

I. The dynamics of quantized particles and classical light fields

We start by writing the total classical Hamiltonian of N particles whose charges and Cartesian positions are denoted as q_j, \mathbf{r}_j in the presence of a classical electromagnetic field,

$$H_{tot} = \sum_j \frac{1}{2} m_j \left(\frac{d\mathbf{r}_j}{dt} \right)^2 + V_C + H_R.$$

V_C is the “Coulomb” energy $V_C = \sum_i q_i \Phi(\mathbf{r}_i)$

where $\Phi(\mathbf{r}_i)$ is the *electrostatic potential* felt by particle i due to the action of all particles with $j < i$,

$$\Phi(\mathbf{r}_i) = \frac{1}{4\pi\epsilon_0} \sum_{j < i} \frac{q_j}{|\mathbf{r}_i - \mathbf{r}_j|},$$

Hence V_C can also be written as,

$$V_C = \frac{1}{4\pi\epsilon_0} \sum_i \sum_{j<i} \frac{q_i q_j}{|\mathbf{r}_i - \mathbf{r}_j|}.$$

H_R of the above is the *cycle averaged* radiative Hamiltonian, given in terms of all the modes amplitudes A_k as,

$$H_R = 2(2\pi)^3 \epsilon_0 \int d^3k k^2 |A_k|^2.$$

where $A(\mathbf{r}, t)$ is the electromagnetic vector potential.

Due to the presence of this vector potential, \mathbf{p}_j - the (generalized) momentum of the j^{th} particle - is given (in Cartesian coordinates) as

$$\mathbf{p}_j = m_j \frac{d\mathbf{r}_j}{dt} + q_j \frac{A(\mathbf{r}_j, t)}{c}.$$

Hence, in terms of \mathbf{p}_j , the total Hamiltonian is given as,

$$H_{tot} = \sum_j \frac{1}{2m_j} \left(\mathbf{p}_j - q_j \frac{A(\mathbf{r}_j, t)}{c} \right)^2 + V_C + H_R.$$

We now quantize the material part by imposing,

$$\mathbf{p}_j \longrightarrow -i\hbar\nabla_j.$$

We have that

$$H_{tot} = \sum_j \frac{1}{2m_j} \left(-i\hbar\nabla_j - \frac{q_j}{c} \mathbf{A}(r_j, t) \right)^2 + V_C + H_R =$$

$$H_{tot} = H_M + H'(t) + H_R.$$

H_R was defined above. H_M , the *material* Hamiltonian, is defined as

$$H_M = \sum_j \frac{-\hbar^2}{2m_j} \nabla_j^2 + V_C.$$

$H'(t)$ is the “interaction Hamiltonian”,

$$H'(t) = \sum_j \frac{iq_j\hbar}{m_jc} \nabla_j \cdot \mathbf{A}(r_j, t) + \frac{q_j^2}{2m_jc^2} A^2(t) =$$

$$\sum_j \frac{iq_j\hbar}{m_jc} \mathbf{A}(r_j, t) \cdot \nabla_j + \frac{q_j^2}{2m_jc^2} A^2(t).$$

where we have used the *Coulomb gauge* ($\nabla \cdot \mathbf{A}(r, t) = 0$)

to obtain that

$$\nabla_j \cdot \mathbf{A}(r_j, t) |\psi\rangle = \mathbf{A}(r_j, t) \cdot \nabla_j |\psi\rangle.$$

We note that (gauge) transformations of the type,

$$\mathbf{A} \rightarrow \mathbf{A}' = \mathbf{A} + \nabla\chi,$$

$$\Phi \rightarrow \Phi' = \Phi - \frac{1}{c} \frac{\partial\chi}{\partial t},$$

where χ is any scalar field, leave the \mathbf{E} and \mathbf{B} fields invariant.

The *Coulomb gauge* is obtained by choosing χ such that

$$\nabla^2 \chi = -\nabla \cdot \mathbf{A}.$$

The above condition does not completely fix the vector and scalar potentials because any additional gauge transformation (“*sub gauge*”) with χ' satisfying $\nabla^2 \chi' = 0$ still leaves $\nabla \cdot \mathbf{A} = 0$.

Choosing a sub-gauge defined via

$$\chi' = -\mathbf{r} \cdot \mathbf{A}(\mathbf{r}, t)$$

hence

$$\nabla\chi' = -\nabla(\mathbf{r} \cdot \mathbf{A}) = -\mathbf{A} - \mathbf{r}(\nabla \cdot \mathbf{A}) - (\mathbf{r} \times \nabla) \times \mathbf{A}$$

and due to the Coulomb gauge

$$\nabla\chi' = -\nabla\mathbf{r} \cdot \mathbf{A} = -\mathbf{A} - (\mathbf{r} \times \nabla) \times \mathbf{A}$$

Neglecting the second term which is associated with the magnetic field (which couples more weakly than the electric field to the material system) we have that

$$\nabla\chi'(\mathbf{r}) \approx -\mathbf{A}.$$

Therefore, in this approximation,

$$\nabla^2\chi' = -\nabla\mathbf{A} = 0,$$

and we are still in the Coulomb gauge.

With the neglect of the magnetic field this Gauge transformation has eliminated \mathbf{A} while modifying $\Phi(\mathbf{r}, t)$ to yield,

$$H_{tot} = \sum_j -\frac{\hbar^2}{2m_j} \nabla_j^2 + \sum_j q_j \left[\Phi(\mathbf{r}_j) + \frac{\mathbf{r}_j}{c} \cdot \frac{\partial \mathbf{A}(\mathbf{r}_j, t)}{\partial t} \right] + H_R$$

Using the relation between the electric field and the vector potential,

$$\sum_j \frac{q_j}{c} \mathbf{r}_j \cdot \frac{\partial \mathbf{A}(\mathbf{r}_j, t)}{\partial t} = - \sum_j q_j \mathbf{r}_j \cdot \mathbf{E}_R(\mathbf{r}_j, t),$$

where \mathbf{E}_R is the *radiative* (“transverse”) component of the electric field, recasts the total Hamiltonian as,

$$H_{tot} = \sum_j -\frac{\hbar^2}{2m_j} \nabla_j^2 + V_C - \sum_j \mathbf{r}_j \cdot \mathbf{E}_R(\mathbf{r}_j, t) + H_R$$

The above form involves the exact charge distribution and the full coordinate dependence of \mathbf{E}_R .

The dipole approximation

The wavelengths of visible radiation, ranging between $0.3\mu m - 0.7\mu m$, are very large compared to molecular sizes. Under these circumstances we can invoke the

$$\text{“dipole approximation”,} \quad \mathbf{E}_R(\mathbf{r}_j, t) \approx \mathbf{E}_R(z, t).$$

where z is some fixed point, (say the molecular c.m.).

