On light matter interaction: The dipole approximation

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Abstract

In this short review, I'm going to present the widely discussed and well-known topic of light interacting with a quantum object.

- **In the first part, I will go through the general derivation of light matter interaction, entering the quantum mechanical description of the phenomena using quantum mechanics (QM) postulates.**
- **In the second part, I will go through few simplifications that bring to an easy way to deal with electromagnetic interactions, exploiting the perturbation theory.**
- **At the end, I will show an easy way to derive the common dipole Hamiltonian, staying within QM formalism.**

In this short paper, I have tried to be consistent with quantum mechanics fundamentals, being as formal as possible.
The aim of this "personal review" is to combine different good derivations I have seen in my young scientific life to generate a different, self-consistent and elegant proof in the form that I would have liked to be taught as a student. However, since in physics what matter is the coherence of the final result, the derivation in itself is only a matter of taste, so I invite the reader to find his/her favorite one.

This paper is in the form of a lecture, a bit pedagogical and descriptive, so I apologize in advance if sometimes I focus the attention on what it seems trivial and well-known to the expert reader. To follow the whole work it is, however, required good knowledge on QM, Classical Physics and all the related Mathematical tools.

A twisted introduction:

As in many good problems we start with a simple question:
Given a non-relativistic quantum system, described via Shrödinger's equation, how it will interact with an electro-magnetic field?
In other words, given a quantum system $|\Psi\rangle$ we want to understand how the dynamic of this system will be modified if an electro-magnetic (EM) field is present.

$$\hat{H}\,|\Psi(t)\rangle = i\hbar\frac{\partial}{\partial t}\,|\Psi(t)\rangle \tag{1}$$

If we stay within the introductory form of QM, the problem makes no sense, indeed, so far, we have no clue what an electromagnetic field is for a quantum system. To go further, we need to remember how the Shrödinger equation was introduced in the first place.
As in all physical theories we need postulates, like $\mathbf{F} = m\mathbf{a}$ in Newtonian mechanics.

In the easiest formulation of QM the **postulate** we are interested in is:
Given a point-like particle[1]*described through its Hamiltonian $H(\boldsymbol{r},\boldsymbol{p},t)$, where $\boldsymbol{r}$ is the particle poistion and $\boldsymbol{p}$ is the particle momentum, the corresponding quantum wave function is described by the partial differential equation (PDE) (1), where you have taken the same Hamiltonian and every time you encounter $\boldsymbol{p}$, particle momentum, you substitute*[2]

What about $\boldsymbol{r}$?
Here the things became more subtle, before **r** was the particle position, now it has become something different, associated with the spatial distribution of the wave function.

Therefore, to evaluate the effect of a classical[3] electromagnetic field we have to derive first the classical Hamiltonian that describes the interaction. Then, once we have applied the postulate on the classical H, we can fully describe the dynamic in a pure quantum environment.

So far this way of reasoning should be very familiar, since it is the most widely adopted and after all it makes sense, doesn't it?

One may think that QM is not that powerful because it always needs a "classic support" to perform its job.
This is a wrong way of reasoning. In fact, despite the appearance, QM do not need any support from classical physics to work.
Indeed, metaphorically speaking, QM is a game, and we need to define the rules of the game, as well as what the game is about, before even thinking to start playing. If the rules are not completely told at the beginning of the match, then we should blame ourselves, or our coach.

Historically classical mechanics, that is a different game with very different rules, comes first, so in this sense, it appears that QM is generated by classical physics. But, if in 1687 Newton had come out with a fully QM description to prove the change of velocity in time of an apple falling in a gravitational field, then he would have obtained an accurate description of reality, as well, with just a little bit of additional effort in explaining it to Newton's colleagues.
The key point, to make a working self-consistent theory, is to define objects and their interactions, think, for instance, to a computer simulation where you can define a whole universe with arbitrary laws.
Then, of course, not all self-consistent theories can be also physics theories[4]. In fact, a physics theory

[1] In principle we should say "system of particles", but we want to keep it simple for the moment, so we go for "single particle".
[2] Why? This time we do not need to find any answer. Of course, we should be curious but quantum mechanics cannot tell us the answer. Here we should open an endless parenthesis on why we need postulate in any scientific theory.
[3] i.e. not quantized.
[4] $F = ma$ and not $F = ma^3$, even if we can simulate objects that respect this "weird" law.

must have connection with an experimental reality and can be "proved"[5] through experiments.

From a pure theoretical physicist perspective we do not need a naive classical physics theory to describe and make sense of nature, but tell to a mechanical engineer to develop a car engine, based only on quantum mechanical considerations.

To conclude, the only thing that one should now understand is the connection between the two descriptions. This connection is the nature we are trying to understand, that will be always independent by the way we are describing it.[6]
This means that, what we have said at the beginning makes sense, after all, so we could follow the well- established way to uses quantum mechanics postulates. However, in principle, instead of the next derivation one could just say:
Defined the quantum object and the object electromagnetic potentials $(\boldsymbol{A}, \phi)$*, then the quantum particle feels the field and change its spatial shape according to...*

[5]We should say "falsified", but this will take us too far from our objective. For the curious see Karl Popper, The Logic of Scientific Discovery.

