'_{cls} = \phi_{ex}(R, t)Q - d \cdot E_{ex}$$

(2.140)

where $d = q\{\frac{M_1 Z_0 - M_2 Z_1}{M_1 + M_2} \cdot R_m - \sum e R_e\}$ and $-\nabla \phi_{ex} = E_{ex}$ is the external electrostatic field.

The first order Stark shift for symmetric top molecules is given by [175]

$$E_{cls}^{(1)} = -E_z d_z \frac{KM}{J(J+1)}$$

(2.141)

where $E_z$ and $d_z$ are the electric field and dipole moment along the field direction, $K$ and $M$ are the angular momentum quantum numbers along the molecular axis and the quantization axis, defined along the electric field direction. For linear molecules where $K = 0$, there is no first order Stark shift. The second order Stark shift given by the second order perturbation is

$$E_{cls}^{(2)} = \frac{(E_z d_z)^2}{2hcB_e} \left\{ \frac{(J^2 - K^2)(J^2 - M^2)}{J^3(2J+1)(2J-1)} - \frac{(J + 1)^2 - K^2)((J + 1)^2 - M^2)}{(J + 1)^3(2J+1)(2J+3)} \right\}$$

(2.142)

For typical rotational constant $B_e = 1cm^{-1}$ dipole moment of $d_z = 1$Debye $^8$ and electric field $E_z = 10^7Vm^{-1}$, the first and second order shifts (in angular frequency) are respectively in the order of $10^{11}s^{-1}$ and $10^{10}s^{-1}$. When the electric field is sufficiently strong that the dipole interaction energy is greater than the rotational spacing, $E_z d_z > hcB_e$, the higher order terms become important.

\footnote{1Debye = 3.3356 $\times 10^{-20}Cm$ in S.I. unit.}

\footnote{The applied external electric field is much smaller than the field between charged particles in molecules, typically $10^{11}Vm^{-1}$.}
Chapter 3

Master Equation and Controlled Dissipation

Dissipation is an important ingredient for achieving cooling in a gas of particles. Large spontaneous decay rate is required for fast laser cooling. It is well-known that the spontaneous emission rate is proportional to cubic of transition frequency $\omega_0^3$, so the decay rates from infrared and microwave transitions in molecules are much lower than the optical transition rate. The fluorescence process is the hindrance to laser cooling of molecules. If spontaneous emissions to a preferred rovibrational level can be enhanced, the internal heating can be reduced. Also, infrared transitions may be incorporated as a dissipation mechanism in laser cooling of molecules if the rate can be significantly enhanced. The spontaneous emitted photons has a spectrum around the resonant frequency. This spectrum can be modified coherently or through quantum interference [250]. Periodic laser pulses is also used to control decoherence rate [255], [256].

The suppression of the spontaneous emission is required in applications for efficient lasers and quantum information processing. Here, in cooling, we are interested in the enhancement of the spontaneous emission rate which is the manifestation of the vacuum fluctuation fields. It can be modified in structured reservoir [257], for example using photonic bandgap material [258], [260]. However, in laser cooling the gas has to be kept away from contact with material surfaces. These are the motivating factors for controlling spontaneous emissions in free space using external laser fields which can provide the a.c. Stark shift to change the transition frequency. This provides a way of controlling the spontaneous emission rate.

The master equation approach has been used long ago by Bloch and Wangness [132] to describe dissipative effects in thermal reservoir. Later, the theory of spontaneous emissions is developed for a system of many two-level atoms using phase space approach [135] and also extended to a collection of harmonic oscillators [136]. The master equation is a standard approach in treating dissipative mechanisms in quantum optics [139] and stochastic systems [140] with Markov approximation and weak driving field assumption.
The kinetic effect of photons affect the center of mass dynamics, which in turns lead to non-Poissonian photon statistics in resonance fluorescence. The theory was elaborated by Cook [227] and later by Stenholm [228] using generalized Bloch equation (with center of mass momentum).

In this Chapter, we are mainly concerned with the effect of spontaneous emissions on the momentum and internal dynamics of a molecule in thermal radiation with and without coherent laser fields. We develop the theory using the projection operator technique [130] and obtain the Nakajima-Zwanzig master equation, which is an integro-differential equation with non-Markovian effect. In thermal reservoir, we obtain the standard master which is valid to first Born approximation. In non-equilibrium reservoir, the first Born-approximation gives additional terms. We show the invalidity of the standard Liouvillean used to describe dissipation in the presence of laser fields and present the derivation of the correct Liouvillean valid for arbitrary laser fields strength which depends on the laser-particle interaction. This leads to the general master equations written in interaction picture and in Schrödinger picture. The results are applied to derive the exact master equation for a two-level system with the inclusions of the center of mass momentum states as well as the Röntgen term [236] into the laser-particle interaction. The decay rate and the momentum spread due to the photon recoils during spontaneous emission are dependent on the laser frequency and intensity. The results are general and can be physically understood using the dressed state model with the a.c. Stark shift. Analytical expressions of transition coefficients for a V-system driven by a laser field are obtained by Laplace transform, which show full non-Markovian and field dependent decay effects. We also study the modification of the spontaneous emission rate of the V-system driven by multiple 2π pulses as proposed by Agarwal et. al. [246] using the Schrödinger equation and including the momentum effect. Non-perturbative results are obtained for the decay rates after odd and even number of 2π pulses.

In the absence of driving fields, we derive a general Liouvillean for multilevel system including center of mass momentum. The Liouvillean is used to study the dynamics of spontaneous emissions from a single excited state to several ground states as in fluorescence process of molecules. In our published paper [2], we used the results to study in details the effect of spontaneous emissions on the momentum spread of cold and dilute gas in thermal radiation. Finally, we present the non-Markovian analytical solution of a two-level system using Laplace transform. For a simple Λ system, we obtain the solutions describing the spontaneously generated coherences.

3.1 Projection Operator Technique

For a system (subscript S) interacting with a large reservoir(subscript R), the state of the reservoir is postulated to be approximately time independent due to any change in the state of the system. We define a projection operator $\mathcal{P} = \hat{\rho}_R \otimes \text{Tr}_R(...) =
\[ \sum_R f_R |R\rangle \langle R| \otimes \text{Tr}_R \{ ... \} \text{ which projects out the reservoir states from the density operator.} \]

The Liouville-von Neumann equation can be written as \[ \frac{\partial}{\partial t} \hat{\rho}(t) = \mathcal{L} \hat{\rho}(t) \] where \[ \mathcal{L} \equiv \frac{1}{i\hbar} \hat{H}(t), \] is the superoperator acting on an operator instead of a state. Thus, we can write the following relations

\[ v = \mathcal{P} \hat{\rho} = \sum_R f_R |R\rangle \langle R| \otimes \text{Tr}_R \{ \sum_i W_i |\Psi_i\rangle \langle \Psi_i| \} \equiv \hat{\rho}_R \otimes \hat{\rho}_S \]  \hspace{1cm} (3.1)

\[ \hat{\rho}_R \equiv \text{Tr}_S \{ \hat{\rho} \} = \text{Tr}_S \{ v \} = \sum_{i,S} W_i \langle S| \Psi_i \rangle \langle \Psi_i| S \rangle \equiv \sum_R f_R |R\rangle \langle R| \]  \hspace{1cm} (3.2)

\[ \hat{\rho}_S \equiv \text{Tr}_R \{ \hat{\rho} \} = \text{Tr}_R \{ v \} = \sum_{i,R} W_i \langle R| \Psi_i \rangle \langle \Psi_i| R \rangle \] \hspace{1cm} (3.3)

\[ \mathcal{P} v = \hat{\rho}_R \otimes \text{Tr}_R \{ \hat{\rho}_R \otimes \hat{\rho}_S \} = v \rightarrow \mathcal{P}^2 = \mathcal{P} \] \hspace{1cm} (3.4)

The complementary projection operator is defined as \( \mathcal{Q} \equiv 1 - \mathcal{P} \) with the following relations

\[ w = \mathcal{Q} \hat{\rho} = \hat{\rho}_{SR} = \hat{\rho} - \hat{\rho}_R \otimes \hat{\rho}_S \] \hspace{1cm} (3.5)

\[ \mathcal{Q} = (1 - \hat{\rho}_R \otimes \text{Tr}_R) = 1 - \mathcal{P} \rightarrow \mathcal{Q}^2 = \mathcal{Q} \] \hspace{1cm} (3.6)

From Eqs. 3.1 and 3.5, we see that \( \mathcal{P} \) 'decorrelate' the density operator into system and reservoir subsystems while \( \mathcal{Q} \) projects out the correlated part, defined as

\[ \hat{\rho}_{SR} = \hat{\rho} - \hat{\rho}_R \otimes \hat{\rho}_S \] \hspace{1cm} (3.7)

cannot be reduced by the tracing process, which destroys any correlation between the system and reservoir since

\[ \text{Tr}_R \{ \hat{\rho}_{SR} \} = \text{Tr}_R \{ \hat{\rho} - \hat{\rho}_R \otimes \hat{\rho}_S \} = \text{Tr}_R \{ \hat{\rho} \} - \hat{\rho}_S = 0 \]
\[ \text{Tr}_S \{ \hat{\rho}_{SR} \} = \text{Tr}_S \{ \hat{\rho} - \hat{\rho}_R \otimes \hat{\rho}_S \} = \text{Tr}_S \{ \hat{\rho} \} - \hat{\rho}_R = 0 \] \hspace{1cm} (3.8)

Using the projection operators on the Liouville-von-Neumann equation, we obtain a pair of coupled differential equations

\[ \mathcal{P} \frac{\partial \hat{\rho}(t)}{\partial t} = \mathcal{P} \mathcal{L} \hat{\rho}(t) \rightarrow \frac{\partial v}{\partial t} - \frac{\partial \mathcal{P}}{\partial t} \hat{\rho}(t) = \mathcal{P} \mathcal{L} (v + w) \] \hspace{1cm} (3.9)

\[ (1 - \mathcal{P}) \frac{\partial \hat{\rho}(t)}{\partial t} = (1 - \mathcal{P}) \mathcal{L} \hat{\rho}(t) \rightarrow \frac{\partial w}{\partial t} - \frac{\partial \mathcal{Q}}{\partial t} \hat{\rho}(t) = \mathcal{Q} \mathcal{L} (v + w) \] \hspace{1cm} (3.10)

\[ \mathcal{L}(t) \equiv \frac{1}{i\hbar} [\hat{H}(t), \ldots] \] \hspace{1cm} (3.11)

The reservoir affects the evolutions of the system. The change in the system reacts back and affects the reservoir. Thus, in general the reservoir may be time dependent \( \hat{\rho}_R(t) \) and so is \( \mathcal{P} \) and we should write \( -\frac{\partial}{\partial t} \hat{\rho}(t) = \frac{\partial v}{\partial t} \hat{\rho}(t) = \frac{\partial \mathcal{P}}{\partial t} \hat{\rho}(t) = \frac{\partial \mathcal{Q}}{\partial t} \hat{\rho}(t) \). By using \( P(t) e^{-\int \mathcal{L}(t) dt} \) -
\[ P(t_o) e^{-\int_{t_o}^{t} L(t')dt'} = \int_{t_o}^{t} A(t') e^{-\int_{t'}^{t} L(t')dt'} \] as the formal solution for \( \frac{dP(t)}{dt} = L(t)P(t) + A(t) \), we have

\[
\begin{align*}
    v(t) &= A(t,0) v(0) + \int_{0}^{t} dt' A(t, t') PL(t) w(t') - \int_{0}^{t} dt' A(t, t') \frac{\partial \rho_R(t')}{\partial t} \otimes \rho_S(t') \quad (3.12) \\
    w(t) &= B(t,0) w(0) + \int_{0}^{t} dt' B(t, t') QL(t') v(t') + \int_{0}^{t} dt' B(t, t') \frac{\partial \rho_R(t')}{\partial t} \otimes \rho_S(t') \quad (3.13)
\end{align*}
\]

where

\[
\begin{align*}
    A(x, y) &= T_{-\epsilon} e^{K_x} d\sigma \mathcal{L}(0) \approx I + \epsilon \int_{y}^{x} dt \mathcal{P} \mathcal{L}(t) + \epsilon^2 \int_{y}^{x} dt \int_{y}^{x} dt' \mathcal{P} \mathcal{L}(t) \mathcal{P} \mathcal{L}(t') + \cdots \quad (3.14) \\
    B(x, y) &= T_{-\epsilon} e^{K_y} d\sigma \mathcal{Q}(0) \approx I + \epsilon \int_{y}^{x} dt \mathcal{Q} \mathcal{L}(t) + \epsilon^2 \int_{y}^{x} dt \int_{y}^{x} dt' \mathcal{Q} \mathcal{L}(t) \mathcal{Q} \mathcal{L}(t') + \cdots \quad (3.15)
\end{align*}
\]

and \( \epsilon = 1 \) serves for tracking the order of the coupling terms. So far, the formalism is exact.

**Constant Reservoir Approximation**: For sufficiently large reservoir and weak interaction with the system, the reservoir state is essentially unaffected by the change in the system and assumes an approximately constant state, that is \( \frac{\partial \rho_R}{\partial t} = 0 \) in Eqs. 3.12 and 3.13 or \( \mathcal{P} \frac{\partial}{\partial t} = \frac{\partial}{\partial t} \mathcal{P} \). By eliminating \( w \) from Eqs. 3.9 we have

\[
\frac{\partial v}{\partial t} = \mathcal{P} \mathcal{L} v + \mathcal{P} \mathcal{L} B(t,0) w(0) + \int_{0}^{t} dt' \mathcal{P} \mathcal{L}(t) B(t, t') QL(t') v(t') \quad (3.16)
\]

For \( t \gg t_c \), the correlation time of system-reservoir, the system and reservoir become uncorrelated at \( t' = 0 \), and the total density operator can be factorized as \( \hat{\rho}(0) = \hat{\rho}_R(0) \otimes \hat{\rho}_S(0) \). From the definition, \( w(0) = \hat{\rho}(0) - \hat{\rho}_R(0) \otimes \hat{\rho}_S(0) = 0 \), and we have the Nakajima-Zwanzig equation [131], [130]

\[
\frac{\partial v}{\partial t} = \mathcal{P} \mathcal{L} v + \int_{0}^{t} dt' \mathcal{K}(t, t') v(t') \\
K(t, t') \doteq \mathcal{P} \mathcal{L}(t) B(t, t') QL(t') \quad (3.17)
\]

where \( \mathcal{P} \mathcal{L} v = \hat{\rho}_R \otimes Tr_R \frac{1}{\mathcal{H}} [\hat{H}(t), \hat{\rho}_R \otimes \hat{\rho}_S] \doteq \hat{\rho}_R \otimes \frac{1}{\mathcal{H}} [\hat{\sigma}(t), \hat{\rho}_S] \) and \( \hat{\sigma}(t) \doteq Tr_R \{ \hat{H}(t) \hat{\rho}_R \} \).

The integral on the right hand side of equation 3.17 includes the non-Markovian effect and the Born corrections to all orders. Equation 3.17 can be expanded as

\[
\frac{\partial \rho_S}{\partial t} = Tr_R \{ \frac{1}{i\hbar} [\hat{H}(t), \hat{\rho}_R \otimes \hat{\rho}_S(t)] \} + \int_{0}^{t} dt' Tr_R \{ \frac{1}{i\hbar} [\hat{H}(t), B(t, t') \frac{1}{i\hbar} [\hat{H}(t'), \hat{\rho}_R \otimes \hat{\rho}_S(t')]] \} - \int_{0}^{t} dt' Tr_R \{ \frac{1}{i\hbar} [\hat{H}(t), B(t, t') \hat{\rho}_R \otimes Tr_R \frac{1}{i\hbar} [\hat{H}(t'), \hat{\rho}_R \otimes \hat{\rho}_S(t')]] \} \quad (3.18)
\]
**First Born Approximation** By approximating \( B(x, y) = T_{-i} \int_y^x ds Q_L(s) \approx I + \lambda \int_y^x ds Q_L(s) \)

we can expand the integrand as

\[
K(t, t') v(t') \approx \mathcal{P}L(t)\mathcal{L}(t') v(t') - \mathcal{P}L(t)\mathcal{P}L(t') v(t') + \lambda \int_t^{t'} ds \mathcal{P}L(t)\mathcal{L}(s)\mathcal{L}(t') v(t') - \lambda \int_t^{t'} ds \mathcal{P}L(t)\mathcal{P}L(s)\mathcal{L}(t') v(t') - \lambda \int_t^{t'} ds \mathcal{P}L(t)\mathcal{L}(s)\mathcal{P}L(t') v(t') + \lambda \int_t^{t'} ds \mathcal{P}L(t)\mathcal{P}L(s)\mathcal{P}L(t') v(t')
\]

(3.19)

The zeroth order approximation corresponds to setting \( B(t, t') = 1 \) or \( \lambda = 0 \) in Eq. 3.19. In the case of thermal reservoir in free space \( \hat{\rho}_R = \{\hat{a}^{\dagger}_{k\lambda} \hat{a}_{k\lambda}\}, \hat{H}(t) \propto \hat{a}^{\dagger}_{k\lambda} \) and \( \hat{a}_{k\lambda} \), we have \( \hat{\sigma}(t) = 0 \) and \( \mathcal{P}L_v = \mathcal{P}L\mathcal{L}\mathcal{L}_v = \mathcal{P}L\hat{O}_S = 0 \) where the system operator \( \hat{O}_S \) is from \( \hat{\rho}_R \otimes \hat{O}_S = \mathcal{P}L\mathcal{L}_v \). Here, the first Born approximation gives the same result as the zeroth Born approximation where Eq. 3.19 reduces to

\[
\frac{\partial v}{\partial t} = \int_0^t dt' \mathcal{P}L(t)\mathcal{L}(t') v(t')
\]

\[
\frac{\partial \hat{\rho}_S(t)}{\partial t} = \frac{1}{(\hbar)^2} \int_0^t dt'' Tr_R[H(t), [\hat{H}(t'), \hat{\rho}_R \otimes \hat{\rho}_S(t')]]
\]

(3.20)

If the reservoir is in non-equilibrium \( \hat{\sigma}(t) \neq 0 \), and the first Born approximation should be used. If we neglect the term with three product \( \mathcal{P}L(t)\mathcal{L}(s)\mathcal{L}(t') v(t') \), we have

\[
\frac{\partial \hat{\rho}_S(t)}{\partial t} = \frac{1}{\hbar} [\hat{\sigma}(t), \hat{\rho}_S(t)]
\]

\[
+ \frac{1}{(\hbar)^2} \int_0^t dt'' Tr_R[H(t), [\hat{H}(t'), \hat{\rho}_R \otimes \hat{\rho}_S(t')]] - \frac{1}{(\hbar)^2} \int_0^t dt'' [\hat{\sigma}(t), [\sigma(t'), \hat{\rho}_S(t')]]
\]

\[
- \lambda \frac{1}{(\hbar)^3} \int_0^t dt'' \int_t^{t'} ds \hat{\rho}_R \otimes [\hat{\sigma}(s), Tr_R[H(t), [\hat{H}(t'), \hat{\rho}_R \otimes \hat{\rho}_S(t')]]]
\]

\[
- \lambda \frac{1}{(\hbar)^3} \int_0^t dt'' \int_t^{t'} ds \hat{\rho}_R \otimes Tr_R[H(t), [\hat{H}(s), \hat{\rho}_R \otimes [\hat{\sigma}(t'), \hat{\rho}_S(t')]]]
\]

\[
+ \lambda \frac{1}{(\hbar)^3} \int_0^t dt'' \int_t^{t'} ds \hat{\rho}_R \otimes [\hat{\sigma}(s), [\hat{\sigma}(t), \hat{\rho}_S(t')]]
\]

(3.21)

Those terms with \( \hat{\sigma}(t) \) in Eq. 3.21 could give rise to new effects which are not present in the case of equilibrium reservoir, for example in structured reservoir [257] or in photonic bandgap structures [259].

### 3.2 Master Equation in Weak Fields

If the system-laser coupling is also weak, we can use the zeroth Born approximation. In interaction picture, the Hamiltonian \( \hat{H}(t) \) can be split into system-laser
interaction $\hat{V}_{SL}$ and system-reservoir interaction $\hat{V}_{SR}$

$$\hat{\sigma}(t) = \hat{V}_{SL}(t) + \hat{\sigma}_{SR}(t)$$

$$\hat{\sigma}_{SR}(t) = \{\hat{V}_{SR}(t)\} = T_{\tau R}\{\hat{V}_{SR}(t)\hat{\rho}_{R}\}$$

(3.22)  

(3.23)

By setting $\lambda \to 0$, and using Eqs. 3.22 and 3.23, Eq. 3.21 becomes

$$\frac{\partial \hat{\rho}_S}{\partial t} = \frac{1}{i\hbar}[\hat{V}_{SL}(t),\hat{\rho}_S] + \left(\frac{1}{2\hbar}\right)^2 \int_0^t dt' T_{\tau R}[\hat{V}_{SR}(t),[\hat{V}_{SR}(t'),\hat{\rho}_{R}\otimes\hat{\rho}_S(t')]]$$

$$+ \frac{1}{2\hbar}[\hat{\sigma}_{SR}(t),\hat{\rho}_S] - \int_0^t dt''[\hat{\sigma}_{SR}(t),[\hat{\sigma}_{SR}(t''),\hat{\rho}_S(t'')]]$$

(3.24)

The second line of Eq. 3.24 seems to gives additional terms when the reservoir is non-thermal. However, the projection operator technique has been based on the assumption (Eq. 3.1) of a radiation reservoir state which is diagonal in the Fock space basis $|n_{k\lambda}\rangle$, in the form $\hat{\rho}_R = \sum_{k\lambda}\hat{f}_{k\lambda}|n_{k\lambda}\rangle\langle n_{k\lambda}|$. This means that $\hat{\rho}_R$ must be a function of $\hat{a}_{k\lambda}^\dagger\hat{a}_{k\lambda}$ or $\hat{a}_{k\lambda}\hat{a}_{k\lambda}^\dagger$ and not $\hat{a}_{k\lambda}$ or $\hat{a}_{k\lambda}^\dagger$. This is satisfied by the radiation reservoir at thermal equilibrium, as given by Eq. 4.64. For the system-reservoir interaction in p,A and multipolar version, $\hat{V}_{SR}$ is a function of $\hat{a}_{k\lambda}$ and $\hat{a}_{k\lambda}^\dagger$ only, so we have $\hat{\sigma}_{SR} = 0$ and the master equation Eq. 3.24 reduces to the standard results in literatures [139],[138], [151]. However, in minimal coupling, the interaction term $A^2$ is a function of $\hat{a}_{k\lambda}^\dagger\hat{a}_{k\lambda}$, $\hat{a}_{k\lambda}\hat{a}_{k\lambda}^\dagger$, $\hat{a}_{k\lambda}\hat{a}_{k\lambda}$ and $\hat{a}_{k\lambda}^\dagger\hat{a}_{k\lambda}^\dagger$ which would give finite $\hat{\sigma}_{SR}$, although as a very small correction. In multipolar version, $\hat{\rho}_R$ has to be transformed as well along with the Hamiltonian, to $\hat{\rho}_R^{\text{mult}} = \hat{T}\hat{\rho}_R\hat{T}^\dagger$ where $\hat{T} = \exp\left(\frac{1}{\hbar}\int \hat{P}(r)\cdot \hat{A}(r)d^3r\right)$. Thus, although $\hat{\rho}_R$ is diagonal, $\hat{\rho}_R^{\text{mult}}$ is not and so $\hat{\sigma}_{SR}^{\text{mult}} = T_{\tau R}\{\hat{V}_{SR}^{\text{mult}}(t)\hat{\rho}_R^{\text{mult}}\}$ is finite.

### 3.3 Repeated Substitution Technique

In this section, we derive the master equation by repeated substitution. The Liouville-von-Neumann equation in interaction picture is

$$\frac{\partial \hat{\rho}_1(t)}{\partial t} = \frac{1}{i\hbar}[\hat{V}_{SR1} + \hat{V}_{SL1}(t),\hat{\rho}_1(t)]$$

(3.25)

where

$$\hat{\rho}_1(t) \triangleq U_1(t)\hat{\rho}(t)U_1(t)$$

$$\hat{V}_{SR1} \triangleq U_1(t)\hat{V}_{SR}\cdot U_1(t)$$

$$U_1(t) \triangleq \hat{T}_e^{\hat{H}_0}[\hat{U}_0(t)\hat{a}(t)\hat{a}(t)]$$

(3.26)  

(3.27)  

(3.28)

and $\hat{T}$ indicates time-ordering operation and $X \in R,L$ with $\hat{H}_0 = \hat{H}_S + \hat{H}_R, \hat{V}_{SR}$ and $\hat{V}_{SL}(t)$ are the interaction-free (molecular system+ reservoir), system-reservoir interaction
and system-laser interaction Hamiltonians respectively. Since \( \hat{H}_o = \hat{H}_S + \hat{H}_R \) contain the free system and reservoir Hamiltonians, we can write \( \frac{d}{dt} \rho_{S,R}(t) = \frac{i}{\hbar} \hat{H}_{S,R}(t) \) with \( U_1(t) = U_S(t)U_R(t) \). Normally, \( \hat{H}_o(t) \) is time independent, so \( U_1(t) \rightarrow e^{i\hat{H}_o t} \).

We want to find a master equation for the system density operator \( \tilde{\rho}_{1S}(t) = Tr_R\{\rho_{1S}(t)\} = Tr_R\{U_R^{-1}(t)\rho(t)U_R(t)\} = U_1^{-1}(t)\tilde{\rho}_S(t)U_1(t) \). By the tracing out the radiation in Eq. 3.25 we have

\[
\frac{d\tilde{\rho}_{1S}(t)}{dt} = \frac{i}{\hbar} [\tilde{V}_{SL1}(t),\tilde{\rho}_{1S}(t)] + \frac{1}{\hbar} Tr_R[\tilde{V}_{SR1}(t),\tilde{\rho}_{1S}(t)].
\]  

(3.29)

Integration of Eq. 3.25 gives \( \tilde{\rho}_1(t) = \tilde{\rho}_1(t_o) + \frac{i}{\hbar} \int_{t_o}^{t} [\tilde{V}_{SL1}(t'),\tilde{\rho}_1(t')] dt' + \frac{1}{\hbar} \int_{t_o}^{t} [\tilde{V}_{SR1}(t'),\tilde{\rho}_1(t')] dt' \) and substituting \( \rho_1(t) \) into Eq. 3.29 we obtain the results identical to Ref. [92]

\[
\frac{d\rho_{1S}(t)}{dt} = \frac{i}{\hbar} [V_{SL1}(t),\rho_{1S}(t)] + \frac{1}{\hbar} Tr_R[V_{SR1}(t),\rho_{1S}(t_o)]
\]

\[+(\frac{1}{\hbar})^2 Tr_R \int_{t_o}^{t} ([V_{SR1}(t),V_{SL1}(t'),\rho_{1S}(t')]) + [V_{SR1}(t),[V_{SR1}(t'),\rho_{1S}(t')]]) dt'.
\]  

(3.30)

As before, we can assume that initially the reservoir and the system become uncorrelated \( \tilde{\rho}_1(t_o) \approx \rho_{1R}(t_o) \otimes \rho_{1S}(t_o) \) at time \( t - t_o >> t_c \). However, the reservoir and the system are always correlated at any time \( t \) so \( \tilde{\rho}_1(t) \neq \rho_{1R}(t) \otimes \rho_{1S}(t) \). Since the reservoir state is a big reservoir, its state is essentially unaltered by the change in the state of the system via the weak coupling and we set it to be time-invariant \( \rho_{1R}(t) \approx \rho_R(t_o) \rightarrow \rho_R \).