H_{tot} now assumes the form,

$$H_{tot} = \sum_j -\frac{\hbar^2}{2m_j} \nabla_j^2 + V_C - \mathbf{d} \cdot \mathbf{E}_R(z, t) + H_R,$$

where \mathbf{d} is the *electric dipole*, $\mathbf{d} = \sum_j q_j \mathbf{r}_j$.

The time dependent Schrödinger equation of the *material wave function* $\Psi(t)$ in the dipole approximation is,

$$i\hbar \frac{d\Psi(t)}{dt} = H(t)\Psi(t) = [H_M + H_{MR}(t)]\Psi(t),$$

where $H(t) = H_M + H_{MR}(t)$ is the part of the Hamiltonian operating on the material wave function, and

$$H_{MR} = -\mathbf{d} \cdot \mathbf{E}_R(z, t).$$

II. Photo-excitation of a Molecule with a Pulse of Light

Using the radiation-free basis set,

$$H_M | E_n \rangle = E_n | E_n \rangle.$$

we can expand $\Psi(t)$ as,

$$\Psi(t) = \sum_n b_n(t) | E_n \rangle e^{-iE_n t/\hbar},$$

with $b_n(t)$ satisfying the following set of ordinary differential equations,

$$\frac{db_m(t)}{dt} = (1/i\hbar) \sum_n b_n(t) e^{i\omega_{m,n}t} \langle E_m | H_{MR}(t) | E_n \rangle .$$

$$\omega_{m,n} \equiv (E_m - E_n)/\hbar.$$

The molecule is initially ($t = -\infty$) in a single state $|E_1\rangle$,

$$b_1(t = -\infty) = 1, \text{ and } b_k(t = -\infty) = 0 \text{ for } k \neq 1,$$

If the perturbation is weak

$$\int_{-\infty}^{\infty} dt |\langle E_i | H_{MR}(t) | E_j \rangle e^{i\omega_{i,j}t} / \hbar \ll 1,$$

$$b_m(t) = -\frac{d_{m,1}}{i\hbar} \int_{-\infty}^t dt' e^{i\omega_{m,1}t'} \varepsilon(z, t') = \\ -\frac{d_{m,1}}{i\hbar} \int_{-\infty}^{\infty} d\omega \epsilon(\omega) \int_{-\infty}^t dt' e^{i(\omega_{m,1}-\omega)t'},$$

where

$$d_{m,1} \equiv \langle E_m | \mathbf{d} \cdot \hat{\mathbf{e}} | E_1 \rangle,$$

and we have factored the electric field vector as $\mathbf{E}_R(z, t) = \hat{\mathbf{e}} \varepsilon(z, t)$

with $\hat{\mathbf{e}}$ being the *polarization* direction and $\varepsilon(z, t) \equiv \int_{-\infty}^{\infty} d\omega \epsilon(\omega) e^{-i\omega t}$

being the magnitude of the field.

The Fourier transform, $\epsilon(\omega)$, can be a complex number, which we write as a product of an absolute value and a phase factor,

$$\epsilon(\omega) \equiv |\epsilon(\omega)| e^{i[\phi(\omega) + \omega z/c]},$$

with $\omega z/c = \mathbf{k} \cdot \mathbf{r}$ along the z (pulse propagation) direction.

To obtain $\Psi(t)$ as $t \rightarrow +\infty$ we use the

$$\int_{-\infty}^{\infty} dt' e^{i[\omega_{m,1} - \omega]t'} = 2\pi \delta(\omega_{m,1} - \omega), \quad \text{identity,}$$

leading to

$$b_m(+\infty) = \frac{2\pi i}{\hbar} d_{m,1} \epsilon(\omega_{m,1}) = \frac{2\pi i}{\hbar} d_{m,1} |\epsilon(\omega_{m,1})| e^{i[\phi(\omega_{m,1}) + \omega_{m,1} z/c]}.$$

At infinite times or after the pulse is gone, a material energy level E_m only absorbs or emits *on resonance* modes, satisfying

$$\omega = \omega_{m,1} \quad \text{OR} \quad \omega = -\omega_{m,1} \quad .$$

This need not be the case while the pulse is *on*.

III: State Preparation During the Pulse

At finite times, while the pulse is on,

$$b_m(t) = \langle E_m | \Psi(t) \rangle = \frac{i}{\hbar} d_{m,1} \int_{-\infty}^t dt' \varepsilon(t') e^{i\omega_{m,1}t'}$$

and the probability of observing the $|E_m\rangle$ state is

$$P_m(t) = |\langle E_m | \Psi(t) \rangle|^2 = |b_m(t)|^2 .$$

In the *single mode* (or Continuous Wave - CW) limit,

$$\bar{\varepsilon}(\omega) = \frac{\epsilon_0}{2} [\delta(\omega - \omega_a) + \delta(\omega + \omega_a)],$$

$$\text{or, } \varepsilon(t) = \pi\epsilon_0 [e^{-i\omega_a t} + e^{i\omega_a t}] = 2\pi\epsilon_0 \cos(\omega_a t).$$

We obtain that

$$b_m(t) = (i/\hbar)d_{m,1} \int_{-\infty}^t dt' \varepsilon(t') e^{i(\omega_{m,1}t')} = \frac{\pi i \epsilon_0 d_{m,1}}{\hbar} A(t),$$

where

$$A(t) = \lim_{T \rightarrow \infty} \int_{-T}^t dt' \left\{ e^{-i(\omega_a - \omega_{m,1})t'} + e^{i(\omega_a + \omega_{m,1})t'} \right\}.$$

For absorption (**emission**) the first (**second**) term is called the “*Rotating Wave*” (RW) term. When we are in “near resonance”, i.e., $\omega_a \approx \omega_{m,1}$ (absorption), or $\omega_a \approx -\omega_{m,1}$ (**emission**) we can invoke the *Rotating Waves Approximation* (RWA) in which we only retain this term.

For absorption we have that

$$A(t) = \frac{e^{i\Delta t}}{i\Delta} - \lim_{T \rightarrow \infty} \frac{e^{-i\Delta T}}{i\Delta},$$

where $\Delta \equiv \omega_{m,1} - \omega$.