[6]The fact that, if we do a "quantum mechanical average" we obtain laws that are similar to the ones of classical mechanics, is just a hint that our beloved QM is a good physical theory that reflects very well nature and not classical mechanics!!!

Part I

Classical particle in an electromagnetic field

Since for human, like us, making sense of quantum mechanics is not an easy task, at all, the best pedagogical way to understand the light-matter interaction is to keep the Quantum-Classical mechanics bridge down. Being aware, however, that is not needed at all!

Therefore, let's put the hat of a classical physicist for a while, it means that, for us, the world is made of point like objects immersed in a space full of arrows, our force field, that interact with the particles through $\mathbf{F} = m\mathbf{a}$.
Consider a point-like particle in position $\mathbf{r}$ of mass m and charge q, and consider a vectorial field $(\mathbf{E}, \mathbf{B})$ that interacts with the particle with a well-known force, the **Lorentz Force**[7].

$$\mathbf{F}(t) = q\mathbf{E}(\mathbf{r}, t) + q\mathbf{v}(t) \times \mathbf{B}(\mathbf{r}, t) \tag{2}$$

Where $\mathbf{v}(t)$ is, clearly, the particle velocity , $\mathbf{E}(\mathbf{r}, t)$ electric field, $\mathbf{B}(\mathbf{r}, t)$ magnetic field. $(\mathbf{E}, \mathbf{B})$ are related through Maxwell equations, with clear meaning of the sources term ρ, charge density, and **J** current density.

$$\nabla \cdot \mathbf{E} = \frac{\rho}{\epsilon_0} \qquad \nabla \cdot \mathbf{B} = 0$$
$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t} \qquad \nabla \times \mathbf{B} = \mu_0\epsilon_0\frac{\partial \mathbf{E}}{\partial t} + \mu_0\mathbf{J}$$

Postulated this 4 vectorial equations for 2 unknown vectorial fields, we can understand that, clearly, some information on the fields are redundant. Therefore, we may look for a more concise description with less variables. It turns out that we can actually describe the same electromagnetic field through the electromagnetic four-potential $(\mathbf{A}, \phi)$:

$$\begin{cases} \mathbf{E}(\mathbf{r}, t) = -\nabla\phi(\mathbf{r}, t) - \dfrac{\partial \mathbf{A}(\mathbf{r}, t)}{\partial t} \\ \mathbf{B}(\mathbf{r}, t) = \nabla \times \mathbf{A}(\mathbf{r}, t) \end{cases}$$

Where $\mathbf{A}(\mathbf{r}, t)$ and $\phi(\mathbf{r}, t)$ can be arbitrary chosen within a certain gauge[8] defined by $\chi(\mathbf{r}, t)$:

$$\begin{cases} \mathbf{A'} = \mathbf{A} + \nabla\chi \\ \phi' = \phi - \dfrac{\partial \chi}{\partial t} \end{cases}$$

For example, one can fix χ so that $\nabla \cdot \mathbf{A} = 0$, this is the, so called, **Coulomb gauge**.

It can be shown that in a different formulation of classical mechanics we can define an object called **Lagrangian** $\mathcal{L}(\mathbf{r}, \mathbf{v}, t)$. This object defines the behavior of a particle[9] in a generic force field and allows to retrieve the Newton's dynamic equation, solving[10]:

$$\frac{d}{dt}\Big(\frac{\partial \mathcal{L}}{\partial \dot{r}_i}\Big) = \frac{\partial \mathcal{L}}{\partial r_i} \tag{3}$$

[7] "That interacts" seems really to be a postulate, and in our case it is. We are postulating the existence of this force and defining its way of working. However, it is a matter of theoretical taste. One relevant point is that sometimes a theory needs to be cleaned up. For example, the Lorentz force is an object that could be retrieved from Maxwell equation, so, in principle, we do not need to postulate both. Physics, fortunately, is based on experiments, therefore following the experimental evidence is always right and legitimate. To be precise even saying that a particle has a propriety called "mass" and a propriety called "charge", in our framework is an axiomatic decision. An interesting direction that physicists have taken is to find one big postulate, under the form of an equation, and to generate everything from it.

[8] To prove it: try to substitute in the vectorial field E B the other potential, you will find a gauge invariance.

[9] Or of an ensemble of particles $\mathcal{L}(\mathbf{r}_i, \mathbf{v}_i, t)$, or, in even more advanced term, a classical field.

[10] For the curious the following equation comes out from the minimization of a functional, the action S. I postpone this discussion for another time, see @

At this point, a consistent definition of the Lagrangian is the one that allows to recover[11] the same dynamical equation of (2).
Therefore the Lagrangian of a single particle (m, q) in a generic em field $(\mathbf{A}, \phi)$ is:

$$\mathcal{L}_{em}(\mathbf{r}, \mathbf{v}, t) = \frac{1}{2}mv^2(t) - q\phi(\mathbf{r}, t) + q\mathbf{v}(t) \cdot \mathbf{A}(\mathbf{r}, t) \tag{4}$$

