Chapter 2

Quantum Interference in Atoms and Molecules: A Review

Quantum interference is one of the most profound effects of quantum mechanics. Feynman referred it as ‘the only mystery’ of quantum mechanics. The field of optical interference has a very old history back in early nineteenth century when Thomas Young performed his famous double slit experiment[1–3]. In general, interference means the superposition of two or more coherent waves resulting in reinforcing or neutralizing effects. Atoms or molecules interacting with electromagnetic fields undergo transitions from initial to final states. Sometimes these may occur through multiple indistinguishable pathways which may interfere enhancing a desired process or suppressing the undesired one under suitable conditions. The coherence signifies the correlation or matching between phases or amplitudes of interfering pathways. Quantum interference has applications in devices such as different types of interferometers [2], super computing quantum device(SQUID), quantum cryptography, quantum computing [4] etc.

Light interacting with a two-level system is a primitive case and has been widely studied [1]. When a multilevel system interacts with electromagnetic fields it can display non-linear optical behaviour which is of great interest for quantum optics researchers. The most simple system is a three-level atomic system. A three-level system can be of three different types: 1) Vee , 2) Lambda and 3) Cascade which are shown in Fig.2.1. Now let us consider a three-level system interacting with two nearly-resonant coherent fields. Each field connects a separate transition, but both transitions share a common energy state. These two pathways can interact
with each other resulting in new and counter-intuitive observations. Interference occurring within a single atom or molecule in the presence of electromagnetic fields can lead to many interesting physical effects such as electromagnetically induced transparency (EIT)[5], coherent population trapping (CPT)[6], lasing without inversion (LWI) [7], Rabi oscillation (RO)[8], Autler Townes splitting (AT) [9], slow light [10], STIRAP [11], vacuum-induced coherence (VIC)[12], quantum beating (QB) [13] etc.

Most of the studies on quantum interference have been done in case of atoms. With the development of the fields of cold and ultra atoms and ions, continuum-bound transitions in atom-molecule coupled system have started to draw attention. In this thesis, our aim is to discuss the quantum interference effects in case atom-molecule coupled system. Our primary focus is on Fano interference. In 1961, Ugo Fano studied the interference among the configurations of discrete level(s) to a continuum [14]. Two ionization pathways interfere leading to an asymmetric peak which is known as Fano profile. This method is useful to discuss the interference effects in atom-molecule coupled system which involves at least one transition from continuum to a bound state. Therefore, we can obtain dressed continuum as discussed in Fano’s theory. In next section, Fano interference will be discussed in

![Diagram of Three-Level Systems](image)
short. Apart from Fano interference, another two interesting quantum interference effects will play key role in chapter 5 and hence they need short introduction in the perspective of atom-molecule coupled systems. They are vacuum induced coherence (VIC) and quantum beating. In the following subsections, we shall discuss these three effects in short.

2.1 Fano Interference

Fano interference [14] is named after famous scientist Ugo Fano. In 1961, Fano studied the coupling of discrete configurations with a continuum of states in case of autoionization. Let us consider a simple case of an autoionizing discrete level interacting with a continuum. Two ionization pathways, one direct and another through autoionizing state, interfere resulting in asymmetric spectral profile.

First, Let us consider an atomic system with discrete level $\phi$ of energy $E_\phi$ and a continuum of states $\psi_{E'}$. Each of these states is assumed to be non degenerate. Next, the energy sub-matrix belonging to the subset of states $\phi$, $\psi_{E'}$ will be
diagonalized. Its elements form a square sub-matrix:

\[ \langle \phi | H | \phi \rangle = E_\phi, \quad (2.1) \]
\[ \langle \psi_{E'} | H | \phi \rangle = V_{E'}, \quad (2.2) \]
\[ \langle \psi_{E} | H | \psi_{E'} \rangle = E' \delta(E - E'). \quad (2.3) \]

The discrete energy level \( E_\phi \) lies within the continuous range of values. Fano treated the problem in dressed picture. The dressed eigenvector of the energy matrix is assumed to have the form:

\[ \chi_{E} = a \phi + \int dE' b_{E'} \psi_{E'}, \quad (2.4) \]

where the dressed coefficients \( a \) and \( b_{E'} \) are the function of \( E \). These coefficients are obtained as solutions of the system of eqs. (2.1) to (2.3):

\[ E_\phi a + \int dE' V_{E'}^* b_{E'} = E a', \quad (2.5) \]
\[ V_{E'} a + E' b_{E'} = E b_{E'}. \quad (2.6) \]