We first deal with the CW case. The limit $T \rightarrow \infty$ is now awkward because it involves an endlessly oscillatory term. We therefore choose to examine the case in which we know that the system existed at $t = 0$ in state $|E_1\rangle$. The lower limit now becomes $T = 0$ and we have that

$$A(t) \equiv \int_0^t dt' e^{i\Delta t'} = \frac{e^{i\Delta t} - 1}{i\Delta}.$$

Hence,

$$b_m(t) = \frac{i\pi\epsilon_0 d_{m,1}}{\hbar} \frac{e^{i\Delta t} - 1}{i\Delta} = \frac{i\pi\epsilon_0 d_{m,1}}{\hbar} e^{i\Delta t/2} \frac{\sin(\Delta t/2)}{\Delta}$$

and

$$P_m(t) = \left(\frac{2\pi\epsilon_0 d_{m,1}}{\hbar} \right)^2 \frac{\sin^2(\Delta t/2)}{\Delta^2}.$$

At short times $\sin^2(\Delta t/2) \approx \Delta^2 t^2/4$ and

$$P_m(t) = \left(\frac{\pi \epsilon_0 d_{m,1} t}{\hbar} \right)^2$$

The rate is defined as

$$R_m(t) \equiv dP_m(t)/dt = 2 \left(\frac{\pi \epsilon_0 d_{m,1}}{\hbar} \right)^2 t$$

Under these circumstances we never reach a *constant rate*.

As $t \rightarrow \infty$, $\frac{\sin(\Delta t/2)}{\Delta} \rightarrow 2\pi\delta(\Delta)$ and we recapture the *resonance condition*

The difficulties arose in going to the CW limit *before* performing the integration.

Realizing that in real life, the CW case is a limit of the pulsed case for infinitely narrow pulses, we now examine the **pulsed** case for which,

$$b_m(t) = (i/\hbar)d_{m,1}\epsilon(\omega_{m,1})c_m(t),$$

where,

$$c_m(t) \equiv \frac{1}{\epsilon(\omega_{m,1})} \int_{-\infty}^{\infty} d\omega \epsilon(\omega) \frac{e^{i(\omega_{m,1}-\omega)t}}{i(\omega_{m,1}-\omega)}.$$

For a Gaussian pulse,

$$\epsilon(t) = \epsilon_a e^{-4 \ln 2 (\Gamma t)^2} e^{-i\omega_a t} + c.c.,$$

$$\text{for which } \epsilon(\omega) = \pi^{-\frac{1}{2}} \epsilon_a \alpha e^{-\alpha^2 (\omega - \omega_a)^2},$$

$$\text{where } \alpha \equiv 1/(4\Gamma \ln^{1/2} 2).$$

we have that,

$$c_m(t) = \text{sgn}(t') 2\pi \left\{ \theta(t) - (1/2) e^{\beta^2} W[\text{sgn}(t)\beta] \right\},$$

where,

$$\beta \equiv \alpha(\omega_{m,1} - \omega_a) + i \frac{t}{2\alpha}.$$

and $W[z]$ is the complex error function.

We have that,

$$c_m(t) \rightarrow 0, \text{ for } t \ll -1/\Gamma,$$

and

$$c_m(t) \rightarrow 2\pi, \text{ for } t \gg 1/\Gamma .$$

Pulse preparation coefficients

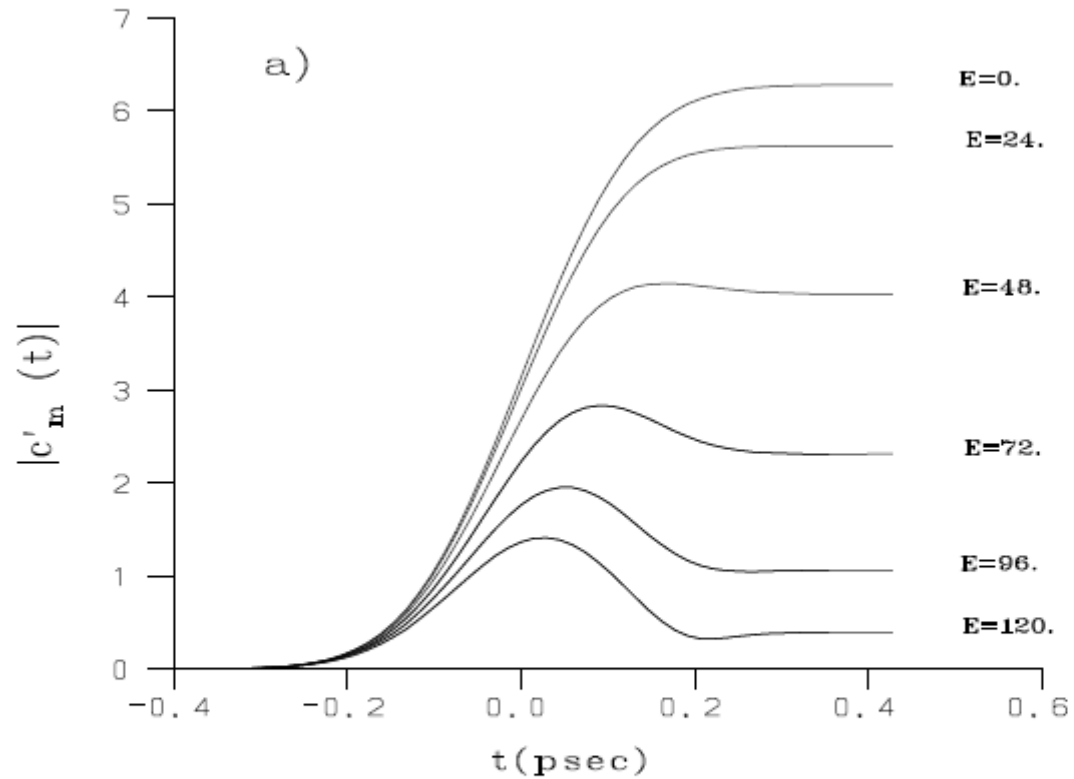


Figure 1: The absolute value of the preparation coefficients divided by the pulse peak amplitude during the pulse.

For $\omega_{m,1}$ near the line center, $c_m(t)$ rises smoothly to its asymptotic value. However at off-center energies $c_m(t)$ does not rise so monotonically: At the end of the pulse, for an absorption process ($E_m > E_1$),

$$\Psi(t \gg 1/\Gamma) = \psi_1 e^{-iE_1 t/\hbar} + \frac{2\pi i}{\hbar} \sum_m \epsilon(\omega_{m,1}) d_{m,1} \psi_m e^{-iE_m t/\hbar}.$$

The absorption of a photon has created a wave packet in which the coefficients of preparation are proportional to the field amplitude at the $\omega_{m,1}$ frequency.

During the excitation pulse

$$\Psi(t) = \psi_1 e^{-iE_1 t/\hbar} + \frac{i}{\hbar} \sum_m c_m(t) \epsilon(\omega_{m,1}) d_{m,1} \psi_m e^{-iE_m t/\hbar}.$$

As shown in Fig. 1, for $\omega_{m,1}$ near the line center, $c_m(t)$ rises smoothly to its asymptotic value of 2π . However at off-center energies $c_m(t)$ does not rise so monotonically: At early times all the c_m 's respond to the field in almost the same manner since the system has insufficient "information" to determine the true spectral composition of the pulse. It therefore "thinks" that it is exposed to a much broader band of frequencies, hence a more slowly varying $\epsilon(\Delta)$. Only at later times does the system "realize" its "mistake" and corrects for it by depleting the off-center $c_m(t)$'s.