We can go even further and use another description of classical mechanics exploiting the **Hamiltonian**, here we should spend a lot of time on the meaning of the Hamiltonian with respect to the Lagrangian. In a very qualitative way, we can say the Hamiltonian is the representation of the system energy and reflects the conservative terms.[12] The Hamiltonian is the Legendre transform of the Lagrangian[13],which means, defined **p**(t) particle momentum:

$$p_i = \frac{\partial \mathcal{L}}{\partial \dot{r}_i} \tag{5}$$

$$\mathbf{p}_{em} = m\mathbf{v} + q\mathbf{A} \tag{6}$$

Then,

$$\mathcal{H}_{em}(\mathbf{p}, \mathbf{r}, t) = \mathbf{p}_{em}(t) \cdot \mathbf{v}(\mathbf{p}, t) - \mathcal{L}_{em}(\mathbf{p}, \mathbf{r}, t) \tag{7}$$

The electromagnetic field particle interaction it can be easily written as:

$$H_{em}(\mathbf{p}, \mathbf{r}, t) = -\frac{1}{2}mv^2(\mathbf{p}, t) + q\phi(\mathbf{r}, t) - q\mathbf{v}(\mathbf{p}, t) \cdot \mathbf{A}(\mathbf{r}, t) + \mathbf{v}(\mathbf{p}, t) \cdot (m\mathbf{v}(\mathbf{p}, t) + q\mathbf{A}(\mathbf{r}, t)) \tag{8}$$

Omitting, for the sake of simplicity, all the dependencies, we can simplify (8), obtaining:

$$\mathcal{H}_{em} = \frac{1}{2}mv^2 + q\phi \tag{9}$$

The previous result justifies the statement on the relation between the Hamiltonian and the mechanical energy, indeed, in the Hamiltonian, we only have conservative terms. At this point, we have reached the end of our classical path, the unnecessary bridge toward QM is made by the postulate that relates **p** with the quantum operator $\hat{\mathbf{p}} = -i\hbar\nabla$.
So from a single particle classical Hamiltonian,

$$\mathcal{H}_{em} = \frac{1}{2}m\Big(\frac{\mathbf{p}}{m} - \frac{q\mathbf{A}}{m}\Big)^2 + q\phi \tag{10}$$

So a part very long calculus, and extremely brilliant tricks to generate a refined portrait of different complicate phenomena, this is all we can get from classical physics.

However, this is not enough, and scientist of the past soon realized that classical physics fails in answering to some questions, therefore they were not satisfied.[14].

[11] See Appendix B for the proof.

[12] This will appear clearer soon, indeed we should not forget that the Lorentz force is non conservative, in the sense that, if a magnetic field moves a particle in a loop, the particle will lose or gain energy. **BUT** for the principle of energy conservation, something else, the field, must, viceversa, gain or lose energy.

[13] We could spend hours in discussing the implications and the meaning of this statement, but at the end the Legendre transform can be seen as a different language to express the same object.

[14] The lack of satisfaction, is judged, by some historians, to be one of the main motor of mankind extremely wide imagination.

For example:
Why different particles with very different masses and charges, but similar in size, respond to different wavelength in very different ways?
If we had not been able to understand it, we would not have developed advanced techniques to recognize different material.

Or, Can matter generate light from a bunch of atoms and can we realize with this new light system that can be used for all sort of things: from extremely precise surgery, to the accurate cut of heavy structure; from the investigation of ultrafast phenomena for fundamental knowledge, to send encoded message through a small fiber and substain our desperate need to communicate with our dearest friends spread all over the world ?

It is hard, to imagine a modern society without the invention of the laser, so it is meaningless to go further with the list of things we would have missed if we had not been able to find a better description of light matter interaction.

The point I want to stress is that, at the time, people weren't satisfied by the classical "physicist hat", still extremely powerful, but too naive. Therefore, great scientists funded and create "new shops" where people, like me, could demand for a different headgear to wear.

Exploiting the postulate mentioned in the introduction, after few trivial steps we can achieve:
The quantum mechanical Hamiltonian of a single particle in an electromagnetic field.

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + q\phi(\mathbf{r},t) + \frac{q^2}{m}A^2(\mathbf{r},t) + i\frac{q\hbar}{2m}\nabla\cdot\mathbf{A}(\mathbf{r},t) + i\frac{q\hbar}{2m}\mathbf{A}(\mathbf{r},t)\cdot\nabla \tag{11}$$

Quantum particle in an electromagnetic field

At this point the bridge is no more needed, therefore we can postulate that a non-relativistic single particle, that is described by its own wave function $|\Psi(t)\rangle$, in an electromagnetic field will evolve following:

$$\hat{H}\,|\Psi(t)\rangle = i\hbar\frac{\partial}{\partial t}\,|\Psi(t)\rangle$$

From now on, we will put aside Dirac notation using only the spatial projection of the wave function.[15]

$$\Psi(\mathbf{r},t) = \langle \mathbf{r}|\Psi(t)\rangle \tag{12}$$

Practically speaking, it is the common wave-function we are all comfortable with.
At this point, we would like to use the previous equation for something different than contemplation, so we may need to simplify our description:

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + q\phi(\mathbf{r},t) + \frac{q^2}{m}A^2(\mathbf{r},t) + i\frac{q\hbar}{2m}\nabla\cdot\mathbf{A}(\mathbf{r},t) + i\frac{q\hbar}{2m}\mathbf{A}(\mathbf{r},t)\cdot\nabla$$