If the reservoir and the system interact weakly, they are approximately decoupled at time \( t_o < t' < t \) and we can write \( \tilde{\rho}_1(t') \approx \rho_R \otimes \tilde{\rho}_{1S}(t') \) in the last term of Eq. 3.30. This assumption is implicitly contained in the project operator technique, through the definition of the projection operator itself of Eq. 3.1. Similarly, if the interaction between the laser and the system is also weak, \( \tilde{\rho}_1 \otimes \tilde{\rho}_{1S}(t') \) can be used in the second last term of Eq. 3.30. Thus, we obtain

\[
\frac{d\tilde{\rho}_{1S}(t)}{dt} = \frac{i}{\hbar} [V_{SL1}(t),\tilde{\rho}_{1S}(t)] + \frac{1}{\hbar} Tr_R(V_{SR1}(t),\tilde{\rho}_{1S}(t_o)]
\]

\[+(\frac{1}{\hbar})^2 \int_{t_o}^{t} [\tilde{\sigma}_{SR1}(t),[V_{SL1}(t'),\tilde{\rho}_{1S}(t')]] dt'
\]

\[+(\frac{1}{\hbar})^2 Tr_R \int_{t_o}^{t} [V_{SR1}(t),[V_{SR1}(t'),\tilde{\rho}_R \otimes \tilde{\rho}_{1S}(t')]]) dt'.
\]  

(3.31)

where \( \tilde{\sigma}_{SR1}(t) \approx Tr_R\{V_{SR1}(t)\rho_{1R}\} = Tr_R\{V_{SR}(t)\tilde{\rho}_R\}. \) If the reservoir is not in thermal equilibrium, \( \tilde{\rho}_{1R} \neq \rho_R \) and \( \tilde{\sigma}_{SR1}(t) \neq 0 \), the evolution of the quantum system is dependent on the initial state \( \tilde{\rho}_{1S}(t_o) \) through the second term in the first line. However, Eq. 3.31 is valid only for weak system-laser coupling because it is generally NOT valid to write \( [V_{SR1}(t),[V_{SL1}(t'),\tilde{\rho}_R \otimes \tilde{\rho}_{1S}(t')]] \), especially if \( V_{SL1}(t') \) is large.
3.4 Master Equation with Arbitrary Field Dependent Dissipative Liouvillean

It has been shown long ago that strong coherent pumping fields are able to modify the resonance fluorescence spectrum [229] and the Lamb shift [149] of two-level atoms using Schrödinger formalism. The interests in the modification of the spontaneous emission spectrum by laser fields and quantum interference have been extended to three-level [230] and four-level [231] systems. There were also attempts to demonstrate the cancellation of spontaneous emissions [232]. However, none of these works used the master equation with the field dependent dissipations or spontaneous emission rate. For continuous wave lasers with the Rabi frequency much lower than the levels spacings, the field dependence in the dissipation can be neglected. However, when the time dependent Rabi frequency or pulses are used, the fields can grossly affect the dynamics of the dissipation. For resonance case, the dressed state picture gives good description of the physical system [233]. The physical system in strong field would be more correctly described by the master equation approach if the field dependent dissipations effect is included.

The standard master equations, like Eq. 3.31, is only valid for weak driving fields. We can find a master equation for arbitrary strength of laser-system interaction if we transform Eq. 3.25 to the dressed picture [137] so that we have only the weak reservoir-system interaction Hamiltonian

$$\frac{\partial \hat{\rho}_2(t)}{\partial t} = \frac{1}{i\hbar} [\hat{V}_{SR2}, \hat{\rho}_2(t)]$$  \hspace{1cm} (3.32)

with

$$\hat{\rho}_2(t) \equiv U_2^+(t)\hat{\rho}_1(t)U_2(t)$$  \hspace{1cm} (3.33)

$$U_2(t) \equiv T_\omega \exp \frac{1}{i\hbar} \{ \int_0^t V_{SL1}(t')dt' \} = \frac{\partial}{\partial t} U_2(t) = \frac{1}{i\hbar} V_{SL1}(t)U_2(t)$$  \hspace{1cm} (3.34)

$$\hat{V}_{SR2} \equiv U_2^+(t)\hat{V}_{SR1}(t)U_2(t)$$  \hspace{1cm} (3.35)

The subscript '1' indicates interaction picture while subscript '2' indicates dressed picture.

From the master equation derived from the projection operator (Eq. 3.20), we can write the master equation for the system in thermal reservoir and laser field as

$$\frac{\partial \hat{\rho}_{2S}(t)}{\partial t} = \frac{1}{\hbar^2} Tr_R \int_0^t dt' [\hat{V}_{SR2}(t), [\hat{V}_{SR2}(t'), \hat{\rho}_R \otimes \hat{\rho}_{2S}(t')]]$$  \hspace{1cm} (3.36)

where $\hat{\rho}_{2S}(t) = Tr_R \{ \hat{\rho}_2(t) \} = U_2^+(t)\hat{\rho}_{1S}(t)U_2(t)$ with $\hat{\rho}_{1S}(t) = Tr_R \{ \hat{\rho}_1(t) \}$ since $U_2(t)$ does not contain the reservoir operators and $\hat{\sigma}(t) = \langle H(t) \rangle = Tr_R \{ \hat{V}_{SR2}(t)\hat{\rho}_R \} = 0.$
3.4.1 Master Equation in Interaction Picture

By using Eq. 3.34 with further algebras on Eq. 3.36 and using $U_2(t')U_2^*(t) = U_2(t', t) = U_2^*(t, t')$, we transform Eq. 3.36 back to the interaction picture, resulting in the master equation valid for arbitrary laser field strength as obtained in Ref. [137],

$$\frac{\partial \hat{\rho}_{S1}(t)}{\partial t} = \frac{1}{i\hbar}[\hat{V}_{SL1}(t), \hat{\rho}_{S1}(t)] + \mathcal{L}_R \hat{\rho}_{S1}(t)$$  \hspace{1cm} (3.37)

$$\mathcal{L}_R \hat{\rho}_{S1}(t) = -\frac{1}{\hbar^2} \int_0^t dt' T_R \{ \hat{V}_{SR1}(t', [W_{SR1}(t', t')], \hat{\rho}_R \otimes \hat{\rho}_{S1}(t')) \}$$  \hspace{1cm} (3.38)

where

$$V_{SR1}(t) \doteq -\hbar \sum_{i, k} \{ S_{ki}(t) R_{ki}(t) + S_{ki}^+(t) R_{ki}^+(t) \}$$  \hspace{1cm} (3.39)

$$W_{SR1}(t, t') \doteq U_2(t, t') \hat{V}_{SR1}(t') U_2^*(t, t')$$  \hspace{1cm} (3.40)

with the radiation operator $R_{ki}(t) \doteq g_{jk} \hat{a}_k e^{-i\omega_{ki} t}$, the system operator $S_{ki}(t) \doteq (S_{ki} e^{-i\omega_{ki} t} + S_{ki}^o e^{i\omega_{ki} t}) \hat{\pi}_k(t)$, the c.m. operator $\hat{\pi}_k(t) \doteq e^{i\mathbf{k} \cdot \mathbf{r}} \hat{P} e^{i\mathbf{P} \cdot \mathbf{r}} = \sum_{\mathbf{P}'} \mathbf{P}' | \mathbf{P}' + \hbar \mathbf{k} \rangle \langle \mathbf{P}' | e^{i\mathbf{P} \cdot \mathbf{r}} e^{i\mathbf{P}' \cdot \mathbf{r}}$ and $\mathbf{k}$ represents the photons modes (including polarizations) while $i$ represents the internal states. The internal and the radiation variables are coupled up through the coupling constant $g_{jk}$ while the center of mass (external) variable is coupled to the radiation variables by the operator $\hat{\pi}_k(t)$.

It is important to note that Markov approximation may not be used for Eq. 3.38 because of the additional $t'$ dependence in $W_{SR1}$ from the laser source. In the standard master equation, the effect of the external driving field on dissipation is neglected by setting $U_2(t', t) \rightarrow 1$ and $W_{SR1}(t, t') \rightarrow \hat{V}_{SR1}(t')$ before employing the Markov approximation.

The Liouvillean of Eq. 3.38 can be expanded as

$$\mathcal{L}_R \hat{\rho}_{S1} = -\int_0^t dt' \sum_{i, k, j, l} \{ \langle R_{ki} R_{ij}^+ \rangle S_{ki} X_{ij}^+ \hat{\rho}_{S1} + \langle R_{ki}^+ R_{ij} \rangle S_{ki}^+ X_{ij} \hat{\rho}_{S1} + \langle R_{ij} R_{ki} \rangle S_{ki} X_{ij}^+ \hat{\rho}_{S1} + \langle R_{ij}^+ R_{ki} \rangle S_{ki}^+ X_{ij} \hat{\rho}_{S1} + \langle R_{ki} R_{ij} \rangle S_{ki}^+ X_{ij}^+ \hat{\rho}_{S1} + \langle R_{ki}^+ R_{ij} \rangle S_{ki} X_{ij}^+ \hat{\rho}_{S1} + \langle R_{ij} R_{ki} \rangle S_{ki}^+ X_{ij} \hat{\rho}_{S1} + \langle R_{ij}^+ R_{ki} \rangle S_{ki} X_{ij} \hat{\rho}_{S1} \}$$  \hspace{1cm} (3.41)

where $X_{ij}(t, t') \doteq U_2(t, t') S_{ki}(t') U_2^*(t, t')$ and $\hat{U}_2(t, t') \doteq T_- e^{\frac{i}{\hbar} \int_{t'}^t dt' \Delta S_L (t')}$.

3.4.2 Master Equation in Schrödinger Picture

The master equation, Eqs. 3.37 in interaction Hamiltonians can be transformed back to the Schrödinger picture. By using the inverse relations of Eqs. 3.33 and 3.35, we obtain
\[
\frac{\partial}{\partial t} \hat{\rho}_S(t) = \frac{1}{i\hbar} [\hat{H}_c(t) + \hat{V}_{SL}(t), \hat{\rho}_S] + U_1(t) L \hat{\rho}_{S1}(t) U_1^\dagger(t) \\
U_1(t) L \hat{\rho}_{S1}(t) U_1^\dagger(t) = -\frac{1}{\hbar^2} \int_0^t d\tau \text{Tr}_R[\hat{V}_{SR}(t), [Q(t, \tau') \hat{V}_{SR}(t'), \hat{\rho}_R \otimes \hat{\rho}_S(t')]]
\]

where \( Q(t, t') = Q(t)Q^\dagger(t') \) and \( Q(t) = U_1(t)U_2(t) = T e^{\frac{i}{\hbar}\int_0^t [\hat{H}_c(t') + \hat{V}_{SL}(t')] dt'}. \)

### 3.4.3 Transformation to Time Independent Form

The evolution operator \( U_2 \) involves the time ordering product and difficult to be evaluated exactly because \( \hat{V}_{SL}(t) \) is explicitly time dependent. By using a unitary operator \( O(t) \) which contains only the system operators, we transform \( \hat{V}_{SL1}(t) \) from interaction picture to the time independent form [146]

\[
\hat{V}_{SL1} = O^\dagger(t) \hat{V}_{SL1}(t) O(t) + i\hbar \frac{dO^\dagger(t)}{dt} O(t) \tag{3.43}
\]

Now, we have \( \frac{\partial}{\partial t} U_2(t) = \frac{1}{i\hbar} \hat{V}_{SL1}(t) U_2(t) \rightarrow \frac{1}{i\hbar} O(t) \hat{V}_{SL1} O^\dagger(t) U_2(t) - O(t) \frac{dO^\dagger(t)}{dt} U_2(t) \) and by multiplying with \( O^\dagger(t) \) from the left, we get \( O^\dagger(t) \frac{\partial}{\partial t} U_2(t) = \frac{1}{i\hbar} \hat{V}_{SL1} O^\dagger(t) U_2(t) - \frac{dO^\dagger(t)}{dt} U_2(t) \) and after defining \( \frac{\partial}{\partial t} \hat{U}_2(t) = \frac{\partial}{\partial t} O^\dagger(t) U_2(t) + O^\dagger(t) \frac{\partial}{\partial t} U_2(t) \), we have

\[
\frac{\partial}{\partial t} \hat{U}_1(t) = \frac{1}{i\hbar} \hat{V}_{SL1} \hat{U}_1(t) \rightarrow \hat{U}_1(t) = e^{\frac{i}{\hbar}\hat{V}_{SL1} t} \tag{3.44}
\]

\[
U_2(t) = O(t) e^{\frac{i}{\hbar}\hat{V}_{SL1} t} \tag{3.45}
\]

By using \( U_2(t, t - \tau) = U_2(t) U_2^\dagger(t - \tau) \) and \( U_2(t, t - \tau) = U_2(t - \tau) U_2^\dagger(t) = U_2(t - \tau, t) \), the term \( W_{SR}(t, \tau) \) in the master equation can be written as

\[
W_{SR}(t, \tau) = U_2(t) U_2^\dagger(t - \tau) \hat{V}_{SR1}(t - \tau) U_2(t - \tau) U_2^\dagger(t) \tag{3.46}
\]

\[
= O(t) e^{\frac{i}{\hbar}\hat{V}_{SL1} t} \{ O^\dagger(t - \tau) \hat{V}_{SR1}(t - \tau) O(t - \tau) \} e^{-\frac{i}{\hbar}\hat{V}_{SL1} t} O^\dagger(t)
\]

Thus we have the master equation with all the operators that can be evaluate exactly.

The field dependent dissipation can also be shown using the Schrödinger equation. The Schrödinger formalism for field dependent dissipation is usually used in the theory concerning Zeno and anti-Zeno effects [321], and the general modification of decay rate through weak temporal perturbations [251]. In the presence of arbitrary laser interaction \( V_{SL}(t) \), the Schrödinger equation Eq. 3.89 becomes

\[
i\hbar \frac{d}{dt} |\Psi(t)\rangle_1 = \{ V_{SL1}(t) + V_{SR1}(t) \} |\Psi(t)\rangle_1 \tag{3.47}
\]
The unitary transformation to the 'dressed' picture (superscript '2') is accomplished in the same way as the transformation from the Schrödinger picture to interaction picture, with the transformed state vector \( |\Psi(t)\rangle_2 = \hat{U}^2_2(t) |\Psi(t)\rangle_1 \) and the unitary operator 
\[
\hat{U}_2(t) = T_\gamma \exp\left\{ \frac{i}{\hbar} \int_{t_0}^{t} dt' V_{SL1}(t') \right\}
\]
giving the Schrödinger equation in dressed picture
\[
i\hbar \frac{d}{dt} |\Psi(t)\rangle_2 = \hat{V}_{SR2}(t) |\Psi(t)\rangle_2 \tag{3.48}
\]
\[
\hat{V}_{SR2}(t) = \hat{U}_2(t)\hat{V}_{SR1}(t)\hat{U}_2^\dagger(t) \tag{3.49}
\]
The time evolution operator \( \hat{U}(t, t_o)_2 = T_\gamma \exp\left\{ \frac{i}{\hbar} \int_{t_o}^{t} dt' \hat{V}_{SR2}(t') \right\} \) is obtained from Eq. 3.48. It determines the evolution of the state vector \( |\Psi(t)\rangle_2 = \hat{U}(t, t_o)_2 |\Psi(t_o)\rangle_2 \) and can be expanded up to the second order in \( \hat{V}_{SR2}(t) \) as
\[
\hat{U}(t, t_o)_2 \approx I + \frac{1}{i\hbar} \int_{t_o}^{t} dt' \hat{V}_{SR2}(t') + \left( \frac{1}{i\hbar} \right)^2 \int_{t_o}^{t} dt' \int_{t_o}^{t'} dt'' \hat{V}_{SR2}(t')\hat{V}_{SR2}(t'') \tag{3.50}
\]
In the absence of laser interactions \( \hat{V}_{SR2} \rightarrow \hat{V}_{SR1} \), and the first order term of Eq. 3.50 gives the Fermi golden rule which describes the one-photon process while the second order term leads to the various scattering (Rayleigh, Raman) events governed by the Kramers-Heisenberg formula [138]. Transition amplitude of the excited state are obtained from \( c_e(t) = \langle e | \Psi(t) \rangle = \langle e | \hat{U}(t, t_o) | \Psi(t_o) \rangle \). The probability in excited state is \( P_e(t) = |c_e(t)|^2 \). For the system is initially in the excited state \( |\Psi(t_o)\rangle = |e\rangle \), we obtain up to second order
\[
c_e^{(1)}(t) = \frac{1}{i\hbar} \int_{t_o}^{t} dt_1 \langle e, R | \hat{U}(t)\hat{V}_{SR}(t)\hat{U}^\dagger(t) | \Psi(t_o) \rangle \tag{3.51}
\]
\[
c_e^{(2)}(t) = \left( \frac{1}{i\hbar} \right)^2 \int_{t_o}^{t} dt_1 \int_{t_o}^{t_1} dt_2 \langle e, R | \hat{U}(t_1)\hat{V}_{SR}^2(t_1)\hat{U}(t_2, t_1)\hat{V}_{SR}^2(t_2)\hat{U}^\dagger(t_2) | \Psi(t_o) \rangle \tag{3.52}
\]
where \( |R \rangle \) is the radiation state and \( \hat{U}(t_2, t_1) = \hat{U}(t_2)\hat{U}^\dagger(t_1) \). The field dependence in the excited state coefficient is contained in the operator \( \hat{U} \). In the usual theory of spontaneous emission, \( \hat{U}(t) \rightarrow I \) gives the field independent spontaneous emission rate.

### 3.5 Exact Master Equation for Two-Level System

Resonance fluorescence for multi-level atom in intense laser beam has been developed using dressed picture [233]. The dressed-atom approach has also been used to describe the dynamics of atom in a non-perturbative interaction with laser light [145]. In the theory of laser cooling of atoms, the driving laser is assumed to be sufficiently weak such it does not affect the Liouvillian for spontaneous emissions. For resonant strong laser fields, this assumption is no longer true as shown in previous Section, since the Liouvillian is dependent on the driving fields. The field dependent dissipation was shown by Argyres and Kelly
long ago. The Liouvillean is also frequency dependent, as shown by Olga, Mandel and Scully for multilevel system [146] using the Pauli master equation and for three-level system [148]. The effect of coherent fields on dissipation in a 3 level system has been worked out using Schrodinger equation and solved using the Laplace transform method [252]. The dissipation can also be described by the correct master equation with field dependent Liouvillean, which was derived by Agarwal[137] and used for a system of two-level atoms in a resonant laser field without quantization of the external degree of freedom (center of mass). The prospect of designing high intensity laser pulse has enabled coherent control of internal molecular degrees of freedom [275] at very short timescale and femtosecond chemistry [154]. This includes controlling spontaneous emission rate with pulses [246] or pulsed observations through Zeno or anti-Zeno effects [321]. Molecules dressed in a strong laser fields has been studied [180] using the Schrodinger equation, where the a.c. Stark shift can modify the internal energy structure. The influence of strong laser fields on cold gases has also been studied [152]. There are also theoretical developments in the manipulations of molecules using intense laser based on Schrödinger equations [162].

However, these works neglect the center of mass momentum dynamics. It would be interesting to study how the momentum dynamics are affected by dissipation in the presence of strong coherent fields. We present the full master equation valid for arbitrarily high intensity and non-resonant frequency, generalized to include the center of mass motion with the Röntgen term. The problem is expected to be complicated, thus we use the two-level system.

### 3.5.1 Dissipative Liouvillean

The laser-system interaction Hamiltonian $V_{SL}(t)$ in interaction picture with counter rotating terms and including the Röntgen term which is due to the small correction to the electric field [238] is given by

$$
\hat{V}_{SL}(\hat{R},t) = -\sum_{L} \hbar \Omega_{L} \{(S^+ e^{-i\Delta_{L}t} + S e^{-i\sigma_{L}t})\hat{I}_{L}(t) + (S e^{i\Delta_{L}t} + S^+ e^{i\sigma_{L}t})\hat{I}_{L}^{\dagger}(t)\} \quad (3.53)
$$

where $\Omega_{L} \equiv dE_{L}$ is the Rabi frequency, $\omega_{L}(\hat{P}) \equiv \omega_{L} - \frac{k_{L} \hat{P}}{M} + \frac{\hbar k_{L}^{2}}{2M}$ is the Doppler and recoil shifted frequency, $\omega_{L}(\hat{P}) = k_{L} \hat{P}$ the transverse Doppler shift, $S = |g\rangle \langle e|$, $q = 0, +1, -1$ for linear, $\sigma^{+}$ and $\sigma^{-}$ polarized lasers, and $\Delta_{L} = \omega_{L} - \omega_{0}$ is the laser detuning. The center of mass (c.m.) operators are given in Appendix III, $\hat{\Pi}_{L}(t) \equiv \hat{\chi}_{L} \hat{\pi}_{L}(t)$, $\hat{\chi}_{L} \equiv \sum_{q=-1,0} \epsilon_{L}^{e} \frac{\omega_{L}}{\omega_{L}} + \kappa_{L}^{e} \frac{\omega_{L}}{\omega_{L}}$ and $\hat{\pi}_{L}(t) \equiv \hat{U}_{cm}(t) e^{i k_{L} \hat{R} \hat{U}_{cm}(t)}$ with $\hat{U}_{cm}(t) \equiv e^{-i \frac{P^{2}}{2M \hbar}}$.

The inclusion of the Röntgen effect in $\hat{\chi}_{L}$ is consistent with the inclusion of the Doppler frequency $\frac{k_{L} \hat{P}}{M}$ in the exponential since both are in the same order ($\sim P/Mc$) relative to the laser frequency. For a single laser beam, it is always possible to choose $\kappa_{L}^{e} = 0$ and define the momentum dependent Rabi frequency $\Omega(\hat{P}) = dE_{L} \epsilon_{L}^{e} \frac{\omega_{L}}{\omega_{L}}$. The
Röntgen term would be important in the case of strong field, where the correction due to Doppler shift is larger than the natural linewidth, \( \delta E_L(P/Mc) > \Gamma_0 \).

By applying the rotating wave approximation (RWA) on Eq. 3.53, we have obtained the analytical expression for evolution operator \( \hat{U}(t, t') = T_{-}e^{\frac{i}{\hbar}\int_{t'}^{t} d\tau \hat{S}_R(\tau)} \) in Appendix IV for finite laser detuning \( \Delta_L \) and with the quantization of the c.m. operators,

\[
\hat{U}(\tau) = \begin{pmatrix}
e^{-i\Delta_L\tau/2}(i\hat{d}(\tau) + \hat{c}(\tau)) & i\hat{\Pi}_L(\tau) e^{-i\Delta_L\tau/2}\hat{c}(\tau) \\
i\hat{\Pi}_L(\tau) e^{i\Delta_L\tau/2}\hat{c}(\tau) & e^{i\Delta_L\tau/2}(-i\hat{d}(\tau) + \hat{c}(\tau)) \end{pmatrix}
\] (3.54)

where we have defined

\[
\hat{d}(\tau) = \frac{\Delta_L}{i2\hbar}(e^{i\hat{\beta}\theta\tau} - e^{-i\hat{\beta}\theta\tau}), \quad \hat{c}(\tau) = \frac{2\Omega_l}{i2\hbar}(e^{i\hat{\beta}\theta\tau} - e^{-i\hat{\beta}\theta\tau}), \quad \hat{c}(\tau) = \frac{1}{2}(e^{i\hat{\beta}\theta\tau} + e^{-i\hat{\beta}\theta\tau})
\] (3.55)

with \( \tau \equiv t - t' \), \( \hat{B} \equiv \sqrt{\Delta_L^2 + \Omega_L^2} \) and \( \hat{\Delta}_L \equiv \Delta_L + \frac{\hbar k^2}{2M} \).

In the RWA, we have set our calculations to be valid up to a maximum detuning \( \omega_L + \omega_0 > 10|\Delta_L| \). From \( (\omega_L + \omega_0)^2 - 100(\omega_L - \omega_0)^2 > 0 \), we find that the range of validity is \( 0.8\omega_0 < \omega_L < 1.2\omega_0 \) or \( |\Delta_L| < 0.2\omega_0 \).

The quantized radiation-system interaction Hamiltonian \( V_{SR}(t) \) in interaction picture is

\[
V_{SR}(t) = -\hbar(S^\dagger e^{i\omega_L t} + S e^{-i\omega_L t}) \sum_{k\lambda} g_{k\lambda}(\hat{a}_{k\lambda} \hat{\Pi}_{k\lambda}(t)e^{-i\omega_{k\lambda} t} + \hat{a}^\dagger_{k\lambda} \hat{\pi}_{k\lambda}(t)e^{i\omega_{k\lambda} t})
\] (3.56)

\[
V_{SR}(t) = -\hbar \sum_{k\lambda} \{S_{k\lambda}(t)R_{k\lambda}(t)+S_{k\lambda}^\dagger(t)R_{k\lambda}^\dagger(t)\}
\] (3.57)

where we define

\[
S_{k\lambda}(t) \equiv g_{k\lambda}(S^\dagger e^{i\omega_L t} + S e^{-i\omega_L t}) \hat{\Pi}_{k\lambda}(t)
\] (3.58)

\[
R_{k\lambda}(t) \equiv \hat{a}_{k\lambda} e^{-i\omega_{k\lambda} t}
\] (3.59)

\[
\hat{\Pi}_{k\lambda}(t) \equiv \hat{\chi}_{k\lambda} \hat{\pi}_{k\lambda}(t)
\] (3.60)

\[
\hat{\chi}_{k\lambda} \equiv \sum_{q=-r,-0} C_q \{e^{i\omega_{k\lambda}} + e^{-i\omega_{k\lambda}}\} \frac{\omega_{k\lambda}}{\omega_{k\lambda}}, \quad \hat{\pi}_{k\lambda}(t) \equiv e^{i\hbar k_{\lambda} \cdot \hat{R} + \frac{\hbar k_{\lambda} \cdot \hat{P}}{2M}}
\] (3.61)

\[
g_{k\lambda} \equiv \frac{d}{2\omega_{k\lambda} M} \omega_{k\lambda}, \quad \omega_{k\lambda}(\hat{P}) \equiv \omega_{k\lambda} - \frac{\hbar k_{\lambda} \cdot \hat{P}}{M} + \frac{\hbar k_{\lambda} \cdot \hat{P}}{2M}, \quad \omega_{k\lambda}(\hat{P}) \equiv k_{\lambda} \frac{\hbar k_{\lambda} \cdot \hat{P}}{M}
\] (3.62)
The Liouvillean, Eq. 3.41 can be evaluated exactly by using Eq. 8.105. The explicit form of $X_{k\lambda}(t,\tau)$ in Eq. 3.41 is written as

$$X_{k\lambda}(t,\tau) \doteq U(t,t')S_{k\lambda}(t')U(t',t) = g_{k\lambda}(F_{k\lambda}e^{-i\omega_0(t-\tau)} + G_{k\lambda}e^{-i\omega_0(t-\tau)} \tag{3.63}$$

$$G_{k\lambda}(t,\tau) \doteq \hat{U}(\tau)\hat{S}_{k\lambda}(t')\hat{U}^\dagger(\tau) \tag{3.64}$$

$$\approx \begin{pmatrix}
\hat{P}_L(\tau)\hat{P}_{k\lambda}(t-\tau)\{\hat{d}(\tau) + i\hat{c}(\tau)\}\hat{r}(\tau) \\
\hat{P}_{k\lambda}(t-\tau)e^{i\Delta_L\tau}\{\hat{c}(\tau) - i\hat{d}(\tau)\}^2
\end{pmatrix}
\begin{pmatrix}
\hat{P}_L(\tau)\hat{P}_{k\lambda}(t-\tau)\{\hat{d}(\tau) + i\hat{c}(\tau)\}\hat{r}(\tau) \\
\hat{P}_{k\lambda}(t-\tau)e^{i\Delta_L\tau}\{\hat{c}(\tau) - i\hat{d}(\tau)\}^2
\end{pmatrix}^{-1}
\hat{U}(\tau)\hat{S}_{k\lambda}(t')\hat{U}^\dagger(\tau) \tag{3.65}$$

The precise $G_{k\lambda}(t,\tau)$ is

$$\begin{pmatrix}
e^{-i\Delta_L\tau/2}\hat{P}_{k\lambda}(t')e^{i\Delta_L\tau/2}(-i\hat{d} + \hat{c}) \\
e^{-i\Delta_L\tau/2}(-i\hat{d} + \hat{c})\hat{P}_{k\lambda}(t)e^{i\Delta_L\tau/2}(-i\hat{d} + \hat{c})
\end{pmatrix}
\begin{pmatrix}
\hat{P}_L(\tau)e^{-i\Delta_L\tau/2}\hat{P}_{k\lambda}(t')\hat{P}_L(\tau)e^{-i\Delta_L\tau/2}
\end{pmatrix}^{-1}
\begin{pmatrix}
e^{i\Delta_L\tau/2}(-i\hat{d} + \hat{c})\hat{P}_{k\lambda}(t')\hat{P}_L(\tau)e^{-i\Delta_L\tau/2}
\end{pmatrix}$$

We note that $\hat{P}_L(\tau)$ and $\hat{P}_{k\lambda}(t')$ contain both $\hat{P}$ and $\hat{R}$, and do not commute with $\hat{B}$, $\hat{D}_L$, $\hat{d}(\tau)$, $\hat{r}(\tau)$ and $\hat{c}(\tau)$ which contain only $\hat{P}$ . However, for $\Delta_L > > \frac{P_k}{M}$ we can assume that they do commute when we neglect the Doppler shift operator and write $\Delta_L \approx \Delta_L, \tilde{B} \approx \sqrt{\Delta_L^2 + 4\Omega_L^2}$. This enables $\hat{d}, \hat{r}, \hat{c}$ to be reduced to c-numbers, which give the results (second line) of Eqs. 8.16 and 3.65.