The formal solution can be written as

\[ b_{E'} = \left[ \frac{1}{E - E'} + z(E) \delta(E - E') \right] V_{E'} a. \quad (2.7) \]

The asymptotic behaviour of \( \chi_{E} \) is now compared to the continuum. If \( \psi_{E} \propto \sin(kr) \), where \( E = \frac{k^2 \pi^2}{2m} \) and \( m \) is the mass of the system, then at asymptotic limit

\[ \int dE' b_{E'} \psi_{E'} \propto -\pi \cos(kr) + z(E) \sin(kr) = \sin(kr + \Delta). \quad (2.8) \]

Here, \( \Delta = -\arctan[\pi/z(E)] \) represents the phase shift due to the interaction between the continuum of states \( \psi_{E} \) and discrete level \( \phi \). \( z(E) \) can be expressed as

\[ z(E) = \frac{E - E_\phi - F(E)}{|V_E|^2} \quad (2.9) \]

where,

\[ F(E) = \mathcal{P} \int dE' \frac{|V_{E'}|^2}{E - E'}. \quad (2.10) \]
\( \mathcal{P} \) stands for the principal value of the integral. The phase shift \( \Delta \) varies by \( \sim \pi \) as \( E \) covers the intervals \( \sim |V_E|^2 \) about the resonance at \( E = E_\phi + F(E) \). Therefore, \( F(E) \) represents shift from resonance position of discrete level \( \phi \). With proper normalization, the dressed amplitudes are given by

\begin{align}
    a &= \frac{\sin \Delta}{\pi V_E}, \\
    b_{E'} &= \frac{V_{E'}}{\pi V_E} \frac{\sin \Delta}{E - E'} - \delta(E - E') \cos \Delta.
\end{align}

(2.11) (2.12)

Now if a transition takes place between a state \(|i\rangle\) and the dressed state \(\chi_E\) and \(T\) be the transition operator, the transition probability amplitude is given by

\[ \langle \chi_E|T|i \rangle = \frac{\sin \Delta}{\pi V_E} \left( \langle \Phi|T|i \rangle - \langle \psi_E|T|i \rangle \right) \cos \Delta \]

where,

\[ \Phi = \phi + \mathcal{P} \int dE' \frac{|V_{E'}\psi_{E'}|}{E - E'} \]

(2.13) (2.14)

is an admixture of the discrete level and the states of the continuum. The sharp variation of \( \Delta \) as \( E \) passes through resonance induces a sharp variation of \( \langle \chi_E|T|i \rangle \). Since \( \sin \Delta \) is an even function and \( \cos \Delta \) is an odd function of \( (E - E_\phi - F(E)) \), their contributions to \( \langle \chi_E|T|i \rangle \) by \( \langle \Phi|T|i \rangle \) and \( \langle \psi_E|T|i \rangle \), respectively, ‘interfere with opposite phase on the two sides of the resonance’ [14], which is a characteristic feature of Fano resonances. The general line shape of of Fano resonance can be written as

\[ S_q(E) = \frac{(\epsilon + q)^2}{(\epsilon^2 + 1)}, \]

(2.15)

Here, the reduced energy \( \epsilon \) is given by

\[ \epsilon = -\cot \Delta = \frac{E - E_\phi - F(E)}{\Gamma/2} \]

(2.16)

and \( q \) is the ratio of indirect resonant scattering and background scattering. The expression (2.15) shows that it gives rise to asymmetric line shapes as described in Fig.2.2. This line shape profile is known as ‘Fano profile’. \( q \) describes the degree of asymmetry in resonance.
We will apply this well known Fano theory to treat the atom-molecule coupled systems.