So far, we have spoken about a generic electromagnetic field. We can assume, at this point, that our universe is made of three elements: an electron, an unspecified frozen nucleus[16], which, for us, only effect is to create an electrostatic field around it, and the electromagnetic field.
We will show that, both the two last phenomena can be already included in our electromagnetic Hamiltonian description.
Indeed,

$$\mathbf{E}_{tot} = \mathbf{E}_{nucleus} + \mathbf{E}_{waves} \tag{13}$$

Then the divergence of this field, according to Maxwell equations is:

$$\nabla\cdot\mathbf{E}_{tot} = \nabla\cdot\mathbf{E}_{nucleus} + \nabla\cdot\mathbf{E}_{waves} = \frac{\rho_l}{\epsilon_0} + 0$$

Where $\rho_l = Ze\delta(\mathbf{r})$ localized nucleus of charge Ze, with e the modulus of the electron charge and Z the number of protons. Therefore, we can split the description in two fields $(\mathbf{A}_{waves}, \phi_{waves})(0, \phi_{nucleus})$:

$$\mathbf{E}_{tot} = -\nabla\phi_{nucleus}(\mathbf{r}) - \nabla\phi_{waves}(\mathbf{r}) - \frac{\partial\mathbf{A}_{waves}(\mathbf{r},t)}{\partial t}$$

$$\mathbf{E}_{nucleus}(\mathbf{r}) = -\nabla\phi_{nucleus}(\mathbf{r}) \tag{14}$$

$$\mathbf{E}_{waves}(\mathbf{r},t) = -\frac{\partial\mathbf{A}_{waves}(\mathbf{r},t)}{\partial t} - \nabla\phi_{waves} \tag{15}$$

Now, we include the Coulomb Gauge, $\nabla\cdot\mathbf{A}_{waves} = 0$, on the wave field, and the electrostatic condition on the field produced by the nucleus[17].
Finally, it can be proved that solving $-\nabla^2\phi_{nucleus} = \frac{Ze}{\epsilon_0}\delta(\mathbf{r})$, we can retrieve the classical Coulomb potential, this is done through Green's functions tool.
At this point, we have a better form of (11), where the subscript have been removed since no more needed:

$$\hat{H} = \hat{H}_0 + \frac{e^2A^2}{2m} - i\frac{e\hbar}{2m}\mathbf{A}\cdot\nabla \tag{16}$$

With $\hat{H}_0 = -\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{4\pi\epsilon_0|\mathbf{r}|}$, almost the classical atomic Hamiltonian[18].

[15] Dirac notation is way more powerful that it seems to be and it's not just a cool way of writing down Shödinger equation. To understand its full potential one should look in the direction of second quantization.

[16] To disclose this properly we should stop and spend many many pages in the discussion. Since we want to arrive somewhere with this discussion, as always, we should close one eye and go further. Being aware, however, that if something will not match the experimental reality we will have to open the "black box" called nucleus.

[17] Electrostatic means that the curl of E is equal to zero, this implies that there is no potential vector. While the elimination of a scalar potential in (15) is **ONLY** due to the Coulomb gauge, this will be proved later on in part III.

[18] Why almost? Well, in this derivation we are wrongly assuming that the proton is not a particle. In other word, the presence of the proton is only tracked by the electric field that it produces in space. This is clearly incorrect, and, we should consider

Part II

Perturbation theory and dipole selection rules

To solve (17) many methods have been developed in the decades.

$$(\hat{H}_0 + \frac{e^2A^2}{2m} - i\frac{e\hbar}{2m}\mathbf{A}\cdot\nabla)\Psi(\mathbf{r},t) = i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r},t) \tag{17}$$

Before proceeding further with the mentioned tool, let's simplify our life by saying that the A^2 is negligible with respect the one linear in A. In more formal term we are assuming:

$$|A_{max}| << \frac{\hbar}{ea} \tag{18}$$

Where a is the typical atomic dimension, $a \approx 0.1$ nm.
Commonly speaking, we are asking that the field is not "too intense"[19]. Therefore, our new problem is:

$$(\hat{H}_0 + \hat{H}_{em})\Psi(\mathbf{r},t) = i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r},t) \tag{19}$$

With:

$$\hat{H}_{em} = -i\frac{e\hbar}{2m}\mathbf{A}\cdot\nabla \tag{20}$$

For sure a direct approach is still not recommended.
A very smart way to face this problem was introduced by a brilliant English physicist, Paul Dirac. This famous physicist developed what is called **time-dependent perturbation theory** to solve this class of problems[20].
At this point we can proceed and start the engine of the perturbation theory, whose formal discussion can be seen in many good QM textbook.

The idea is simple: we have our $\hat{H}_0$ unperturbed Hamiltonian that describes the system in a condition where the electro-magnetic field is absent. So, the first step is to find the solution of this unperturbed problem. After variable separation and other very simple steps we end up with a complete set of orthonormal wave-functions $\psi_k(\mathbf{r})$, by solving:

$$\hat{H}_0\psi_k(\mathbf{r}) = \hbar\omega_k\psi_k(\mathbf{r}) \tag{21}$$

This set can describe the evolution of a generic wave-function $\Psi_{unperturbed}(\mathbf{r},t)$ that describe the unperturbed system, only, by superposition of these eigenstates times their energetic temporal dependence[21].

$$\Psi_{unperturbed}(\mathbf{r},t) = \sum_k c_k\psi_k(\mathbf{r})e^{-i\omega_k t} \tag{22}$$

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also the nucleus as a massive particle. Therefore, solving a QM two-body problem and splitting the electron and nucleus wave function we obtain (16), with m reduced mass. However, if the nucleus is much heavier than the electron, our model is fairly correct. Thus, we leave more advanced consideration on the topic for another time. A final comment is on the beauty of equation (11), with very general considerations we have derived all relevant aspect of particle-field interaction

[19] With respect to a certain quantity defined in (18).