The density operator for the thermal reservoir $[138] \hat{\rho}_R = \prod_{k\lambda}(1 - e^{-\frac{\omega_{k\lambda}}{kT}})e^{-\frac{\omega_{k\lambda}}{kT}}\sum_m [n_{k\lambda}]^\dagger [n_{k\lambda}]$ gives

$$TR\{\hat{a}_{k\lambda}^\dagger \hat{a}_{k\lambda}\} = (\bar{\rho}_{k\lambda} + 1)\delta_{k\lambda k'\lambda'} \tag{3.66}$$

$$TR\{\hat{a}_{k\lambda}^\dagger \hat{a}_{k\lambda}\} = \bar{\rho}_{k\lambda} \delta_{k\lambda k'\lambda'} \tag{3.67}$$

where $\bar{\rho}_{k\lambda} \doteq (e^y - 1)^{-1} e^{\frac{\omega_{k\lambda}}{kT}}$. Only those terms with $\hat{a}_{k\lambda}^\dagger \hat{a}_{k\lambda}$ and $\hat{a}_{k\lambda}^\dagger \hat{a}_{k\lambda}$ give non-vanishing two-time averages. After straightforward algebras using Eqs. 3.37, 3.56 and Eqs. 3.63-3.65, we obtain

$$L\hat{\rho}_S(t) = \int_0^t dt' \sum_{k\lambda} \hat{F}_{k\lambda}(t,t') \tag{3.68}$$

$$\hat{F}_{k\lambda}(t,\tau) \doteq -(\bar{\rho}_{k\lambda} + 1) e^{-i\omega_{k\lambda}(t-\tau)} S_{k\lambda}(t) X_{k\lambda}^\dagger(t)\hat{\rho}_S(t-\tau) + \bar{\rho}_{k\lambda} e^{-i\omega_{k\lambda}(t-\tau)} S_{k\lambda}^\dagger(t) X_{k\lambda}(t,\tau) \hat{\rho}_S(t-\tau)
+ \bar{\rho}_{k\lambda} e^{-i\omega_{k\lambda}(t-\tau)} \hat{S}_{k\lambda}(t) \hat{\rho}_S(t-\tau) X_{k\lambda}^\dagger(t) + (\bar{\rho}_{k\lambda} + 1) e^{i\omega_{k\lambda}(t-\tau)} S_{k\lambda}^\dagger(t) \hat{\rho}_S(t-\tau) X_{k\lambda}^\dagger(t)\hat{\rho}_S(t-\tau) X_{k\lambda}(t,\tau)
+ \bar{\rho}_{k\lambda} e^{i\omega_{k\lambda}(t-\tau)} X_{k\lambda}(t,\tau) \hat{\rho}_S(t-\tau) S_{k\lambda}^\dagger(t) + (\bar{\rho}_{k\lambda} + 1) e^{-i\omega_{k\lambda}(t-\tau)} X_{k\lambda}^\dagger(t,\tau) \hat{\rho}_S(t-\tau) S_{k\lambda}(t)$$

In the following, we neglect the counter-rotating terms $e^{i(\omega_{k\lambda} + \omega_0)\tau}$ (rotating wave approximation) which contribute only to the radiative level shifts and can be absorbed into the
levels spacing. By replacing $S_{k\lambda}$ and $X_{k\lambda}$ from Eq. 3.58 and Eq. 3.63 into Eq. 3.68, we obtain the master equation in RWA,

\[
L\dot{\rho}_S(t) = -\int_0^t d\tau \sum_{k\lambda} g_{k\lambda}^2 \{(\overline{\rho}_{k\lambda} + 1)e^{-i\Delta_{k\lambda} T} \tilde{H}_{k\lambda}(t)[S^\dagger + \frac{S_t e^{2i\omega_0 t}}{2}]F_{k\lambda}^\dagger(t, \tau)\dot{\rho}_S + \overline{\rho}_{k\lambda} e^{i\Delta_{k\lambda} T} \tilde{H}_{k\lambda}^\dagger(t) [S + S_t e^{-2i\omega_0 t}] F_{k\lambda}(t, \tau)\dot{\rho}_S(t)\} \\
+ \int_0^t d\tau \sum_{k\lambda} g_{k\lambda}^2 \{\overline{\rho}_{k\lambda} e^{-i\Delta_{k\lambda} T} \tilde{H}_{k\lambda}(t)[S^\dagger + \frac{S_t e^{-2i\omega_0 t}}{2}]F_{k\lambda}^\dagger(t, \tau)\dot{\rho}_S(t) + \overline{\rho}_{k\lambda} e^{i\Delta_{k\lambda} T} \tilde{H}_{k\lambda}^\dagger(t) [S + S_t e^{2i\omega_0 t}] \dot{\rho}_S(t)F_{k\lambda}(t, \tau)\} + H.c.
\]

(3.69)

The underlined terms $e^{\pm 2i\omega_0 t}$ are the secular terms which average to zero for timescale $\delta t >> 1/2\omega_o$ and will be neglected. By inserting Eq. 3.65 into Eq. 3.69, we obtain

\[
L\dot{\rho}_S(t) = -\{T_{A,\bar{r}+1} S^\dagger S \tilde{H}_{k\lambda}(t) \tilde{H}_{k\lambda}^\dagger(t, \tau) \rho_{\bar{S}} - T_{B,\bar{r}+1} S^\dagger \tilde{H}_{k\lambda}(t) \tilde{H}_{k\lambda}^\dagger(t, \tau) \tilde{H}_{L}(t, \tau) \rho_{\bar{S}} \} \\
+ \{T_{B,r} S^\dagger S \tilde{H}_{k\lambda}^\dagger(t) \tilde{H}_{k\lambda}(t, \tau) \rho_{\bar{S}} - T_{A,r} \tilde{H}_{k\lambda}^\dagger(t) \tilde{H}_{k\lambda}(t, \tau) SS^\dagger \rho_{\bar{S}} \} \\
+ T_{A,\bar{r}+1} S^\dagger S \tilde{H}_{k\lambda}(t) \tilde{H}_{k\lambda}^\dagger(t, \tau) \tilde{H}_{L}(t, \tau) - T_{B,\bar{r}+1} \tilde{H}_{k\lambda}^\dagger(t) S^\dagger \tilde{H}_{k\lambda}(t) SS^\dagger \tilde{H}_{k\lambda}(t, \tau) \tilde{H}_{L}(t, \tau) \\
+ T_{C,r} \tilde{H}_{k\lambda}^\dagger(t) \tilde{H}_{k\lambda}(t, \tau) \tilde{H}_{L}(t, \tau) - T_{A,r} \tilde{H}_{k\lambda}^\dagger(t) \tilde{H}_{k\lambda}(t, \tau) SS^\dagger \tilde{H}_{k\lambda}(t, \tau) \tilde{H}_{L}(t, \tau) \\
+ T_{A,\bar{r}+1} \tilde{H}_{k\lambda}^\dagger(t) S^\dagger \tilde{H}_{k\lambda}(t) \tilde{H}_{L}(t, \tau) - T_{B,\bar{r}+1} \tilde{H}_{k\lambda}^\dagger(t) S \tilde{H}_{k\lambda}(t) SS^\dagger \tilde{H}_{L}(t, \tau) \tilde{H}_{k\lambda}(t, \tau) \\
+ H.c. \ (\text{Hermitian conjugates})
\]

(3.70)

where we have defined

\[
T_{A,\pi+1} \equiv \int_0^\ell dt \sum_{k\lambda} g_{k\lambda}^2 (\overline{\rho}_{k\lambda}(+1)) e^{-i\Delta_{k\lambda} T} e^{i\Delta_{k\lambda} T} (c - id)^2 = \frac{1}{2} (1 - \delta^2) K_{\pi+1}(\omega_o + \Delta_L)
\]

\[
+ \frac{1}{4} (1 + \delta)^2 K_{\pi+1}(\omega_o + \Delta_L - R) + \frac{1}{4} (1 - \delta)^2 K_{\pi+1}(\omega_o + \Delta_L + R)
\]

(3.71)

\[
T_{B,\pi+1} \equiv \int_0^\ell dt \sum_{k\lambda} g_{k\lambda}^2 (\overline{\rho}_{k\lambda}(+1)) e^{-i\Delta_{k\lambda} T} (d + ic) r
\]

(3.72)

\[
\frac{\Omega L}{B} \frac{1}{2} \{- (1 + \delta) K_{\pi+1}(\omega_o - R) + (1 - \delta) K_{\pi+1}(\omega_o + R) + 2\delta K_{\pi+1}(\omega_o)\}
\]

\[
T_{C,\pi+1} \equiv \int_0^\ell dt \sum_{k\lambda} g_{k\lambda}^2 (\overline{\rho}_{k\lambda}(+1)) e^{-i\Delta_{k\lambda} T} e^{-i\Delta_{k\lambda} T} r^2
\]

(3.73)

\[
= \frac{\Omega^2}{B^2} \{- K_{\pi+1}(\omega_o - \Delta_L + R) - K_{\pi+1}(\omega_o - \Delta_L - R) + 2 K_{\pi+1}(\omega_o - \Delta_L)\}
\]
\[ K_{\pi^{(1)}}(x) = \int_0^t dt' \sum_{k\lambda} g_{k\lambda}^2 \tilde{\rho}_{k\lambda}(+1)e^{-i(\omega_{k\lambda}-x)t} \rightarrow \left\{ \frac{\Gamma(x)\bar{\pi}(x)(+1) - i\Lambda_{\pi^{(1)}}(x)}{2} \right\} \] (3.74)

\[ \Gamma(x) = 2\pi \sum_{k\lambda} g_{k\lambda}^2 \delta(\omega_{k\lambda} - x) \rightarrow \frac{\partial^3 x}{3\varepsilon_{\perp}n_{\perp}c^3} \text{the decay rate,} \] (3.75)

\[ \Lambda_{\pi^{(1)}}(x) = 2\pi \sum_{k\lambda} g_{k\lambda}^2 \tilde{\rho}_{k\lambda}(+1) \frac{\varphi}{\omega_{k\lambda} - x} \text{the radiative shift,} \] (3.76)

\[ \bar{\pi}(x) = (\exp\left\{ \frac{\hbar x}{k_BT} \right\} - 1)^{-1} \text{the mean thermal number.} \] (3.77)

Equation 3.70 is the central result. It is valid for two-level system within the rotating wave approximation, secular approximation and Born-Markov approximation for arbitrary field intensity and frequency. There are additional terms associated with \( T_B, \bar{\pi}^{(1)} \) and \( T_C, \bar{\pi}^{(1)} \) as compared to the conventional results. The \( T \)'s are operators as they represent the time \( \tau \) integral operation on \( \hat{\rho}_S(\tau) \) and \( \bar{\Pi}(\tau) \) as well as photon wavevector/polarization \( k\lambda \) summation on \( \bar{\Pi} \). If we substitute the explicit expressions for the operators \( \bar{\Pi}_{k\lambda} \) Eq. 3.60 into Eq. 3.70, we obtain the master equation with the c.m. momentum in a more transparent manner, but much more complicated. However, this can be simplified if we neglect the complicated time dependent exponentials terms due to the small Doppler and recoil frequencies in Eq. 3.70. Hence, we obtain,

\[ L_{\rho_{ee}}(\mathbf{P}, t) = -\left( T_{A,n+1} + T_{A,n+1}^* \right) \rho_{ee}(\mathbf{P}, t) + (T_{A,n} + T_{A,n}^* \rho_{gg}(\mathbf{P} - \hbar \mathbf{k}, t) \right) + T_{B,n+1} \rho_{ge}(\mathbf{P} - \hbar \mathbf{k}_L, \mathbf{P}, t) + T_{B,n+1}^* \rho_{eg}(\mathbf{P}, \mathbf{P} - \hbar \mathbf{k}_L, t) \] (3.78)

\[ L_{\rho_{gg}}(\mathbf{P}, t) = (T_{A,n+1} + T_{A,n+1}^* \rho_{ee}(\mathbf{P} + \hbar \mathbf{k}, t) - (T_{A,n} + T_{A,n}^* \rho_{gg}(\mathbf{P}, t) \right) - T_{B,n+1} \rho_{ge}(\mathbf{P} + \hbar \mathbf{k} - \hbar \mathbf{k}_L, \mathbf{P} + \hbar \mathbf{k}, t) - T_{B,n+1}^* \rho_{eg}(\mathbf{P} + \hbar \mathbf{k}, \mathbf{P} - \hbar \mathbf{k}_L + \hbar \mathbf{k}, t) \] (3.79)

\[ L_{\rho_{eg}}(\mathbf{P}', \mathbf{P}, t) = -T_{A,n+1} \rho_{eg}(\mathbf{P}', \mathbf{P}, t) + T_{B,n} \rho_{gg}(\mathbf{P}' - \hbar \mathbf{k}_L, \mathbf{P}, t) - T_{B,n} \rho_{gg}(\mathbf{P}' + \hbar \mathbf{k}_L - \hbar \mathbf{k}, t) \] (3.80)

\[ \rho_{ab}(\mathbf{P}_a, \mathbf{P}_b, t) \doteq (\mathbf{P}_a | \hat{\rho}_{ab}(t) | \mathbf{P}_b). \]

\(^1\bar{\pi}^{(1)} \text{ means } \pi \text{ or } (\pi + 1)\)
By operating $K_{\pi}(x)$ on the generalized matrix elements $\langle P_i + \hbar k | \hat{\rho}_{ij} | P_j + \hbar k \rangle$ gives a generic expression for each term within the $T$ operators:

$$K_{\pi}(x)\langle P_i + \hbar k | \hat{\rho}_{ij} | P_j + \hbar k \rangle = \frac{1}{2} \Gamma(x)\pi(x) \frac{3}{8\pi} \int_{0}^{2\pi} d\phi \int_{0}^{\pi} d\theta N_{\pi}(\theta) \langle P_i + \hbar \tilde{k}x/c | \hat{\rho}_{ij} | P_j + \hbar \tilde{k}x/c \rangle$$

$$-\frac{1}{2} \sum_{k\lambda} \frac{g_{k\lambda}^2 \bar{n}_{k\lambda}}{\omega_{k\lambda}} \int_{0}^{2\pi} d\phi \int_{0}^{\pi} d\theta N_{\pi}(\theta) \langle P_i + \hbar \tilde{k}x_{k\lambda}/c | \hat{\rho}_{ij} | P_j + \hbar \tilde{k}x_{k\lambda}/c \rangle (3.81)$$

where $\tilde{k}$ is dependent on $\phi, \theta$. The first term on the right hand side of Eq. 3.81 shows that the recoil momentum $\hbar \tilde{k}x/c$ is generally dependent on the laser detuning and intensity through the coupling with the reservoir radiation, for example $x = \omega_o - \Delta_L + \sqrt{\Omega_L^2 + \Delta_L^2}$. It provides an additional degree for controlling the center of mass motion of particles with laser frequency and intensity in the strong field regime. From Eqs. 3.78-3.80, we also see that the terms with $T_{B,\bar{n}}$ and $T_{C,\bar{n}}$ involve not only the recoil momentum from the vacuum reservoir photon but also an additional recoil from the laser photons $\hbar k_L$.

### 3.5.2 Neglecting Center of Mass Recoil

By neglecting the center of mass recoils momenta, the generalized Liouvillean 3.70 becomes:

$$L\hat{\rho}_S(t) = (T_{A,\bar{n}+1} + T_{A,\bar{n}+1}^*) \hat{\rho}_S S\dagger - T_{A,\bar{n}+1} S\dagger \hat{\rho}_S S - T_{A,\bar{n}+1}^* \hat{\rho}_S S\dagger S$$

$$+ (T_{A,\bar{n}} + T_{A,\bar{n}}^*) \hat{\rho}_S S\dagger - T_{A,\bar{n}} S\dagger \hat{\rho}_S S - T_{A,\bar{n}}^* \hat{\rho}_S S\dagger S$$

$$+ T_{C,\bar{n}+1} S\dagger \hat{\rho}_S S + T_{C,\bar{n}+1}^* \hat{\rho}_S S$$

$$+ T_{B,\bar{n}} [S\hat{\rho}_S, S] + T_{B,\bar{n}} [S\dagger, \hat{\rho}_S S\dagger] + T_{B,\bar{n}+1}[S\hat{\rho}_S, S\dagger] + T_{B,\bar{n}+1}^* [S, \hat{\rho}_S S\dagger]$$

(3.82)

The first three lines in Eq. 3.82 are identical to the results for decay in a squeezed vacuum [219]. The last line contains additional terms with $T_B$ due to the coherences induced by strong laser fields and contribute to the dynamics of the populations. The decay rates are proportional to the effective level spacings which depend on both Rabi frequency and the laser detuning. This may provide a channel for coherent control the evolution of the populations and spontaneous decay process.

For zero thermal photons $\bar{n} = 0$ and resonant case, $\Delta_L = 0$, Eq. 3.82 gives Agarwal’s results [137],

$$L\rho_{ee} = -\frac{1}{4}(2\Omega_o + \Gamma_+)\rho_{ee} + \frac{1}{4}K_-\rho_{ge} + \frac{1}{4}K_-^*\rho_{eg}$$

$$L\rho_{gg} = \frac{1}{4}(2\Omega_o + \Gamma_+)\rho_{ee} - \frac{1}{4}K_-\rho_{ge} - \frac{1}{4}K_-^*\rho_{eg}$$

$$L\rho_{eg} = -\frac{1}{4}(2K_o + K_+)\rho_{eg} + \frac{1}{4}(2K_o - K_+)\rho_{ge} + \frac{1}{4}K_-$$

(3.83)
where we have used \( T_{A,R+1} + T_{A,R-1}^* = \Gamma_{A,R+1} \rightarrow \frac{1}{4}(2\Gamma(\omega_0) + \Gamma_1), T_B \rightarrow \frac{1}{4}K_-, T_C \rightarrow \frac{1}{4}(2K(\omega_0) - K_+ ) \) with

\[
K_\pm \equiv K(\omega_0 + R) \pm K(\omega_0 - R) \quad \text{and} \quad \Gamma_1 \equiv \Gamma(\omega_0 + R) + \Gamma(\omega_0 - R). \tag{3.84}
\]

Equations 3.83 correspond to the results obtained by constructing the dressed states : with doubling of the excited states \( |e, +\rangle, |e, -\rangle \) and doubling of the ground states \( |g, +\rangle, |g, -\rangle \) with the energies \( \omega_e + R, \omega_e - R, \omega_g + R \) and \( \omega_g - R \) respectively. The levels doubling create 4 channels of decays, one with frequency \( \omega_o + R, \) two with \( \omega_o \) and one with \( \omega_o - R. \) The existence of the additional decay channels has been pointed out in Ref. [249] which uses intense and low frequency fields to suppress the decay. The populations become dependent on the coherences between \( |e, +\rangle \) and \( |g, -\rangle \); and between \( |e, -\rangle \) and \( |g, +\rangle. \) These are the field induced coherences with the same dipole transition which depend on the rate \( K(\omega_0 + R) \) and \( K(\omega_0 - R) \) instead of the driving field, similar to the interference of the spontaneous decays of different dipole transitions [244], [243]. For finite detuning, similar interpretation can be drawn from analysis of Eq. 3.82.

In the weak field limit, \( \Omega_L \approx \Gamma, \Delta_L \ll R >> \Omega_L \) and \( \delta \approx 1; \) we have \( T_{A,R(1)} \rightarrow K_{\sigma(1)}(\omega_0) \) and \( T_{B,R,\sigma(1)} \rightarrow 0, T_{C,\sigma(1)} \rightarrow 0 \) and the standard results are recovered \( L_{\rho ee}(t) = -\Gamma_o(\bar{n}_o + 1)\rho_{ee} + \Gamma_o\bar{n}_o\rho_{gg}, L_{\rho_{gg}}(t) = \Gamma_o(\bar{n}_o + 1)\rho_{gg} - \Gamma_o\bar{n}_o\rho_{gg} \) and \( L_{\rho_{eg}}(t) = -\frac{1}{2}\{\Gamma_o(2\bar{n}_o + 1) - i\Delta_{\sigma(1)}(\omega_0)\}\rho_{eg}. \) Thus, from Eqs. 3.72 and 3.73, the necessary condition for using the simplified standard results in weak field limit is

\[
\omega_0 << |\Delta_L \pm \sqrt{\Omega_L^2 + \Delta_L^2}| \tag{3.85}
\]

The terms on the right hand side correspond to the light shifts of the levels. So, the weak field condition means that the light shift should be negligible compared to the level spacing.

### 3.6 Coherent Control of Spontaneous Emission Rate

The system is a ‘\( V' \) scheme with one sided laser coupling (see Fig. 3.1) with an excited state \( |e\rangle \) coupled by radiation to the ground state \( |g\rangle \) and an the third state \( |\tau\rangle \) coupled by multiple 2\( \pi \)-pulses to state \( |\tau\rangle \). The free Hamiltonian \( H_o \), laser interaction \( V_{SL}(\hat{R}, t) \) and radiation interaction \( V_{SR}(\hat{R}, t) \) Hamiltonians in interaction picture are respectively

\[
H_o = \frac{\hat{p}_e^2}{2M} + \hbar \omega_e |e\rangle\langle e| + \hbar \omega_g |g\rangle\langle g| + \hbar \omega_\tau |\tau\rangle\langle \tau| + \sum_{k, \lambda} (\hat{a}_{k\lambda}^\dagger \hat{a}_{k\lambda} + \frac{1}{2})\hbar \omega_{k\lambda} \tag{3.86}
\]

\[
V_{SL}^z(\hat{R}, t) = -\hbar \frac{1}{2} \Omega(t) |\tau\rangle \langle g| \pi_L e^{-i\Delta_L t} + |g\rangle \langle \tau| \pi_L^\dagger e^{i\Delta_L t}) \tag{3.87}
\]

\[
V_{SR}^z(\hat{R}, t) = -\hbar \sum_{k, \lambda} g_{k\lambda} (|e\rangle \langle g| \hat{a}_{k\lambda} \bar{n}_{k\lambda} e^{-i \varphi_{k\lambda}(t)} + |g\rangle \langle e| \hat{a}_{k\lambda}^\dagger \bar{n}_{k\lambda} e^{i \varphi_{k\lambda}(t)}))^2 \tag{3.88}
\]
Figure 3.1: Three-level V-scheme with one-sided strong laser coupling and one-sided spontaneous emission.

where \( \hat{\pi}_{k\lambda}(t) \equiv e^{ik\lambda \cdot (\hat{\mathbf{r}} + \hat{\mathbf{p}}/m)} = e^{ik\lambda \cdot \hat{\mathbf{R}}} e^{\hat{\mathbf{P}}/2 \hbar} e^{-\hbar \hat{\mathbf{P}}^2/(2\hbar)} \) is the center of mass operator, \( \hbar \mathbf{C}_{k\lambda} \equiv \sqrt{\hbar^2/2e}\mathbb{C}_{2}\mathbb{C}_{\lambda} \) is the vacuum coupling, \( \Delta_{k\lambda} \equiv \Delta_{k\lambda} - \omega_{k\lambda}^{P} + \omega_{k\lambda}^{R} \), \( \Delta_{k\lambda} \equiv \omega_{k\lambda} - \omega_{\lambda} \), \( \omega_{k\lambda}^{P} \equiv \frac{k_{\lambda} \cdot \mathbf{p}}{\hbar} \) the Doppler frequency, \( \omega_{k\lambda}^{R} \equiv \frac{\hbar^2}{2M} \) the recoil frequency and \( \Theta_{k\lambda}(t) \equiv \Phi(t) + \Delta_{k\lambda} t \). Parameters for laser fields are analogously defined. The time-dependent phase \( \Phi(t) \) may be due to the levels modulation by external perturbations \([248],[247]\). In the following, we concentrate on the effect of laser fields on spontaneous emission and set \( \Phi(t) \) to zero.

