Time Evolution of Matter States

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The Time-Evolution Operator

The time-evolution of a wavefunction is determined by the effect of a time evolution operator through the relation

$$\Psi(\vec{r},t) = U(t)\Psi(\vec{r},t), \text{ with } U(0) = 1. \tag{1}$$

Using this in the Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}\Psi(\vec{r},t) = \mathcal{H}\Psi(\vec{r},t) \Longrightarrow i\hbar\left(\frac{\partial}{\partial t}U(t)\right)\Psi(\vec{r},0) = \mathcal{H}U(t)\Psi(\vec{r},0), \tag{2}$$

yields the differential equation for U

$$i\hbar\frac{\partial}{\partial t}U(t) = \mathcal{H}U(t). \tag{3}$$

If $\mathcal{H}$ is independent of time, the solution is the simple time dependent phase factor of a stationary state

$$U(t) = e^{-\frac{i}{\hbar}\mathcal{H}t}. \tag{4}$$

Since the stationary state $\Psi(0)$ is an eigenfunction of $\mathcal{H}$ with eigenvalue E,

$$U(t)\Psi(0) = e^{-\frac{i}{\hbar}\mathcal{H}t}\Psi(0) = e^{-\frac{i}{\hbar}Et}\Psi(0). \tag{5}$$

When the Hamiltonian is a general function of time

$$U(t) = U(0) - \frac{i}{\hbar}\int_0^t \mathcal{H}\, d(t')U(t')dt'. \tag{6}$$

The solution to this integral equation can be obtained by interation. The first order approximation can be obtained by substituting the zero order approximation $U(0) = 1$ into the integral

$$U(t) = 1 - \frac{i}{\hbar}\int_0^t \mathcal{H}(t')\, dt'. \tag{7}$$

The second order approximation is obtained by replacing $U(t)$ in the integral with the first order expression

$$U(t) = 1 - \frac{i}{\hbar}\int_0^t \mathcal{H}(t')dt' + \left(-\frac{i}{\hbar}\right)^2\int_0^t\int_0^{t'} \mathcal{H}(t')\mathcal{H}(t'')dt''dt', \tag{8}$$

and so forth

$$U(t) = 1 - \frac{i}{\hbar}\int_0^t \mathcal{H}(t_1)\,dt_1 + \left(-\frac{i}{\hbar}\right)^2 \int_0^t \int_0^{t_1} \mathcal{H}(t_1)\mathcal{H}(t_2)\,dt_1\,dt_2 + \left(-\frac{i}{\hbar}\right)^3 \int_0^t \int_0^{t_1} \int_0^{t_2} \mathcal{H}(t_1)\mathcal{H}(t_2)\mathcal{H}(t_3)\,dt_1\,dt_2\,dt_3 + \cdots , \quad (9)$$

When $\mathcal{H} = \mathcal{H}_o + V(t)$, $U(t)$ can be written in the form

$$U(t) = U_o(t)U_v(t), \text{ where } U_o(t) = e^{-\frac{i}{\hbar}\mathcal{H}_o t}. \quad (10)$$

Using this definition in the Schrodinger equation yields

$$i\hbar\left[\left(\frac{\partial}{\partial t}U_o\right)U_v + U_o\left(\frac{\partial}{\partial t}U_v\right)\right] = \mathcal{H}U_oU_v = \mathcal{H}_oU_oU_v + V(t)U_oU_v. \quad (11)$$