[20] As we will see this will oblige us to introduce simplifications, this will be performed without too much worries. But, in principle, we should be damn scared every time we throw away a term from an equation. Pursuing this approach is mathematically noble, but it will froze the progress. To win this fear, we should understand what does it mean "to simplify" an already accurate description of nature? This is another very interesting thing to discuss... To give you a very solid perspective on the topic I will leave you with the world of Paul Dirac himself:
The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble. It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation..
Word to the wise.

[21] Here the reader should be familiar with the basic concept that characterizes QM.

Since, we have a different system, i.e. perturbed system, then the (22) is no more a good description of a generic particle dynamic. However, the eigenstates are still orthonomal basis of the Hilbert space, so we can always write the generic time evolution of the most general particle of the bounded system as:

$$\Psi(\mathbf{r},t)=\sum_k c_k(t)\psi_k(\mathbf{r})e^{-i\omega_k t} \tag{23}$$

Now, we turn on the field, $\hat{H}_{em}$, and we want to see how the generic $\Psi(\mathbf{r},t)$ will change. So far, the word perturbation is not needed, at all, indeed the following calculus are very general. However, as it will become clear at the very end, we can exploit the perturbation theory result only if the perturbation is small. The key point of perturbation theory is that our $\hat{H}_{em}$ is, indeed, a perturbation. Therefore, it must be small with respect to the energy of the meaningful energies of H_0, simply speaking the field should not being able to ionize our medium, otherwise perturbation theory, in this form[22], cannot be applied. If one simply plug (23) in (19):

$$(\hat{H}_0+\hat{H}_{em})\sum_k c_k(t)\psi_k(\mathbf{r})e^{-i\omega_k t}=i\hbar\frac{\partial}{\partial t}\sum_k c_k(t)\psi_k(\mathbf{r})e^{-i\omega_k t} \tag{24}$$

For linearity, exploiting the fact that $\hat{H}_{em}(\mathbf{r},t)$ does not introduce any temporal derivative, and (21).

$$\sum_k c_k(t)(\hat{H}_0+\hat{H}_{em})\psi_k(\mathbf{r})e^{-i\omega_k t}=i\hbar\sum_k(\dot{c}_k(t)\psi_k(\mathbf{r})e^{-i\omega_k t}-i\omega_k c_k(t)\psi_k(\mathbf{r})e^{-i\omega_k t})$$

$$\sum_k c_k(t)(\hbar\omega_k+\hat{H}_{em})\psi_k(\mathbf{r})e^{-i\omega_k t}=i\hbar(\sum_k \dot{c}_k(t)\psi_k(\mathbf{r})e^{-i\omega_k t}+\sum_k \hbar\omega_k c_k(t)\psi_k(\mathbf{r})e^{-i\omega_k t})$$

The first and the latter term annihilate each other, so we remain with an equation that is in all sense equivalent to (19), i.e. no approximation have been made.

$$\sum_k c_k(t)\hat{H}_{em}\psi_k(\mathbf{r})e^{-i\omega_k t}=i\hbar\sum_k \dot{c}_k(t)\psi_k(\mathbf{r})e^{-i\omega_k t} \tag{25}$$

So far not so good. We had a complex PDE equation with one big unknown, Ψ, now we, still, have a single ODE equation but with a higher number of unknown $c_k(t)$.
A counter-intuitively bright idea is to increase the number of equations to be solved. This can be done by integrating[23] left and right by $\int d^3r\psi_j^*(\mathbf{r})e^{+i\omega_j t}$.
The j-th equation can be now written as, exchanging the sum with the integral[24]

$$\sum_k c_k(t)\int d^3r\psi_j^*(\mathbf{r})\hat{H}_{em}\psi_k(\mathbf{r})e^{-i(\omega_k-\omega_j)t}=i\hbar\sum_k \dot{c}_k(t)\int d^3r\psi_j^*(\mathbf{r})\psi_k(\mathbf{r})e^{-i(\omega_k-\omega_j)t}$$

For the property of orthogonality of eigenstates:

$$\int d^3r\psi_j^*(\mathbf{r})\psi_k(\mathbf{r})=\delta_{kj}$$

Where δ_{kj} is the Kronecker's delta.
Therefore,

$$\dot{c}_j(t)=\frac{1}{i\hbar}\sum_k c_k(t)e^{-i(\omega_k-\omega_j)t}\int d^3r\psi_j^*(\mathbf{r})\hat{H}_{em}\psi_k(\mathbf{r}) \tag{26}$$

[22]We can reverse the problem, saying that H_0 is the perturbation and $\hat{H}_{em}$ is the unperturbed condition, this works fine only if the two energetic terms are not comparable. In this middle regime the analytic treatment is tough.

[23]In Dirac formalism this can be expressed in term of bra, provided that $|\psi_k\rangle$ is a ket vector. Here we are not using it for the reason expressed in (12). Remembering that Dirac formalism is not just a cool way of writing down QM.