### 3.6.1 Non-Markovian Effect with Laser Field from Schrödinger Equation

The Schrödinger equation in interaction picture (superscript ‘t’) describes the evolution of the truncated Hilbert space ansatz state vector \( |\Psi(t)\rangle \) of a quantum system of particle interacting with the reservoir,

\[
\dot{\Psi}(\mathbf{P}, t) = \begin{align*}
\{\mathcal{V}_{SL}^t(\hat{\mathbf{R}}, t) + \mathcal{V}_{SR}^t(\hat{\mathbf{R}}, t)\} |\Psi(\mathbf{P}, t)\rangle \\
|\Psi(\mathbf{P}, t)\rangle &\equiv a(\mathbf{P}, t)|e, \mathbf{P}, \{0\}\rangle + \sum_{k\lambda} b_{k\lambda}(\mathbf{P} - \hbar \mathbf{k}, t)|g, \mathbf{P} - \hbar \mathbf{k}, \{1\}_{k\lambda}\rangle \\
&\quad + \sum_{k\lambda} c_{k\lambda}(\mathbf{P} - \hbar \mathbf{k} + \hbar \mathbf{k}_L, t)|r, \mathbf{P} - \hbar \mathbf{k} + \hbar \mathbf{k}_L, \{1\}_{k\lambda}\rangle
\end{align*}
\]  

(3.89)

(3.90)

where \( |e, \mathbf{P}, \{0\}\rangle = \prod_{k\lambda} |e, \mathbf{P}, 0_{k\lambda}\rangle \) is the basis for the particle with momentum \( \mathbf{P} \) in the excited internal state and the vacuum radiation state. The ansatz corresponds to the rotating wave approximation (RWA) where the basis describe the energy conserving processes; for example, the coexistence of a ground internal state and the creation of a photon with mode
\[ k \lambda \] has the probability \( |b_{k\lambda}|^2 \). The ansatz and the Schrödinger equation lead to the coupled equations

\[
\frac{d}{dt} a(P, t) = - \sum_{k, \lambda} g_{k, \lambda} b_{k, \lambda}(P - \hbar k, t) e^{-i \Delta k t} \tag{3.91}
\]

\[
\frac{d}{dt} b_{k, \lambda}(P - \hbar k, t) = i \Omega(t) c_{k, \lambda}(P - \hbar k + \hbar k_L, t) e^{i \Delta L t} + g_{k, \lambda}^* a(P, t) e^{i \Delta k t} \tag{3.92}
\]

\[
\frac{d}{dt} c_{k, \lambda}(P - \hbar k + \hbar k_L, t) = i \Omega(t) e^{-i \Delta L t} b_{k, \lambda}(P - \hbar k, t) \tag{3.93}
\]

The exponential time dependent term can be eliminated by replacing \( \bar{b}_{k, \lambda} = b_{k, \lambda} e^{-i \Delta k t} \) and \( \bar{c}_{k, \lambda} = c_{k, \lambda} e^{-i \Delta k L t} \) with \( \bar{\Delta}_{kL} = \bar{\Delta}_{k \lambda} - \bar{\Delta}_L \), Eqs. 3.91 and 3.92 become

\[
\frac{d}{dt} a = - \sum_{k, \lambda} g_{k, \lambda} \bar{b}_{k, \lambda} \tag{3.94}
\]

\[
\frac{d}{dt} \bar{b}_{k, \lambda} = -i \Delta_{kL} \bar{b}_{k, \lambda} + g_{k, \lambda}^* a + i \Omega(t) \bar{c}_{k, \lambda} \tag{3.95}
\]

\[
\frac{d}{dt} \bar{c}_{k, \lambda} = -i \Delta_{kL} \bar{c}_{k, \lambda} + i \Omega(t) \bar{b}_{k, \lambda} \tag{3.96}
\]

with the Laplace transform equations for arbitrary time dependent laser field \( \Omega(t) \)

\[
sA(s) = a(0) - \sum_{k, \lambda} g_{k, \lambda} B_{k, \lambda}(s) \tag{3.97}
\]

\[
sB_{k, \lambda}(s) = \bar{b}_{k, \lambda}(0) - i \Delta_{kL} B_{k, \lambda}(s) + g_{k, \lambda}^* A(s) + L \{ i \Omega(t) \bar{c}_{k, \lambda}(t) \} \tag{3.98}
\]

\[
sC_{k, \lambda}(s) = \bar{c}_{k, \lambda}(0) - i \Delta_{kL} C_{k, \lambda}(s) + L \{ i \Omega(t) \bar{b}_{k, \lambda} \} \tag{3.99}
\]

The coefficients \( A(s), B_{k, \lambda}(s) \) and \( C_{k, \lambda}(s) \) are the Laplace transforms of the coupled Volterra equations. For time independent field \( \Omega \), we can eliminate \( C_{k, \lambda} \) from Eqs. 3.98 and 3.99 and get

\[
A(s) = (s + \gamma(s, \Omega))^{-1}\{ a(0) - \sum_{k, \lambda} g_{k, \lambda} \{ (s + i \Delta_{kL}) \bar{b}_{k, \lambda}(0) + i \Omega \bar{c}_{k, \lambda}(0) \} \} \tag{3.100} \]

\[
B_{k, \lambda}(s) = \frac{(s + i \Delta_{kL}) g_{k, \lambda}^*}{M_{k, \lambda}(s)(s + \gamma(s, \Omega))} \{ a(0) - \sum_{k', \lambda'} g_{k', \lambda'} \{ (s + i \Delta_{k'L}) \bar{b}_{k', \lambda'}(0) + i \Omega \bar{c}_{k', \lambda'}(0) \} \} \tag{3.101}
\]

\[
C_{k, \lambda}(s) = \frac{i \Omega g_{k, \lambda}^*}{M_{k, \lambda}(s)(s + \gamma(s, \Omega))} \{ a(0) - \sum_{k', \lambda'} g_{k', \lambda'} \{ (s + i \Delta_{k'L}) \bar{b}_{k', \lambda'}(0) + i \Omega \bar{c}_{k', \lambda'}(0) \} \} \tag{3.102}
\]
where

\[
M_{k\lambda}(s, \Omega) \equiv (s + i\Delta_{k\lambda})(s + i\Delta_{kL}) + \Omega^2 \quad (3.103)
\]

\[
\gamma(s, \Omega) = \sum_{k', \lambda'} \frac{(s + i\Delta_{k'\lambda'})(s + i\Delta_{k'L})}{M_{k'\lambda'}(s)} \quad (3.104)
\]

In general, the terms involving \( \bar{b}_{k\lambda}(0) \) and \( \bar{c}_{k\lambda}(0) \) are not zero, the evaluations of these terms become the problems. Assuming initial conditions of \( \bar{b}_{k\lambda}(0) = \bar{c}_{k\lambda}(0) = 0 \), Eqs. 3.100-3.102 simplify to

\[
A(s) = a(0)\{s + \gamma(s, \Omega)\}^{-1} \quad (3.105)
\]

\[
B_{k\lambda}(s) = \frac{(s + i\Delta_{kL})g_{k\lambda}^* a(0)}{M_{k\lambda}(s)\{s + \gamma(s, \Omega)\}} \quad (3.106)
\]

\[
C_{k\lambda}(s) = \frac{i\Omega g_{k\lambda}^* a(0)}{M_{k\lambda}(s)\{s + \gamma(s, \Omega)\}} \quad (3.107)
\]

The Laplace transforms of the transition coefficients depend on the laser Rabi frequency inside \( M_{k\lambda}(s) \). Equations 3.105-3.107 are exact within the rotating wave approximation and contain the full non-Markovian effect. They apply to free space reservoir as well as structured reservoir.

For resonant case \( \omega_L = \omega_0 \), we have \( \Delta_{kL} = \Delta_k \) and Eq. 3.104 becomes

\[
\gamma(s, \Omega) = \sum_{k, \lambda} g_{k\lambda} g_{k\lambda}^* \frac{(s + i\Delta_k)}{(s + i\Delta_k)^2 + \Omega^2} - \frac{\Gamma}{2\pi\omega_0^m} \int_0^{\omega_c} \frac{(s + i\Delta)\omega^m d\omega}{(s + i\Delta)^2 + \Omega^2} \quad (3.108)
\]

where \( m = 1 \) for p.A version and \( m = 3 \) for d.E version.

When \( s \) is small, we can use \( \frac{1}{s - i\Delta_k} \to \pi \delta(\Delta_k) + i \frac{\Delta_k}{s} \) and \( \lim_{s \to 0} \frac{\Delta_k}{s} = \Delta_k \) to obtain

\[
\gamma(s, \Omega) \to \frac{\Gamma}{2\pi} \left\{ \left(1 - \frac{\Omega}{\omega_0}\right)^m + \left(1 + \frac{\Omega}{\omega_0}\right)^m \right\} - \frac{\Gamma}{2\pi\omega_0^m} \int_0^{\omega_c} \frac{\Delta^m d\omega}{\Delta^2 - \Omega^2} \quad (3.109)
\]

Equation 3.109 recovers the results of Ref. [252] and with the energy shift. When minimal coupling version is used (\( m=1 \)), the exponential decay rate is independent of laser field since \( \gamma(s, \Omega) \to \frac{\Gamma}{2} \). This result is consistent with Ref. [252] which has also shown the field dependence for the electric quadrupole and magnetic dipole couplings. When the dipole coupling version is used (\( m=3 \)), we can expand \( \Omega \) as a small parameter and obtain the field dependent decay rate \( \gamma(s, \Omega) \to \frac{\Gamma}{2}(1 + 3\frac{\Omega^2}{\omega_0^2}) \) as in Ref. [253]. The field dependent decay rate may be interpreted as due to the light shift of the energy levels. The qualitatively

\footnote{This corresponds to the Markov approximation.}
different results from the two coupling versions is unacceptable. The wrong result from the dipole coupling occur because the states are not transformed. It has been shown that both versions should yield the same result if the states are properly transformed [206]. In the absence of laser field, we set $\Omega \to 0$ and Eq. 3.109 gives the same Wigner-Weisskopf results for both versions ($m=1$ and $m=3$).

### 3.6.2 Modified Spontaneous Emission Rate with Multiple $2\pi$-pulses

Agarwal [246] has shown that repeated application of $2\pi$-pulses can accelerate the decay from an excited state, using the perturbative approach. This motivates for coherent control of spontaneous emission rate. In the following, we present a non-perturbative calculations of the state vector coefficients using iterative solutions of the Schrödinger equation above. In the absence of laser field (or $\omega_0 >> \Omega$), the formal solution of Eq. 3.95 is

$$\bar{\epsilon}_{k\lambda}(\mathbf{P} - \hbar \mathbf{k}, t) = \bar{\epsilon}_{k\lambda}(\mathbf{P} - \hbar \mathbf{k}, t_0) e^{-i \Delta \omega_0 (t - t_0)} + g_{k\lambda}^* \int_{t_0}^t a(\mathbf{P}, t') e^{-i \Delta \omega_0 (t-t')} dt'$$

(3.110)

which is substituted into Eq. 3.94 to give the integro-differential equation

$$\frac{d}{dt} a(\mathbf{P}, t) = - \sum_{k, \lambda} g_{k\lambda} \bar{\epsilon}_{k\lambda}(\mathbf{P} - \hbar \mathbf{k}, t_0) e^{-i \Delta \omega_0 (t-t_0)}$$

$$- \int_{t_0}^t a(\mathbf{P}, t') \sum_{k, \lambda} g_{k\lambda}^* g_{k\lambda} e^{-i \Delta \omega_0 (t-t')} dt$$

(3.111)

The photon mode summation is transformed to integral as derived in Appendix II Eq. 8.55

$$\sum_{k, \lambda} g_{k\lambda} g_{k\lambda} \ldots \to \frac{\Gamma}{2\pi} \sum_{q = 1, -1, 0} C_q C_{-q} \int \! N_q(\theta) d\Omega \int_0^{\omega_c} f(\omega) d\omega \ldots$$

(3.112)

where $f(\omega) = \frac{\omega^3}{\omega_0^4}$ in dipole interaction framework and $\frac{\omega^3}{\omega_0^4}$ in minimal coupling framework, and $\omega_c$ is the cut-off frequency.

By using $\frac{3}{8\pi} \int N_q(\theta) d\Omega = 1$ and $\sum_{q = 1, -1, 0} C_q C_{-q} = 1$, Eq. 3.111 becomes

$$\frac{d}{dt} a(\mathbf{P}, t) = - \int_{t_0}^t F(\tau) a(\mathbf{P}, t - \tau) d\tau - \sum_{k, \lambda} g_{k\lambda} \bar{\epsilon}_{k\lambda}(\mathbf{P} - \hbar \mathbf{k}, t_0) e^{-i \Delta \omega_0 (t-t_0)}$$

(3.113)

where $F(\tau) \approx \sum_{k, \lambda} g_{k\lambda}^* g_{k\lambda} e^{-i \Delta \omega_0 (t-t')} \to \frac{\Gamma}{2\pi} \int_0^{\omega_c} d\omega \frac{\omega^3}{\omega_0^4} e^{-i \Delta \tau}$, $t' = t - \tau$, with $m = 1$ (p.A version) , 3 (d.E version) and $\Gamma \approx \frac{d^2 \omega_0^3}{d\omega_0^3 \delta(\omega)}$ is the free space decay rate. In Markov approximation, $a(t)$ is assumed to vary much slower than $e^{-i \Delta \tau}$ so that it can be taken out of the $\tau$-integration. In the time frame $\Delta t >> 1$, we can use $\lim_{t \to \infty} \int_0^t e^{-i \Delta \tau} d\tau \to \pi \delta(\Delta) + i \frac{\Delta}{\Delta}$
and obtain $\int_0^t F(\tau)d\tau \rightarrow \frac{F}{\pi\hbar} \int_0^\infty d\omega \frac{\sin m}{\omega^m} \{\pi \delta(\Delta) + i \frac{\hbar}{m}\}$. The solutions for the coefficients of the state vector are

$$a(P, t) = a(P, t_0)e^{-\frac{\pi i}{\hbar}(t-t_0)} - \sum_{k, \lambda} g_{k\lambda}^* b_{k\lambda}(P-\hbar k, t_0) \frac{e^{-i \Delta \omega \alpha t} (e^{\Gamma t} - e^{-\Gamma t})}{C_{k\lambda}} \tag{3.114}$$

$$b_{k\lambda}(P-\hbar k, t) = \tilde{b}_{k\lambda}(P-\hbar k, t_0)e^{-i \Delta \omega \alpha t} + a(P, t_0) \frac{g_{k\lambda}^* e^{-i \Delta \omega \alpha t} e^{\Gamma t} - e^{-\Gamma t}}{C_{k\lambda}} \tag{3.115}$$

$$b_{k\lambda}(P-\hbar k, t) = b_{k\lambda}(P-\hbar k, t_0) + g_{k\lambda}^* a(P, t_0) \frac{e^{\frac{\pi i}{\hbar} t} (e^{\Gamma t} - e^{-\Gamma t})}{C_{k\lambda}} \tag{3.116}$$

where $C_{k\lambda} = (i \Delta \omega - \frac{\Gamma}{2})$, $\Delta = \frac{\pi \hbar}{\Gamma} \int_0^\infty \omega^m d\omega$ and $\Gamma' = \Gamma + i \Lambda$. The level shift $\Lambda$ can be absorbed into $\Delta_{k\lambda}$. So, we can write $C_{k\lambda} = (i \Delta_{k\lambda} - \frac{\Gamma}{2})$.

When the ground state is initially empty, $b_{k\lambda} = 0$ and from Eqs. 3.114 and 3.116, we can obtain the density matrix elements from the pure state $\hat{\rho}(t) = \langle \Psi(P, t) \rangle \langle \Psi(P, t) \rangle$. The four matrix elements are:

$$\rho_{ee}(P, t) = |a(P, t_0)|^2 = e^{-\Gamma(t-t_0)} \tag{3.117}$$

$$\rho_{gg}(P, t) = \sum_{k\lambda} [b_{k\lambda}(P-\hbar k, t_0)]^2 = \rho_{ee}(P, t_0) \sum_{k\lambda} |g_{k\lambda}|^2 \frac{e^{\frac{\pi i}{\hbar} t} (e^{\Gamma t} - e^{-\Gamma t})}{C_{k\lambda}} \tag{3.118}$$

$$\rho_{ge}(P, t) = \sum_{k\lambda} b_{k\lambda}(P-\hbar k, t) a^*(P, t) = |a(P, t_0)|^2 e^{-\frac{\pi i}{\hbar} t} e^{\Gamma t} \sum_{k, \lambda} g_{k\lambda}^* (e^{\Gamma t} - e^{-\Gamma t}) \tag{3.119}$$

where we have defined $\rho_{ee}(P, t_0) \doteq |a(P, t_0)|^2$, and $\rho_{gg}(P, t_0) \doteq \sum_{k\lambda} [b_{k\lambda}(P-\hbar k, t_0)]^2$. From Eq. 3.119, we see that $\rho_{ge}(P, t_0) = 0$. From the forthcoming Eq. 4.30, we have $\rho_{ge}(P, t) = 0$. So, $\sum_{k, \lambda} g_{k\lambda}^* (e^{\Gamma t} - e^{-\Gamma t})$ in Eq. 3.119 must vanish in the frequency integration. It involves the functions $\int_0^\infty \sin(\omega - \omega_0) \omega^3/2 d\omega$ and $\int_0^\infty \cos(\omega - \omega_0) \omega^3/2 d\omega$ for a version of $g_{k\lambda}^*$. Since $\frac{\cos(\omega - \omega_0)}{\sin(\omega - \omega_0)} \omega^3/2$ is nearly an odd function around $\omega_0$ and rapidly vanishes away from $\omega_0$, its integral is essentially zero for large time. The $\sin(\omega - \omega_0) \omega^3/2$ oscillates rapidly for large $t$ with increasing amplitudes as $\omega$ increases, thus averaging to zero.

By using $Tr\{\rho(t)\} = 1$ and $\int d^3 P \rho_{ee}(P, t_0) + \rho_{gg}(P-\hbar k, t_0) = 1$, we find

$$\sum_{k, \lambda} |g_{k\lambda}|^2 \{e^{-\Gamma(t-t_0)} + 1 - 2e^{-\frac{\pi i}{\hbar} t} \cos \Delta_{k\lambda}(t-t_0)\} \Delta_{k\lambda} + (\frac{\Gamma t}{2})^2 = 1 - e^{-\Gamma(t-t_0)} \tag{3.120}$$

This enables Eq. 3.118 to be simplified into $\rho_{gg}(P-\hbar k, t) = \rho_{gg}(P-\hbar k, t_0) + \rho_{ee}(P, t_0)(1 - e^{-\Gamma(t-t_0)})$ which agrees with Eq. 4.30 for $\hbar = 0$ (absolute zero vacuum reservoir).

We shall proceed with the $V-$scheme (where $E_e, E_r > E_g$) and applying multiple $2\pi$-pulses between the state $|g\rangle$ and a third state $|r\rangle$ to calculate the decay probability. The
effect of $2\pi$-pulse ($\Omega t = 2\pi$) is to flip the coefficients $b$ and $c$ of states $|g\rangle$ and state $|r\rangle$ respectively from positive to negative. This is shown in Eq. 8.108 in Appendix IV. Thus, the full unitary operation after the application of $2\pi$-pulse is

$$\hat{U}(t) = |e\rangle\langle e| \otimes e^{i\Omega(t)}|g\rangle\langle g| |r\rangle$$

(3.121)

This gives

$$\begin{pmatrix}
a(P, NT^+)
\hline
b(P-hk, NT^+)
\hline
c(P-hk, NT^+)
\end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\
0 & -1 & 0 \\
0 & 0 & -1 \end{pmatrix} \begin{pmatrix}
a(P, NT^-) \\
b(P-hk, NT^-) \\
c(P-hk, NT^-) \\
\end{pmatrix} = \begin{pmatrix} a(P, NT^-) \\
-b(P-hk, NT^-) \\
-c(P-hk, NT^-) \end{pmatrix}$$

Let $T$ be the period between the pulses, with $\tau = T^+ - T^-$ as the duration of each pulse, much shorter than the period such that we can take $T^+ \simeq T^- = T$. During the first period of free decay, we set $t_0 = 0, t = T^-$ in Eqs 3.114 and 3.116 and obtain

$$a(P, T^-) = a(P, 0)e^{\frac{-i\omega}{\tau} T^-}$$

(3.122)

$$b_{k\lambda}(P-hk, T^-) = b_{k\lambda}(P-hk, 0) + a(P, 0)\frac{g_{k\lambda}^*}{C_{k\lambda}}(e^{C_{k\lambda} T^-} - 1)$$

(3.123)

The first $2\pi$-pulse is applied from $T^- \rightarrow T^+$, and we have

$$a(P, T^+) = a(P, T^-)e^{\frac{-i\omega}{\tau} T^+}$$

(3.124)

$$b_{k\lambda}(P-hk, T^+) = -b_{k\lambda}(P-hk, T^-)$$

(3.125)

The second period of free decay from $t_0 = T^+$ to $t = 2T^-$ gives

$$a(P, 2T^-) = a(P, T^+)e^{\frac{-i\omega}{\tau}(2T^- - T^+)} = a(P, 0)e^{-\frac{i\omega}{\tau}2T^-}$$

(3.126)

$$b_{k\lambda}(P-hk, 2T^-) = -b_{k\lambda}(P-hk, 0) + a(P, 0)\frac{g_{k\lambda}^*}{C_{k\lambda}}\{(e^{C_{k\lambda} 2T^-} - e^{C_{k\lambda} T^+}) - (e^{C_{k\lambda} T^-} - 1)\} \simeq -b_{k\lambda}(P-hk, 0) + a(P, 0)\frac{g_{k\lambda}^*}{C_{k\lambda}}(e^{C_{k\lambda} T} - 1)(e^{C_{k\lambda} T} - 1)$$

(3.127)

The second $2\pi$-pulse from $t_0 = 2T^- \rightarrow t = 2T^+$ leads to

$$a(P, 2T^+) = a(P, 0)e^{-\frac{i\omega}{\tau}2T^+}$$

(3.128)

$$b_{k\lambda}(P-hk, 2T^+) = -b_{k\lambda}(P-hk, 2T^-)$$

(3.129)

\footnote{In the following, we suppress the momentum dependence to shorten the equations whenever necessary.}

$$b_{k\lambda}(NT^-) = b_{k\lambda}((N-1)T^+) + a(0)\frac{g_{k\lambda}^*}{C_{k\lambda}}(e^{C_{k\lambda} T} - 1)\langle e^{C_{k\lambda} (N-1)T} \rangle$$

(3.130)

$$b_{k\lambda}(NT^+) = -b_{k\lambda}(NT^-)$$

(3.131)
For even $N = 2M$, the iterations of Eqs. 3.130 and 3.131 give

$$b_{k\lambda}(NT^-) = -b_{k\lambda}(0) - \frac{a(0)\xi_{k\lambda}}{C_{k\lambda}} \left(-e^{C_{k\lambda}(N-1)T} + e^{C_{k\lambda}(N-2)T} + \cdots + e^{C_{k\lambda}2T} - e^{C_{k\lambda}T} + 1\right)\left(e^{C_{k\lambda}T} - 1\right)$$

(3.132)

By using $e^{C_{k\lambda}(M-1)2T} + e^{C_{k\lambda}4T} + e^{C_{k\lambda}2T} + 1 = \frac{1-e^{M2C_{k\lambda}T}}{1-e^{C_{k\lambda}T}}$ we have

$$b_{k\lambda}(NT^-) = -b_{k\lambda}(0) - \frac{a(0)\xi_{k\lambda}}{C_{k\lambda}} \frac{(e^{C_{k\lambda}T} - 1)}{(e^{C_{k\lambda}T} + 1)}\left(1 - e^{NC_{k\lambda}T}\right)$$

(3.133)

For odd $N = 2M + 1$, the coefficient becomes

$$b_{k\lambda}(NT^-) = b_{k\lambda}(0) + \frac{a(0)\xi_{k\lambda}}{C_{k\lambda}} \left(\frac{e^{C_{k\lambda}(N-1)T} - e^{C_{k\lambda}(N-2)T} - \cdots - e^{C_{k\lambda}T} - e^{C_{k\lambda}T} + 1}{e^{C_{k\lambda}T} + 1}\right)$$

(3.134)

By using $(C_{k\lambda}(N-1)T) + e^{C_{k\lambda}(N-2)T} + e^{C_{k\lambda}T} = e^{C_{k\lambda}T} \frac{1-e^{M2C_{k\lambda}T}}{1-e^{C_{k\lambda}T}} + e^{C_{k\lambda}T}$ we have

$$b_{k\lambda}(NT^-) = b_{k\lambda}(0) + \left(\frac{a(0)\xi_{k\lambda}}{C_{k\lambda}} \frac{(e^{C_{k\lambda}T} - 1)}{(e^{C_{k\lambda}T} + 1)}\left(1 + e^{NC_{k\lambda}T}\right)\right)$$

(3.135)

The transient coefficient at time $t$ just after $NT^+$ for even and odd $N$ are respectively

$$b_{k\lambda}(t) = b_{k\lambda}(0) + \frac{a(0)\xi_{k\lambda}}{C_{k\lambda}} \left(\frac{(e^{C_{k\lambda}T} - 1)}{(e^{C_{k\lambda}T} + 1)}\left(1 - e^{NC_{k\lambda}T}\right)\right)$$

(3.136)

$$b_{k\lambda}(t) = -b_{k\lambda}(0) + \frac{a(0)\xi_{k\lambda}}{C_{k\lambda}} \left(\frac{(e^{C_{k\lambda}T} - 1)}{(e^{C_{k\lambda}T} + 1)}\left(1 + e^{NC_{k\lambda}T}\right)\right)$$

(3.137)

If initially, the ground state is empty, $b_{k\lambda}(0) = 0$ and the probability in ground state with the photon mode $k\lambda$ is

$$|b_{k\lambda}(NT^+)|^2 = |a(\mathbf{P})|^2 \left|\frac{\xi_{k\lambda}}{C_{k\lambda}} \left(e^{C_{k\lambda}T} - 1\right)\right|^2 \frac{\Gamma(2NT)}{2} + \cos \Delta_{k\lambda} NT$$

(3.138)

$$F_{k\lambda} = \frac{\sinh^2 \frac{\Gamma}{2} T + \sinh \frac{\Gamma}{2} \Delta_{k\lambda} T}{\sinh^2 \frac{\Gamma}{2} T + \sinh \frac{\Gamma}{2} \Delta_{k\lambda} T}$$

(3.139)

where we have used $(e^{(i\Delta_{k\lambda} - \frac{\Gamma}{2})T} \pm 1)(e^{(-i\Delta_{k\lambda} - \frac{\Gamma}{2})T} \pm 1)e^{\frac{\Gamma}{2} T} = e^{-\frac{\Gamma}{2} T} \pm 2 \Delta_{k\lambda} T$ and $e^{\frac{\Gamma}{2} T} = 2 \cosh \frac{\Gamma}{2} T \pm 2 \cos \Delta_{k\lambda} T$. The term $F_{k\lambda}$ modifies the decay rate. The term in the braces ( ) of Eq. 3.138 can be rewritten as $(\sinh \frac{\Gamma}{4} NT \pm \sinh \frac{1}{2} \Delta_{k\lambda} NT)$ for even $N$ and $(\sinh \frac{\Gamma}{4} NT \pm \sinh \frac{1}{2} \Delta_{k\lambda} NT)$ for odd $N$. 


\[ \cos^2 \frac{\Delta_{\lambda} N T}{2} \] for odd \( N \). Hence, the probability in ground state is obtained by tracing over all photon modes

\[
\rho_{gg}(P - \hbar k, N T^+) = \rho_{ee}(P, 0) \sum_{k, \lambda} 4 \frac{F_{k \lambda} \gamma_{k \lambda}^2}{\Delta_{k \lambda}^2 + (\frac{1}{2})^2} e^{\frac{-\Delta_{k \lambda} NT}{2}} \left\{ \sinh^2 \frac{\Gamma}{4} N T + \frac{\sin^2 \frac{\Delta_{\lambda} N T}{2} \cos^2 \frac{\Delta_{\lambda} N T}{2}}{\cos^2 \frac{\Delta_{\lambda} N T}{2}} \right\}
\]

(3.140)

where \( \rho_{ee}(P, 0) \equiv |a(P)|^2 \).

By converting the mode to continuous summation using Eq. 8.55, and using the spectral response \( \zeta(\omega) = (1 + (\omega / \omega_c)^2)^4 \) given by Moses [203] for free space to obtain convergence, we can rewrite Eq. 3.140 as

\[
\rho_{gg}(P - \hbar k, N T^+) = \rho_{ee}(P, 0) \frac{\Gamma}{2\pi} \int_0^{\omega_c} \frac{\omega^m}{\omega_0^m} \frac{4F_{k \lambda} e^{\frac{-\Delta_{k \lambda} NT}{2}}}{\Delta_{k \lambda}^2 + (\frac{1}{2})^2} \left\{ \sinh^2 \frac{N \Gamma T}{4} + \left( \frac{\sin^2 \frac{\Delta_{\lambda} N T}{2} \cos^2 \frac{\Delta_{\lambda} N T}{2}}{\cos^2 \frac{\Delta_{\lambda} N T}{2}} \right) \right\} d\omega
\]

(3.141)

where \( \omega_c \sim c / a_B \sim 10^{10} \text{s}^{-1} \) is the cutoff-frequency, and \( a_B \) is the Bohr radius, with \( m = 1, 3 \).

The above results are obtained in Markov approximation during the free decaying stage. On overall, it is a non-Markovian effect since the iterations are accumulated from all past histories. The summation over all radiation modes is done after accumulating the 2\( \pi \)-pulses flipping effects from all previous times on the ground state coefficient \( b_{k \lambda} \). The period of the pulses \( T \) should be longer than \( \omega_c^{-1} \) such that the Markovian approximation applies.

In the absence of the pulses, Eq. 3.116 gives the free decay results

\[
b_{k \lambda}(P - \hbar k, N T) = b_{k \lambda}(P - \hbar k, 0) + a(P, 0) \frac{\gamma_{k \lambda}}{C_{k \lambda}} (e^{C_{k \lambda} N T} - 1)
\]

(3.142)

\[
\rho_{gg}(P - \hbar k, N T) = \rho_{ee}(P, 0) \sum_{k, \lambda} \frac{|\gamma_{k \lambda}|^2 (1 + e^{-\frac{\Delta_{k \lambda} NT}{2}} - 2e^{-\frac{\Delta_{k \lambda} NT}{2}} \cos \frac{\Delta_{k \lambda} NT}{2})}{\Delta_{k \lambda}^2 + (\frac{1}{2})^2}
\]

(3.143)

and from Eq. 3.120, we see that Eq. 3.143 is exactly the free decay solution \( \rho_{gg}(P - \hbar k, N T) = \rho_{ee}(P, 0)(1 - e^{-\Gamma NT}) \) and it is identical to Eq. 3.141 but without the factor \( F_{k \lambda} \).

