Lecture 12

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Gauge Transformations of the Time Dependent Schrödinger Equation

Before we can talk about atomic processes is strong fields we need to talk about different gauges and how they enter the Schrödinger problem. We remember the time dependent Schrödinger Equation (TDSE) for a single electron in a electromagnetic field:

$$i\hbar\partial_t\psi(\boldsymbol{r},t) = \left[\frac{\hat{\boldsymbol{p}}^2}{2m} + \frac{e}{2m}\left(\boldsymbol{A}(\hat{\boldsymbol{r}},t)\cdot\hat{\boldsymbol{p}} + \hat{\boldsymbol{p}}\cdot\boldsymbol{A}(\hat{\boldsymbol{r}},t)\right) + \frac{e^2}{2m}\boldsymbol{A}^2(\hat{\boldsymbol{r}},t)\right]\psi(\boldsymbol{r},t). \tag{1}$$

As we already know, this equation is invariant unter gauge transformations of type:

$$\boldsymbol{A} \to \boldsymbol{A}' = \boldsymbol{A} + \nabla f \tag{2a}$$

$$\phi \to \phi' = \phi - \partial_t f \tag{2b}$$

$$\psi \to \phi' = e^{-\frac{ie}{\hbar}f}\psi. \tag{2c}$$

From now on we will assume that we can work in dipole approximation and, thus, neglect all spatial dependencies of the vector potential $\boldsymbol{A}(\boldsymbol{r},t) = \boldsymbol{A}(t)$. Therefore we find $\nabla\boldsymbol{A}(t) = 0$. But be careful! Although the divergence of the vector potential vanishes, resembling the Coulomb gauge condition, we have not chosen any gauge yet. Moreover let us assume the absence of any sources (static charges) so that $\phi = 0$. With these approximations the TDSE simplifies to:

$$i\hbar\partial_t\psi(\boldsymbol{r},t) = \left(\underbrace{\frac{\hat{\boldsymbol{p}}^2}{2m}}_{\hat{H}_0} + \underbrace{\frac{e}{m}\boldsymbol{A}(\hat{\boldsymbol{r}},t)\cdot\hat{\boldsymbol{p}} + \frac{e^2}{2m}\boldsymbol{A}^2(\hat{\boldsymbol{r}},t)}_{\hat{H}_{int}}\right)\psi(\boldsymbol{r},t). \tag{3}$$

The first important gauge, we need to know for the interaction between electrons and electromagnetic fields is the *velocity gauge*. In this case we choose:

$$f = -\frac{r}{2m}\int_{-\infty}^{t}\boldsymbol{A}^2(t')dt'. \tag{4}$$

And we find:

$$\boldsymbol{A}' = \boldsymbol{A}, \tag{5a}$$

$$\phi' = \frac{e}{2m}\boldsymbol{A}^2. \tag{5b}$$

Therefore the TDSE for the wave function $\psi^V(\boldsymbol{r}, t)$ in velocity gauge becomes

$$i\hbar\partial_t\psi^V(\boldsymbol{r}, t) = \left(\hat{H}_0 + \frac{e}{m}\boldsymbol{A}(t)\cdot\hat{\boldsymbol{p}}\right)\psi^V(\boldsymbol{r}, t). \tag{6}$$

Now it becomes clear why this gauge is called velocity gauge. Looking at the interaction Hamiltonian we see that the vector potential $\boldsymbol{A}(t)$ couples to the operator $\frac{\hat{\boldsymbol{p}}}{m}$, which is, in classical mechanics, the velocity $\boldsymbol{v}$.

The second important gauge we need to know is the *length gauge* resulting from the transformation:

$$f = -\boldsymbol{A}(t)\cdot\boldsymbol{r}, \tag{7}$$

thus we get

$$\boldsymbol{A}' = 0, \tag{8a}$$

$$\phi' = \partial_t\boldsymbol{A}(t)\cdot\boldsymbol{r} = -\boldsymbol{E}(t)\cdot\boldsymbol{r}, \tag{8b}$$

which gives us the TDSE in length gauge:

$$i\hbar\partial_t\psi^L(\boldsymbol{r}, t) = \left(\hat{H}_0 + e\boldsymbol{E}(t)\cdot\boldsymbol{r}\right)\psi^L(\boldsymbol{r}, t) \tag{9}$$

The Kramers-Transformation

In order to describe electrons in an electromagnetic field it is very useful to make a coordinate transformation into the so-called *Kramers-Henneberger frame*.