Then, (**??**) leads to

$$\mathcal{H}_oU_oU_v + i\hbar U_o\frac{\partial}{\partial t}U_v = \mathcal{H}_oU_oU_v + V(t)U_oU_v\ , \quad (12)$$

or simply

$$i\hbar U_o\frac{\partial}{\partial t}U_v = V(t)U_oU_v\ . \quad (13)$$

Operating on the left with $U_o^\dagger$ yields the relation

$$i\hbar\frac{\partial}{\partial t}U_v = U_0^\dagger V(t)U_oU_v = V_H(t)U_v\ , \quad (14)$$

where $V_H(t)$ is the Heisenberg representation of the operator V(t). Solving the resulting integral equation by iteration yields

$$U_v(t) = 1 - \frac{i}{\hbar}\int_0^t V_H(t_1)\,dt_1 + \left(-\frac{i}{\hbar}\right)^2 \int_0^t \int_0^{t_1} V_H(t_1)V_H(t_2)\,dt_1\,dt_2 + \left(-\frac{i}{\hbar}\right)^3 \int_0^t \int_0^{t_1} \int_0^{t_2} V_H(t_1)V_H(t_2)V_H(t_3)\,dt_1\,dt_2\,dt_3 + \cdots\ . \quad (15)$$

When there is no applied time-dependent electromagnetic field or other perturbation, then the Hamiltonian may consist of two terms: one large operator $\mathcal{H}_o$ for which the eigenstates can be found, and one small operator $V =$ *constant operator* considered to be a perturbation. Then the expression for U is again **??** but the time dependence of the integrands is particulary simple.

Expansion of Ψ in a basis of pseudo-stationary states

Commonly, we know only the set of eigenstates $[\phi_l \ : \ l = 1, 2, \ldots]$ of an approximate time-independent Hamiltonian $\mathcal{H}_a$, with $\mathcal{H}_a\phi_l = \varepsilon_l\phi_l$. Even when the total Hamiltonian has no time dependence, Ψ will be a time-dependent linear combination of the basis functions. Suppose that $\mathcal{H}_o = \mathcal{H}_a + \mathcal{H}_p$, where $\mathcal{H}_p$ represents a small time-independent perturbation, such as spin-orbit coupling. Then

$$\Psi(t) = \sum_k c_k(t)\phi_k = \sum_k c_k(t)|k_a\rangle \ , \tag{16}$$

where the set of coefficients $[c_k]$ is determined by perturbation theory or a variational approach, and the subscript a on the index k indicates that the function $|k_a\rangle$ is an eigenstate of $\mathcal{H}_a$. Using the concept of a vector space, the set $[\,|k_a\rangle\,]$ is presumed to be a complete basis for the description of any state vector $|\Psi\rangle$. An important general expression for the coefficients is

$$c_k(t) = \langle k_a|\Psi(t)\rangle \ , \tag{17}$$

which is simply the projection of Ψ on to the $|k_a\rangle$ axis. Now suppose that we know that at time $t = 0$ the system is in a definite eigenstate of $\mathcal{H}_a$, that is $\Psi(0) = |l_a\rangle$. We also know that

$$\Psi(t) = U(t)\Psi(0) = U\Psi_o \ . \tag{18}$$

So,

$$c_k(t) = \langle k|\Psi(t)\rangle = \langle k|U\Psi_o\rangle = \langle k_a|U|l_a\rangle = U_{kl} \ . \tag{19}$$

The zero-order expression for $c_k(t)$ arises from the zero-order approximation for U, that is $U(t) = U_oU_v = U_o$. Then

$$c_k(t) = \langle k_a|U_o|l_a\rangle = \langle k_a|e^{-\frac{i}{\hbar}\mathcal{H}_at}|l_a\rangle = e^{-\frac{i}{\hbar}\varepsilon_lt}\langle k_a|l_a\rangle = e^{-\frac{i}{\hbar}\varepsilon_lt}\delta_{kl} \ . \tag{20}$$