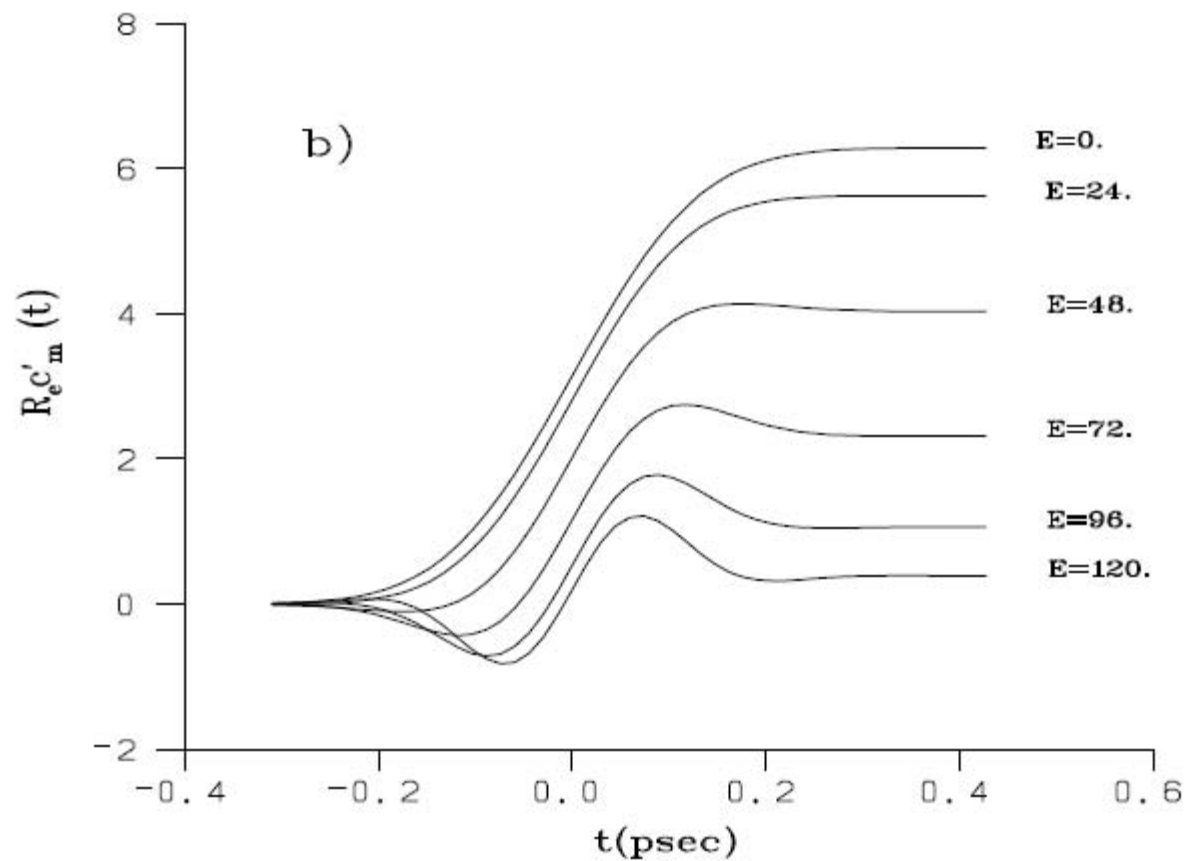


Figure 2: The real part of the preparation coefficients divided by the pulse peak amplitude during the pulse.

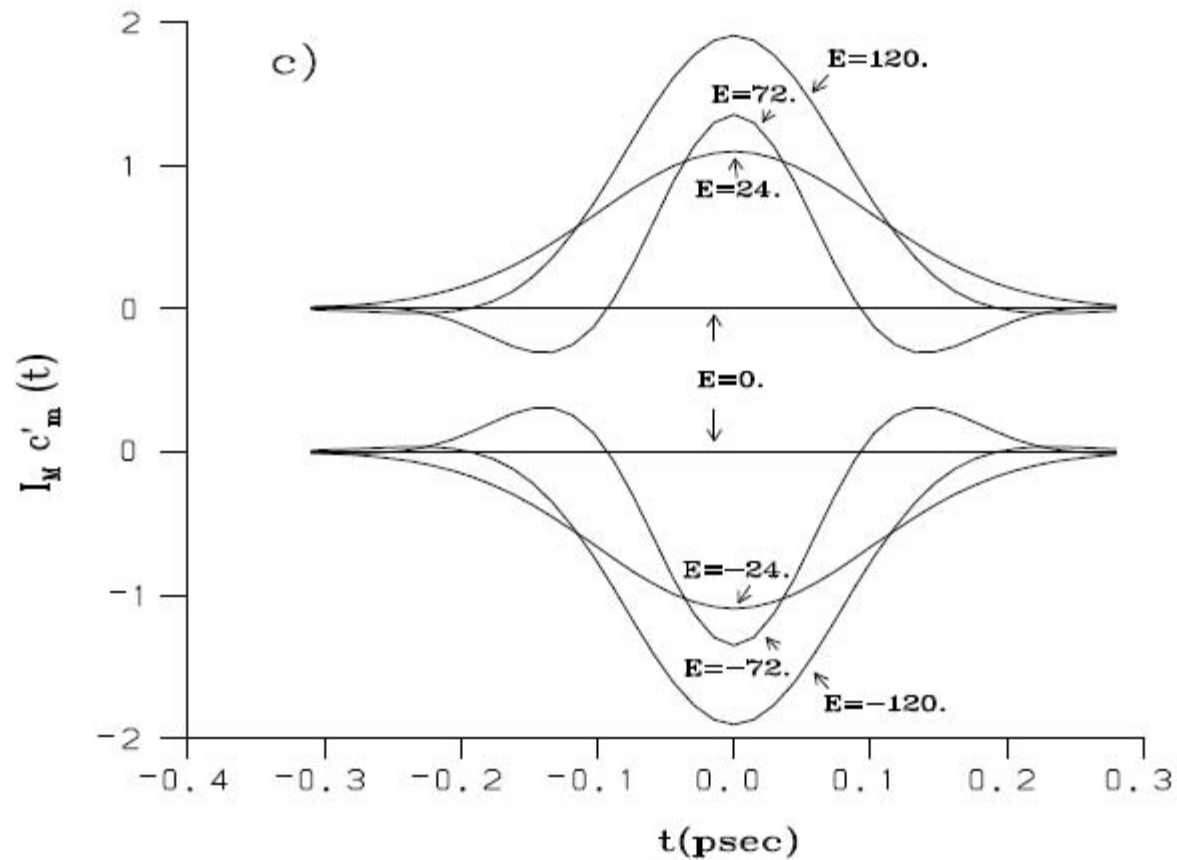


Figure 3: The imaginary part of the preparation coefficients divided by the pulse peak amplitude during the pulse.