Starting with the TDSE in velocity gauge we perform a unitary transformation of the wavefunction introducing a time-dependent translation $\boldsymbol{\alpha}(t)\cdot\hat{\boldsymbol{p}}$

$$\psi^{KH}(\boldsymbol{r}, t) = e^{\frac{i}{\hbar}\boldsymbol{\alpha}(t)\cdot\boldsymbol{p}}\psi^V(\boldsymbol{r}, t), \tag{10}$$

where

$$\boldsymbol{\alpha}(t) = -\frac{e}{m}\int_{-\infty}^{t}\boldsymbol{A}(t')dt'. \tag{11}$$

Whe know from classical electrodynamics that $\boldsymbol{\alpha}(t)$ corresponds to the translation of a charge in an electromagnetic field (ponderomotive shift). Its meaning becomes evident looking at the TDSE in the Kramers-Henneberger frame:

$$i\hbar\partial_t\psi^{KH}(\boldsymbol{r}, t) = \hat{H}_0\psi^{KH}(\boldsymbol{r}, t). \tag{12}$$

The equation above is the Schrödinger equation for a free electron with momentum $\boldsymbol{p}$. All effects from the external dipole field are covered by the special choice of coordinates.

Electrons in a laser field - The Volkov Wave Funktion

With Eq. (12) we have found a very convenient way to describe a free electron propagating in a laser field. The only approximation we made so far is the assumption that the vector potential $\boldsymbol{A}(t)$ does not depend on any spatial degrees of freedom. But: The solution of Eq. (12) we know already. It is just a plane wave:

$$\psi^{KH}(\boldsymbol{r},t) = (2\pi)^{-\frac{3}{2}} e^{-\frac{i}{\hbar}(\boldsymbol{p}\cdot\boldsymbol{r} - E_p t)} \tag{13}$$

What we need to do now is transform the wave function back into the rest frame of the observer. Therefore we perform the inverse transformation of Eq. (10):

$$\begin{aligned}\psi^{V}(\boldsymbol{r},t) &= e^{-\frac{i}{\hbar}\boldsymbol{\alpha}(t)\cdot\boldsymbol{p}}\psi^{KH}(\boldsymbol{r},t) \\ &= (2\pi)^{-\frac{3}{2}} e^{\frac{i}{\hbar}[\boldsymbol{p}\cdot\boldsymbol{r} - \boldsymbol{\alpha}(t)\cdot\boldsymbol{p} - E_p t]} \\ &= (2\pi)^{-\frac{3}{2}} e^{\frac{i}{\hbar}[\boldsymbol{p}\cdot\boldsymbol{r} + \frac{e}{m}\int_{-\infty}^{t}\boldsymbol{A}(t')dt'\cdot\boldsymbol{p} - E_p t]}.\end{aligned} \tag{14}$$

This solution of the TDSE is the *Volkov wave fucntion*, describing an electron in a (strong) laser field. Actually it is worth to note that in the relativistic case we do not need to make the assumption that $\boldsymbol{A}(t)$ is a dipole field. Instead, we can solve the free Dirac-Maxwell problem for any vector potential that is homogenous in the plane transverse to its propagation direction, i.e. a plane wave for example.

Strong Field Ionization and Strong Field Approximation

In this section we want to use the results obtained previously to describe the ionization of an atom by a strong laser field. The ionization probability proportional the matrix element

$$M_{fi} = \langle \psi_{\boldsymbol{p}} | \psi_{nlm} \rangle \tag{15}$$

where $\psi_{\boldsymbol{p}}(\boldsymbol{r})$ is the wavefunction of an electron with asymptotic momentum $\boldsymbol{p}$ in the continuum and $\psi_{nlm}(\boldsymbol{r})$ is a bound state with principal quantum number n, orbital angular momentum l and projection m. But to wich Hamiltonian do these states belong? In wich Hilbert space do they live?