So, the state of the system does not change. The first order term in U_v contributes

$$c_k(t) = \langle k_a|U_o\left(-\frac{i}{\hbar}\int_0^t e^{\frac{i}{\hbar}\mathcal{H}_at'}\mathcal{H}_pe^{-\frac{i}{\hbar}\mathcal{H}_at'}\,dt'\right)|l_a\rangle \ , \tag{21}$$

or

$$c_k(t) = -\frac{i}{\hbar}e^{-\frac{i}{\hbar}\varepsilon_lt}\int_0^t \langle k_a|e^{\frac{i}{\hbar}\mathcal{H}_at'}\mathcal{H}_pe^{-\frac{i}{\hbar}\mathcal{H}_at'}|l_a\rangle\,dt' \ , \tag{22}$$

or

$$c_k(t) = -\frac{i}{\hbar}e^{-\frac{i}{\hbar}\varepsilon_lt}\langle k_a|\mathcal{H}_p|l_a\rangle\int_0^t e^{\frac{i}{\hbar}(\varepsilon_k-\varepsilon_l)t'}\,dt' = -\frac{i}{\hbar}e^{-\frac{i}{\hbar}\varepsilon_lt}\langle k_a|\mathcal{H}_p|l_a\rangle\left(\frac{-i\hbar}{\epsilon_k-\epsilon_l}\right)\left(e^{\frac{i}{\hbar}(\varepsilon_k-\varepsilon_l)t}-1\right) \ . \tag{23}$$

The probability of the state $|k_a\rangle$ is

$$|c_k(t)|^2 = \frac{2}{(\epsilon_k-\epsilon_l)^2}|\langle k_a|\mathcal{H}_p|l_a\rangle|^2\left(1-\cos\left(\frac{(\epsilon_k-\epsilon_l)}{\hbar}t\right)\right) \ , \tag{24}$$

which is just the first-order time-independent perturbation result. This looks pathological as $(\epsilon_k - \epsilon_l) \to 0$, but it really is not since $\cos x = 1 - x^2/2 + \cdots$. The most useful application of this expression is for the case of $\epsilon_k - \epsilon_l \approx 0$. Then

$$|c_k(t)|^2 = \frac{|\langle k_a|\mathcal{H}_p|l_a\rangle|^2t^2}{\hbar^2} \, . \tag{25}$$

$U(t)$ for the EM Field-Matter Interation

It is customary to consider the interaction between the electromagnetic field and matter to be weak relative to the interactions among the matter particles themselves, and this is certainly the case for typical nonlinear optical phenomena. Therefore, we write

$$\mathcal{H} = \mathcal{H}_m + \mathcal{H}_I(t) + \mathcal{H}_F \,, \tag{26}$$

where $\mathcal{H}_m$ describes the matter, $\mathcal{H}_F$ describes the field and $\mathcal{H}_I(t)$ describes the interaction. If $\mathcal{H}_I(t) = 0$, then $\mathcal{H}$ has two independent terms, so the total wavefunction is a simple product of matter and field states,

$$\Psi(t) = \psi(t)\xi(t) \,. \tag{27}$$

We will assume that the Schrödinger equation for the matter has been solved and that the wavefunction for the matter is

$$\Psi(t) = \sum_l c_l(t)\phi_l = \sum_l c_l(t)|l_m\rangle \ , \tag{28}$$

which describes a wave packet or coherent superposition of the stationary state solutions $[|k_m\rangle]$. The field wavefunction is

$$\xi = \prod_k |n_k\rangle \prod_{k'} |0_{k'}\rangle \,, \tag{29}$$

where k ranges over modes of the radiation field that are of interest and k' refers to all other modes. A coherent state function would be prefered, but the number state function makes the algebra simpler. The coherence of the radiation field can be handled at a later stage.