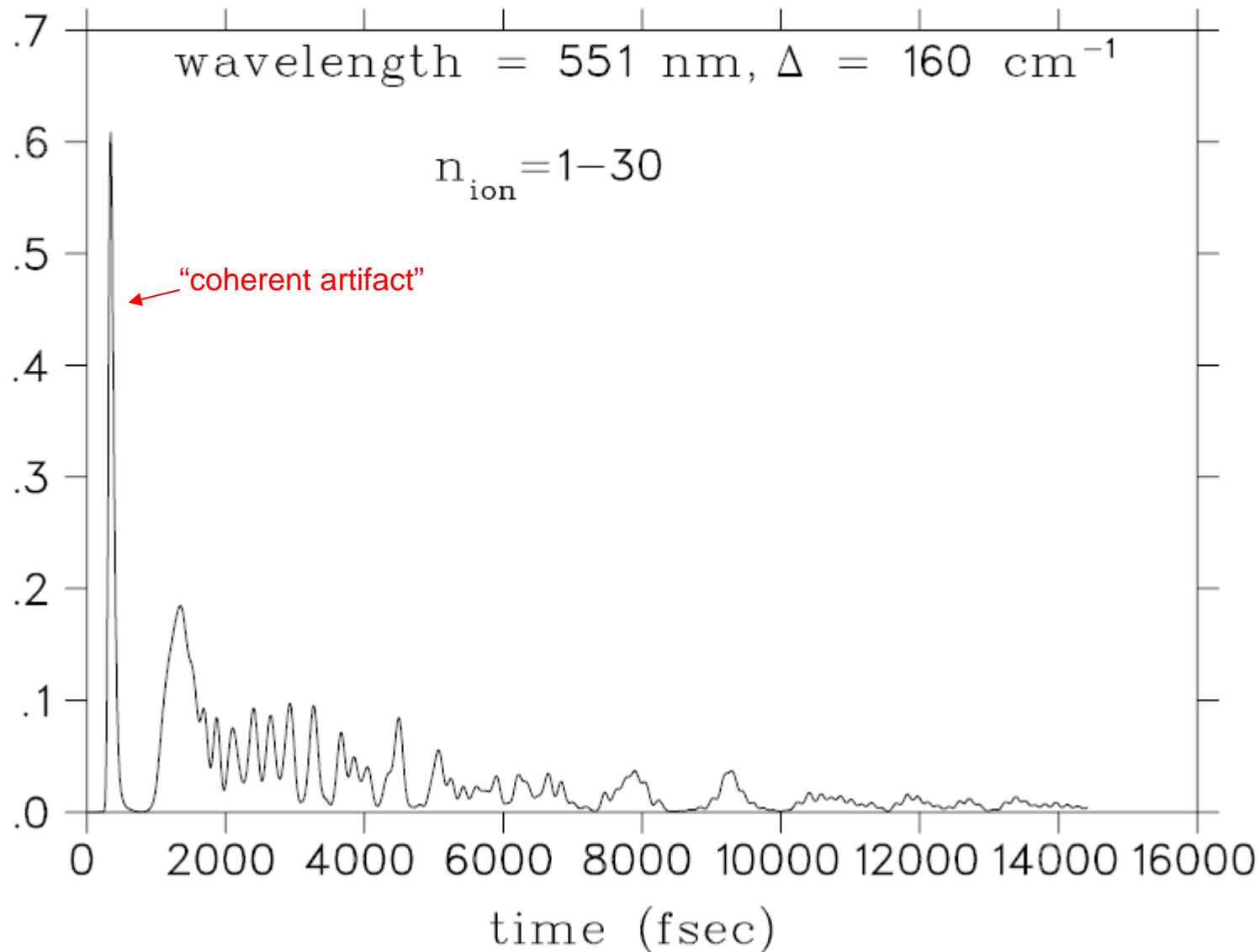
In the extreme case of detuning i.e., when $\epsilon(\omega_{m,1}) \approx 0$, although the probability of observing the level after the pulse is essentially zero, $c_m(t)$ during the pulse is not necessarily zero. This means that the level in question gets populated and de-populated during the pulse. In the usual jargon what we have described here is a *virtual* state. The above description of a *light dispersion* process gives a physically meaningful content to the concept of a virtual state, which is often treated as a pure mathematical construct.