As we know from previous lectures, the Hamiltonian of a hydrogen-like atom in an electromagnetic field is (in dipole approximation):

$$\begin{aligned}\hat{H} &= \frac{1}{2m}\left(\hat{\boldsymbol{p}} + e\boldsymbol{A}(t)\right)^2 - \frac{Ze^2}{\hat{r}} \\ &= \frac{\hat{\boldsymbol{p}}^2}{2m} + \frac{e}{m}\boldsymbol{A}(t)\cdot\hat{\boldsymbol{p}} + \frac{e^2}{2m}\boldsymbol{A}(t)^2 - \frac{Ze^2}{\hat{r}}\end{aligned} \tag{16}$$

Ideally both wave functions $\psi_{\boldsymbol{p}}(\boldsymbol{r},t)$ and $\psi_{nlm}(\boldsymbol{r},t)$ would be eigenfunctions of this Hamiltonian. Unfortunately the corresponding Schrödinger equation cannot be solved analytically. Indeed it is already numerically quite challenging to solve this problem in one

dimension and there are very advanced programs for its solution in 3D, running on clusters. So we need to apply some approximatins. One approximation that is extremely successful even today is the so-calles *Strong Field approximation* (SFA). It relies on the following two assumptions:

- The laser field is strong enough so that the atomic Coulomb potential can be neglected for continuum states.
- The binding potential is strong so that the laser field can be neglected for bound states.

This means our initial and final wave functions are solutions of two different Schrödinger equations

$$i\hbar\partial_t\psi_{nlm}(\boldsymbol{r},t) = \left(\frac{\hat{\boldsymbol{p}}^2}{2m} - \frac{Ze^2}{\hat{r}}\right)\psi_{nlm}(\boldsymbol{r},t), \tag{17a}$$

$$i\hbar\partial_t\psi_{\boldsymbol{p}}(\boldsymbol{r},t) = \frac{1}{2m}\left(\hat{\boldsymbol{p}} + e\boldsymbol{A}(t)\right)\psi_{\boldsymbol{p}}(\boldsymbol{r},t). \tag{17b}$$

Now you see the beauty of this approximation: We already know both wave functions. Either from the QM I lecture or from the previous section. We just need to decide from wich state the ionization shall occur and how our laser field $\boldsymbol{A}(t)$ exactly looks like and we are ready to calculate the transition matrix element M_{fi}. So let us, for simplicity, assume that the atom is initially in its $1s$ ground state:

$$\psi_{100} = \sqrt{\frac{Z^3}{\pi a_0^3}} e^{-\frac{Zr}{a_0}} e^{-\frac{i}{\hbar}E_{1s}t}. \tag{18}$$

Moreover let the laser field be a continiuous wave with the vector potential

$$\boldsymbol{A}(t) = \frac{E_0}{\omega}\boldsymbol{\epsilon}\cos\omega t, \tag{19}$$

where $\boldsymbol{\epsilon}$ is the polarization of the laser and E_0 the maximum amplitude of its electric field. Thus the ponderomotive shift yields

$$\boldsymbol{\alpha}(t) = -\frac{eE_0}{m\omega}\boldsymbol{\epsilon}\int_{-\infty}^{t}\cos\omega t' dt' \quad = -\frac{eE_0}{m\omega^2}\boldsymbol{\epsilon}\sin\omega t, \tag{20}$$

where we assumed that the laser field has been switched on adiabatically [1] at $t = -\infty$. Given these assumptions we can write down the Volkov wave function in velocity gauge:

$$\psi^V_{\boldsymbol{p}}(\boldsymbol{r},t) = (2\pi)^{-\frac{3}{2}} e^{\frac{i}{\hbar}[\boldsymbol{p}\cdot\boldsymbol{r} + \frac{eE_0}{m\omega^2}\boldsymbol{\epsilon}\cdot\boldsymbol{p}\sin\omega t - E_p t]}. \tag{21}$$

[1] Adiabatically switching means here a very slow change of the electric field such that the state of the electron is not changed. It can be understood in a way that the largest Fourier component of the switching envelope is too small to lift the atom to an excited state.