### 3.7 Master Equation for Multilevels Without Driving Fields

In this Section, we use Eq. 3.38 to obtain the dissipative Liouvillean for a multilevel system coupled to thermal radiation field in the absence of driving fields. The results are used to describe the fluorescence of a molecule undergoing spontaneous emissions from a single excited electronic state to the ground rovibrational states. By setting
\[ U_2(t', t) \rightarrow I, X_{kj}(t, t') \rightarrow S_{kj}(t'), W_{SR1}(t, t') \rightarrow V_{SR1}(t') \] in Eq. 3.38 and using Eq. 8.26 with the transition involving a pair of states \(|\alpha\rangle \leftrightarrow |\beta\rangle\) being represented by the index \(i\) or \(j\), we obtain the master equation with quantized c.m. momentum variable after lengthy but straightforward calculations

\[
L\hat{\rho}(t) = \int_0^t d\tau \sum_{i,j,k,P',P''} g_{ik}g_{j} f_{i,j,k,P',P''}(t, \tau)
\]

(3.144)

where \( f_{i,j,k}(t, \tau) = \)

\[-\{(\mathcal{P}_k + 1)e^{i\omega_{k}\tau} + \mathcal{P}_k e^{-i\omega_{k}\tau}\} \times
\]

\[
(e^{-i\omega_{i}\tau} e^{-i\omega_{i}\tau} S_j S_j + e^{i\omega_{i}\tau} e^{-i\omega_{i}\tau} S_j S_j + S_j S_j e^{i\omega_{i}\tau} e^{-i\omega_{i}\tau} + S_j S_j e^{-i\omega_{i}\tau} e^{i\omega_{i}\tau})|P\rangle\langle P'\rangle |\hat{\rho}(t)\rangle
\]

\[
+ \mathcal{P}_k e^{-i\omega_{k}\tau} e^{i\omega_{i}\tau} t \times
\]

\[
\{S_j S_j S_j S_j e^{i\omega_{i}\tau} e^{-i\omega_{i}\tau} + S_j S_j S_j S_j e^{-i\omega_{i}\tau} e^{i\omega_{i}\tau} + S_j S_j S_j S_j e^{i\omega_{i}\tau} e^{-i\omega_{i}\tau} + S_j S_j S_j S_j e^{-i\omega_{i}\tau} e^{i\omega_{i}\tau}\}
\]

(3.145)

and the Hermitian conjugate \(H.c. = \)

\[-\{(\mathcal{P}_k + 1)e^{i\omega_{k}\tau} + \mathcal{P}_k e^{-i\omega_{k}\tau}\} \times
\]

\[
\hat{\rho}(t)|P\rangle\langle P'|\langle S_j S_j S_j S_j e^{i\omega_{i}\tau} e^{-i\omega_{i}\tau} + S_j S_j S_j S_j e^{-i\omega_{i}\tau} e^{i\omega_{i}\tau} + S_j S_j S_j S_j e^{i\omega_{i}\tau} e^{-i\omega_{i}\tau} + S_j S_j S_j S_j e^{-i\omega_{i}\tau} e^{i\omega_{i}\tau}\}
\]

\[
+ \mathcal{P}_k e^{i\omega_{k}\tau} e^{-i\omega_{i}\tau} t \times
\]

\[
\{S_j S_j S_j S_j e^{i\omega_{i}\tau} e^{-i\omega_{i}\tau} + S_j S_j S_j S_j e^{-i\omega_{i}\tau} e^{i\omega_{i}\tau} + S_j S_j S_j S_j e^{i\omega_{i}\tau} e^{-i\omega_{i}\tau} + S_j S_j S_j S_j e^{-i\omega_{i}\tau} e^{i\omega_{i}\tau}\}
\]

(3.145)

where \( \hat{\rho}(t)|P\rangle\langle P'|\langle H.c. = \)

\[
\hat{\rho}(t)|P\rangle\langle P'|\langle S_j S_j S_j S_j e^{i\omega_{i}\tau} e^{-i\omega_{i}\tau} + S_j S_j S_j S_j e^{-i\omega_{i}\tau} e^{i\omega_{i}\tau} + S_j S_j S_j S_j e^{i\omega_{i}\tau} e^{-i\omega_{i}\tau} + S_j S_j S_j S_j e^{-i\omega_{i}\tau} e^{i\omega_{i}\tau}\}
\]

(3.145)

3.7.1 Secular and Rotating Wave Approximations

Equation 3.145 is essentially an exact master equation describing the dissipation of a multilevel system. Subsequently, we neglect the rapidly oscillating terms \( e^{i\omega_{i}\tau} e^{i\omega_{i}\tau} \) for timescale \( \omega_{i}\tau >> 1 \) under the secular approximation and the Liouvillian becomes
\[ F_{i,j,k}(t, \tau) = -\{(\Omega_{\text{LW}} + 1)e^{-i\omega_{\text{LW}} t} + \Omega_{\text{LW}} e^{i\omega_{\text{LW}} t}\} \times \]

\[ (e^{-i\omega_{\text{adj}} t} e^{-i\omega_{\text{adj}} t} S_i S_j^+ + e^{i\omega_{\text{adj}} t} e^{i\omega_{\text{adj}} t} S_i^+ S_j^+) |P'| \langle P'| \bar{\rho}_S(t - \tau) \]

\[ + \Omega_{\text{LW}} e^{-i\omega_{\text{LW}} t} e^{i\omega_{\text{LW}} (t - \tau)} \times \]

\[ (\bar{\rho}_S|P'_{-h} h\rangle S_i^+ e^{-i\omega_{\text{adj}} t} + \bar{\rho}_S|P'_{+h} h\rangle S_i e^{i\omega_{\text{adj}} t} e^{-i\omega_{\text{adj}} t} \rangle \]

\[ + (\Omega_{\text{LW}} + 1) e^{i\omega_{\text{LW}} t} e^{i\omega_{\text{LW}} (t - \tau)} \times \]

\[ (\bar{\rho}_S|P'_{+h} h\rangle S_i^+ e^{-i\omega_{\text{adj}} t} + \bar{\rho}_S|P'_{+h} h\rangle S_i e^{i\omega_{\text{adj}} t} e^{-i\omega_{\text{adj}} t} \rangle \]

\[ - \{(\Omega_{\text{LW}} + 1)e^{-i\omega_{\text{LW}} t} e^{i\omega_{\text{LW}} t} \} \times \]

\[ \bar{\rho}_S(t - \tau) |P'| \langle S_j S_i^+ e^{i\omega_{\text{adj}} t} e^{i\omega_{\text{adj}} t} S_j^+ S_i^+ |P'| \bar{\rho}_S \]

\[ + \Omega_{\text{LW}} e^{i\omega_{\text{LW}} t} e^{i\omega_{\text{LW}} (t - \tau)} \times \]

\[ (\bar{\rho}_S|P'_{-h} h\rangle S_i e^{-i\omega_{\text{adj}} t} + \bar{\rho}_S|P'_{+h} h\rangle S_i e^{i\omega_{\text{adj}} t} e^{-i\omega_{\text{adj}} t} \rangle \]

\[ + (\Omega_{\text{LW}} + 1) e^{i\omega_{\text{LW}} t} e^{i\omega_{\text{LW}} (t - \tau)} \times \]

\[ (\bar{\rho}_S|P'_{+h} h\rangle S_i e^{-i\omega_{\text{adj}} t} + \bar{\rho}_S|P'_{+h} h\rangle S_i e^{i\omega_{\text{adj}} t} e^{-i\omega_{\text{adj}} t} \rangle \]

(3.146)

The terms \( e^{i\omega_{\text{adj}} t} \) only contribute to the radiative level shift and can be absorbed by renormalizing the energy levels. For simplicity, we neglect these terms under rotating wave approximation and obtain

\[ F_{i,j,k}(t, \tau) = -\{(\Omega_{\text{LW}} + 1)e^{-i\Delta_{\text{adj}} t} e^{i\omega_{\text{adj}} t} S_i S_j^+ |P'| \langle P'| \bar{\rho}_S + \Omega_{\text{LW}} e^{i\Delta_{\text{adj}} t} e^{-i\omega_{\text{adj}} t} S_i S_j^+ |P'| \bar{\rho}_S \}

\[ + \Omega_{\text{LW}} e^{i\omega_{\text{adj}} t} e^{i\omega_{\text{adj}} (t - \tau)} \times \]

\[ (\bar{\rho}_S|P'_{-h} h\rangle S_i^+ e^{-i\omega_{\text{adj}} t} + \bar{\rho}_S|P'_{+h} h\rangle S_i e^{i\omega_{\text{adj}} t} e^{-i\omega_{\text{adj}} t} \rangle \]

\[ + (\Omega_{\text{LW}} + 1) e^{i\omega_{\text{adj}} t} e^{i\omega_{\text{adj}} (t - \tau)} \times \]

\[ (\bar{\rho}_S|P'_{+h} h\rangle S_i e^{-i\omega_{\text{adj}} t} + \bar{\rho}_S|P'_{+h} h\rangle S_i e^{i\omega_{\text{adj}} t} e^{-i\omega_{\text{adj}} t} \rangle \]

\[ - \{(\Omega_{\text{LW}} + 1)\rho_{S}^{i\text{P}}|P'| S_j^+ S_i e^{-i\omega_{\text{adj}} t} e^{i\Delta_{\text{adj}} t} + \Omega_{\text{LW}} \rho_{S}^{i\text{P}}|P'| S_j S_i^+ e^{i\omega_{\text{adj}} t} e^{-i\Delta_{\text{adj}} t} \}

\[ + \Omega_{\text{LW}} e^{i\Delta_{\text{adj}} t} e^{i\omega_{\text{adj}} (t - \tau)} \times \]

\[ (\bar{\rho}_S|P'_{-h} h\rangle S_i^+ e^{i\omega_{\text{adj}} t} + \bar{\rho}_S|P'_{+h} h\rangle S_i e^{-i\omega_{\text{adj}} t} e^{i\omega_{\text{adj}} t} \rangle \]

\[ + (\Omega_{\text{LW}} + 1) e^{-i\Delta_{\text{adj}} t} e^{i\omega_{\text{adj}} (t - \tau)} \times \]

\[ e^{-i\omega_{\text{adj}} t} r \rangle S_i^+ S_j e^{i\omega_{\text{adj}} t} \rangle \]

(3.147)

where \( \Delta_{\text{adj}}^{\pm} = \omega_{\text{adj}} - \omega_{\text{adj}} \). The time dependent exponential terms \( e^{i\omega_{\text{adj}} t} \) gives the slow transient modulation or quantum beat of the spontaneous emission dynamics for small levels spacings \( \omega_{\text{adj}} = \omega_{\text{adj}} - \omega_{\text{adj}} \).

In the semiclassical regime, the \( h\hbar \) term is neglected by assuming \( h\hbar \ll P \) or setting \( \hbar \to 0 \). Then the exponential \( \exp\{i(\omega_{\text{LW}} - \omega_{\text{LW}})t\} \) averages to zero for timescale much greater than \( |\omega_{\text{LW}} - \omega_{\text{LW}}|^{-1} \) unless \( P' = P'' \) and we can set \( \sum_{P', P''} |\rho_{S}^{i\text{P}}(P', P'') \approx \sum_{P, P''} |P'\rangle \langle P'| \rho_{S} |P''\rangle \langle P''| \delta_{P', P''} \to \rho_{S} \). In the microwave or infrared regime, we can also neglect the Doppler shift compared to the transition frequency and set \( \Delta^{+}_{\text{adj}} \to \Delta \).
The dissipative Liouville equation becomes

\[
\mathcal{L}\tilde{\rho}_{S}(t) = \left\{ (\kappa_{\pi}^+ + \kappa_{\pi}^-) e^{i\omega_{\text{od}} t} S_j^+ \tilde{\rho}_{S} + \kappa_{\pi} e^{-i\omega_{\text{od}} t} S_i S_j^+ \tilde{\rho}_{S} \right\}
\]

\[
- \left\{ (\kappa_{\pi} + \kappa_{o}) \tilde{\rho}_{S} S_j^+ S_i e^{-i\omega_{\text{od}} t} + \kappa_{\pi}^2 \tilde{\rho}_{S} S_j S_i^+ e^{i\omega_{\text{od}} t} \right\}
\]

\[
+ \left\{ \kappa_{\pi}^+ S_j^+ \tilde{\rho}_{S} S_i e^{i\omega_{\text{od}} t} + (\kappa_{\pi} + \kappa_{o}) \tilde{\rho}_{S} S_i S_j^+ e^{i\omega_{\text{od}} t} \right\}
\]

\[
+ \left\{ \kappa_{\pi}^+ S_j \tilde{\rho}_{S} S_i e^{-i\omega_{\text{od}} t} + (\kappa_{\pi}^2 + \kappa_{\pi}^+ \kappa_{o}) \tilde{\rho}_{S} S_i S_j^+ e^{i\omega_{\text{od}} t} \right\}
\]

(3.148)

where \(\kappa_{\pi} \equiv \sum_{i,j,k} g_{ik} g_{jk} \tau_{ik} \int_{0}^{\Delta} d\tau e^{i\Delta_{ij}\tau}\) and \(\kappa_{o} \equiv \sum_{i,j,k} g_{ik} g_{jk} \int_{0}^{\Delta} d\tau e^{i\Delta_{ij}\tau}\).

### 3.7.2 Decay from Single Excited State–Fluorescence

For a system with one excited state \(|\tilde{\eta}\rangle\) and \(n\) dipole allowed ground states \(|\tilde{i}\rangle\), \(i = 1, 2, \ldots, n\), we replace \(S_{i} = |\tilde{i}\rangle\langle\tilde{\eta}|\) and obtain

\[
\mathcal{F}_{i,j,k}(t, \tau) = \left\{ (\tau_{ik} + 1) e^{-i\Delta_{jk}\tau} e^{-i\omega_{\text{od}} \tau} e^{-i\omega_{\text{od}} \tau} \right\}
\]

\[
\left\{ \kappa_{\pi} e^{i\Delta_{jk}\tau} e^{-i\omega_{\text{od}} \tau} \right\}
\]

\[
\left\{ \kappa_{i} \right\}
\]

\[
\left\{ \kappa_{o} \right\}
\]

(3.149)

By taking the matrix elements of Eqs. 3.149 and 3.144, we obtain the populations

\[
\frac{\partial \rho_{\text{ce}}(P, t)}{\partial t} = \left\{ \sum_{i,k} |g_{ik}|^2 (\tau_{ik} + 1) \int_{0}^{\Delta} d\tau \cos \Delta_{i,k}\tau \rho_{\text{ce}}(P, t - \tau) \right\}
\]

\[
+ \sum_{j,k} g_{ik} g_{jk} \tau_{ik} \rho_{ij}(P - \hbar k, t - \tau) e^{i\omega_{\text{od}} \tau} \int_{0}^{\Delta} d\tau (e^{-i\Delta_{jk}\tau} + e^{i\Delta_{jk}\tau})
\]

(3.150)

\[
\frac{\partial \rho_{\text{gg}}(P, t)}{\partial t} = \left\{ \sum_{j,k} g_{ik} g_{jk} \tau_{ik} \int_{0}^{\Delta} d\tau \left\{ e^{i\Delta_{jk}\tau} e^{i\omega_{\text{od}} \tau} \rho_{ij}(P, t - \tau) + \rho_{ij}(P, t - \tau) e^{i\omega_{\text{od}} \tau} \right\}
\right\}
\]

\[
+ \sum_{j,k} |g_{ik}|^2 (\tau_{ik} + 1) \int_{0}^{\Delta} d\tau \cos \Delta_{i,k}\tau \rho_{\text{ce}}(P + \hbar k, t - \tau)
\]

(3.151)
and the coherences

\[
\frac{\partial \rho_{gg}(P,t)}{\partial t} = -\sum_{j,k} \int_{0}^{t} d\tau \{ g_{jk} g_{jk} \bar{n}_{k} e^{i \Delta_{jk} P \tau} e^{-i \omega_{0j} t} \rho_{jg}(P,t-\tau) + \sum_{j,k} \int_{0}^{t} d\tau g_{jk} g_{jk} \bar{n}_{k} e^{-i \Delta_{jk} P \tau} e^{i \omega_{0j} t} \rho_{jg}(P,t-\tau) \} + \sum_{j,k} g_{jk} g_{jk} \int_{0}^{t} d\tau (\bar{n}_{k} + 1) \rho_{cc}(P + \hbar k,t-\tau) \{ e^{i \Delta_{jk} P \tau} e^{-i \omega_{0j} t} + e^{-i \Delta_{jk} P \tau} e^{i \omega_{0j} t} \} \]

(3.152)

\[
\frac{\partial \rho_{eg}(P,t)}{\partial t} = -\sum_{j,k} |g_{jk}|^{2} \int_{0}^{t} d\tau (\bar{n}_{k} + 1) e^{-i \Delta_{jk} P \tau} \rho_{eg}(P,t-\tau) - \sum_{j,k} g_{jk} g_{jk} \int_{0}^{t} d\tau \bar{n}_{k} \rho_{eg}(P,t-\tau) e^{i \omega_{0j} t} e^{-i \Delta_{jk} P \tau} \]

(3.153)

For more than one ground states, the non-vanishing terms of \( g_{jk} g_{jk} \) for \( j \neq i \) give rise to quantum interferences between the ground levels if the dipole moments are non-orthogonal [243],[244]. The quantum coherence is due to the interference of the decaying channels, termed as spontaneously generated coherence (SGC). The decay dynamics are shown to be slower in the presence of interference between the decaying channels [242].

### 3.7.3 Spontaneously Generated Coherences for \( \Lambda \) System

For two ground levels, the system becomes a three level \( \Lambda \) scheme \( |e\rangle, |1\rangle, |2\rangle \). By neglecting the Doppler and recoil shifts, Eqs. 3.150-3.153 reduce to

\[
\frac{\partial \rho_{ee}(t)}{\partial t} = \sum_{i=1,2} \{ \Gamma_{0,i} \bar{n}_{0,i} \rho_{ii}(t) - \Gamma_{0,i} (\bar{n}_{0,i} + 1) \rho_{ee}(t) \} + \frac{(\Gamma_{1,02} \bar{n}_{0,2} + \Gamma_{2,01} \bar{n}_{0,1})}{2} \{ \rho_{12}(t) e^{i \omega_{012} t} + \rho_{21}(t) e^{-i \omega_{012} t} \}
\]

\[
\frac{\partial \rho_{11}(t)}{\partial t} = -\Gamma_{0,1} \bar{n}_{0,1} \rho_{11}(t) + \Gamma_{0,1} (\bar{n}_{0,1} + 1) \rho_{ee}(t) - \frac{\Gamma_{1,02} \bar{n}_{0,2}}{2} \{ e^{-i \omega_{012} t} \rho_{21}(t) + \rho_{12}(t) e^{i \omega_{012} t} \}
\]

\[
\frac{\partial \rho_{12}(t)}{\partial t} = -\frac{\Gamma_{0,1} \bar{n}_{0,1}}{2} \rho_{12}(t) - \frac{\Gamma_{1,02} \bar{n}_{0,2}}{2} e^{-i \omega_{012} t} \rho_{22}(t) - \frac{\Gamma_{2,01}}{2} \rho_{12}(t) - \frac{\Gamma_{0,2} \bar{n}_{0,2}}{2} (e^{-i \omega_{012} t} - e^{i \omega_{012} t})
\]

(3.154)

where \( \Gamma_{i,j} \equiv 2\pi \sum_{k} g_{ik} g_{jk} \delta(\omega - \omega_{oj}) \), \( \Gamma_{ii} \equiv 2\pi \sum_{k} |g_{ik}|^{2} \delta(\omega - \omega_{0i}) \), \( \bar{n}_{0i} \equiv (e^{\hbar \omega_{0i}/kBT} - 1)^{-1} \)

and \( \omega_{0i} = (E_{e} - E_{i})/\hbar \) with \( i,j = 1,2 \). For \( \bar{n}_{0i} = 0 \), Eqs. 3.154 are greatly simplified as
\[
\frac{\partial \rho_{e\alpha}(t)}{\partial t} = -\rho_{ee}(t) \sum_{i=1,2} \Gamma_{\alpha}^i \\
\frac{\partial \rho_{11}(t)}{\partial t} = \Gamma_{\alpha} \rho_{ee}(t) \\
\frac{\partial \rho_{12}(t)}{\partial t} = \frac{1}{2} \rho_{ee}(t) \left\{ \Gamma_{1,\alpha} e^{-i\omega_{\alpha 2} t} + \Gamma_{2,\alpha} e^{i\omega_{\alpha 2} t} \right\} \\
\frac{\partial \rho_{e1}(t)}{\partial t} = -\rho_{e1}(t) \frac{1}{2} \left( \Gamma_{1,\beta} + \Gamma_{2,\beta} \right) \\
\frac{\partial \rho_{e2}(t)}{\partial t} = -\rho_{e2}(t) \frac{1}{2} \left( \Gamma_{2,\alpha} + \Gamma_{3,\alpha} \right)
\]

(3.155)

The excited-ground coherence is also dependent on the decay rate to other ground state as shown from the last 2 equations. The time dependent solutions of Eqs. 3.155 are easily obtained as

\[
\rho_{ee}(t) = \rho_{ee}(0) e^{-\left(\Gamma_{\alpha} + \Gamma_{\beta}\right)t} \\
\rho_{11}(t) = \rho_{11}(0) + \Gamma_{\alpha} \rho_{ee}(0) \frac{1 - e^{-\left(\Gamma_{\alpha} + \Gamma_{\beta}\right)t}}{\Gamma_{\alpha} + \Gamma_{\beta}} \\
\rho_{12}(t) = \rho_{12}(0) + \frac{1}{2} \rho_{ee}(0) \left\{ \frac{1 - e^{-\left(\Gamma_{\alpha} + \Gamma_{\beta} + \omega_{\alpha 2}\right)t}}{\Gamma_{\alpha} + \Gamma_{\beta} + \omega_{\alpha 2}} \right\} \left( \Gamma_{1,\beta} + \Gamma_{2,\beta} \right) \\
\rho_{e1}(t) = \rho_{e1}(0) e^{-\left(\Gamma_{\alpha} + \Gamma_{\beta}\right)t/2}
\]

(3.156)

We shall use these results in the next chapter to obtain the transient internal entropy during spontaneous decay to many lower levels for the purpose of illustrations. This system can describe the infrared rovibrational transitions in molecules, for example: from state \(|n = 1, J = 0\) to \(|n = 0, J = \pm\). For optical spontaneous emissions, more ground states have to be included and there may be some interfering decay channels for certain molecules.

### 3.8 Momentum Effects in Free Spontaneous Emissions

In the case of no SGC, we have used Eqs. 3.149 to study the decay dynamics and the stationary states of a cold and dilute gas with two-level multi-ground states undergoing spontaneously decaying in thermal radiation and in Markov approximation (see paper [2]). Earlier, the effect of Doppler shift on the wavepacket evolution was studied using Schrödinger formalism [240].

The momentum and transient dynamics of a two-level system interacting with the thermal radiation is governed by the Bloch equations derived from Eq. 3.149
\[
\frac{\partial \rho_{\text{ee}}(\mathbf{P}, t)}{\partial t} = \sum_{k, \lambda} |g_{k\lambda}|^2 \int_0^t d\tau \cos \Delta_{\mathbf{k} \mathbf{P}, \tau}^+ \{\overline{\rho}_{\text{ee}}(\mathbf{P} + \hbar \mathbf{k}, t) - (\overline{\rho}_{\text{ee}} + 1) \rho_{\text{ee}}(\mathbf{P}, t)\} \tag{3.157}
\]

\[
\frac{\partial \rho_{gg}(\mathbf{P}, t)}{\partial t} = \sum_{k, \lambda} |g_{k\lambda}|^2 \int_0^t d\tau \cos \Delta_{\mathbf{k} \mathbf{P}, \tau}^+ \{(\overline{\rho}_{\text{ee}} + 1) \rho_{\text{ee}}(\mathbf{P}, t) - \overline{\rho}_{\text{gg}}(\mathbf{P}, t)\} \tag{3.158}
\]

\[
\frac{\partial \rho_{eg}(\mathbf{P}, t)}{\partial t} = \sum_{k, \lambda} |g_{k\lambda}|^2 \int_0^t d\tau \exp(\Delta_{\mathbf{k} \mathbf{P}, \tau}^+) (\overline{\rho}_{\text{ee}} + 1) \rho_{eg}(\mathbf{P}, t) \tag{3.159}
\]

where \(\rho_{\text{ee}}(\mathbf{P} \pm \hbar \mathbf{k}, t) \doteq \langle a, \mathbf{P} \pm \hbar \mathbf{k} | \rho(t) | a, \mathbf{P} \pm \hbar \mathbf{k} \rangle\) and \(\Delta_{\mathbf{k} \mathbf{P}, \tau}^\pm \doteq \omega_k - \omega_0 - \frac{\mathbf{P} \cdot \mathbf{r}}{M c} \pm \frac{\hbar \omega_0}{2Mc} \omega_k^2\).

For \(t >> 1/\Delta_{\mathbf{k} \mathbf{P}}^\pm\), we can replace \(\int_0^t d\tau \cos \Delta_{\mathbf{k} \mathbf{P}, \tau}^\pm \to \pi \delta(\Delta_{\mathbf{k} \mathbf{P}}^\pm)\). Since \(\Delta_{\mathbf{k} \mathbf{P}}^\pm\) is a quadratic function of \(\omega_k\) with two roots

\[
\omega_{\text{op}, 1}^\pm = \frac{\omega_0}{w} \left\{ -u_{\text{OP}} \mp \sqrt{u_{\text{OP}}^2 + 2w} \right\} \tag{3.160}
\]

\[
\omega_{\text{op}, 2}^\pm = \frac{\omega_0}{w} \left\{ -u_{\text{OP}} \mp \sqrt{u_{\text{OP}}^2 + 2w} \right\} \tag{3.161}
\]

We use \(\delta(\pm \frac{\hbar}{2Mc}(\omega - a)(\omega - b)) = \frac{1}{\pm \frac{\hbar}{2Mc}|a - b|} \{\delta(\omega - a) + \delta(\omega - b)\}\) and obtain

\[
\delta(\Delta_{\mathbf{k} \mathbf{P}}^\pm) = \{\delta(\omega_k - \omega_{\text{op}, 1}^\pm) + \delta(\omega_k - \omega_{\text{op}, 2}^\pm)\} / \sqrt{u_{\text{op}}^2 + 2w} \tag{3.162}
\]

where \(u_{\text{op}} = (1 - d_{\text{op}}), d_{\text{op}} = \frac{\mathbf{P} \cdot \mathbf{r}}{Mc} \) and \(w = \frac{\hbar \omega_0}{2Mc}\).