[24]If the fear has suddenly taken over you, see Fubini-Tonelli theorem.

To recap: from one PDE with one unknown, we reach a single ODE with several unknowns, not happy, we have arrived at our last exact formulation of (19), where we have several coupled ODE with several unknowns.
This seems awful but sometimes, as the Descartes's method taught, splitting a huge problem in small little problems can make your life much easier, and this is the case.

To convince you, we can use the powerful matrix formalism to reformulate the problem, in that case Dirac notation became extremely useful and as well as a space-saving necessity[25].
We rewrite (26) as:

$$\dot{c}_j(t) = \frac{1}{i\hbar}\sum_k c_k(t) e^{-i(\omega_k-\omega_j)t}\langle\psi_j|\hat{H}_{em}|\psi_k\rangle \tag{27}$$

Clearly, (27) belongs to a bigger system of equation, this system can be written as:

$$\dot{\mathbf{C}}(t) = \frac{1}{i\hbar}\mathbf{H}_{em}\mathbf{C}(t) \tag{28}$$

Where $\mathbf{C}(t)$ is the vector containing c_i, $\mathbf{H}_{em}$ is a matrix[26] whose elements are:

$$\mathbf{H}_{em} = \begin{bmatrix} \langle\Psi_1|\hat{H}_{em}|\Psi_1\rangle & \langle\Psi_1|\hat{H}_{em}|\Psi_2\rangle & \cdots & \langle\Psi_1|\hat{H}_{em}|\Psi_n\rangle \\ \langle\Psi_2|\hat{H}_{em}|\Psi_1\rangle & \langle\Psi_2|\hat{H}_{em}|\Psi_2\rangle & \cdots & \langle\Psi_2|\hat{H}_{em}|\Psi_n\rangle \\ \vdots & \vdots & \ddots & \vdots \\ \langle\Psi_n|\hat{H}_{em}|\Psi_1\rangle & \langle\Psi_n|\hat{H}_{em}|\Psi_2\rangle & \cdots & \langle\Psi_n|\hat{H}_{em}|\Psi_n\rangle \end{bmatrix}$$

Where $|\Psi_k\rangle = |\psi_k\rangle\, e^{-i\omega_k t}$.
This procedure is not perturbation theory, therefore no approximation have been made so far. Indeed, the problem can be solved, even numerically with an almost **exact** solution. Indeed, if we diagonalize $\mathbf{H}_{em} = \Gamma\Lambda\Gamma^{-1}$, then we end up with a system of simple decoupled ODE equations. This is a possible way to proceed, but we have to know numerically each matrix element.

What follow is the core of perturbation theory, however in the next section we will only focus on the matrix elements, hoping that the reader is familiar of the use of perturbation theory to discuss a two-level system, if not, well, it can be clearly understood that all the physics that characterize our system and the solution is embedded in $\langle\psi_j|\hat{H}_{em}|\psi_k\rangle$. At the beginning of the section we have declared that an approximation of equation (19) was desperately needed. However, so far, we have just circumnavigate the problem without making any approximation.

Now the genius of Dirac comes to play: *since (27) is a system of coupled equations, is there a way of decoupling them ?*
If we are really talking about a small perturbation, then we can think at the system as if the unperturbed states are still eigenstates of the new one. Therefore, it makes sense[27] to see how the perturbation changes the occupation probability of the j-level, $|c_j(t)|^2$.
At this point we have to play some tricks. The meaning of all of this is to collect terms with similar "order of relevance" and to evaluate terms with the same "order of relevance", this will be clear soon.
To stress the meaning of perturbation we can say that:

$$\hat{H}_{em} = \lambda\hat{H'}_{em}$$

[25]To be rigorous we should include also the spin wavefunction χ, we will neglect this relevant details, since so far is unused information

[26]At this point a good question is: *Which is the size of this matrix?* In principle the matrix has no finite size, since the eigenstates are infinite. However, as in most quantum real system we can stop to count after a certain number of levels. Two level system, three level system and so on.

[27]The phrase "to make sense" has been chosen ad hoc. From a mathematical perspective there are no problems at all. We can in principle do whatever we like, since we are respecting all the rules even in (28) even if the eigenstate basis chosen has nothing to do with the $\hat{H}_{em}$. From a physical sense to say something meaningful we need a small perturbation that do not change too much the problem. In this way a series of simplification known as perturbation theory can be done.

With this step we are not adding anything to our discussion, is just a way of highlighting the smallness of the perturbation and it will be useful to set the order of relevance of the different terms. At this point, the effect of this small perturbation on the coefficients can be split in a series of contribution with decreasing relevance:

$$c_j(t) = c_j^{(0)} + \lambda c_j^{(1)}(t) + \lambda^2 c_j^{(2)}(t) + \lambda^3 c_j^{(3)}(t) + ... + \lambda^i c_j^{(i)}(t) + ... \tag{29}$$

Where $c_j^{(0)}$ can be regarded as the unperturbed initial condition, a well known term fixed by boundaries. If we put (29) in (27) and we collect all the terms with the same power of λ, we achieve the final result of perturbation theory:

$$\dot{c}_j^{(1)}(t) = \frac{1}{i\hbar} \sum_k c_k^{(0)} e^{-i(\omega_k - \omega_j)t} \langle \psi_j | \hat{H}_{em} | \psi_k \rangle \tag{30}$$

This result can be used freely, what will be meaningful, from now on, is the proprieties of the field.