However before we can use this wave function to calculate the matrix element, we need to simplify this wavefunction. To achieve this we make use of the Jacobi-Anger expansion:

$$e^{\frac{ieE_0}{\hbar m\omega^2}\boldsymbol{\epsilon}\cdot\boldsymbol{p}\sin\omega t} = \sum_{N=-\infty}^{\infty} J_N\left(\frac{eE_0}{\hbar m\omega^2}\boldsymbol{\epsilon}\cdot\boldsymbol{p}\right)e^{iN\omega t}, \tag{22}$$

where $J_N(z)$ is the Bessel function of the first kind. With this expansion we get:

$$\psi_{\boldsymbol{p}}^V(\boldsymbol{r},t) = (2\pi)^{-\frac{3}{2}}\sum_{N=-\infty}^{\infty} J_N\left(\frac{eE_0}{\hbar m\omega^2}\boldsymbol{\epsilon}\cdot\boldsymbol{p}\right)e^{\frac{i}{\hbar}(\boldsymbol{p}\cdot\boldsymbol{r}+N\hbar\omega t-E_p t)}. \tag{23}$$

Plugging this into the matrix element we arrive at the following formula:

$$\begin{aligned} M_{fi} &= \pi^{-2}\left(\frac{Z}{2a_0}\right)^{\frac{3}{2}}\int_{-\infty}^{\infty} e^{\frac{i}{\hbar}(E_p t-E_{1s}t-\frac{eE_0}{m\omega^2}\boldsymbol{\epsilon}\cdot\boldsymbol{p}\sin\omega t)}dt\int e^{-\frac{i}{\hbar}\boldsymbol{p}\cdot\boldsymbol{r}}e^{-\frac{Zr}{a_0}}d^3\boldsymbol{r} \\ &= \pi^{-2}\left(\frac{Z}{2a_0}\right)^{\frac{3}{2}}\sum_{N=-\infty}^{\infty} J_N\left(\frac{eE_0}{\hbar m\omega^2}\boldsymbol{\epsilon}\cdot\boldsymbol{p}\right)\int_{-\infty}^{\infty} e^{\frac{i}{\hbar}(E_p-N\hbar\omega-E_{1s})t}dt\int e^{-\frac{i}{\hbar}\boldsymbol{p}\cdot\boldsymbol{r}}e^{-\frac{Zr}{a_0}}d^3\boldsymbol{r}. \end{aligned} \tag{24}$$

While you will solve the spatial integral at home, let us call it $\tau(Z,\boldsymbol{p})$ for the moment, the time integral is rightly solved giving the energy conservation condition:

$$\int_{-\infty}^{\infty} e^{\frac{i}{\hbar}(E_p-N\hbar\omega-E_{1s})t}dt = 2\pi\hbar\delta(E_p-N\hbar\omega-E_{1s}) \tag{25}$$

From this condition we can already learn several things. First we can interpret the index N as the number of photons that the electron exchanges with the external field, since with each N we add or substract the energy of one photon from the total energy bilance. Moreover we can identify a minimal photon number that is needed to ionize the atom. We can calculate it by setting the energy of the continuum electron exactly to the ionization potential I_p. This gives us the minimal photon number:

$$N_{min} = \frac{I_p - E_{1s}}{\hbar\omega} \tag{26}$$

But how does the matrix element behave for larger photon numbers? Or, practically asked: How many terms of the summation do I need to take into account? Indeed there is a cut-off photon number, after wich the cross section of the ionization process will drop to zero exponentially. We can estimate this number by performing a *stationary phase analysis* of the time dependend phase in the first line of Eq. (24). This analysis is based on the assumption that only those parts of the function contribute significantly to the result, where the exponential does not oscillate. Therefore we are looking for points, where the following condition is fullfilled:

$$\partial_t\left(E_p t - E_{1s}t - \frac{eE_0}{m\omega^2}\boldsymbol{\epsilon}\cdot\boldsymbol{p}\sin\omega t\right) = 0, \tag{27}$$

after the time derivative we get:

$$E_p - E_{1s} - \frac{eE_0}{m\omega}\boldsymbol{\epsilon}\cdot\boldsymbol{p}\cos\omega t = 0, \tag{28}$$

wich can be reformulated into the inequality:

$$|E_p - E_{1s}| = \left|\frac{eE_0}{m\omega}\boldsymbol{\epsilon}\cdot\boldsymbol{p}\cos\omega t\right| \leq \frac{eE_0}{m\omega}p. \tag{29}$$

With the energy conservation condition (25) we find:

$$\begin{aligned} N\hbar\omega &\leq \frac{eE_0}{m\omega}p \\ N &\leq \frac{eE_0}{\hbar m\omega^2}p \end{aligned} \tag{30}$$

as the cut-off condition. Now we already know a lot about the ionization of atoms in a laser field, without having calculated anything serious yet! Let us finally introduce some common terms by writing down the probability of the process. Following Fermi's golden Rule it is given by:

$$\begin{aligned} \frac{dw}{d\Omega} =& |M_{fi}|^2 \\ =& 2\hbar\left(\frac{Z}{2\pi a_0}\right)^3 \sum_{N=-\infty}^{\infty}\sum_{N'=-\infty}^{\infty} J_N\left(\frac{eE_0}{\hbar m\omega^2}\boldsymbol{\epsilon}\cdot\boldsymbol{p}\right) J_{N'}\left(\frac{eE_0}{\hbar m\omega^2}\boldsymbol{\epsilon}\cdot\boldsymbol{p}\right) \\ & \times \delta(E_p - N\hbar\omega - E_{1s})\delta(E_p - N'\hbar\omega - E_{1s})\left|\tau(Z,\boldsymbol{p})\right|^2 \\ =& 2\hbar\left(\frac{Z}{2\pi a_0}\right)^3 \sum_{N=-\infty}^{\infty} \delta(E_p - N\hbar\omega - E_{1s})\left|J_N\left(\frac{eE_0}{\hbar m\omega^2}\boldsymbol{\epsilon}\cdot\boldsymbol{p}\right)\tau(Z,\boldsymbol{p})\right|^2 \\ =& 2\pi\hbar\sum_{N=-\infty}^{\infty} \delta(E_p - N\hbar\omega - E_{1s})\left|\mathcal{M}_{fi}^{(N)}\right|^2, \end{aligned} \tag{31}$$

where we defined the *partial matrix element* $\mathcal{M}_{fi}^{(N)}$. Moreover we want to distinguish two cases (cf. Fig. 1). The first case is, where $N = N_{min}$ and $N > 1$, i.e. where the number of ionizing photons corresponds exactly to the number needed to lift the electron over the ionization threshold and, moreover, more than one photon is needed to ionize the atom. In this case we speak of *multi-photon ionization* (MPI). If, however, the electron absorbs more photons than needed for the ionization leading to a final electron energy E_p that is by more than $\hbar\omega$ larger than I_p, we speak of *above threshold ionization.* One can think of one or more "ionization" steps taking place already in the continuum.

High harmonic generation

High harmonic generation (HHG) is one of the most convenient processes to generate coherent XUV and soft X-ray pulses. Nowadays it is realized with tabletop equipment.