The total Hamiltonian is

$$\mathcal{H} = \sum_{l=1}^{n_e+n_n} \frac{1}{2m_l}\left[\vec{p_l} - q_l\vec{A}(\vec{r_l},t)\right]^2 + \sum_{i\neq j}^{n_e+n_n} \frac{q_i q_j}{4\pi\epsilon_\circ r_{ij}} + \sum_k^{modes} \hbar\omega_k \left(a_k^\dagger a_k + \frac{1}{2}\right) \,. \tag{30}$$

Considering the interaction of the radiation field only with the electrons, the interaction energy operator is

$$\mathcal{H}_I = \sum_{l=1}^{n_e} \frac{-e}{m}\left(\vec{p_l}\cdot\vec{A}(\vec{r_l},t) + \vec{A}(\vec{r_l},t)\cdot\vec{p_l}\right) + \sum_{l=1}^{n_e} \frac{e^2}{2m}\vec{A}(\vec{r_l},t)\cdot\vec{A}(\vec{r_l},t) \,, \tag{31}$$

and the total Hamiltonian is

$$\mathcal{H} = \sum_{l=1}^{n_e+n_n} \frac{p_l^2}{2m_l} + \sum_{i\neq j}^{n_e+n_n} \frac{q_i q_j}{4\pi\epsilon_\circ r_{ij}} + \mathcal{H}_I(t) + \sum_k^{modes} \hbar\omega_k \left(a_k^\dagger a_k + \frac{1}{2}\right) \ , \tag{32}$$

or

$$\mathcal{H} = \mathcal{H}_\circ + \mathcal{H}_I(t) + \mathcal{H}_F \,. \tag{33}$$

A time-evolution operator is now

$$U(t) = U_\circ(t)U_v(t), \text{ where } U_\circ(t) = e^{-\frac{i}{\hbar}(\mathcal{H}_\circ+\mathcal{H}_F)t} \tag{34}$$

and U_v is defined by eq. 16.

The operator

$$V_H(t) = U_\circ^\dagger(t)\mathcal{H}_I(t)U_\circ(t) \tag{35}$$

must now be carefully defined. First, specify $\mathcal{H}_I$ precisely. The term involving A^2 will be ignored as not being important for this discussion. Since we are working in the Coulomb gauge $\vec{\nabla}\cdot\vec{A} = 0$, and

$$\vec{p}\cdot\vec{A} = -i\hbar\vec{\nabla}\cdot\vec{A} = -i\hbar\left[(\vec{\nabla}\cdot\vec{A}) + \vec{A}\cdot\vec{\nabla}\right] = -i\hbar\vec{A}\cdot\vec{\nabla} = \vec{A}\cdot\vec{p} \tag{36}$$

as an operator relation. Therefore,

$$\mathcal{H}_I = \sum_{l=1}^{n_e} -\frac{2e}{m}\vec{A}(\vec{r_l},t)\cdot\vec{p_l}\,. \tag{37}$$

This is refered to as the momentum form of the interaction Hamiltonian. The vector potential $\vec{A}$ is a simple multiplicative operator as far as the matter states are concerned but contains annihilation and creation operators for the field states. So, consider only the matter operators for the moment. Using $\vec{p_l} = -i\hbar\vec{\nabla}_l$ as an operator on a matter state $|l_m\rangle$ chills the spine. Fortunately, the simple commutator relations

$$[x,p_x] = [y,p_y] = [z,p_z] = i\hbar\,, \tag{38}$$

$$[x,p_x^2] = 2i\hbar p_x,\ [y,p_y^2] = 2i\hbar p_y,\ [z,p_z] = 2i\hbar p_z \tag{39}$$

provide a way to replace $\vec{p}$ with $\vec{r}$. We will need to evaluate integrals of the form $\langle k'_m|\vec{p_l}|k_m\rangle$. Using

$$[\vec{r_j},\mathcal{H}_\circ] = \sum_{l=1}^{n_e}\frac{1}{2m}[\vec{r_j},p_l^2] = \frac{2i\hbar\vec{p_j}}{2m}\,, \tag{40}$$

we find that

$$\langle k'|\vec{p_l}|k\rangle = \frac{m}{i\hbar}\langle k'|[\vec{r_l},\mathcal{H}_\circ]|k\rangle = \frac{m}{i\hbar}\langle k'|\vec{r_l}\mathcal{H}_\circ - \mathcal{H}_\circ\vec{r_l}|k\rangle\,, \tag{41}$$

or

$$\langle k'|\vec{p_l}|k\rangle = \frac{m}{i\hbar}(E_k - E'_k)\langle k'|\vec{r_l}|k\rangle = im(\omega'_k - \omega_k)\langle k'|\vec{r_l}|k\rangle = im\omega_{k'k}\langle k'|\vec{r_l}|k\rangle\,. \tag{42}$$