### 2.2 Spontaneous Emission and Vacuum-Induced Coherence

Vacuum-induced coherence (VIC) takes place due to the interference between two pathways of transitions in system-vacuum interaction \[12\]. Vacuum does not mean some absolutely empty space. It is actually quantized three-dimensional multimode electromagnetic field. Normally, a vacuum state is denoted as $|0_{ks}\rangle$, where $k$ and $s$ denote vacuum field wave vector and polarization. Let us consider a two level atom interacting with the vacuum field. Just as light field drives an excited atom to emit stimulated emission, interaction of an atom with the electromagnetic vacuum results in spontaneous emission. As a result, state of the field changes from $|0_{ks}\rangle \rightarrow |1_{ks}\rangle$. 1 signifies the emission of photon and the system moves from an excited to a ground state as shown in Fig.\[2.3\]. The overall state vector can be written as \[1\]
\[ |\psi(t)\rangle = c_a(t)|a,0_k\rangle + \sum_k c_{b,k}(t)|b,1_{ks}\rangle, \quad (2.17) \]

where \( c_a \) and \( c_{b,k,\text{s}} \) are the coefficients of corresponding states. The interaction Hamiltonian is given by

\[ H_{\text{int}} = \sum_k [g_{ks} \hat{S}^+ \hat{a}_k e^{i(\omega - \nu_{ks})t} + H.C.]. \quad (2.18) \]

Here \( \omega \) and \( \nu_{ks} \) is the atomic transition frequency and frequency of the field, \( \hat{a}_k \) is the lowering operator of field and \( \hat{S}^+ \) is the raising operator of the atom. \( g_{ks} = -\langle a|\vec{d} \cdot \vec{E}_{\text{vac}}|b\rangle \) is the dipole coupling with \( \vec{d} \) being the atomic dipole moment and \( \vec{E}_{\text{vac}} = \sqrt{\hbar \nu_{ks}/2\epsilon_0 V} \vec{\epsilon}_s \). \( \hbar \nu_{ks}/2\epsilon_0 V \) is the amplitude of vacuum field, \( \vec{\epsilon}_s \) is the electric field polarization vector and \( V \) is the quantization volume. \(|g_{ks}|^2 \) may be written as

\[ |g_{ks}|^2 = \frac{\hbar \nu_{ks}}{2\epsilon_0 V} |d_1|^2 \cos^2 \theta \quad (2.19) \]

where, \( \theta \) is the angle between \( \vec{d} \) and \( \vec{\epsilon}_s \). From the Schrödinger equation \( |\dot{\psi}(t)\rangle = -(i/\hbar)H_{\text{int}}|\psi(t)\rangle \), one can obtain

\[ \dot{c}_a(t) = -\sum_{ks} |g_{ks}|^2 \int_0^t dt' e^{i(\omega - \nu_{ks})(t-t')} c_a(t'). \quad (2.20) \]

The summation over the modes of vacuum fields can be converted to an integral

\[ \sum_k \rightarrow 2 \frac{V}{(2\pi)^3} \int_0^\infty dk \int_0^\pi d\theta \sin \theta \int_0^{2\pi} d\phi. \quad (2.21) \]

Integrating over \( \theta \) and \( \phi \) and putting \( k = \nu_{ks}/c \), the Eq. (2.20) becomes

\[ \dot{c}_a(t) = -\frac{4d^2}{(2\pi)^2 6\hbar^2 c^3} \int_0^\infty d\nu_{ks} \nu_{ks}^3 \int_0^t dt' e^{i(\omega - \nu_{ks})(t-t')} c_a(t'). \quad (2.22) \]

Considering that the frequency of the vacuum field is centered around atomic transition frequency, \( \nu_{ks}^3 \) is replaced by \( \omega^3 \) and the lower limit in the \( \nu_{ks} \) integration by \(-\infty\). The \( d\nu_{ks} \) integral can be solved as

\[ \int_{-\infty}^\infty d\nu_{ks} e^{i(\omega - \nu_{ks})(t-t')} = 2\pi \delta(t-t'). \quad (2.23) \]
So, under Wigner-Weisskopf approximation one can write
\[ \dot{c}_a(t) = -\frac{\gamma}{2} c_a(t) \] (2.24)
where,
\[ \gamma = \frac{1}{4\pi\epsilon_0} \frac{4\omega^3 d^2}{3\hbar^3} \] (2.25)
is the spontaneous decay constant. So this is the origin of spontaneous emission.

Now for demonstration of VIC, let us consider a Vee-type system consisting of two excited states \( |2\rangle \) and \( |3\rangle \) and a ground state \( |1\rangle \) (as depicted in Fig.2.1(a)). The coupling of the system with the background vacuum fields causes spontaneous decay from the excited states to the same ground state. Now these two spontaneous emission pathways can interfere resulting in VIC. This effect can modify and even quench the spontaneous emission. Several studies have suggested to control the spontaneous emission by using external fields in atomic systems [12, 15–22]. Using VIC, Hegerfeldt and Plenio showed periodic dark states and quantum beats in a near-degenerate Vee-system [15]. VIC may lead to the modification and sometimes suppression of resonance fluorescence [15–17]. Elimination of spectral line and even the cancellation of spontaneous emission have been demonstrated as an application of VIC [18]. It may lead to phase sensitive absorption and emission profile [23–25]. It also has been found effective for controlling decoherence in quantum information processing [26].