Part III

The dipole approximation Hamiltonian

What is left to do in this section is to make some final simplifications on the perturbation, remembering that $\mathbf{A}(\mathbf{r},t)$ is a vectorial field:

$$\hat{H}_{em} = -i\frac{e\hbar}{2m}\mathbf{A}(\mathbf{r},t)\cdot\nabla$$

What is commonly performed is the **multipole expansion**. Under the hypothesis of a linearly polarized plane vector potential, with **e** polarization vector.

$$\mathbf{A}(\mathbf{r},t) = A(t)e^{i\mathbf{k}\cdot\mathbf{r}-i\omega t}\mathbf{e} + cc = A(t)e^{-i\omega t}[1 + i\mathbf{k}\cdot\mathbf{r} - \frac{1}{2}(\mathbf{k}\cdot\mathbf{r})^2 + ...]\mathbf{e} + cc \tag{31}$$

If we can infer: $\mathbf{k}\cdot\mathbf{r} << 1$, then we can stop at the zero order.

This is the **electric dipole approximation**, that allows to write a time-dependent perturbation[28].
Thanks to this huge simplification that can be freely use only if the wavelength of the impinging wave is much bigger with respect atomic dimensions.

$$\hat{H}_{em} = -i\frac{e\hbar}{2m}\mathbf{A}(t)\cdot\nabla \tag{32}$$

In this last part we are going to manipulate a bit the matrix elements, without attempting to solve it. The outcome allows to understand some proprieties that characterize the interaction. We will show, in particular, how different choices of gauge will condition the form of the Hamiltonian.
For simplicity we focus only on the effect of gauge transformation on the electromagnetic field, neglecting completely the electrostatic interaction, that is already embedded in $\hat{H}_0$.
In previous part we have claimed, if you take this:

$$\hat{H} = \hat{H}_0 + \frac{q^2}{m}A^2(\mathbf{r},t) + i\frac{q\hbar}{2m}\nabla\cdot\mathbf{A}(\mathbf{r},t) + i\frac{q\hbar}{2m}\mathbf{A}(\mathbf{r},t)\cdot\nabla + q\phi(\mathbf{r},t) \tag{33}$$

And once you apply Coulomb gauge, $\nabla\cdot\mathbf{A} = 0$, then you can throw away two terms $i\frac{q\hbar}{2m}\nabla\cdot\mathbf{A}(\mathbf{r},t)$ and $q\phi(\mathbf{r},t)$.
For sure, nobody has doubt on the first, for the latter we should spend few lines about it.
Without wasting words, one should observe that we are looking at a wave generated by no local source, then:

$$\begin{aligned}
&\mathbf{E}(\mathbf{r},t) = -\frac{\partial\mathbf{A}(\mathbf{r},t)}{\partial t} - \nabla\phi(\mathbf{r},t)\\
&\nabla\cdot\mathbf{E}(\mathbf{r},t) = 0\\
&\nabla\cdot\mathbf{E}(\mathbf{r},t) = -\frac{\partial}{\partial t}\nabla\cdot\mathbf{A}(\mathbf{r},t) - \nabla^2\phi(\mathbf{r},t) = 0\\
&\nabla^2\phi(\mathbf{r},t) = 0
\end{aligned}$$

This reasonably implies $\phi(\mathbf{r},t) = 0$.

At this point we can discuss the matrix element, that we are going to rewrite in the following form for simplicity.

$$\langle\psi_j|\hat{H}_{em}|\psi_k\rangle = \langle j|\hat{H}_{em}|k\rangle \tag{34}$$

[28] For the sake of completeness, the linear term is the so called quadrupole-magnetic dipole term.

Within the Coulomb gauge, the dipole approximation and neglecting A^2:

$$\langle j|\hat{H}_{em}|k\rangle = \frac{e}{2m}\mathbf{A}(t)\cdot\langle j|\hat{\mathbf{p}}|k\rangle \tag{35}$$

The equation (35) already gives us relevant hints on the proprieties of the matrix element, e.g. the fact that the polarization of the wave must be among direction where $\langle j|\hat{\mathbf{p}}|k\rangle$ is not null. If we exploit the commutator $[\mathbf{r},\hat{H}_0] = i\frac{\hbar}{m}\hat{\mathbf{p}}$, proved in appendix then:

$$\langle j|\hat{H}_{em}|k\rangle = \frac{ie}{2\hbar}(\epsilon_j - \epsilon_k)\mathbf{A}(t)\cdot\langle j|\mathbf{r}|k\rangle \tag{36}$$

Where, clearly, $\hbar\omega_n = \epsilon_n$. The result is extremely relevant and can be used in plenty of real physics situation, e.g. it fixes the dipole selection rules[29].