More thoughtful analyses yield the same result. This replacement of $\vec{p}$ with $\vec{r}$ will be used later.

Notice that $\mathcal{H}_I$ is a sum of one-electron operators. Electrons interact with the field individually, and the results are additive. Without any loss in generality, the interaction of only a single particle will be considered.$\mathcal{H}_I$. Thus

$$\mathcal{H}_I = -\frac{2e}{m}\vec{A}(\vec{r},t)\cdot\vec{p}. \tag{43}$$

Now, turn to the quantized field operator $\vec{A}$. From an earlier discussion,

$$\vec{A}(\vec{r},t) = \sum_j^{modes} A_j\left[a_j\hat{\epsilon_j}\,e^{i(\tilde{k_j}\cdot\tilde{r}-\omega_j t)} + a_j^\dagger\hat{\epsilon_j}\,e^{-i(\tilde{k_j}\cdot\tilde{r}-\omega_j t)}\right]. \tag{44}$$

Both creation a and annihilation $a^\dagger$ operators appear for all the polarizations and wave vectors $\vec{k}$. In a two-photon process, governed by the second term in equation 16, many products of these operators would appear. We can restrict the contributions to $\vec{A}$ to only those operators which yield changes in the field which are measurable or expected. Thus, for a two-photon absorption of photons of modes $(\omega_1,\hat{\epsilon_1})$ and $(\omega_2,\hat{\epsilon_2})$, we can use

$$\vec{A}(\vec{r},t) = A_1\,a_1\hat{\epsilon_1}\,e^{i(\tilde{k_1}\cdot\tilde{r}-\omega_1 t)} + A_2\,a_2\hat{\epsilon_2}\,e^{i(\tilde{k_2}\cdot\tilde{r}-\omega_2 t)}\,. \tag{45}$$

Similarly, for sum-frequency generation (or second harmonic generation), photons of modes $(\omega_1,\hat{\epsilon_1})$ and $(\omega_2,\hat{\epsilon_2})$ are annihilated, and one photon of mode $(\omega_3,\hat{\epsilon_3})$ is created. So, we can use

$$\vec{A}(\vec{r},t) = A_1\,a_1\hat{\epsilon_1}\,e^{i(\tilde{k_1}\cdot\tilde{r}-\omega_1 t)} + A_2\,a_2\hat{\epsilon_2}\,e^{i(\tilde{k_2}\cdot\tilde{r}-\omega_2 t)} + A_3\,a_3^\dagger\hat{\epsilon_3}\,e^{-i(\tilde{k_3}\cdot\tilde{r}-\omega_3 t)}\,. \tag{46}$$

All this can now be used to construct V_H,

$$V_H(t) = U_\circ^\dagger(t)\mathcal{H}_I(t)U_\circ(t) = e^{-\frac{i}{\hbar}(\mathcal{H}_\circ+\mathcal{H}_F)t}\mathcal{H}_I(t)e^{\frac{i}{\hbar}(\mathcal{H}_\circ+\mathcal{H}_F)t}\,. \tag{47}$$

Continuing,

$$V_H(t) = e^{-\frac{i}{\hbar}(\mathcal{H}_\circ+\mathcal{H}_F)t}\left[-\frac{2e}{m}\vec{A}(\vec{r},t)\cdot\vec{p}\right]e^{\frac{i}{\hbar}(\mathcal{H}_\circ+\mathcal{H}_F)t}\,. \tag{48}$$