Since \(u_{\text{op}} >> w\), we can expand the roots as

\[
\omega_{\text{op}, 1}^\pm = \frac{\omega_0}{w} \left\{ u_{\text{op}} \mp \frac{w}{2u_{\text{op}}^2} \right\} \tag{3.163}
\]

\[
\omega_{\text{op}, 2}^\pm = \frac{\omega_0}{w} \left\{ u_{\text{op}} \mp \frac{w}{2u_{\text{op}}^2} \right\} \tag{3.164}
\]

Since \(u_{\text{op}} \sim 1\) but \(w << 1\), the second root is in the order of \(\frac{Mc^2}{\hbar} \sim 10^{20} \text{s}^{-1}\) corresponds to unphysical large resonant frequency beyond the limit of electromagnetic spectrum. Thus, Eq. 3.162 becomes

\[
\delta(\Delta_{\mathbf{k} \mathbf{P}}^\pm) = \delta(\omega_k - \omega_{\text{op}, 1}^\pm) / \sqrt{u_{\text{op}}^2 + 2w} \tag{3.165}
\]

By neglecting \(w\) in Eqs. 3.165 and 3.163, the delta function becomes \(\delta(\Delta_{\mathbf{k} \mathbf{P}}^\pm) \approx \delta(\omega - \omega_{\text{op}})/u_{\text{op}}\). Now, \(\sum |g_{k\lambda}|^2 \int_0^t d\tau \cos \Delta_{\mathbf{k} \mathbf{P}, \tau}^\pm\) in Eqs. 3.157-3.159 can be evaluated by using Eqs. 8.57 and 8.60 from Appendix II, giving the momentum dependent decay rate,

\[
\Gamma(\mathbf{P}) = \frac{3\Gamma}{8\pi} \int_0^{2\pi} d\omega \frac{\omega^m}{\omega_0^m} \int d\Omega N_q(\theta) \delta(\Delta_{\mathbf{k} \mathbf{P}}^\pm) - \frac{3\Gamma}{8\pi} \int d\Omega N_q(\theta)(1 - \frac{\mathbf{P} \cdot \mathbf{r}}{Mc})^{-(m+1)} \tag{3.166}
\]
where \( m = 1 \) for p.A (minimal coupling) version and \( m = 3 \) for d.E (multipolar) version, with
\[
\Gamma = \sum_{\rho=1}^{3} \sum_{\sigma=-1}^{1} \sum_{\alpha=-1}^{1} \sum_{\beta=1}^{3} |C_{q}(\rho,\sigma,\alpha,\beta)|^2
\]
the decay rate of a resting molecule or the rate as observed in the frame moving with the molecule\(^5\). By choosing the momentum to be along the z-axis \( \mathbf{P} = \hat{z} P \), Eq. 3.166 can be evaluated analytically for \( \pi \) - and \( \sigma \)- transitions,
\[
\Gamma^{\text{mult}}(\mathbf{P})_{q=0} = \Gamma(1 - \beta^2)^{-2} \approx \Gamma(1 + 2\beta^2 + 3\beta^4 + ...)
\]
(3.167)
\[
\Gamma^{\text{mult}}(\mathbf{P})_{q=\pm} = \Gamma \frac{1 + \beta^2}{(1 - \beta^2)^3} \approx \Gamma(1 + 4\beta^2 + 9\beta^4 + ...)
\]
(3.168)
where \( \beta = P/Mc \). Again, for the same conditions as above with the minimal coupling version, we have
\[
\Gamma^{\text{min}}(\mathbf{P})_{q=0} = \Gamma \frac{3}{4} \left( \frac{1 + \beta^2}{\beta^3} - \frac{4\beta}{\beta^3} \right) \approx \Gamma(1 + \frac{3}{5}\beta^2 + \frac{3}{7}\beta^4 + ...)
\]
(3.169)
\[
\Gamma^{\text{min}}(\mathbf{P})_{q=\pm} = \frac{3}{4} \left( \frac{2}{\beta^2} \right) \frac{1}{(1 - \beta^2)} \ln \frac{\beta + 1}{\beta - 1} \approx \Gamma(1 + \frac{6}{5}\beta^2 + \frac{9}{7}\beta^4 + ...)
\]
(3.170)
In both versions of interactions, the decay rates obtained are in even powers of momentum. But both versions of interactions and both types of transitions are incorrect qualitatively because the decay rates \( \Gamma(\mathbf{P}) \) increase with particle momentum \( P \). This is in contradiction\(^6\) with the special theory of relativity which predicts that the decay rate of the moving molecule should be subjected to a time-dilation as observed from the laboratory frame, as
\[
\Gamma(\mathbf{P}) = \Gamma \sqrt{1 - (\frac{P}{Mc})^2} \approx \Gamma(1 - \frac{1}{2}\beta^2 - \frac{1}{3}\beta^3 - \frac{1}{4}\beta^4 + ...)
\]
which decreases as the momentum increases.

We can show that the inclusion of the momentum dependence in \( \omega_{\alpha} \) would lead to correct result for the minimal coupling version. Let us consider a particle with initial momentum \( P \) along z-axis, emits a photon with momentum \( \hbar k \) and end up with final momentum \( P_f \). The energy and momentum conservations give
\[

\begin{align*}
\hbar \omega_{\alpha} & = \left( 1 - \frac{(P_x)^2}{2Mc^2} \right) + \frac{P_y^2}{2Mc^2} = Mc^2 \sqrt{1 + \left( \frac{P}{Mc} \right)^2 + \hbar k c} \\
(P_{fx} + \hbar k \sin \theta \cos \varphi, P_{fy} + \hbar k \sin \theta \sin \varphi, P_{fz} + \hbar k \cos \theta) & = (0, 0, P)
\end{align*}
\]
(3.171)
(3.172)
The expansions of up to second order in momenta give the non-relativistic energy conservation
\(^5\) The additional summation index \( g \) is due to the dipole components in the molecular frame.
\(^6\) The problem of the momentum dependent decay rate with non-relativistic dipolar interaction Hamiltonian was first pointed out by Wilkens [234], but he did not argue it this way.
\[ kc - \omega_c(1 - \frac{1}{2}\beta^2) - \frac{kP\cos \theta}{M} + \frac{\hbar k^2}{2M} = 0 \]  
(3.173)

in terms of photon frequency \( kc \), momentum dependent level spacing \( \omega_c(1 - \frac{1}{2}\beta^2) \), Doppler frequency \( \frac{kP\cos \theta}{M} \) and recoil frequency \( \frac{\hbar k^2}{2M} \).

Thus, the delta function becomes \( \delta(\Delta_{kP}^\pm) \approx \delta(\omega - \frac{\omega_c}{u_{\Omega P}}) \) where \( \gamma^{-1} = \sqrt{1 - \beta^2} \). Equation 3.166 needs to be corrected as \( \Gamma_{q\gamma} \rightarrow \Gamma_{q}/\gamma^3 \) which leads to correct qualitative results for p.A version: \( \Gamma_{q=0}^{\text{min}} \approx \Gamma(1 - \frac{9}{16}\beta^2 - \frac{33}{70}\beta^4 - \frac{9}{14}\beta^6) \) and \( \Gamma_{q=\pm}^{\text{min}} \approx \Gamma(1 - \frac{3}{10}\beta^2 - \frac{18}{35}\beta^4 - \frac{27}{14}\beta^6) \). But, for d.E version, the results are still incorrect qualitatively \( \Gamma_{q=0}^{\text{mutt}} \approx \Gamma(1 + \frac{1}{2}\beta^2 - \frac{9}{14}\beta^6) \) and \( \Gamma_{q=\pm}^{\text{mutt}} \approx \Gamma(1 + \frac{5}{2}\beta^2 + 3\beta^4 - \frac{27}{2}\beta^6) \) because the Röntgen correction term is not included to the d.E Hamiltonian. Wilkens [235] has shown that the inclusion of the Röntgen term leads to the results consistent with the special relativity, up to second order in \( P/Mc \). Thus, the form of the minimal coupling interaction Hamiltonian is the same for any particle momentum, it is relativistically invariant. However, the multipolar version d.E interaction must be supplemented by the Röntgen term, for moving particles.

### 3.8.1 Röntgen Term and Relativistic Effect on Spontaneous Emission Rate

The correct derivation in consistency with time-dilation was given by Ref. [239]. The exact special relativistic (superscript ‘SR’) correction to Eq. 3.166 is obtained when the aberration effect is taken into account through the relations [241], [235]

\[ \frac{d\Omega}{d\Omega} = \frac{d(\cos \theta)}{d(\cos \theta)} = (1 - \beta^2)(1 - \mathbf{k} \cdot \mathbf{\beta})^{-2} \]  
(3.174)

\[ N_q(\theta') = \delta_{q,0}\sin^2 \theta' + \delta_{q,\pm}(1 - \frac{1}{2}\sin^2 \theta') \]  
(3.175)

\[ \sin^2 \theta' = (1 - \beta^2)(1 - \mathbf{k} \cdot \mathbf{\beta})^{-2}\sin^2 \theta \]  
(3.176)

where \( d\Omega = \sin \theta d\theta d\phi \) and the primed variables are the new variables which depend on the particle momentum. Hence, we have the momentum dependent decay operator which would act on angular dependent function for both polarizations.

\[ \hat{\Gamma}_{q=0}^{\text{SR}}(\mathbf{P}) = (1 - \beta^2)\frac{3I}{8\pi} \int d\Omega (1 - \mathbf{k} \cdot \mathbf{\beta})^{-4}\sin^2 \theta \ldots \]  
(3.177)

\[ \hat{\Gamma}_{q=\pm}^{\text{SR}}(\mathbf{P}) = (1 - \beta^2)\frac{3I}{8\pi} \int d\Omega (1 - \mathbf{k} \cdot \mathbf{\beta})^{-2}(1 - \frac{\sin^2 \theta}{2}(1 - \beta^2)(1 - \mathbf{k} \cdot \mathbf{\beta})^{-2}) \]  
(3.178)

We can always choose the momentum to be along the z-axis \( \beta = \hat{z} P/Mc \). Hence, it can be easily shown from Eqs. 3.177 and 3.178 that \( \Gamma^{SR}(\mathbf{P}) = \Gamma \sqrt{1 - \left(\frac{P}{mc}\right)^2} \) for all \( q = 0, \pm 1 \).
The Röntgen term from the Hamiltonian in Appendix I, Eq. 8.34 leads to momentum dependent coupling \( g_{k\lambda} \), and the Bloch coupled equations Eqs. 3.157-3.159 are modified as

\[
\frac{\partial \rho_{cc}(P,t)}{\partial t} = \sum_{k\lambda} 2\pi \delta(\Delta_{kP}^+)|g_{k\lambda}(P)|^2 \{ \bar{n}_{k\lambda} \rho_{gg}(P,\hbar k,t) - (\bar{n}_{k\lambda} + 1) \rho_{cc}(P,t) \}
\]

\[
\frac{\partial \rho_{gg}(P,t)}{\partial t} = \sum_{k\lambda} 2\pi \delta(\Delta_{kP}^-)|g_{k\lambda}(P+\hbar k,t)|^2 \{ (\bar{n}_{k\lambda} + 1) \rho_{cc}(P+\hbar k,t) - \bar{n}_{k\lambda} \rho_{gg}(P,t) \}
\]

\[
\frac{\partial \rho_{eg}(P,t)}{\partial t} = \sum_{k\lambda} g_{k\lambda}(P) g^*_{k\lambda}(P+\hbar k) \int_0^t d\tau \exp(\Delta_{kP}^{-}\tau)(\bar{n}_{k\lambda} + 1) \rho_{eg}(P,t)
\]

(3.179a)

where \( g_{k\lambda}(P) \equiv d \sqrt{\frac{\omega_{\lambda\lambda}^2}{\pi \sigma_{\lambda\lambda}}} \sum_{q=-1,0} C_q \{ \epsilon_{k\lambda q}^* \frac{\omega_{\lambda\lambda}(P)}{\omega_{\lambda\lambda}} + \epsilon_q \frac{\omega_{\lambda\lambda}(P)}{\omega_{\lambda\lambda}} \} = \sqrt{\frac{\omega_{\lambda\lambda}}{2\pi \sigma_{\lambda\lambda}}} ((d \times \bar{\beta}) \cdot (\kappa \times \tilde{\varepsilon}_{k\lambda}) + (d \cdot \tilde{\varepsilon}_{k\lambda})(1 + \frac{\hbar \kappa}{2\pi \sigma_{\lambda\lambda}})).

### 3.8.2 Non-Markovian Effect in Free Spontaneous Emissions

The Wigner-Weisskopf exponential decay of spontaneous emissions is the results of Markovian theory of dissipation. It has been shown that exponential decay is not physical [91]. This is true for many other unstable systems [87]. The long time decay rate was shown to deviate from exponential in the long times [89] and short times [90]. The non-exponential character is the manifestation of the non-Markovian nature of particle-reservoir interactions.

For two-level states system, we can include the anti-rotating terms into Eqs. 3.157 and 3.158 and use the Laplace transform to obtain analytical solutions. We concentrate on the transient dynamics and neglect the momentum dependence by writing the Laplace transforms of the coupled equations for the populations as (ARW terms are labelled with superscript "a")

\[
x_{cc}(s) - \frac{1}{s} \rho_{cc}(0) = \{ \tau_{11}(s) + \tau_{01}^{1\sigma} \} x_{gg}(s) - \{ \tau_{11}(s) + \tau_{01}^{1\sigma} \} x_{cc}(s)
\]

\[
x_{gg}(s) - \frac{1}{s} \rho_{gg}(0) = -\{ \tau_{11}(s) + \tau_{01}^{1\sigma} \} x_{gg}(s) + \{ \tau_{11}(s) + \tau_{01}^{1\sigma} \} x_{cc}(s)
\]

where \( x_{cc}(s) = \int_0^\infty \rho_{cc}(t) e^{-st} dt \) is the Laplace transform of the populations, \( \tau(s) = 2 \int_0^\infty \frac{D(\omega) E(\omega)}{s^2 + \Delta^2} d\omega \) and \( \tau_{1\sigma}(s) = 2 \int_0^\infty \frac{n(\omega) D(\omega) E(\omega)}{s^2 + \Delta^2} d\omega \) for the RWA parts, while \( \tau_0^{1\sigma}(s) = 2 \int_0^\infty \frac{D(\omega) E(\omega)}{s^2 + \Delta^2} d\omega \) for the ARW parts.

The solutions of Eqs. 3.180-3.181 in Laplace transforms are

\[
\begin{pmatrix}
x_{cc}(s)
\end{pmatrix} = \frac{1}{s} \begin{pmatrix}
\tau_{11} + \tau_{01}^{1\sigma} + \tau_{1\sigma} + \tau_{01}^{1\sigma}
\end{pmatrix} \begin{pmatrix}
\tau_{11} + \tau_{01}^{1\sigma}
\end{pmatrix}^{-1} \begin{pmatrix}
\tau_{11} + \tau_{01}^{1\sigma} + \tau_{1\sigma}
\end{pmatrix} \begin{pmatrix}
\rho_{cc}(0)
\end{pmatrix}
\]

\[
\begin{pmatrix}
x_{gg}(s)
\end{pmatrix}
\]

(3.182)
Further analytical solutions from Eq. 3.182 would be too cumbersome. Hence, Eq. 3.182 provides the general starting point for further analysis of the decay dynamics. The exact inverse Laplace transforms can only be performed numerically, Wodkiewicz and Eberly [86], and Knight and Milonni and Knight [89] have shown that a correction term to the exponential decay is proportional to $1/t^2$ which dominates at long times. They used the monimal coupling (p.A) version for the coupling.

By neglecting the ARW parts, and setting $\pi_k \to 0$, Eqs. 3.182 can be further simplified as

$$x_{ee}(s) = \frac{1}{1 + 2I(s)} \frac{1}{s} \rho_{ee}(0) \quad (3.183)$$

$$x_{gg}(s) = \frac{2I(s)}{1 + 2I(s)} \frac{1}{s} \rho_{ee}(0) + \frac{1}{s} \rho_{gg}(0). \quad (3.184)$$

where

$$I(s) = \int_0^{\omega_c} d\omega \frac{D(\omega)|g(\omega)|^2}{s^2 + \Delta^2} \zeta(\omega) \to \frac{\Gamma}{2\pi\omega_c^m} \int_0^{\omega_c} \frac{\zeta(\omega)\omega^m}{s^2 + (\omega - \omega_o)^2} d\omega \quad (3.185)$$

and $\omega_c \sim c/a_B$ ($a_B$ is the Bohr radius) is the cutoff frequency of the electromagnetic spectrum, $m = 1$ for minimal coupling (p.A) and $m = 3$ in dipole coupling (d.E) with the spectral response $\zeta(\omega) = (1 + (\frac{\omega}{\omega_o})^2)^4$ inserted to obtain convergence as in Ref. [203]. For $\omega_c \gg \omega_o$, $\zeta(\omega) \to 1$ and $m = 1$, the integral can be evaluated exactly

$$I(s) = \frac{\Gamma}{2\pi\omega_o} \left\{ \frac{1}{2} \ln \left( \frac{s^2 + (\omega_o - \omega_o)^2}{s^2 + \omega_o^2} \right) + \omega_o \left( \frac{\omega_o - \omega_o}{s} + \arctan \frac{\omega_o}{s} \right) \right\}. \quad (3.186)$$

The population is obtain via the inverse transform $\rho_{ee}(t) = \frac{\rho_{ee}(0)}{2\pi s} \int_{c-i\infty}^{c+i\infty} e^{st} \{s + 2sI(s)\}^{-1} ds$.

For $s < \omega_o \ll \omega_c$, we can expand $\ln \left( \frac{s^2 + (\omega_o - \omega_o)^2}{s^2 + \omega_o^2} \right) \approx 2 \ln \frac{\omega_o}{\omega_o} - \frac{1}{\omega_o^2} s^2 + \frac{1}{2\omega_o^2} s^4$ and set $\arctan \frac{\omega_o - \omega_o}{s} \to \pi/2$. Thus, we obtain

$$x_{ee}(s) = \left\{ s \left( 1 + \frac{\Gamma}{2\pi \omega_o} 2 \ln \frac{\omega_o}{\omega_o} - \frac{\Gamma}{2\pi \omega_o} s^3 + \frac{\Gamma}{2\pi} (\pi + 2 \arctan \frac{\omega_o}{s}) \right) \right\}^{-1} \rho_{ee}(0) \quad (3.187)$$

$$\approx \left\{ s + \frac{\Gamma}{2\pi} (\pi + 2 \arctan \frac{\omega_o}{s}) \right\}^{-1} \rho_{ee}(0) \quad (3.188)$$

The inverse transforms of Eq. 3.187 has a branch point in Riemannian space at $s = 0^-$. For $s \ll \omega_o$ or $t \gg \frac{1}{\omega_c}$, it is a good approximation to set $\frac{\omega_o}{s} \to \infty$ and Eq. 3.188 gives the exponential decay law

$$\rho_{ee}(t) \to \frac{\rho_{ee}(0)}{2\pi t} \int_{c-i\infty}^{c+i\infty} e^{st} \left\{ s + \frac{\Gamma}{2\pi} (\pi + \frac{\pi}{s}) \right\}^{-1} ds = \rho_{ee}(0) \exp(-\Gamma t). \quad (3.189)$$

Thus, the exponential decay is the result of neglecting the contributions from the branch point, which also corresponds to the non-Markovian effect.
Chapter 4

Entropy, Phase Space and Thermodynamics in Cooling

In laser cooling, the momentum width is usually used to define and measure the extent of cooling. The concept of entropy applies irrespective of whether the system is in equilibrium or non-equilibrium conditions. However, it is not widely used in the analysis of most laser cooling works, with two exceptions in Refs. [117] and [118] where the radiation entropy was quantified. They have shown that the entropy reduction rate of the atomic beam by laser cooling is at least 10^6 times smaller than the radiation entropy generated by the random photons scattering through spontaneous emissions. Thus, the efficiency of laser cooling is extremely poor, estimated to be about 10^{-5}. This shows that laser cooling is not an energy-efficient process to remove the entropy.

There are subtle differences and interrelations between various physical concepts which are related to the terminology of 'cooling'. The measurable quantities are: momentum width $\Delta P$, probability momentum distribution $f(P)$, von Neumann entropy $S$, Renyi entropy $S^R$, phase space density $\rho_{\text{p}}$, and Wigner function $W$. How are these quantities related? How do they change in a unitary process and a dissipative process? This chapter is essentially devoted towards answering these questions.

We show that the Wigner function can change even in unitary process and behaves like a compressible fluid, in contrast to the classical phase space. The momentum and spatial probability densities can be obtained from the Wigner function. By including the internal states, we derive the expression for the classical phase space density in terms of the thermal de Broglie wavelength and spatial density of each internal state. The general properties of the subsystems von Neumann entropies are given. We obtain the relationship between $f(P, t)$ and the center of mass subsystem entropy $S_{\text{cm}}$ for discrete and continuous variables. The rate of entropy change or entropy production for the system and subsystems are expressed in terms of $\frac{d}{dt}f(P, t), f(P, t)$ and the dissipative Liouvillian $Lp$. Simpler relationships are obtained with the Renyi entropy. We also obtain the relationship between the Wigner function $W$ and the $S_{\text{cm}}$. We show that for Renyi entropy, $\frac{d}{dt}S^R_{\text{cm}} = 0$ even if
\( \frac{d}{dt} W \neq 0 \) in a unitary process. We show how the transient internal entropy of a fluorescence process can be evaluated. The equilibrium center of mass entropy for a single particle and many non-interacting particles are derived from the Gibbs ensemble state. The equilibrium entropy for thermal photon, harmonic oscillator for vibrational motion and rotational motion of molecules are derived. We find that the thermal radiation entropy is proportional to cube of the thermal temperature. Finally, we review the works on quantum heat engine and refrigerator based on laser particle interactions and it relations to the laws of thermodynamics.

### 4.1 Phase Space and Quasi Phase Space

The translational cooling or heating effect of a gas can be inferred from the momentum probability distribution of a gas. In classical regime, the phase space probability distribution \( \rho(\mathbf{r}, \mathbf{p}, t) \) provides complete information for the temporal evolution of particles in phase space. The distribution evolves according to the classical Liouville theorem [108], which is derived based on the assumption that the phase points vary continuously and from the Hamilton’s equations of motion \( \frac{d}{dt} \mathbf{r} = \nabla_p H(\mathbf{r}, \mathbf{p}, t), \frac{d}{dt} \mathbf{p} = \frac{\partial}{\partial \mathbf{r}} H(\mathbf{r}, \mathbf{p}, t) \), giving

\[
\frac{d}{dt} \rho(\mathbf{r}, \mathbf{p}, t) = 0 = \frac{\partial}{\partial \mathbf{r}} \rho(\mathbf{r}, \mathbf{p}, t) - \{ \nabla_r H \cdot \nabla_p - \nabla_p H \cdot \nabla_r \} \rho(\mathbf{r}, \mathbf{p}, t)
\]

(4.1)

It means that the classical phase space density \( \rho(\mathbf{r}, \mathbf{p}, t) \) is unchanged and behaves much like an incompressible fluid through the action of the Hamiltonian \( H \) which describes non-dissipative processes.

Although the phase space is defined both in the classical and quantum regimes, the phase space density is entirely classical. In quantum regime, the phase space probability or density is strictly undefined because the uncertainty principle forbids simultaneous knowledge of position and momentum due to the non-commutivity between the momentum and spatial variables. Instead, we can only define a quasiprobability distribution in phase space, namely the Wigner function, \( W(\mathbf{r}, \mathbf{p}, t) \) [315]. Although \( W(\mathbf{r}, \mathbf{p}, t) \) is real and gives the correct expectation value \( \langle \hat{O}(t) \rangle = \int \int \hat{O}(\mathbf{r}, \mathbf{p}, t) W(\mathbf{r}, \mathbf{p}, t) d^3 \mathbf{p} d^3 \mathbf{r} \), it may not be everywhere positive in phase space.

The dynamical equation for the Wigner function in a unitary process characterized by real (Hermitean) Hamiltonian \( \hat{V} \) is given by [221]

\[
\frac{\partial W(x, p, t)}{\partial t} = -\frac{p}{M} \frac{\partial W(x, p, t)}{\partial x} + \frac{\partial V(x, t)}{\partial x} \frac{\partial W(x, p, t)}{\partial p} + O(\hbar)
\]

(4.2)

where \( V(x, t) \doteq \text{Tr} \{ \langle x, t | \hat{V}(\hat{x}, t) | x, t \rangle \} \) and \( O(\hbar) \approx \sum_{n=1}^{\infty} \frac{1}{(2n+1)^2} (\frac{i\hbar}{2})^{2n+1} \frac{\partial^{2n+1} V(\mathbf{x}, t)}{\partial x^{n+1}} \frac{\partial^{2n+1} W(\mathbf{x}, \mathbf{p}, t)}{\partial p^{n+1}} \).

If we compare Eq. 4.2 with the Liouville’s theorem, we find that \( W(x, p, t) \) does not behave exactly like the classical \( \rho(\mathbf{r}, \mathbf{p}, t) \) due to the extra term \( O(\hbar) \). From the chain
rule for differentiation $\frac{dW(x,p,t)}{dt} = \frac{\partial W(x,p,t)}{\partial t} + \frac{\partial p}{\partial x} \frac{\partial W(x,p,t)}{\partial x} + \frac{\partial p}{\partial p} \frac{\partial W(x,p,t)}{\partial p}$ we have $\frac{dp}{dt} = \frac{P}{\hbar}$ and $\frac{d\rho}{dt} = -\frac{\partial V(x,t)}{\partial x}$ which is expected classically. However, we have $\frac{dW(x,p,t)}{dt} = O(\hbar)$, (instead of zero) an unexpected result. Thus, we can say that, in quantum regime the quasi-phase space density can change or is ‘compressible’ even if the process is unitary or non-dissipative. This is entirely a quantum effect because if we set $\hbar \to 0$, Eq. 4.2 reduces to the classical form, Eq. 4.1. For harmonic potential, $O(\hbar) = 0$ and the Wigner function evolves exactly the same way like a classical particle.

### 4.2 Momentum and Spatial Probability Densities

In quantum regime, the Wigner function is related to the spatial probability distribution $f(r,t)$ and the momentum probability distribution $f(p,t)$ by

$$f(r,t) = \int W(r,p,t)d^3p = dN/dV_r$$

$$f(p,t) = \int W(r,p,t)d^3r = dN/dV_p$$

where $\int f(r,t)d^3r = \int f(p,t)d^3p = N$ is the number of particles in phase space. For a mixed state system we have

$$f(r,t) = \sum_i P_i(t)\Psi_i^*(r,t)\Psi_i(r,t) = \sum_{i,a,b} P_i(t)\psi_{ia}^*\psi_{ib}(r,t)\psi_{ib}(r,t)$$

By using $\Psi_i(r,t) = \sum_{a} c_{ia}\psi_{ia}(r,t)$, we can write $N = \sum_{a} N_{a}$ and $f(r,t) = \sum_{i} f_{a}(r,t)$, where $f_{a}(r,t) = |\psi_{a}(r,t)|^2 \sum_{i} P_{i}|c_{ia}|^2$ is the spatial density of particles in state $|a\rangle$ and $N_{a} = \int f_{a}(r,t)d^3r$ is the number of particles in internal state $|a\rangle$ with $\sum_{i} P_{i}(t) = 1$. The term $|\psi_{a}(r,t)|^2$ gives the probability distribution in space while $\sum_{i} P_{i}|c_{ia}|^2$ gives the fraction of the population in state $|a\rangle$ by averaging over all possible mixed states depending on the weight $P_{i}$.

In classical regime, we can define the mean phase space density for a system in single internal state around a classical momentum $\vec{p}$ and position $\vec{r}$ point from the Wigner distribution, $W(r,p,t) \to \rho(\vec{r},\vec{p},t)$. Thus we have the expression of the phase space density for a system in many internal states,

$$\rho(\vec{r},\vec{p},t) = \sum_{a} \frac{n_{a}(\vec{p},t)}{V_{p,a}(\vec{r},t)}$$

where $n_{a}(\vec{p},t)$ is the volume density in states $|a\rangle$ and $V_{p,a}(\vec{r},t)$ the momentum volume in state $|a\rangle$. 
The thermal de Broglie wavelengths $\Lambda_i$ of a gas with momentum widths $\Delta P_{i,a} \doteq \sqrt{2Mk_BT_{i,a}}$ are related to the effective temperatures $T_i$ by

$$\Lambda_{i,a}(\mathbf{r},t) = \frac{\hbar}{\Delta P_{i,a}(\mathbf{r},t)} = \frac{\hbar^2}{2Mk_BT_{i,a}(\mathbf{r},t)}$$  \hspace{1cm} (4.7)

where $i \in x, y, z$. By writing the momentum volume as $V_{\mathbf{p},a}(\mathbf{r},t) = \Delta P_{x,a}\Delta P_{y,a}\Delta P_{z,a}$, Eq. 4.6 can be written as

$$\rho(\mathbf{r},\mathbf{p},t) = \sum_a \frac{n_a(\mathbf{p},t)}{h^3} \Lambda_{x,a}(\mathbf{r},t)\Lambda_{y,a}(\mathbf{r},t)\Lambda_{z,a}(\mathbf{r},t)$$  \hspace{1cm} (4.8)

The optical molasses in the magneto-optical trap (MOT) [305] has typical spatial density of $10^{11} \text{cm}^{-3}$. This is lower than the density of the optical lattice sites in optical regime which is about $\lambda^{-3} \sim 10^{15} \text{cm}^{-3}$. The typical temperature of the molasses is about $1 \mu \text{K}$. The phase space density is normally defined in dimensionless quantity as $\bar{p} \doteq h^3 \rho \sim n \Lambda^3$. In magneto-optical trap, the phase space density is $\sim 5 \times 10^{-6}$ [306]. This is a factor of 6 lower than the BEC limit which is around unity. However, the increase in the spatial density will increase reabsorptions of incoherent radiation from nearby atoms which cause heating and this limit the phase space density. One way of overcoming this problem is by using far detuned optical lattice [216].