It is really common to find a different expression for $\hat{H}_{em}$.
Instead of (32), as our perturbation, we may work in a different gauge $(\mathbf{A}', \phi')$:

$$\begin{cases} \mathbf{A'} = \mathbf{A} + \nabla\chi \\ \phi' = \phi - \dfrac{\partial\chi}{\partial t} \end{cases}$$

For simplicity we are going to consider a monochromatic wave, aware, however, that the generic envelope generalization is straightforward. Let's consider the dipole approximation, and remember the relation in the Coulomb gauge between **E** and **A**, then we have:

$$\mathbf{A}(t) = \frac{1}{2}A_0 e^{-i\omega t}\mathbf{e} + cc = \frac{E_0}{2i\omega}e^{-i\omega t}\mathbf{e} + cc = -\frac{E_0}{\omega}\sin(\omega t)\mathbf{e} \tag{37}$$

At this point if we set the gauge so that:

$$\chi(\mathbf{r},t) = \mathbf{r}\cdot\frac{E_0}{\omega}\sin(\omega t)\mathbf{e} \tag{38}$$

Then the new gauge will give the following four-vector potential:

$$\begin{cases} \mathbf{A'} = \frac{E_0}{\omega}(-\sin(\omega t) + \sin(\omega t)) = 0 \\ \phi' = 0 - \mathbf{r}\cdot(\mathbf{E}_0)\frac{1}{\omega}\omega\cos(\omega t) \end{cases}$$

Unexpectedly, the new gauge provided:

$$\phi'(\mathbf{r},t) = -\mathbf{r}\cdot\mathbf{E}_0 cos(\omega t) = \tag{39}$$

This result comes out, strictly, from the monochromatic wave case. However, it is not hard to imagine performing Fourier transform on $A(t)$, this will cause a different time dependency of $\chi(\mathbf{r},t)$, but at the end, for linearity we will end up with very similar results. Thus, it can be proved that in general:

$$\phi'(\mathbf{r},t) = -\mathbf{r}\cdot\mathbf{E}(t) \tag{40}$$

Plugging the new four-vector, that has become a simple scalar field[30], in the (33):

$$\hat{H} = \hat{H}_0 - q\mathbf{r}\cdot\mathbf{E}(t) \tag{41}$$

Therefore, the new Hamiltonian, called **Electric Dipole Hamiltonian**, completely equivalent to (32), can be used to evaluate the effect of perturbation on a simple quantum system.

$$\hat{H}_{dipole} = -\hat{\mu}\cdot\mathbf{E}(t) \tag{42}$$

With $\hat{\mu} = q\mathbf{r}$.

[29]The only transactions allowed, i.e. the state in which the electric field has an effect, are the one that do not conserve the parity of the states. This appears clear if we look at (27). This is of course strictly true in the dipole approximation

[30]This is only son of the dipole approximation, without the least the result make no sense.

Conclusion

The journey might seem tough, but it is worthwhile. Writing down, in a personal way, this old and extremely well known piece of Physics, I have understood how hard is to be clear in an explanation. I have also found a lot difficult to understand where to stop in the different discussions and go on. Indeed, a topic treated in few pages could be extended into an entire chapter, or even a book, if you don't give for granted few results or use the powerful phrase " It can be proved ". It is, however, vital to go through all these result, or at least to know exactly where you should look if one day you want to be sure about what you have always assumed to be true. We are in an era where almost all the scientific knowledge is available online, where if you want to prove something you just have to "Google it", that is awesome!

So why a person should lose its time on proving again and alone old-fashioned Physics?

Personally, because I have realized, few years ago, that without that tool I was not able to face an empty blackboard and do some Physics. A tool cannot substitute our imagination neither our ability to go through the old-fashioned Physics. What is helping me in this tortuous path is to remember the fundamentals:

- What is a postulate, what can be proven starting from that postulate and which is the mathematical tools needed.
- The principle of self-consistency in a mathematical theory, the role of experimental proofs in the corroboration process of the same theory.
- The limits of an approximation but its importance for practical purpose.
- And more than everything the trust in the Scientific method, when properly applied.

Fortunately, we are not alone, there is a Scientific community and there are centuries of "old-fashioned" knowledge.
"*We are dwarfs standing on the shoulders of giants*", after all, and thanks to that we totally have the potentiality, and the tools, to reach higher level of comprehension of the reality surrounding us.

Appendix

[A] Commutator $[r, H_0]$

If we take,

$$[\mathbf{r}, H_0] = [\mathbf{r}, V(\mathbf{r})] + [\mathbf{r}, -\frac{\hbar^2}{2m}\nabla^2] \tag{43}$$

Then we analyze components by components, evaluating the application on a generic scalar function $f(\mathbf{r})$:

$$[x, \nabla^2] = x\nabla^2 f(\mathbf{r}) - \nabla^2(f(\mathbf{r})x) = x\nabla^2 f(\mathbf{r}) - \nabla(\nabla x f(\mathbf{r}) + x\nabla f(\mathbf{r}) \tag{44}$$

Now only using $\nabla x = (1, 0, 0)$:

$$[x, \nabla^2] = x\nabla^2 f(\mathbf{r}) - \frac{\partial}{\partial x} f(\mathbf{r}) - \nabla x \cdot \nabla f(\mathbf{r}) - x\nabla^2 f(\mathbf{r}) \tag{45}$$

Immediately,

$$[x, \nabla^2] = -2\frac{\partial}{\partial x} \tag{46}$$

Therefore:

$$[\mathbf{r}, H_0] = -\frac{\hbar^2}{m}\nabla = i\frac{\hbar}{m}\mathbf{p} \tag{47}$$