1+2 Photoionization of IBr. Coupling=90 cm^{-1}

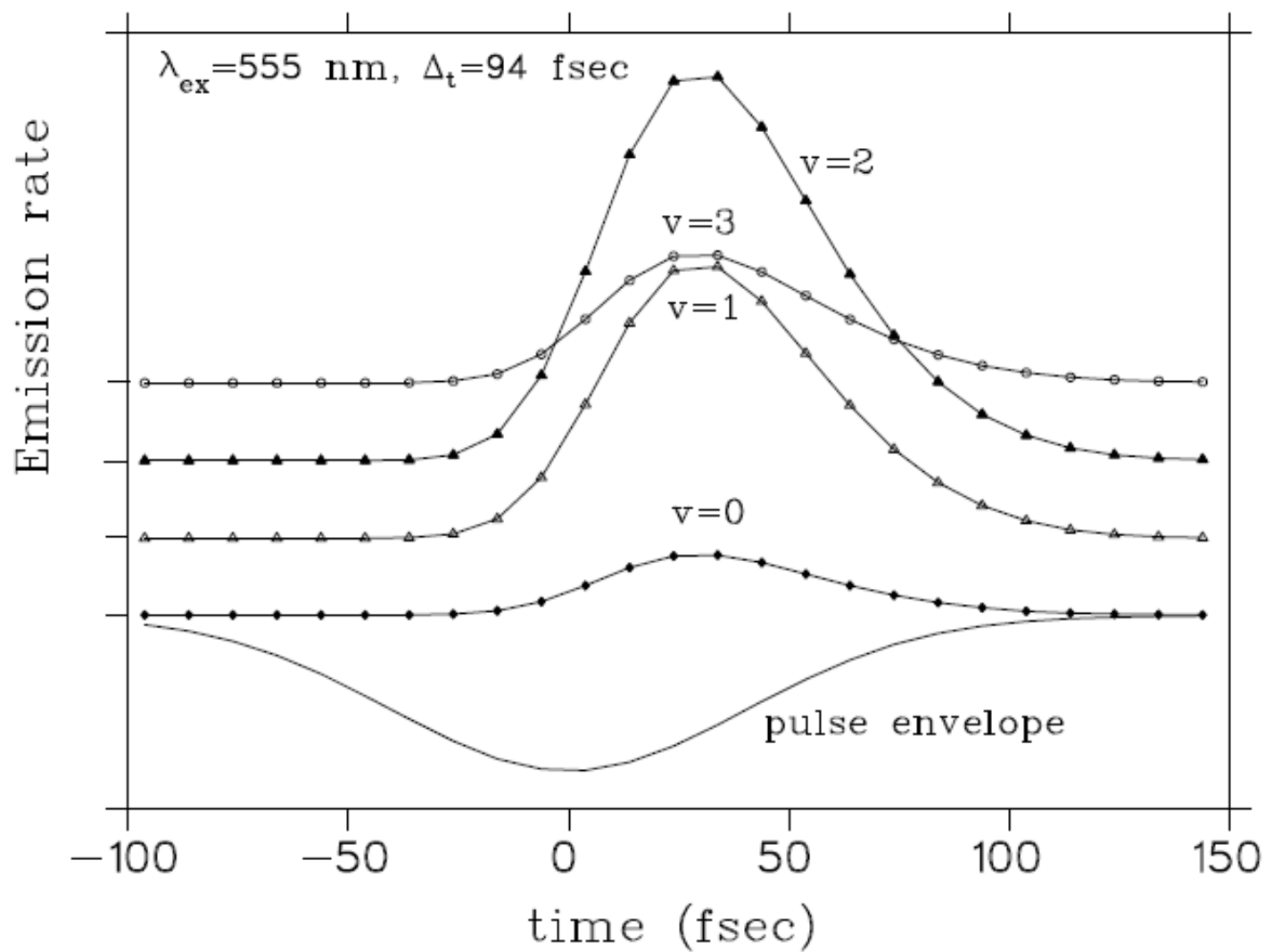
wavelength = 551 nm, $\Delta = 160 \text{ cm}^{-1}$

$n_{\text{ion}} = 1-30$

Ionization Rate



Resonance Raman of IBr



At the end of the pulse, $\Psi(t)$, obtained by substituting the resonance condition in the expansion of $\Psi(t)$ in the $|E_n\rangle$ states, is given for an absorption process ($E_m > E_1$) by,

$$\Psi(t \gg 1/\Gamma) = \psi_1 e^{-iE_1 t/\hbar} + (2\pi i/\hbar) \sum_m \epsilon(\omega_{m,1}) d_{m,1} \psi_m e^{-iE_m t/\hbar}.$$

Thus, after the pulse, the absorption of a photon has created a wavepacket in which the coefficients of preparation are proportional to the field amplitude at the $\omega_{m,1}$ frequency.

During the excitation pulse the above picture must be corrected and we obtain that,

$$\Psi(t) = \psi_1 e^{-iE_1 t/\hbar} + (i/\hbar) \sum_m c_m(t) \epsilon(\omega_{m,1}) d_{m,1} \psi_m e^{-iE_m t/\hbar}.$$

IV. Photodissociation and Scattering Theory

We now discuss scattering theory and photodissociation with a pulse of light, both associated with the presence of a continuous spectrum.

When the spectrum of the material Hamiltonian has a continuous part we have that

$$[E_i - H_M]|E_i\rangle = [E - H_M]|E, n\rangle = 0,$$

where m designate any additional quantum number. In the presence of a laser pulse whose electric field is parametrized as,

$$\mathbf{E}_R(t) = \hat{\epsilon} \mathcal{R}_e \epsilon(t) e^{-i\omega_a t},$$

where ω_a , called “carrier” frequency, represents the average frequency in the spectrum of the pulse $\epsilon(\omega)$. $\epsilon(t)$ is called the “envelope” of the pulse.

We expand the full time-dependent wave function as,

$$\Psi(t) = b_1(t)|E_1\rangle e^{-iE_1t/\hbar} + \sum_n \int dE b_{E,n}(t)|E, n\rangle e^{-iEt/\hbar},$$

In first order perturbation theory this expression becomes,

$$\Psi(t) = \frac{2\pi i}{\hbar} \sum_n \int dE \epsilon(\omega_{E,1}) \langle E, n | d | E_1 \rangle | E, n \rangle e^{-iEt/\hbar}.$$

The normalization of the constituent states

$$\langle E', m | E, n \rangle = \delta(E - E') \delta_{m,n}.$$

$\psi_m(E, R) \equiv \langle R | E, n \rangle$ has dimensions of $[L]^{-1/2} [E]^{-1/2}$.

A triatomic molecule - ABC , which breaks apart to yield, the ($q = 1$) $A + BC$ channel or ($q = 2$) $B + AC$ channel.

H_M is composed of three parts,

$$H_M = K_{\mathbf{R}} + K_{\mathbf{r}} + W(\mathbf{R}, \mathbf{r}).$$

where

$$K_{\mathbf{R}} = \frac{-\hbar^2}{2\mu} \nabla_{\mathbf{R}}^2, \quad K_{\mathbf{r}} = \frac{-\hbar^2}{2m} \nabla_{\mathbf{r}}^2,$$

μ and m being the reduced masses,

$$\mu = m_A(m_B + m_C)/(m_A + m_B + m_C), \quad m = m_B m_C / (m_B + m_C).$$

and $v(r)$ is the asymptotic limit of $W(\mathbf{R}, \mathbf{r})$ as A departs from $B - C$,

$$v(r) = \lim_{R \rightarrow \infty} W(\mathbf{R}, \mathbf{r}).$$

The $A - BC$ interaction potential, defined as,

$$V(\mathbf{R}, \mathbf{r}) \equiv W(\mathbf{R}, \mathbf{r}) - v(r)$$

vanishes as $R \rightarrow \infty$,

$$\lim_{R \rightarrow \infty} V(\mathbf{R}, \mathbf{r}) = 0.$$

Defining the $B - C$ Hamiltonian as,

$$h_{\mathbf{r}} \equiv K_{\mathbf{r}} + v(r)$$

we have that

$$H_M = K_{\mathbf{R}} + h_{\mathbf{r}} + V(\mathbf{R}, \mathbf{r}).$$

The interaction potential $V(\mathbf{R}, \mathbf{r})$ couples the motion of the A atom to the motion of the BC .