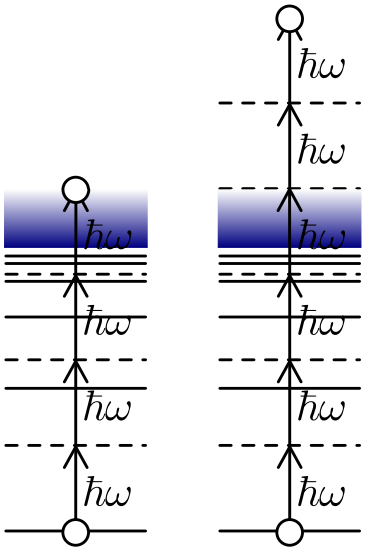

Figure 1: Illustration of multi photon ionization (left sketch) and above threshold ionization (right sketch).

The high harmonic pulses are generated by focusing a high intensity infrared laser into a gas cell in wich the harmonics are generated.

In 1993 Paul Corkum came up with a semiclassical model to explain the main effects of HHG. In this model the whole process is split into three steps (cf. Fig. 2). In the first step the atomic binding potential is modified by the laser field so that the electron can tunnel ionize. After the ionization the electron is accelerated in the laser field and recollides with the atom. The energy excess is emitted as high harmonic radiation. Let

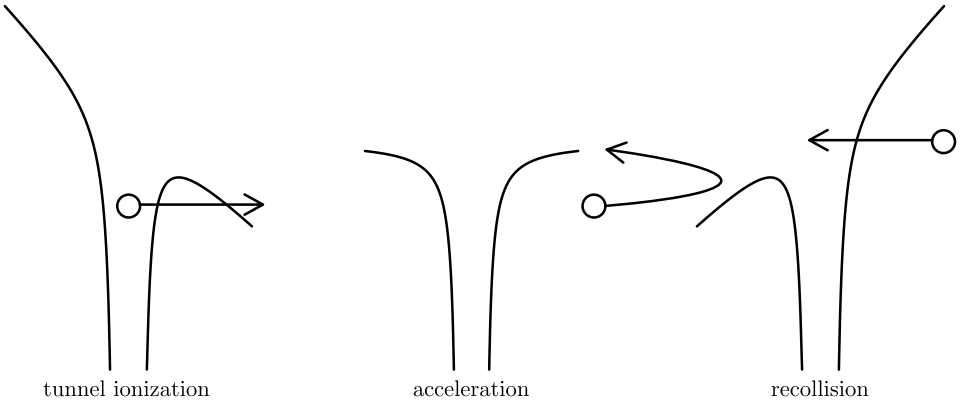

Figure 2: The three step model for high harmonic generation.

us reduce this problem to the 1D case, where a laser field polarized linearly along the z-axis:

$$E(t) = E_0 \cos \omega t. \tag{32}$$

Furthermore, let's assume the electron is ionized at $t = t_i$ and, from this moment on,

propagates classically in the laser field. Let us assume that the electron fullfills the following initial conditions:

$$z(t_i) = 0 \tag{33a}$$

$$\dot{z}(t_i) = 0 \tag{33b}$$

With these we can solve the classical equations of motion and obtain:

$$z(t) = \frac{eE_0}{m\omega^2} \left[(\cos\omega t - \cos\omega t_i) + (\omega t - \omega t_i) \sin\omega t_i \right]. \tag{34}$$

The corresponding kinetic energy is:

$$E_{kin} = 2U_p(\sin\omega t - \sin\omega t_i)^2, \tag{35}$$

where $U_p = \frac{e^2 E_0^2}{4m\omega^2}$ is the ponderomotive energy, defined as the cycle-averaged energy of an electron in an electromagnetic field.

The time(s) t_r at wich the electron recombines with the atom can be found by finding the roots of Eq. (34). You will show as a homework that there are two possible recombination times within the first half-cycle of the laser ($0 \leq \omega t_r \leq \pi$). Moreover it can be shown, that the maximum harmonic energy is:

$$\hbar\omega_{max} = I_p + 3.17U_p \tag{36}$$

A similar expression for the maximum high harmonic energy can be obtained by performing a stationary phase analysis of the matrix element of the HHG process. This corresponds to the so-called *Lewenstein model* and yields a HHG cut-off energy:

$$\hbar\omega_{max} \approx 1.13I_p + 3.17U_p \tag{37}$$

Compton scattering and Klein-Nishina cross-section