If cooling were defined as a measure of the momentum width, it is well-known that this can be achieved by unitary or non dissipative process, for example by rotation or distortion of the phase space distribution Refs. [66],[15],[16] without changing the quasiphase space density. Here, the reduction in the momentum width must be accompanied by the increase in the spatial width or reduction in the gas density. For Gaussian momentum distribution $e^{-p^2/\sigma_p^2}$, the momentum width is well defined as the (FWHM) full width at half maximum as $\Delta P \doteq 2\sqrt{\ln 2}\sigma$ (see Fig. 4.1). We can then define an effective temperature associated to the momentum width of the gas as $T_{cf} = (\Delta P)^2/2Mk_B$. However, for an arbitrary distribution, quantitative definition of the width is not possible. Therefore, the cooling effect is hard to be ascertained.

### 4.3 General Properties of Subsystem Entropies

Generally, entropy is the measure of : a)dispersion, b)uncertainty and c)degree of mixture of states or possible outcomes in statistical events. The concept of entropy can be used to measure cooling. It applies either in equilibrium or non-equilibrium conditions. However, the entropy can change or flow in two ways: a)via dissipation or b) unitary process. (see Fig. 4.2) The former is necessarily irreversible which involves non-unitary evolution, such as the coupling of the system to the reservoir. The latter involves the coupling between two or more subsystems where entropy can be transferred between the subsystems through a unitary process. Any system with entropy can serve either as an entropy source or entropy sink. In the case of a system of photon-molecule interactions,
Figure 4.1: Gaussian distribution with the definition of the momentum width at half maximum.

there are three main subsystems entropies which are coupled together: a) \( S_r \), from the radiation b) \( S_{cm} \), from the external center of mass (c.m.) translational motion c) \( S_I \), from the internal molecular states (electronic, vibrational-rotational or nuclear degrees).

The fundamental properties of quantum entropy have been given in the text by Linblad [111], while the classical entropy was reviewed by Wehr [114]. For a single particle system density operator, \( Tr\{\rho(t)\} = 1 \) where the trace is over all basis states in the Hilbert space spanned by the radiation (\( R \)), internal (\( I \)) and external (\( cm \)) subsystems. The quantum (von Neumann) entropy [112] is defined as

\[
S(t) = -k_B Tr\{\hat{\rho}(t) \ln \hat{\rho}(t)\} \geq 0
\]  

(4.9)

The system, internal and external subsystems density operators are defined (for continuous and discretized momentum) respectively as

\[
\hat{\rho}_S(t) = Tr_R\{\hat{\rho}(t)\} = \int d^P \int d^{P'} \sum_{a,b} \rho_{ab}(P, P', t) |a, P\rangle \langle b, P'| \\
\hat{\rho}_I(t) = Tr_{cm}\{\hat{\rho}_S(t)\} = \sum_{a,b} \int \rho_{ab}(P, P, t) d^3P |a\rangle \langle b| \\
\hat{\rho}_{cm}(t) = Tr_I\{\hat{\rho}_S(t)\} = \int d^3P \int d^3P' \sum_{a} \rho_{ad}(P, P', t) |P\rangle \langle P'| 
\]

(4.10)

(4.11)

(4.12)

where \( \rho_{ab}(P, P', t) = \langle a, P|\hat{\rho}_S(t)|b, P'\rangle \) and \( Tr_R\{\hat{\rho}(t)\} = \sum_{n,k,\lambda} \langle n_{k,\lambda}|\hat{\rho}(t)|n_{k,\lambda}\rangle \). The general density matrix can be written as \( \hat{\rho}(t) = \sum_{n,k,\lambda: P,a} \sum_{n',k',\lambda': P',b} \langle n_{k,\lambda}|a, P|\hat{\rho}(t)|n'_{k',\lambda'}, b, P'\rangle|n_{k,\lambda}, a, P\rangle\langle n'_{k',\lambda'}, b, P'|. \)
We have assumed the momentum to be a continuous variable. For computation purpose, the momentum variable is represented by discrete points where it is useful to replace $\int d^3P$ with $\sum_P$. The corresponding system entropy, internal entropy and external entropy are defined as

\begin{align}
S_S(t) & \doteq -k_B Tr_S \{ \tilde{\rho}_S(t) \ln \tilde{\rho}_S(t) \} \\
S_I(t) & \doteq -k_B Tr_I \{ \tilde{\rho}_I(t) \ln \tilde{\rho}_I(t) \} \\
S_{cm}(t) & \doteq -k_B Tr_{cm} \{ \tilde{\rho}_{cm}(t) \ln \tilde{\rho}_{cm}(t) \}
\end{align}

In free space, the populations are diagonal in momentum space $\rho_{aa}(\mathbf{P}, \mathbf{P}', t) = \delta_{\mathbf{P} \cdot \mathbf{P}'} \rho_{aa}(\mathbf{P}, \mathbf{P}, t)$, so we can obtain the relation between the external entropy and the momentum probability density $f(\mathbf{P}, t) \doteq \sum_a \rho_{aa}(\mathbf{P}, \mathbf{P}, t)$. For discrete momentum,

\begin{equation}
S_{cm}(t) \doteq -k_B \sum_{\mathbf{P}} f(\mathbf{P}, t) \ln f(\mathbf{P}, t)
\end{equation}

and for continuous momentum, we define the relative external entropy,

\begin{equation}
S_{cm}(t|0) \doteq -k_B \int f(\mathbf{P}, t) \ln \frac{f(\mathbf{P}, t)}{f(\mathbf{P}, 0)} d^3P
\end{equation}

Similarly, since the populations are diagonal in the c.m. momentum states, for $a = b$, we have $\rho_{ab}(\mathbf{P}, \mathbf{P}, t) = \rho_{aa}(\mathbf{P}, \mathbf{P}, t)$, but for $a \neq b$, we have $\rho_{ab}(\mathbf{P}, \mathbf{P}, t) = 0$. Therefore
\[ \rho_{ab}(\mathbf{P}, \mathbf{P}, t) = \delta_{ab} \rho_{aa}(\mathbf{P}, \mathbf{P}, t) \] and we define \( \rho_{aa}(t) \equiv \delta_{ab} \int \rho_{ab}(\mathbf{P}, \mathbf{P}, t) d^3 P \leftrightarrow \sum_{\mathbf{P}} \rho_{aa}(\mathbf{P}, \mathbf{P}, t) \)

and Eq. 4.14 becomes

\[ S_I(t) = -k_B \sum_a \rho_{aa}(t) \ln \rho_{aa}(t) \]  \hspace{1cm} (4.18)

From the definition of \( f(\mathbf{P}, t) \) and Eq. 3.37 or 3.42, we obtain the rate of momentum probability density in terms of the dissipative Liouvillean

\[ \frac{\partial}{\partial t} f(\mathbf{P}, t) = Tr_S \{ |\mathbf{P} \rangle \langle \mathbf{P}| \frac{\partial}{\partial t} \hat{\rho}_S \} = \langle \mathbf{P} | Tr_I \{ U(t) \hat{L} \hat{\rho}_{S1}(t) U_1^\dagger(t) \} | \mathbf{P} \rangle \]  \hspace{1cm} (4.19)

Equation 4.19 shows that the probability momentum distribution can only change if the is dissipation. No amount of coherent interactions alone can change \( f(\mathbf{P}, t) \) and the c.m. entropy, Eq. 4.16.

**Entropy in terms of density operator eigenvalues** Let \( f(\hat{\rho}) = \hat{\rho} \ln \hat{\rho} \). By unitary transformation, \( f(\hat{\rho}) \) can be diagonalized as \( f(\hat{\rho}_D) = U^\dagger f(\hat{\rho}) U = f(U^\dagger \hat{\rho} U) \). A diagonal density operator in the new basis \( |d \rangle \) is \( \hat{\rho}_D = U^\dagger \hat{\rho} U = \sum_d w_d |d \rangle \langle d| \), where \( \{w_d\} \) are the eigenvalues for \( \hat{\rho}_D \). From the spectral decomposition theorem, \( f(\hat{A}) = \sum_{n=0}^\infty f(a_n) |\psi_n \rangle \langle \psi_n| \), we have \( f(\hat{\rho}_D) = \hat{\rho}_D \ln \hat{\rho}_D = \sum_{d=0}^\infty w_d \ln w_d |d \rangle \langle d| \). Therefore, the entropy becomes \( S = -k_B \text{Tr} \{ U f(\hat{\rho}_D) U^\dagger \} = -k_B \text{Tr} \{ f(\hat{\rho}_D) \} \) and we can write it in the scalar form as the Shannon information entropy

\[ S(t) = -k_B \sum_{d=0}^\infty w_d(t) \ln w_d(t) \]  \hspace{1cm} (4.20)

Thus, the entropy is independent of the representation of the basis and can be expressed in scalar form when \( \hat{\rho} \) is diagonalizable.

**Additivity of Entropy for Uncorrelated Subsystems** If the subsystems are uncorrelated, we can write \( \hat{\rho}_S(t) = \hat{\rho}_I(t) \otimes \hat{\rho}_{cm}(t) \). The system entropy becomes

\[ S_S(t) = -k_B \text{Tr}_cm \{ \hat{\rho}_{cm}(t) \} Tr_I \{ \hat{\rho}_I(t) \ln \hat{\rho}_I(t) \} - k_B Tr_I \{ \hat{\rho}_I(t) \} Tr_cm \{ \hat{\rho}_{cm}(t) \ln \hat{\rho}_{cm}(t) \}. \]  \hspace{1cm} (4.21)

By using the von Neumann conditions \( Tr_cm \{ \hat{\rho}_{cm}(t) \} = Tr_I \{ \hat{\rho}_I(t) \} = 1 \), and Eqs. 4.14 and 4.15, we obtain the additivity of entropy

\[ S_S(\hat{\rho}_I(t) \otimes \hat{\rho}_{cm}(t)) = S_I(t) + S_{cm}(t) \]  \hspace{1cm} (4.22)
Zero Entropy for Pure State  For pure state, \( \hat{\rho}_S = |\Psi\rangle \langle \Psi| \), the diagonalized operator remains pure as 
\[
\hat{\rho}_D = U^\dagger |\Psi\rangle \langle \Psi| U = |D\rangle \langle D| = \sum_d w_d |d\rangle \langle d| \delta_{d,D} \text{ and we have } S_S = -k_B \sum_{d=0}^\infty w_d \ln w_d \delta_{d,D} = -k_B \ln 1 = 0. \text{ Thus,}
\]
\[
S_S(|\Psi\rangle \langle \Psi|) = 0. \tag{4.23}
\]
If the total system and all subsystems are pure, the state vector is decomposed as 
\[|\Psi_i\rangle \equiv |\psi_i\rangle \otimes |p_i\rangle.\]

A Mixed Subsystem Uncorrelated to a Pure Subsystem  A general mixed state density operator is 
\[\hat{\rho}_S = \sum_i W_i |\Psi_i\rangle \langle \Psi_i|\]. If the internal state is pure and uncorrelated
with external mixed state, we have 
\[
\hat{\rho}_S = \sum_i G(p_i) |p_i\rangle \langle p_i| \otimes |\psi_i\rangle \langle \psi_i| \equiv \hat{\rho}_{cm} \otimes \hat{\rho}_I. \text{ From Eq.}
\]
\[4.22 \text{ and } 4.23, \text{ we have}
\]
\[
S_I = 0, S = S_{cm}. \tag{4.24}
\]

Entropy is Unchanged by Unitary Transformation  Unitary evolution of 
\( \hat{\rho} \) is described by 
\[\hat{\rho}' = U^\dagger \hat{\rho} U, \] and the entropy evolves from 
\[S(t) = -k_B Tr\{\hat{\rho}(t) \ln \hat{\rho}(t)\} \text{ to}
\]
\[S'(t) = -k_B Tr\{U^\dagger \hat{\rho} U \ln U^\dagger \hat{\rho} U\} = -k_B Tr\{U U^\dagger \hat{\rho} U \ln \hat{\rho}\} = -k_B Tr\{U U^\dagger \hat{\rho} U \ln \hat{\rho}\}
\]
\[
S = S'. \tag{4.25}
\]
The quantum Liouville equation 
\[\frac{\partial}{\partial t} \hat{\rho}(t) = \frac{1}{i\hbar}[H, \hat{\rho}(t)] \] describes the unitary evolution of the
global quantum system of radiation and particle. The quantum state of the global system evolves in a unitary manner, represented by 
\[\hat{\rho}(t) = U^\dagger \hat{\rho}(0) U \text{ with } U = T e^{-\frac{1}{i\hbar} \int_{t_0}^t dt' H(t')}, \] as the
unitary operator. Therefore, the global entropy is constant.

Araki-Lieb Inequality for Subsystem Entropies  Another important property of entropy is the Araki-Lieb or triangle inequality
\[115, \]
\[
|S_I - S_{cm}| \leq S_S \leq S_I + S_{cm}. \tag{4.26}
\]
The inequality applies when the subsystems are entangled or correlated. Thus, the quantity 
\[I_c = S_I + S_{cm} - S_S \text{ can be defined } [116] \text{ as the measure of quantum correlation between the center of mass states and the internal states. For a pure state system, the correlation is maximum, with } I_c = 2S_I = 2S_{cm}.
\]
If the system evolves unitarily to new \( S_I', S_{cm} \) and \( S_S \), Eq. 4.25 gives \( S_S = S'_S \).
From Eq. 4.26, we have 
\[|S_I - S_{cm}'| \leq S_S \leq S_I + S_{cm}'. \] By subtracting this with Eq. 4.26, we have 
\[0 \leq (S_I + S_{cm}') - (S_I + S_{cm}). \] Thus, in order to reduce the \( cm \), entropy \( S_{cm}' - S_{cm} < 0 \), we need to increase the internal entropy by at least the same amount \( S_I - S_I(t) \geq 0 \).
If initially the internal subsystem is in pure state $S_I = 0$, the unitary evolution will have to create an internal mixed state with a finite internal entropy $S'_I \geq 0$ in order to reduce the external entropy. If the system is in pure state, $S_S = 0$, Eq. 4.26 gives $S_I = S_{cm}$. This means that even if the gas system has no entropy, it may populate many internal states and large momentum width (externally hot).

The global system (see Fig. 4.2) is composed of particle system (molecular/atomic gas) interacting with the environment (thermal radiation) is a closed system. The entropy of the closed global system can only increase, in accordance to the 2nd law of thermodynamics. The global system can be regarded as composed of two systems: particle and radiation. The particle system is an open system, open to interactions with radiation. The radiation system is open changes due to the particle system. But any changes would be small and rapidly disappear since the radiation system (thermal vacuum) is large and so, maintains a state close to equilibrium with the maximum radiation entropy. The particle-radiation interaction is characterized as irreversible in time if dissipation is involved. During dissipation process, the global entropy must increase until the dissipation ceases when the particle system and the environment reach equilibrium with maximum global entropy.

Entropy can flow two ways between the particle system to the environment as long as the global entropy is constant or increase. Laser cooling is intended to induce the flow of entropy from particles to the environment. The external laser fields provides work to the particle system-radiation for removing the system entropy $S_S$ from the heat source (particles) to the heat sink (radiation) through a dissipative mechanism, namely optical spontaneous emissions. Since the number of occupied internal states does not increase throughout the cooling, the particle center of mass entropy is reduced. Molecules have additional motional degrees of freedom from vibration and rotation, but these are included with the electronic states as the internal degrees.

Trapped gas [304] is physically decoupled from any matter. The only channel of dissipation is via interactions with vacuum fields which lead to spontaneous emissions. If the spontaneous emission is suppressed; there will be no dissipation, the system entropy is constant and there is no entropy flow to or from the environment. However, the entropy of the subsystems can be either increased or decreased through a unitary process. This enables the transfer of entropy from one subsystem to another even by coherent laser interactions alone. It is the basis of cooling certain degree of freedom without dissipation [301].

### 4.3.1 Comparisons of Renyi and von Neumann Entropies

The Renyi entropy is the measure of purity of a system and is defined as [113]

$$S^R(t) = Tr\{\hat{p}^2(t)\} \leq 1$$  \hspace{1cm} (4.27)

For qubit ensemble with probability $-1 \leq x \leq 1$ the Renyi entropy $S^R_{qubit} = x^2 + (1 - x)^2$ has a minimum. In contrary, the von Neumann entropy $S_{qubit} = -x \ln x - (1 - x) \ln(1 - x)$
Figure 4.3: Comparison of the a) Renyi entropy with a minimum and b) von Neumann entropy with a maximum for qubit system.

has a maximum.

Although both the von Neumann entropy and the Renyi entropy are the measure of dispersion of states, the former increases with increasing dispersion while the latter decreases. It has been pointed out in Ref. [73] that $S^R$ is a more appropriate measure of phase space density for the purpose of achieving Bose-Einstein Condensation (BEC) via evaporative cooling. This is because $S^R$ does not change due to the loss of particles during evaporative cooling, while $S$ does. We will show in that $S$ is dependent on the number of particles for equilibrium ensemble of non-interacting gas. The cooling scheme in this thesis does not involve the loss of particles, so both are equally suited for measuring the extend of cooling. Analytical results can be obtained more easily with Renyi entropy although it is not related to the thermodynamic entropy, as the von Neumann entropy.

4.3.2 Entropy Production Rate

In this section, we obtain the entropy production rate of the particle system. It determines how fast entropy can be transferred between the environment and the particle system and is useful to estimate the rate of laser cooling. The entropy production rate of the system is evaluated as

$$\frac{d}{dt}S_e(t) = -k_B Tr_e\left\{ \frac{dU^\dagger}{dt}U \hat{\rho}_e^d(t) (\ln \hat{\rho}_e^d(t) + 1) \right\} - k_B Tr_e\{ \hat{\rho}_e^d(t)U \frac{dU}{dt}(\ln \hat{\rho}_e^d(t) + 1) \} - k_B Tr_e\{ U^\dagger \hat{H} \hat{\rho}_e^d(t) (\ln \hat{\rho}_e^d(t) + 1) \} - k_B Tr_e\{ U^\dagger \hat{L} \hat{\rho}_e^d(t)U (\ln \hat{\rho}_e^d(t) + 1) \}$$

where $e \in S, I, cm$ and $\hat{\rho}_e^d(t) \triangleq U^\dagger \hat{\rho}_e U$ is diagonalized density matrix. The first and second lines are zero since $\hat{\rho}_e^d(t)$ and $\ln \hat{\rho}_e^d(t)$ commutes and finally by using $\ln \hat{\rho}_e^d(t) = U^\dagger \ln \hat{\rho}_e(t)U$ we have
\[ \frac{d}{dt} S_c(t) = -k_B Tr_c \{ \mathcal{L}\dot{\rho}_c(t) [\ln \dot{\rho}_c(t) + 1] \} \]  

(4.28a)

The duration required to reduce the entropy from \( S_{c_0} \) at time \( t = 0 \) to zero is \( \tau \), which satisfies \( \int_0^\tau \frac{d}{dt} S_c dt = -S_{c_0} \).

It is well-known that the master equation for internal states of a two-level system interacting with a thermal reservoir has the Lindblad form [110]. From Eq. 3.149,3.157-3.159, we can obtain the typical master equation in thermal radiation [220],

\[
\frac{\partial \rho(t)}{\partial t} = \mathcal{L}\rho(t) = \frac{\Gamma(\Omega + 1)}{2} \left( -\rho(t)S^+ S^- - S^+ S^- \rho(t) + 2S^- \rho(t) S^+ \right) + \frac{\Gamma(\Omega + 1)}{2} \left( -\dot{\rho}(t)S^- S^+ - S^- S^+ \dot{\rho}(t) + 2S^+ \dot{\rho}(t) S^- \right) = \left( \begin{array}{c c c} -\Gamma(\Omega + 1)\rho_{cc}(t) + \Gamma^2 \rho_{pp}(t) & -\frac{\Gamma(\Omega + 1)}{2} \rho_{cp}(t) \\ \frac{\Gamma(\Omega + 1)}{2} \rho_{cp}(t) & \Gamma(\Omega + 1)\rho_{cc}(t) - \Gamma^2 \rho_{pp}(t) \end{array} \right) \]  

(4.29)

with the solutions

\[
\rho_{cc}(t) = \frac{1}{2} \left( 1 + e^{-\gamma t} - \frac{1 - e^{-\gamma t}}{2\Omega + 1} \right) \rho_{cc}(0) + \frac{\pi(1 - e^{-\gamma t})}{2\Omega + 1} \rho_{pp}(0)
\]

\[
\rho_{pp}(t) = \frac{\Omega + 1}{2\Omega + 1} \rho_{cc}(0) + \frac{1}{2} \left( 1 + e^{-\gamma t} + \frac{1 - e^{-\gamma t}}{2\Omega + 1} \right) \rho_{pp}(0)
\]

\[
\rho_{cp}(t) = \rho_{cp}(0) e^{-\gamma t}
\]

(4.30)

where \( \rho_{ab}(t) = \int \rho_{ab}(\mathbf{P}, t) d^3 P \) are the externally traced matrix elements and \( \gamma = \frac{1}{2} \Gamma(2\Omega + 1) \). The internal entropy production rate from interaction of two-level system with thermal reservoir is readily computed

\[
\frac{dS_i(t)}{dt} = -k_B \Gamma \left( \pi \rho_{pp}(t) - (\Omega + 1) \rho_{cc}(t) \right) \ln \frac{\rho_{cc}(t)}{\rho_{pp}(t)}
\]

(4.31a)

Thus, the internal entropy production rate is proportional to the decay rate \( \Gamma \).

From Eq. 4.16, the external entropy production rate gives the rate of translational cooling, written in discrete and continuous variables

\[
\frac{d}{dt} S_{cm}(t) = -k_B \sum_\mathbf{P} \frac{\partial f(\mathbf{P}, t)}{\partial t} \{ \ln f(\mathbf{P}, t) + 1 \}
\]

(4.32)

\[
\frac{d}{dt} S_{cm}(0) = -k_B \int \frac{\partial f(\mathbf{P}, t)}{\partial t} \{ \ln f(\mathbf{P}, t) + 1 \} d^3 P
\]

(4.33)

Thus, the translational cooling rate is directly proportional to the rate of increase in the momentum probability density.

The Renyi entropy production rate can be easily evaluated as

\[
\frac{d}{dt} S_R^c(t) = Tr_c \{ \mathcal{L}\dot{\rho}_c(t) \dot{\rho}_c(t) + \dot{\rho}_c(t) \mathcal{L}\dot{\rho}_c(t) \}
\]

(4.34)
4.3.3 Internal Entropy during Fluorescence

In the cooling of gas, we are mainly interested in reducing c.m. (external) sub-system entropy, and possibly the internal entropy too. Therefore, the evaluation of both subsystem entropies is important. Equations 4.16-6.19 can be used to describe the transient entropies of a fluorescence process. The evaluation of \( S_{\text{cm}}(t) \) requires numerical approach to solve for \( f(\mathbf{p}, \mathbf{t}) \).

Here, we evaluate the internal entropy of an example of the optical spontaneous emissions from a single excited electronic state \( |e\rangle \) to the ground vibronic states \( |i\rangle \) with the Franck-Condon factor \( F_i \) and \( \sum_i F_i = 1 \).

The solutions for the populations are obtained from Eqs. 3.156 as \( \rho_{ee}(t) = \rho_{ee}(0)e^{-\Gamma t}, \rho_{ii}(t) = \rho_{ii}(0) + \rho_{ee}(0) \frac{\Gamma}{\Gamma_i} (1 - e^{-\Gamma t}) \) where \( \Gamma = \sum_i \Gamma_i \). If we assume \( \Gamma_i = F_i \Gamma \), we have \( \rho_{ii}(t) = \rho_{ii}(0) + F_i \rho_{ee}(0)(1 - e^{-\Gamma t}) \) and the internal entropy is evaluated from

\[
S_i(t) = -k_B \rho_{ee}(t) \ln \rho_{ee}(t) - k_B \sum_i \rho_{ii}(t) \ln \rho_{ii}(t) \tag{4.35}
\]

If \( \rho_{ii}(0) = 0 \), we have

\[
S_i(t) = -k_B \rho_{ee}(0)e^{-\Gamma t} \{ \ln \rho_{ee}(0) - \Gamma t \} - k_B \rho_{ee}(0)(1 - e^{-\Gamma t}) \{ \sum_i F_i \ln F_i + \ln \{ \rho_{ee}(0)(1 - e^{-\Gamma t}) \} \} \tag{4.36}
\]

4.4 Entropy-Wigner Function Relationships

In cooling of molecules, we wish to reduce \( S_{\text{cm}} \) and possibly \( S_I \) as well. The c.m. entropy \( S_{\text{cm}} \) is associated with the quasi phase space density \( W(\mathbf{R}, \mathbf{P}, t) \) of the translational motion through \( f(\mathbf{P}, t) = \int W(\mathbf{R}, \mathbf{P}, t) d^3 R \) and Eq. 4.16

\[
S_{\text{cm}}(t|0) = -k_B \int \int W(\mathbf{r}, \mathbf{p}, t) d^3 \mathbf{r} d^3 \mathbf{p} \ln \frac{W(\mathbf{r}, \mathbf{p}, t) d^3 \mathbf{r} d^3 \mathbf{p}}{W(\mathbf{r}, \mathbf{p}, 0) d^3 \mathbf{r} d^3 \mathbf{p}} \tag{4.37}
\]

Therefore it is useful to find the relationship between entropy and the Wigner function as a quasi phase space density. In Ref. [109], the relationship between entropy and classical phase space in classical regime was outlined. It is argued that unitary evolution cannot change the phase space. Here, we derive the exact relationship between Renyi quantum entropy and the Wigner function. The following property has been derived in Ref. [221]

\[
Tr\{\hat{\rho}_1(t)\hat{\rho}_2(t)\} = (2\pi \hbar)^3 \int \int W_1(\mathbf{r}, \mathbf{p}, t) W_2(\mathbf{r}, \mathbf{p}, t) d^3 \mathbf{p} d^3 \mathbf{r} \tag{4.38}
\]

By letting \( \hat{\rho}_1(t) = \hat{\rho}_2(t) \), we find
\[ S_{\text{Renyi}} = Tr\{\rho^2(t)\} = (2\pi \hbar)^3 \sum_{a,b} \int \int W_{ab}(r,p,t)W_{ba}(r,p,t) d^3p d^3r \leq 1 \quad (4.39) \]

\[ \frac{dS_{\text{Renyi}}}{dt} = (2\pi \hbar)^3 \sum_{a,b} \int \int \{W_{ab} \frac{dW_{ba}}{dt} + W_{ba} \frac{dW_{ab}}{dt}\} d^3p d^3r \quad (4.40) \]

In a unitary process, \( \frac{dS_{\text{Renyi}}}{dt} = 0 \) even if \( \frac{dW(r,p,t)}{dt} = O(\hbar) \neq 0 \) as we have shown from Eq. 4.2. If we neglect the internal states, we see that \( \frac{\partial^{n+1} W(r,p,t)}{\partial r^{n+1}} \) and \( W(r,p,t) \) have opposite parities in momentum space, so their product is an odd function and the integral over the momentum space vanishes \( \int \frac{\partial^{n+1} W(r,p,t)}{\partial r^{n+1}} W(x,p,t) d^3p = 0 \) irrespective of the nature of the potential \( V(x,t) \).

### 4.5 Cooling Based on Thermodynamics

Most existing cooling schemes like laser cooling do not employ the process of thermalization. The processes are dynamical and non-equilibrium. Thus, thermodynamics does not apply and temperature is undefined. The internal and external degrees are not in equilibrium during cooling process.

However, in the cooling of gas the initial ensemble of molecular gas is can be close to thermal equilibrium. Here, temperature and thermodynamics apply. We can derive the entropy, the energy and thermodynamic temperature from the equilibrium density operator for the external c.m. state, the internal electronic-vibrational-rotational states of a molecule, as well as the thermal radiation. It is important to know the equilibrium quantum states, the mean energy and entropy of the external and internal degrees of the gas, which can be compared with their transient and final values. The knowledge of the equilibrium entropy of a system can be used to estimate the required cooling duration if we also know the entropy production rate \( dS/dt \) as computed earlier.

Several schemes which reduce the kinetic energy of atoms merely by adiabatically reducing the trap potential are called "cooling" schemes [54], [55], [56]. It seems that these schemes cannot be termed as cooling since there is no clear dissipative mechanism involved. However, the trapping potential is changed slowly or adiabatically either in depth or in the shape. In this process, the system remains in quasi-equilibrium and thermodynamics is applicable. In fact, the interparticle interactions and collisions continually provide the thermalization through micro-irreversibility mechanism for keeping the system in quasi-equilibrium. Thus, the removal of energy (kinetic or internal) alone also removes the entropy.