The eigenstates, of the free Hamiltonian

$$H_0 \equiv K_{\mathbf{R}} + h_{\mathbf{r}},$$

denoted as $|E, m; 0\rangle$, satisfy the

$$[E - H_0]|E, m; 0\rangle = 0,$$

eigenvalue relations. They are given as products

$$|E, m; 0\rangle = |e_m\rangle |E - e_m\rangle$$

where $[e_m - h_{\mathbf{r}}]|e_m\rangle = 0,$

with e_m denoting the *internal* (electronic, vibrational, rotational) energy of the $B - C$ diatomic, and

$$[E - e_m - K_{\mathbf{R}}]|E - e_m\rangle = 0,$$

describing the free (translational) motion of A relative to BC .

$$\left[E - e_m + \hbar^2 / (2\mu) \nabla_{\mathbf{R}}^2 \right] \langle \mathbf{R} | E - e_m \rangle = 0$$

is a plane wave of kinetic energy $E - e_m$,

$$\langle \mathbf{R} | E - e_m \rangle = e^{i\mathbf{k}_m \cdot \mathbf{R}},$$

where $k_m = \{2\mu(E - e_m)\}^{1/2} / \hbar.$

The free states are normalized as,

$$\langle E', m; 0 | E, n; 0 \rangle = \delta(E - E') \delta_{m,n}.$$

Relating the free states to the fully interacting states:

$$[E - H_0] | E, n \rangle = V | E, n \rangle,$$

can be solved formally as, $| E, n \rangle = [E - H_0]^{-1} V | E, n \rangle$

to which we need to add a general solution $| E, n; 0 \rangle$ of the homogeneous part that equation.

We obtain that $|E, n\rangle = |E, n; 0\rangle + [E - H_0]^{-1}V|E, n\rangle$

Using the spectral resolution,

$$[E - H_0]^{-1} = \int dE' \frac{|E', n; 0\rangle\langle E', n; 0|}{E - E'},$$

we have that,

$$|E, n\rangle = |E, n; 0\rangle + \int dE' \frac{|E', n; 0\rangle\langle E', n; 0|V|E, n\rangle}{E - E'}$$

The $\int dE'$ is ill defined in the Riemann sense. In the Cauchy sense we consider the limit of a series of well defined Riemann integrals by adding a small $i\epsilon$ imaginary part to E , calculating the integrals and finally letting $\epsilon \rightarrow 0$. The limiting value thus obtained depends on the sign of ϵ . We consider adding $i\epsilon$ or subtracting $i\epsilon$, with $\epsilon > 0$.

$$|E, n^\pm\rangle = |E, n; 0\rangle + \lim_{\epsilon \rightarrow 0} [E \pm i\epsilon - H_0]^{-1}V|E, n^\pm\rangle.$$

Each is the Lippmann-Schwinger equation. The $+$ solution is the *outgoing* solution, and the $-$ solution as the *incoming* solution. Each solution is an independent solution of the full Schrödinger equation. They are not independent on (and definitely not orthogonal to) one another, so we can use either one or the other.

After the pulse we have that

$$\Psi(t) = \frac{2\pi i}{\hbar} \sum_n \int dE e^{-iEt/\hbar} \epsilon(\omega_{E,1}) \langle E, n^\pm | d | E_1 \rangle \cdot \left\{ |E, n; 0\rangle + [E \pm i\epsilon - H_0]^{-1} V |E, n^\pm\rangle \right\}.$$

Using the spectral resolution of $[E \pm i\epsilon - H_0]^{-1}$ the probability of finding a free state $|E', m; 0\rangle$ at time t is

$$\langle E', m; 0 | \Psi(t) = \frac{2\pi i}{\hbar} \sum_n \int dE e^{-iEt/\hbar} \epsilon(\omega_{E,1}) \langle E, n^\pm | d | E_1 \rangle \cdot \left\{ \langle E' m; 0 | E, n; 0 \rangle + \frac{\langle E' m; 0 | V | E, n^\pm \rangle}{E \pm i\epsilon - E'} \right\}.$$

Using the normalization of the free states

$$\langle E', m; 0 | \Psi(t) = \frac{2\pi i}{\hbar} e^{-iE't/\hbar} \left\{ \epsilon(\omega_{E',1}) \langle E', m^\pm | d | E_1 \rangle + \sum_n \int dE e^{-iEt/\hbar} \epsilon(\omega_{E,1}) \frac{\langle E, n^\pm | d | E_1 \rangle \langle E' m; 0 | V | E, n^\pm \rangle}{E \pm i\epsilon - E'} \right\}.$$

In the $t \rightarrow \infty$ limit the integration over E can be performed analytically by the contour integration depicted in Fig. 4

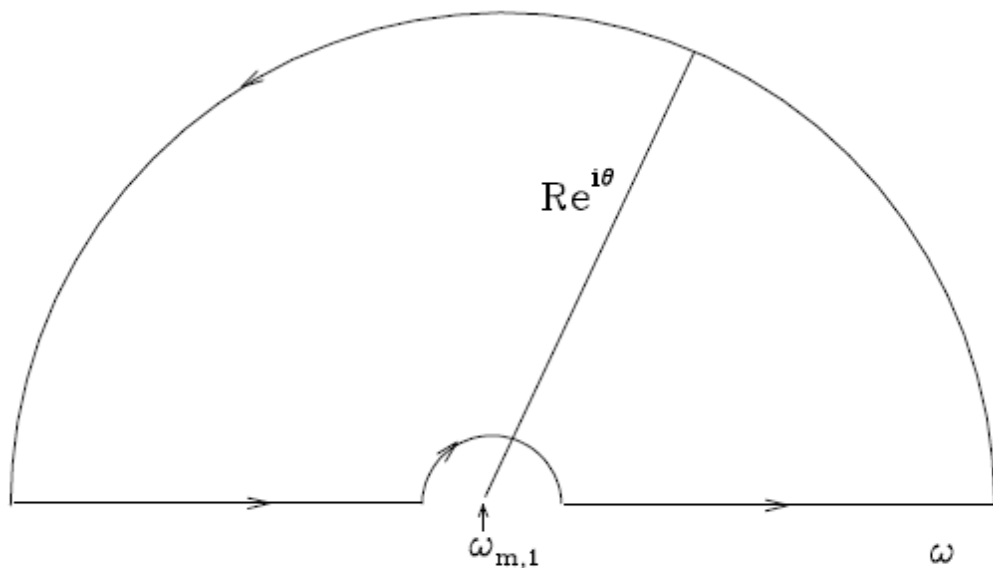


Figure 4: Contour integration used to explore the long time limit.

