Propagator

July 11, 2025

Assuming that the vector potential has the form of Eq. (**??**) and is switched on at the initial time $t = t_0$, let the atom start in the state $|i\rangle$, obeying $\hat{H}_0 |i\rangle = E_i |i\rangle$.

For $t > 0$ we expand the wave packet as

$$|\Psi(\vec{r}, t)\rangle = \sum_j C_j(t) \; |\psi_j(\vec{r})\rangle \,, \tag{1}$$

with the normalization condition $\sum_j |C_j(t)|^2 = 1$. In a sufficiently large simulation box the basis $\{|\psi_j\rangle\}$ includes both bound and continuum states[1].

Substituting Eq. (1) into Eq. (**??**) and projecting with $\langle\psi_k(\vec{r})|$ yields the coupled first-order differential equations

$$\dot{C}_k(t) = \frac{\mathrm{i}}{\hbar} \sum_j \big(E_j \delta_{jk} + V_{jk}(t)\big)\, C_j(t), \tag{2}$$

where

$$V_{jk}(t) = \langle j|\, \hat{V}(t)\, |k\rangle = \begin{cases} \langle j|\, \vec{r}\cdot\vec{F}(t)\, |k\rangle \,, & \text{length gauge,} \\ \langle j|\, \vec{p}\cdot\vec{A}(t)\, |k\rangle \,, & \text{velocity gauge.} \end{cases} \tag{3}$$

The system is solved with the initial condition $C_i(0) = 1$ (all other amplitudes zero).

$$d_{jk} = \begin{cases} \langle j|\, \vec{r}\cdot\vec{\epsilon}\, |k\rangle \,, & \text{length gauge,} \\ \langle j|\, \vec{p}\cdot\vec{\epsilon}\, |k\rangle \,, & \text{velocity gauge.} \end{cases} \tag{4}$$

Gauge transformation relates the two dipole forms through

$$\langle j|\, \vec{p}\, |k\rangle = \mathrm{i}\frac{\mu}{\hbar}(E_j - E_k)\; \langle j|\, \vec{r}\, |k\rangle \,, \tag{5}$$

using $[\hat{H}, \hat{r}] = -\mathrm{i}\frac{\hbar}{\mu}\hat{p}$.

A practical propagator for Eq. (2) employs a truncated Taylor expansion of $H_{jk} = E_j\delta_{jk} + V_{jk}$:

$$\begin{aligned} C_j(t+\delta t) &= \sum_k \Big[\exp\Big(-\frac{\mathrm{i}}{\hbar}\mathbf{H}\,\delta t\Big)\Big]_{jk} C_k(t) \\ &= C_j(t) - \frac{\mathrm{i}\,\delta t}{\hbar}\sum_k H_{jk}C_k(t) - \frac{(\delta t)^2}{2\hbar^2}\sum_{k,l} H_{jk}H_{kl}C_l(t) + \dots \end{aligned} \tag{6}$$

Because the truncated series is not unitary, δt must be small enough that $\sum_j |C_j(t)|^2$ remains unity.

The probability of finding the electron in $|j\rangle$ at time t is

$$P_{i\to j}(t) = |C_j(t)|^2. \tag{7}$$

Taking $t \to \infty$, the photoelectron spectrum becomes

$$p(E) = \frac{1}{\sqrt{2\pi\,\delta E}} \sum_j |C_j(t\to\infty)|^2 \exp\Big[-\Big(\tfrac{E-E_j}{\delta E}\Big)^2\Big], \tag{8}$$

where δE is chosen on the order of the eigenvalue spacing. The total ionization probability is then

$$P_{\text{ion}} = \int \mathrm{d}E\, p(E). \tag{9}$$

References

[1] S. Azizi, "Three aspects of photo-ionization in ultrashort pulses," *Ph.D. thesis,* Technische Universität Dresden (2023).