#### 4.5.1 Equilibrium State and Entropy

At equilibrium, the average energy and entropy of the system are constant of time. Using the Lagrange multiplier \( \sum_x m_x \frac{\partial}{\partial u_i} X\{\{u_i\}\} = 0 \), we can find the multipliers \( m_x \) which
give the extremum values for the parameters $X \in N, E, S$ having a common variables $\{N_c\}$ as given by

$$Tr\{\hat{\rho}_{eq}\} = \sum_e w_e = 1 \iff N = \sum_e g_e n_e = \sum N_c \quad (4.41)$$

$$\langle \hat{H} \rangle_{eq} = Tr\{\hat{\rho}_{eq} \hat{H}\} = \sum_e w_e E_e \iff \sum N_e E_e = E. \quad (4.42)$$

$$S_{eq} = -k_B Tr\{\hat{\rho}_{eq} \ln \hat{\rho}_{eq}\} = -k_B \sum_e w_e \ln w_e \iff -k_B \sum N_e \ln N_e \quad (4.43)$$

where $w_e$ is probability of occupation in energy level $E_e$.

For many-particle system ($\iff$), $N$ is the total number of particles, $N_c = g_e n_e$ is the number of particles in energy level $E_e$, with degeneracy $g_e$ and $n_e$ is the number of particles in each level $|e, M_e\rangle$ of the degenerated level. So, the probability in each level and each state are $P_e = \frac{N_e}{N}$ and $p_e = \frac{n_e}{N}$ respectively. This gives $\hat{\rho}_{eq} = e^{-\left(1+\lambda\right)e^{-\beta \hat{H}}}$, Using $Tr\{\hat{\rho}(t)\} = 1$, we have $e^{-\left(1+\lambda\right)} = 1/\sum g_e e^{-\beta E_e}$ and we can write the equilibrium state, energy and entropy as:

$$\hat{\rho}_{eq} = e^{-\beta \hat{H}} / Z \text{ with partition function } Z = \text{Tr}\{e^{-\beta \hat{H}}\} \text{ and } \beta = 1/k_B T \quad (4.44)$$

$$\langle \hat{H} \rangle_{eq} = \text{Tr}\{\hat{\rho}_{eq} \hat{H}\} = -\frac{d}{d\beta} (\ln Z) \text{ with } \frac{dZ}{d\beta} = -\text{Tr}\{\hat{H} e^{-\beta \hat{H}}\} = -Z \langle \hat{H} \rangle_{eq} \quad (4.45)$$

$$S_{eq} = k_B \left\{ \beta \langle \hat{H} \rangle_{eq} + \ln Z \right\} \quad (4.46)$$

Thus, at thermodynamic equilibrium the energy is proportional to entropy (Eq. 4.46). This shows that the reduction of energy (kinetic or internal) alone corresponds to reduction of the entropy and cooling. Equation 4.46 also conforms with the the definition of thermodynamic temperature \cite{293} $\frac{\partial U}{\partial S} = 1/k_B \beta = T$. However, the equilibrium Renyi entropy is $S_{eq}^R = k_B Tr\{e^{-2\beta \hat{H}}\} / Z^2$ which does not correspond to the thermodynamic temperature. Recently, the quantum entropy is used to derive the 2nd law of thermodynamics \cite{302}. Thus, the von Neumann entropy is related to thermodynamics but the Renyi entropy is not.

**Harmonic Oscillator State (Low Molecular Vibrations)**

A particle in a harmonic trap or the low vibrational states of a molecule can be described by the harmonic oscillator Hamiltonian $\hat{H}(t) = (\hat{\alpha}^\dagger \hat{\alpha} + \frac{1}{2})\hbar \nu \equiv \sum(n + \frac{1}{2})\hbar \nu |n\rangle \langle n|$ with eigenvalue $E_n(t) = (n + \frac{1}{2})\hbar \nu$ where $\hat{\alpha}^\dagger \hat{\alpha} \equiv \sum n |n\rangle \langle n|$. The equilibrium density matrix for harmonic oscillator is
\[ \hat{\rho}_{\text{osc,eq}} = e^{-\beta(\hat{b} \hat{b} + \frac{1}{2} \hat{H})} / Z = \sum_n W_n |n\rangle \langle n| = (1 - e^{-\beta \hat{H}}) e^{-\beta \hat{b} \hat{b}} \] 

(4.47)

where \( W_n \equiv (1 - e^{-\beta \hat{H}}) e^{-\beta \hat{b} \hat{b}} = \frac{1}{(1 + \bar{n}) \left( \frac{\bar{n}}{1 + \bar{n}} \right)^n } \) is the eigenenergy for state \(|n\rangle\), \( Z = e^{-\frac{1}{2} \beta \hat{b} \hat{b}} (1 - e^{-\beta \hat{H}})^{-1} \) and \( \bar{n} \equiv (e^{\beta \hat{H}} - 1)^{-1} \).

The average energy can be written in various forms

\[ \langle \hat{H} \rangle_{eq} = \frac{1}{2} \hbar \omega + \frac{\hbar \omega}{(e^{\beta \hbar \omega} - 1)} = \hbar \omega \left( \frac{1}{2} + \bar{n} \right) = \frac{1}{\beta} \left( \bar{n} + \frac{1}{2} \right) \ln \left( \frac{1}{\bar{n}} + 1 \right) = \frac{\hbar \omega (e^{\beta \hbar \omega} + 1)}{2} = \frac{\hbar \omega}{2} \coth \left( \frac{\beta \hbar \omega}{2} \right) \]

(4.48)

so it is clear that \( \bar{n} \) is identified as the mean occupation number. The equilibrium entropy follows directly from Eq. 4.46,

\[ S_{eq} = k_B \left\{ \frac{\beta \hbar \omega}{2} \coth \left( \frac{\beta \hbar \omega}{2} \right) - \frac{\beta \hbar \omega}{2} - \ln(1 - e^{-\beta \hbar \omega}) \right\} \]

\[ = k_B \left\{ \frac{\beta \hbar \omega}{e^{\beta \hbar \omega} - 1} - \ln(1 - e^{-\beta \hbar \omega}) \right\} = k_B \left\{ (1 + \bar{n}) \ln(1 + \bar{n}) - \bar{n} \ln \bar{n} \right\} \]

(4.49)

For \( N \) number of noninteracting 3D harmonic oscillators, (%)

\[ S_{eq} = N k_B \left\{ \frac{1}{e^{\beta \hbar \omega} - 1} - 3 \ln(1 - e^{-\beta \hbar \omega}) - \ln N + 1 \right\} \]

The equilibrium Renyi entropy is \( S^R_{eq} = k_B Tr\left\{ (1 - e^{-\beta \hbar \omega})^2 e^{-2 \beta \hbar \omega \hat{b} \hat{b}} \right\} = k_B (1 - e^{-\beta \hbar \omega})^2 \sum_n e^{-2 \beta \hbar \omega n} = k_B \left( \frac{1 - e^{-\beta \hbar \omega}}{1 + e^{-\beta \hbar \omega}} \right) = k_B \tanh \left( \frac{\beta \hbar \omega}{2} \right), \text{ with } \frac{\partial \langle \hat{H} \rangle_{eq}}{\partial \beta} \neq T. \text{ Thus, the Renyi entropy does not correspond to thermodynamic quantities.} \]

**Gibbs State of Translational Degree**

The Hamiltonian for a translational kinetic energy of a particle in free space is

\[ \hat{H} = \hat{p}^2 / 2M = \sum_j \langle p_j | p_j \rangle / 2M \]

with \( \hat{p} | p_j \rangle = p_j | p_j \rangle \) and \( \hat{p}^2 = \sum_j p_j^2 | p_j \rangle \langle p_j | \) for discrete values. The equilibrium state of the translational degree of freedom is called the Gibbs state with

\[ \hat{\rho}_{\text{cm,eq}} = \frac{1}{Z} \sum_j e^{-\beta \hat{p}_j^2 / 2M} | p_j \rangle \langle p_j | \]

(4.50)

\[ Z = Tr\left\{ e^{-\beta \hat{p}^2 / 2M} \right\} = \sum_j e^{-\beta \hat{p}_j^2 / 2M} \]

(4.51)

\[ \langle \hat{H} \rangle_{eq} = - \frac{d}{d\beta} (\ln Z) = \frac{1}{Z} \sum_j K_j e^{-\beta K_j} \]

where \( K_j = p_j^2 / 2M \)

(4.52)

\[ S_{eq} = k_B \left\{ \frac{\beta}{Z} \sum_j K_j e^{-\beta K_j} + \ln \left( \sum_j e^{-\beta K_j} \right) \right\} \]

(4.53)
In continuous variable, we make the replacement $\sum_k \rightarrow \left(\frac{V}{\hbar^3}\right)^4 \int_0^\infty p^2 e^{-\beta p^2/2M} dp \int_0^\pi d\theta \int_0^{2\pi} d\phi$ with $V$ as the volume occupied by the particle and Eqs. 4.50-4.53 transform as

$$\dot{\rho}_{cm,eq} = \frac{V}{\hbar^3} \frac{4\pi}{Z} \int_0^\infty \{p^2 e^{-\beta p^2/2M}\}|p\rangle \langle p| dp$$

$$Z = \frac{V}{\hbar^3} \int_0^\infty dp \int_0^\pi d\theta \sin \theta \int_0^{2\pi} d\phi \frac{p^2 e^{-\beta p^2/2M}}{\hbar^3} = V \left(\frac{2\pi M k_B T}{\hbar^2}\right)^{3/2} = \frac{V}{N^3}$$

$$\langle \hat{H} \rangle_{eq} = -\frac{d}{d\beta} \left(\frac{3}{2} \ln V + \frac{3}{2} \ln \left(\frac{2\pi M k_B T}{\hbar^2}\right)\right) = \frac{3}{2} k_B T$$

$$S_{eq} = k_B \left(\frac{3}{2} + \frac{3}{2} \ln \left(\frac{2\pi M k_B T}{\hbar^2}\right) + \ln V\right)$$

where $\Lambda = h/\sqrt{2\pi M k_B T}$ is the translational de Broglie wavelength. The equilibrium Renyi entropy is can be evaluated as

$$S_R^L = \frac{A^6}{V^2} \frac{V}{\hbar^3} \int_0^\infty p^2 e^{-\beta p^2/2M} dp = k_B \frac{A^3}{V} = k_B / Z$$

The above derivations are for single particle. For a system of $N$ non-interacting identical particles we can write the many particle free Hamiltonian in terms of the single particle Hamiltonian $\hat{H}_N = N \hat{H}$ and use

$$\sum_k \rightarrow \frac{1}{N!} \hbar^3 N \prod_i \int d^3 p_i d^3 r_i \ldots \rightarrow \frac{1}{N!} \left(\frac{V}{\hbar^3}\right) \int_0^\infty dp \int_0^\pi d\theta \sin \theta \int_0^{2\pi} d\phi \ldots \right)^N$$

Thus, Eqs. 4.54-4.56 become

$$\dot{\rho}_{cm,eq} = \frac{1}{Z_N N!} \left\{\frac{V}{\hbar^3} \int_0^\infty p^2 e^{-\beta p^2/2M} |p\rangle \langle p| \int_0^\pi d\theta \sin \theta \int_0^{2\pi} d\phi \right\}^N$$

$$Z_N = Z^N / N!$$

$$\langle \hat{H} \rangle_{N,eq} = N \langle \hat{H} \rangle_{eq}$$

By using the Stirling approximation $\ln N! \approx N \ln N - N$, we have the entropy for a system of $N$ non-interacting particles

$$S_{eq} = k_B \{\beta N \langle \hat{H} \rangle_{eq} \ln Z + N Z / N!\} = N k_B \{\beta \langle \hat{H} \rangle_{eq} + \ln Z - \ln N + 1\}$$

$$= N k_B \left\{\frac{5}{2} + \ln\left(\frac{V}{N^3}\right)\right\} = N k_B \left\{\frac{5}{2} + \ln(N \hbar^3 / \rho_\Omega)\right\}$$

where we have used Eq. 4.8, to define the classical phase space density as $\rho = nA^3/\hbar^3$ and $n = N/V$. If we defined the phase space volume as $\rho_\Omega = N/\rho$, we have the result in Ref. [109], $S_{eq} = N k_B \left\{\frac{5}{2} + \ln(N \hbar^3 / \rho_\Omega)\right\}$.

We see that the von Neumann entropy depends on the number of particles, as mentioned in the previous Section. The equilibrium translational entropy is large if the temperature and volume are large and the phase space density is low.
Thermal Reservoir State

The multimode thermal photons state is given by [126], which is the combination of harmonic oscillators

$$
\hat{\rho}_{R,eq} = e^{-\frac{\sum_{k,\lambda} \frac{\hbar}{2p} (\hat{a}^{\dagger}_{k,\lambda} \hat{a}_{k,\lambda} + \frac{1}{2})}{\hbar}} / Tr \left( \prod_{k,\lambda} e^{-\frac{\hbar}{2p} (\hat{a}^{\dagger}_{k,\lambda} \hat{a}_{k,\lambda} + \frac{1}{2})} \right) = \prod_{k,\lambda} (1 - e^{-\frac{\hbar}{2p} x}) e^{-\frac{\hbar}{2p} x^{2} \hat{a}^{\dagger}_{k,\lambda} \hat{a}_{k,\lambda}}
$$

(4.64)

Since $\hat{a}^{\dagger}_{k,\lambda} \hat{a}_{k,\lambda}$ is a diagonal operator in the basis $\{|n_{k,\lambda}\rangle\}$, the spectral decomposition theorem [218] allows us to write $e^{-x_{k,\lambda} \hat{a}^{\dagger}_{k,\lambda} \hat{a}_{k,\lambda}} = \sum_{n_{k,\lambda}} |n_{k,\lambda}\rangle \langle n_{k,\lambda}| e^{-x_{k,\lambda} n_{k,\lambda}}$ where we have used $\hat{a}^{\dagger}_{k,\lambda} \hat{a}_{k,\lambda} = \sum_{n_{k,\lambda}} |n_{k,\lambda}\rangle \langle n_{k,\lambda}|$ and $x_{k,\lambda} = \frac{\hbar \omega_{k,\lambda}}{k_{B} T}$.

In free space, we convert to integration using Eq. 8.54 (Appendix II) and derive the thermal entropy using $S_{R} = -k_{B} Tr_{R}\{\hat{\rho}_{R} \ln \hat{\rho}_{R}\}$. We cannot use $S_{eq} = k_{B} \beta \langle \hat{H}_{eq} \rangle + \ln Z$ because the number of thermal photons is not fixed and therefore cannot be normalized. $Tr\{\hat{\rho}_{R}\} \neq 1$. The entropy is calculated as follows:

$$
S_{R} = - \frac{V}{(2\pi c)^{3}} 2(4\pi)k_{B} \left( \frac{k_{B} T}{\hbar} \right)^{3} \int_{0}^{\infty} x^2 \ln(1 - e^{-x}) - x^3 (e^x - 1)^{-1} dx \quad (4.65)
$$

where we have used $\sum_{n=0}^{\infty} e^{-nx} = (1 - e^{-x})^{-1}$ and $\sum_{n=0}^{\infty} n e^{-nx} = - \frac{d}{dx} ((1 - e^{-x})^{-1})$ with $x = \frac{\hbar \omega}{k_{B} T}$.

By using $\int_{0}^{\infty} x^2 \ln(1 - e^{-x}) dx = \frac{1}{15} \pi^{4}$, $\int_{0}^{\infty} \frac{d}{dx} \{x^3 \ln(1 - e^{-x})\} dx = 3x^2 \ln(1 - e^{-x}) + x^3 (e^x - 1)^{-1}$ and $\int_{0}^{\infty} \left( \frac{d}{dx} \{x^3 \ln(1 - e^{-x})\} \right) dx = - \frac{4}{45} \pi^{4}$, we can evaluate Eq. 4.65 as

$$
S_{R} = \frac{4}{45} \pi^{2} \frac{V k_{B}^{4} T^{3}}{c^{3}} \quad (4.66)
$$

From the radiation Hamiltonian $\hat{H}_{R} = \sum_{k,\lambda} \hbar \omega_{k,\lambda} (\sum_{n_{k,\lambda}} |n_{k,\lambda}\rangle \langle n_{k,\lambda}| + \frac{1}{2})$, we have the mean energy

$$
U = Tr\{\hat{\rho}_{R,eq} \hat{H}_{R}\} = \sum_{k,\lambda} (1 - e^{-\frac{\hbar \omega_{k,\lambda}}{2p} T}) \hbar \omega_{k,\lambda} \sum_{n_{k,\lambda}} (n_{k,\lambda} + \frac{1}{2}) e^{-\frac{\hbar \omega_{k,\lambda}}{2p} n_{k,\lambda} \hbar T} = \sum_{k,\lambda} \hbar \omega_{k,\lambda} \left( \bar{n}_{k,\lambda} + \frac{1}{2} \right)
$$

(4.67)

where $\bar{n}_{k,\lambda} = (e^{\beta \hbar \omega_{k,\lambda}} - 1)^{-1}$ is the mean thermal photon number for mode-$k\lambda$. By neglect the diverging zero point energy and converting the summation to integration, we obtain the Stefan-Boltzmann law

$$
U \rightarrow 2(4\pi) \frac{V}{(2\pi c)^{3}} \int_{0}^{\infty} (e^{\frac{\hbar \omega}{2p} T} - 1)^{-1} \hbar \omega^{3} d\omega = \frac{\pi^{2}}{15} \frac{V}{c^{3}} \frac{1}{k_{B}^{3}} T^{4} \quad (4.68)
$$

The numerical factor of Eq. 4.68 is exactly the same as that derived by Planck in 1914 (Ref. [292], p. 171) which was written in another form $U/V = 48\pi\alpha \frac{k_{B} T}{\hbar^{3}}$ where $\alpha = \sum_{n=1}^{\infty} \frac{1}{n^{3}} \approx 1.0823$. 


Molecular Internal State

The equilibrium state for the internal state of a molecule can be written as

$$ \hat{\rho}_{I,eq} = e^{-E_{\lambda,\Sigma,v,J,\Omega} / k_B T} / \sum_{\lambda,\Sigma,v,J,\Omega} e^{-E_{\lambda,\Sigma,v,J,\Omega} / k_B T} \quad (4.69) $$

$$ E_{\lambda,\Sigma,v,J,\Omega} = \hbar c \{ T_c (\Lambda, \Sigma) + A \Omega^2 \} + \hbar c \{ \omega_e (v + \frac{1}{2}) - \omega_e x_e (v + \frac{1}{2})^2 \} + \hbar c \{ B_v \{ J(J + 1) - \Omega^2 \} - D_v \{ J(J + 1) - \Omega^2 \}^2 \} \quad (4.70) $$

where $E_{\lambda,\Sigma,v,J,\Omega}$ is the molecular eigenenergy.

The internal state can be decoupled into electronic, vibrational and rotational parts as $\hat{\rho}_{I,eq} = \hat{\rho}_{el,eq} \hat{\rho}_{vib,eq} \hat{\rho}_{rot,eq}$ if the rotational electronic coupling is neglected, as for the case $\Omega = 0$.

$$ \hat{\rho}_{el,eq} = e^{-E_{\lambda,\Sigma,\Omega} \hbar \Omega / k_B T} / \sum_{\lambda,\Sigma} e^{-E_{\lambda,\Sigma,\Omega} \hbar \Omega / k_B T} \quad (4.71) $$

$$ \hat{\rho}_{vib,eq}(v) = e^{-E_v \hbar v / k_B T} / \sum_v e^{-E_v \hbar v / k_B T} \rightarrow (1 - e^{-\hbar \omega_v / k_B T}) \quad (4.72) $$

$$ \hat{\rho}_{rot,eq}(J) = e^{-E_J \hbar J \hbar J / k_B T} / \sum_J (2J + 1) e^{-E_J \hbar J / k_B T} \rightarrow \frac{\hbar c B_v}{\hbar c B_v} \frac{\hbar c B_v}{\hbar c B_v} \quad (4.73) $$

where $E_{\lambda,\Sigma,\Omega} = \hbar c \{ T_c (\Lambda, \Sigma) + A \Omega^2 \}, E_v = \hbar c \{ \omega_e (v + \frac{1}{2}) - \omega_e x_e (v + \frac{1}{2})^2 \}$ and $E_J = \hbar c \{ B_v \{ J(J + 1) - D_v \{ J(J + 1) \}^2 \}$ are the eigenenergies of the electronic, vibrational and rotational states.

At temperature 1K and typical molecular parameters [171] of $\hbar c T_e \sim 10^{15} \text{s}^{-1}, \hbar c \omega_e \sim 10^{15} \text{s}^{-1}$ and $\hbar c B_v \sim 10^{11} \text{s}^{-1}$, only a single ground electronic state and the ground vibrational state are mainly occupied, but typically 5-10 rotational levels are significantly occupied.

4.5.2 Thermodynamic Cooling Concepts

The populations and entropies of the above equilibrium states vary with temperature. Thus, the internal populations of a system can be controlled by thermal contact with thermal heat source which transfers heat to the system or heat sink which dissipates heat away from the system. Several works have shown the applicability of thermodynamics in the physics of cooling. It is useful to analyze these works and see how the underlying principles can be applied for cooling of molecular gas in equilibrium regime. The earliest scheme is adiabatic demagnetization cooling of solid which is based on two thermodynamical processes [25]. First, the solid is in contact with a heat sink and in strong magnetic field $H$, an internal level is split into upper and lower energy levels $E_1 = \Delta \mu \hbar$ (antiparallel) and $E_2 = -\Delta \mu \hbar$ (parallel) respectively, where $\Delta \mu$ is the fine splitting due to intrinsic interactions within the solid. The mean internal energy $U_{\text{spin}} = -\Delta \mu \hbar \tan \frac{\Delta \mu \hbar}{2k_B T}$. 
and the entropy $S_{\text{spin}} = k_B \{-\frac{\Delta H + \mu H}{2k_B T_f} \tanh \frac{\Delta H + \mu H}{2k_B T_f} + \ln(2 \cosh \frac{\Delta H + \mu H}{2k_B T_f})\}$ reduce with magnetic field, so populations tend toward the lower quantum state. The temperature is the same as the heat sink and unchanged (isothermal) but the entropy is dissipated to the heat sink. This process is termed isothermal magnetization. The second process is isentropic demagnetization, where the solid is insulated from any heat bath so that its total entropy is unchanged. As the magnetic field is reduced to zero, we have a lower final temperature $T_f$ from $S_{\text{spin}} \approx k_B \{-\frac{\Delta H}{2k_B T_f} \tanh \frac{\Delta H}{2k_B T_f} + \ln(2 \cosh \frac{\Delta H}{2k_B T_f})\}$.

Similar principle lies behind the three-level quantum masers engine of Scovil and Dubois [295], [297], [296] which also connects the concept of negative temperature and Carnot engine. The idea lies on controlling the populations at thermal equilibrium by exposing each transition to a thermal source/sink at certain temperature. At steady state (equilibrium), the populations of the states $|e\rangle$, $|o\rangle$ and $|g\rangle$ (with $E_e > E_o > E_g$) are governed by the Maxwell-Boltzmann distribution as

\[
\tilde{\rho}_{ee} = \tilde{\rho}_{gg} e^{-\hbar \omega_g/k_B T_g} = \tilde{\rho}_{gg} \frac{\bar{n}_{eg}}{\bar{n}_{eg} + 1} \tag{4.74}
\]

\[
\tilde{\rho}_{oo} = \tilde{\rho}_{gg} e^{-\hbar \omega_g/k_B T_g} = \tilde{\rho}_{gg} \frac{\bar{n}_{og}}{\bar{n}_{og} + 1} \tag{4.75}
\]

\[
\tilde{\rho}_{ee} = \tilde{\rho}_{oo} e^{-\hbar \omega_o/k_B T_o} = \tilde{\rho}_{oo} \frac{\bar{n}_{eo}}{\bar{n}_{eo} + 1} = \tilde{\rho}_{gg} \frac{\bar{n}_{og}}{\bar{n}_{og} + 1} \frac{\bar{n}_{eo}}{\bar{n}_{eo} + 1} \tag{4.76}
\]

where $\bar{n}_{og} = \left(e^{\hbar \omega_g/k_B T_g} - 1\right)^{-1}$, $\bar{n}_{eg} = \left(e^{\hbar \omega_g/k_B T_g} - 1\right)^{-1}$, $\bar{n}_{eo} = \left(e^{\hbar \omega_o/k_B T_o} - 1\right)^{-1}$ are the mean photon numbers of frequencies $\omega_g, \omega_{eg}, \omega_e$ from the thermal radiation at temperatures $T_g, T_{eg}, T_o$. Since $\tilde{\rho}_{ee} \tilde{\rho}_{gg} \tilde{\rho}_{oo} = 1$, we have

\[
(1 + \frac{1}{\bar{n}_{og}})(1 + \frac{1}{\bar{n}_{eg}}) = 1 + \frac{1}{\bar{n}_{eg}} = e^{\hbar \omega_g/k_B T_g} e^{\hbar \omega_o/k_B T_o} = e^{\hbar \omega_g/k_B T_g} \tag{4.77}
\]

and $\ln \tilde{\rho}_{ee} + \ln \tilde{\rho}_{gg} + \ln \tilde{\rho}_{oo} = 0$ gives the quantum analog of the second and the first laws of thermodynamics, respectively

\[
\frac{E_e - E_g}{T_{eg}} + \frac{E_o - E_g}{T_{og}} + \frac{E_e - E_o}{T_{eo}} \iff \sum_i \frac{dQ_i}{T_i} \geq 0 \tag{4.78}
\]

\[
\omega_{eg} + \omega_{eo} + \omega_{og} \iff \sum_i dQ_i = 0 \tag{4.79}
\]

The equality of Eq. 4.78 holds for reversible processes, which applies also during equilibrium. By coupling two of the three transitions to thermal baths, for example at $T_{eg}$ and $T_{og}$, we obtain the value of $T_{eo}$ which can be negative (implies a population inversion from Eq. 4.76).

In the recent paper of Scoily [298], he devised a scheme which extracts work in the form of maser radiation from a thermal heat bath. It is a kind of perpetual 'quantum maser engine'. Two-level atoms coming out of the thermal reservoir have positive thermal
temperature. The Stern Gerlach apparatus is used to separate the atoms in the excited state from the atoms in the ground state. The atoms in the excited state are passed through a strongly coupled (lossless) cavity and the Rabi transition produces coherent radiation as pure work in the form of maser photons, with the outgoing atoms in the ground state. The atoms are recycled back to the thermal reservoir and the cycle of extracting pure work repeats. The Stern-Gerlach and cavity processes are unitary but the internal entropy has been reduced to zero. This seems physically unjustified from entropy point of view. When the center of mass (c.m.) entropy of the atoms is taken into considerations along with the reduction of the internal entropy, we can understand that the reduction of the internal entropy is the expense of increasing the external c.m. entropy, although the system entropy is unchanged through the unitary process. The underlying physics of this work is crucial in relation to our present work for cooling (Chapter 6) based on the exchange of entropies between two subsystem, namely the internal and external degrees of freedom. The cavity process itself is against the Kelvin-Planck statement; that heat from reservoir cannot be completely transformed into work. The Kelvin-Planck statement has been modified by Ramsey [294] taking into account the definitive existence of negative temperature:

- Kelvin-Planck-Ramsey statement: Heat from a positive temperature reservoir cannot be completely transformed into work and work cannot be completely discarded as heat into a negative temperature reservoir.

Physically, it is possible to completely transform heat from a negative temperature system (inverted atoms) into work. On first sight, the whole process also seems to be against the 2nd law of thermodynamics; that no pure work can be extracted without generating any heat as a residual. Actually, the overall c.m. entropy of the atoms is higher after the Stern-Gerlach and cavity processes. This corresponds to the residual heat. Thus, the physical process would be consistent with thermodynamics only when all possible subsystems are taken into account. The second and third equivalent statements of the 2nd law of thermodynamics are:

- Clausius statement: It is impossible for heat to flow completely from a lower temperature source to higher temperature sink without producing other effects. This statement may be violated (Ref. [300]) for strong coupling between particles and quantum thermal bath.

- Caratheodory statement[293]: The entropy of a system which is exposed to irreversible process can only increase.