Noting that in that limit, the integrand on a large semi-circle in the lower part of the complex- E plane is zero, due to the fact that when $E = Re^{i\theta}$, with $\theta < 0$,

$$e^{-iEt/\hbar} = e^{-iRe^{i\theta}t/\hbar} = e^{-iR \cos \theta t/\hbar} e^{R \sin \theta t/\hbar} \xrightarrow{t \rightarrow \infty} 0.$$

The real E integration remains unchanged by supplementing it with integration along the above large semi-circle in the lower half E -plane. Since in the $-i\epsilon$ case, the integrand has a pole at $E = E' + i\epsilon$ which is outside the closed contour, the whole integral is zero. We obtain that,

$$\lim_{t \rightarrow \infty} \langle E', m; 0 | \Psi(t) = \frac{2\pi i}{\hbar} \epsilon(\omega_{E',1}) e^{-iE't/\hbar} \langle E', m^- | d | E_1 \rangle.$$

Hence the coefficients of expansion of the full wavepacket in terms of the $|E, m^- \rangle$ states, tell us immediately what is the probability of observing states $|E, m; 0 \rangle$ in the distant future.

V. Photodissociation beyond perturbation theory

In going beyond perturbation theory we first discuss strong field photodissociation from a single (“precursor”) state. we again consider a molecule breaking up into two or more structured fragments, $A - B \longrightarrow A + B$.

We expand $\Psi(t)$, obtaining the usual set of o.d.e.,

$$i\hbar \frac{db_{E,n}}{dt} = -d(E, n|1)\varepsilon(t)b_1(t) \exp [i(\omega_{E,1} - \omega_a)t],$$

$$i\hbar \frac{db_1}{dt} = - \int dE \sum_n d(1|E, n)\varepsilon(t)b_{E,n}(t) \exp[-i(\omega_{E,1} - \omega_a)t]$$

where $\omega_{E,1} \equiv (E - E_1)/\hbar$, and we have invoked the rotating wave approximation.

Substituting the formal solution

$$b_{E,n}(t) = \frac{-1}{i\hbar} d(E, n|1) \int_{-\infty}^t dt' \varepsilon(t') b_1(t') e^{i(\omega_{E,1} - \omega_a)t'},$$

we obtain that,

$$\frac{db_1}{dt} = - \int \frac{dE}{\hbar^2} A_1(E) \varepsilon(t) \int_{-\infty}^t dt' \varepsilon(t') e^{-i(\omega_{E,1} - \omega_a)(t-t')} b_1(t').$$

where $A_1(E) \equiv \sum_n |d(E, n|1)|^2$ is the absorption *spectrum* from state $|E_1\rangle$. According to this *integro-differential* equation the change in b_1 at time t depends on its history at all preceding times $t' < t$. The $\varepsilon(t') e^{-i(\omega_{E,1} - \omega_a)(t-t')}$ factor is called the “memory-Kernel” of the integral equation.

Given the Fourier transform of the spectrum $A_1(E)$

$$F_1(t - t') \equiv \int dE \sum_n |d(E, n|1)|^2 e^{-i\omega_{E,1}(t-t')} = \int dE A_1(E) e^{-i\omega_{E,1}(t-t')},$$

we have that

$$\frac{db_1}{dt} = \frac{-1}{\hbar^2} \varepsilon(t) \int_{-\infty}^t dt' e^{i\omega_a(t-t')} \varepsilon(t') F_1(t-t') b_1(t').$$

If $A_1(E)$ is slowly varying we can replace it by its value $A_1(E_a)$ at the center energy of the pulse ($E_a = E_1 + \hbar\omega_a$). In that case the above equation transforms into,

$$F_1(t-t') \approx A_1(E_a) \int dE e^{-i\omega_{E,1}(t-t')} = \hbar \int d\omega_{E,1} e^{-i\omega_{E,1}(t-t')} = 2\pi\hbar A_1(E_a) \delta(t-t').$$

Using this equation and remembering that we integrate t' from $-\infty$ to the singularity point t , which introduces a factor of $\frac{1}{2}$,

we obtain that

$$\frac{db_1}{dt} = -\frac{\bar{d}}{\hbar} |\varepsilon(t)|^2 b_1(t),$$

whose solution is

$$b_1(t) = b_1(-\infty) \exp \left[-\frac{\bar{d}}{\hbar} \int_{-\infty}^t \varepsilon^2(t') dt' \right].$$

The above is a statement of what may be termed the “slowly varying continuum approximation” (SVCA). We see that in this approximation $b_1(t)$ decreases monotonically with time, though not necessarily as an exponential function.

The SVCA need not be assumed for the continuum coefficients themselves, because once we know $b_1(t)$ we can solve for $b_{E,n}(t)$ with no further approximation.

Assuming that $b_1(-\infty) = 1$,

the $b_{E,n}$ coefficients are given as,

$$b_{E,n}(t) = \frac{-1}{i\hbar} d(E, n|1) \int_{-\infty}^t dt' \varepsilon(t') \exp[i(\omega_{E,1} - \omega_a)t'] \cdot \exp \left[-\frac{\bar{d}}{\hbar} \int_{-\infty}^{t'} \varepsilon^2(t'') dt'' \right].$$

We now show that $F_1(t)$ is proportional to the temporal correlation function of a wavepacket formed by an instantaneous pulse. Setting $\epsilon(\omega) = \epsilon_a$, a constant, we obtain

$$\epsilon(t) = \int d\omega \epsilon(\omega) e^{-i\omega t} = \epsilon_a \int_{-\infty}^{\infty} d\omega e^{-i\omega t} = 2\pi\epsilon_a \delta(t).$$

Given such a pulse, the wave function created from initial state $|E_1\rangle$ is given at $t = 0$ as

$$|\Psi_1(0)\rangle = \frac{2\pi i \epsilon_a}{\hbar} \sum_m \int dE' |E', m^-\rangle \langle E', m^- | d | E_1 \rangle.$$

At subsequent times it evolves to

$$|\Psi_1(t)\rangle = \frac{2\pi i \epsilon_a}{\hbar} \sum_n \int dE |E, n^-\rangle \langle E, n^- | d | E_1 \rangle e^{-iEt/\hbar}.$$

Using the $\langle E', m^- | E, n^- \rangle = \delta(E - E') \delta_{m,n}$ orthonormality,

$$\langle \Psi_1(0) | \Psi_1(t) \rangle = \left(\frac{2\pi\epsilon_a}{\hbar} \right)^2 \sum_n \int dE |\langle E_1 | d | E, n^- \rangle|^2 e^{-iEt/\hbar} =$$

$$\left(\frac{2\pi\epsilon_a}{\hbar} \right)^2 \int dE A_1(E) e^{-iEt/\hbar} = \left(\frac{2\pi\epsilon_a}{\hbar} \right)^2 F_1(t)$$

Thus, the Fourier transform of the spectrum is also the correlation function between a wave packet excited at $t = 0$ from the $|E_1\rangle$ state by the shortest possible pulse - a $\delta(t)$ pulse - and its value at subsequent times t . The Fourier transform of the absorption spectrum is a **self probe** at ultrashort times for a process in which the system is excited by **the shortest possible pulse!**