All these schemes relies on two stringent conditions. First, The frequency splitting between two excited states must not exceed the natural line width of transitions, which means that the excited states must be near-degenerate. Second, the dipole moments \( \vec{d}_1 \) and \( \vec{d}_2 \) associated with transitions \( |2\rangle \rightarrow |1\rangle \) and \( |3\rangle \rightarrow |1\rangle \), respectively must be non-orthogonal. If these two conditions are fulfilled, the resultant interference term can be written as
\[ \gamma_{ij} = \sqrt{\gamma_i \gamma_j} \frac{\vec{d}_i \cdot \vec{d}_j}{|\vec{d}_i||\vec{d}_j|}, \] (2.26)
here \( i \) is not equal to \( j \). This term changes the system dynamics. To meet up both the requirements is very hard for atomic systems. A possible realization of VIC for an excited atom interacting with an anisotropic vacuum [27–29] and utilizing the \( j = 1/2 \rightarrow j = 1/2 \) transition in \(^{198}\text{Hg}^+\) and \(^{139}\text{Ba}^+\) [30, 31] has been
suggested. On the other hand molecules are the natural candidates for observing VIC \[32\]. The required orthogonality criteria is easily satisfied if the two excited states belong to same electronic configuration, but differs only in rotational or vibrational quantum numbers. But only a few ventures have been made in case of molecules \[33\].

Atom-molecule coupled system may provide itself as a better candidate. Using photoassociation (PA) spectroscopy, low-lying rotational levels in an excited electronic level can be selectively populated. VIC will be significant if (i) the ground state has no hyperfine interaction, (ii) these is no bound state close to ground state dissociation threshold and (iii) excited molecular levels have a long lifetime.

To the best of our knowledge VIC in such PA systems has not been addressed. In this thesis, VIC in the context of atom-molecule coupled systems will be discussed for the first time by us \[32\]. In chapter 5, this will be demonstrated in detail.

### 2.3 Quantum Beats

The phenomena of quantum beats are important for studying the quantum interference in the multilevel atomic or molecular systems. Quantum beats in radiation intensity arise from coherent superposition of two long-lived excited states. Such state superpositions and their manipulations are of considerable recent interest to create long-lived molecular-state qubits. The possibility of using quantum beats as a spectroscopic measure for quantum superposition was discussed as early as in 1933 \[13\]. Experimentally, spectroscopic study of quantum beats started since 1960s \[34\]. The use of lasers to create quantum superposition and detect resulting quantum beats in fluorescence started in early 1970s \[35\]. Forty years ago, Haroche, Paisner and Schawlow \[36\] demonstrated quantum beats in fluorescence light emitted from the excited hyperfine levels of a Cs atom as a signature of quantum superposition between the excited atomic states. Since then quantum beats in fluorescence spectroscopy have been studied in a variety of physical situations \[1, 15\]. These techniques open up new possibilities for studying excited state properties, state preparation and manipulation as well as collisional and spectroscopic aspects of ultra-cold atoms and molecules.

Let us consider a Vee-type system, as shown in Fig.2.1(a). When the excited states \(|2\rangle\) and \(|3\rangle\) being coherently excited by an external source decay to the
same final state $|1\rangle$ with slightly different radiation frequencies, the interference between these two transition pathways gives rise to a periodic modulation of the intensity of emitted radiation with a modified frequency given by the difference of two frequencies. This phenomena is known as quantum beating. Quantum beats are manifested as oscillations in the emitted radiation intensity $I_{qb}$ from two correlated excited states as a function of time which is given by [2, 15, 37]

$$I_{qb}(t) = \gamma (\rho_{33}(t) + \rho_{22}(t) + 2\text{Re}[\rho_{23}(t))]. \quad (2.27)$$

Here $\rho_{nn}$ is the population of the excited state $|n\rangle$ and $\rho_{23}$ is the coherence between $|2\rangle$ and $|3\rangle$. We consider, $\gamma_2 = \gamma_3 = \gamma$, where $\gamma_n$ is the spontaneous line width of $|n\rangle$th excited state.
References