We are now ready to make use of the second order term for $U_v(t)$,

$$U_v(t) = \left(-\frac{i}{\hbar}\right)^2\int_0^t\int_0^{t_1} V_H(t_1)V_H(t_2)\,dt_1\,dt_2\,. \tag{49}$$

First, consider how this operator will be used. From **??**,

$$\Psi(t) = U(t)\psi(0)\xi(0)\,, \tag{50}$$

we see that we need to specify the initial state of the system. Ordinarily, this would be given as $|a\rangle\xi_a$, where $|a\rangle$ is a stationary state of the matter Hamiltonian and ξ_a is a product of number states of the field. We will be looking for evidence of a particular final state $|f\rangle\xi_f$. Thus, we want to project $\Psi(t)$ onto the $|f\rangle\xi_f$ axis. Generally,

$$\Psi(t) = \sum_l c_l(t)|k_a\rangle \;= U(t)\psi(0)\xi(0)\,, \tag{51}$$

so,

$$c_f(t) = \langle f\xi_f|\Psi(t)\rangle = \langle f\xi_f|U(t)|a\xi_a\rangle = U_{fa}\,. \tag{52}$$

Using the product form for U yields

$$U_{fa} = \langle f\xi_f|U_\circ(t)U_v(t)|a\xi_a\rangle = \langle f\xi_f|e^{-\frac{i}{\hbar}(\mathcal{H}_\circ+\mathcal{H}_F)t}U_v(t)|a\xi_a\rangle\,. \tag{53}$$

Operating to the left with $U_\circ$,

$$U_{fa} = e^{-\frac{i}{\hbar}E_f t}\langle f\xi_f|U_v(t)|a\xi_a\rangle\,. \tag{54}$$

Using only the second order term for U_v,

$$U_{fa} = e^{-\frac{i}{\hbar}E_f t}\langle f\xi_f|U_v(t)|a\xi_a\rangle\,. \tag{55}$$

Continuing

$$U_{fa} = \left(-\frac{i}{\hbar}\right)^2 e^{-\frac{i}{\hbar}E_f t}\int_0^t\int_0^{t_1}\langle f\xi_f|V_H(t_1)V_H(t_2)|a\xi_a\rangle\,dt_1\,dt_2\,, \tag{56}$$

we arrive at the glorious equation

$$U_{fa} = \left(-\frac{i}{\hbar}\right)^2 e^{-\frac{i}{\hbar}E_f t}$$
$$\int_0^t\int_0^{t_1}\langle f\xi_f|e^{-\frac{i}{\hbar}(\mathcal{H}_\circ+\mathcal{H}_F)t_1}\left[-\frac{2e}{m}\vec{A}(\vec{r},t_1)\cdot\vec{p}\right]\left[-\frac{2e}{m}\vec{A}(\vec{r},t_2)\cdot\vec{p}\right]e^{\frac{i}{\hbar}(\mathcal{H}_\circ+\mathcal{H}_F)t_2}|a\xi_a\rangle\,dt_1\,dt_2\,. \tag{57}$$

If we use the third-order term for U_v, we arrive at the even more glorious equation

$$U_{fa} = \left(-\frac{i}{\hbar}\right)^3 e^{-\frac{i}{\hbar}E_f t}$$
$$\int_0^t\int_0^{t_1}\int_0^{t_2}\langle f\xi_f|e^{-\frac{i}{\hbar}(\mathcal{H}_\circ+\mathcal{H}_F)t_1}\left[-\frac{2e}{m}\vec{A}(\vec{r},t_1)\cdot\vec{p}\right]\left[-\frac{2e}{m}\vec{A}(\vec{r},t_2)\cdot\vec{p}\right]$$
$$\left[-\frac{2e}{m}\vec{A}(\vec{r},t_3)\cdot\vec{p}\right]e^{\frac{i}{\hbar}(\mathcal{H}_\circ+\mathcal{H}_F)t_3}|a\xi_a\rangle\,dt_1\,dt_2\,dt_3\,. \tag{58}$$

And gloriouser sill is the fourth-order equation

$$U_{fa} = \left(-\frac{i}{\hbar}\right)^4 e^{-\frac{i}{\hbar}E_f t} \int_0^t \int_0^{t_1} \int_0^{t_2} \int_0^{t_3} \langle f\xi_f | e^{-\frac{i}{\hbar}(\mathcal{H}_\circ + \mathcal{H}_F)t_1} \left[-\frac{2e}{m}\vec{A}(\vec{r},t_1)\cdot\vec{p}\right] \left[-\frac{2e}{m}\vec{A}(\vec{r},t_2)\cdot\vec{p}\right] \left[-\frac{2e}{m}\vec{A}(\vec{r},t_3)\cdot\vec{p}\right] \left[-\frac{2e}{m}\vec{A}(\vec{r},t_4)\cdot\vec{p}\right] e^{\frac{i}{\hbar}(\mathcal{H}_\circ + \mathcal{H}_F)t_4} |a\xi_a\rangle \, dt_1 \, dt_2 \, dt_3 \, dt_4 \,. \quad (59)$$

Two-Photon Absorption

To find the probability of finding the system in state $|f\xi_f\rangle$ at time t we need to take the absolute square of the glorious equation. To evaluate

$$U_{fa} = \left(-\frac{i}{\hbar}\right)^2 e^{-\frac{i}{\hbar}E_f t} \int_0^t \int_0^{t_1} e^{-\frac{i}{\hbar}E_f t_1} \langle f\xi_f | \left[-\frac{2e}{m}\vec{A}(\vec{r},t_1)\cdot\vec{p}\right] \left[-\frac{2e}{m}\vec{A}(\vec{r},t_2)\cdot\vec{p}\right] |a\xi_a\rangle e^{\frac{i}{\hbar}E_a t_2} \, dt_1 \, dt_2 \,, \quad (60)$$

we will insert a complete set of states between the two operators

$$\sum_j \langle f\xi_f | \left[-\frac{2e}{m}\vec{A}(\vec{r},t_1)\cdot\vec{p}\right] |j\xi_j\rangle\langle j\xi_j| \left[-\frac{2e}{m}\vec{A}(\vec{r},t_2)\cdot\vec{p}\right] |a\xi_a\rangle \,. \quad (61)$$

Focusing on just the t_2 integral,

$$-\frac{2e}{m}\int_0^{t_1} \langle j\xi_j | \left[A_1\, a_1 \hat{\epsilon_1}\, e^{i(\tilde{k}_1\cdot\tilde{r}-\omega_1 t_2)} + A_2\, a_2 \hat{\epsilon_2}\, e^{i(\tilde{k}_2\cdot\tilde{r}-\omega_2 t_2)}\right]\cdot\vec{p}|a\xi_a\rangle e^{\frac{i}{\hbar}E_a t_2}\, dt_2$$
$$= -\frac{2e}{m}\int_0^{t_1} \langle j\xi_j | A_1\, a_1 \hat{\epsilon_1}\, e^{i(\tilde{k}_1\cdot\tilde{r}-\omega_1 t_2)}\cdot\tilde{p}|a\xi_a\rangle e^{\frac{i}{\hbar}E_a t_2}\, dt_2$$
$$-\frac{2e}{m}\int_0^{t_1} \langle j\xi_j | A_2\, a_2 \hat{\epsilon_2}\, e^{i(\tilde{k}_2\cdot\tilde{r}-\omega_2 t_2)}\cdot\tilde{p}|a\xi_a\rangle e^{\frac{i}{\hbar}E_a t_2}\, dt_2 \,. \quad (62)$$

Thus, we have two different time-orderings: ω_1 followed by ω_2 and vice versa.