Lecture I   1. Introduction

Atomic units (au)

	1 a.u. =
Length	$a_0 = 0.529$ Å (Bohr radius)
Velocity	$v_0 = \alpha c$ (e^- speed in lowest Bohr orb.)
Time	$a_0/v_0 = 24.2$ as (1 fs = 41 a.u.)
Frequency	$v_0/a_0 = 4.13 \cdot 10^{16}$ Hz
Intensity ($\frac{1}{2}\varepsilon_0 c E^2$)	$3.54 \cdot 10^{16}$ W/cm² (max. of lin. pol. $\vec{E}$ field)
Elect. field strength	$e/a_0^2 = 5.14 \cdot 10^9$ V/cm
Magn. field strength	$2.35 \cdot 10^5$ T
Elect. dipole moment	$e a_0 = 2.54$ D (Debye)
Energy	27.21 eV = 2 Ry
	(1 eV = 8065.54 cm^{-1})

Some conversion & formulae

e^- de Broglie wave length $\lambda = 1$ Å $\hat{=}\ E_e = 150$ eV

e^- momentum $p = 1$ au $\hat{=}\ E_e = \frac{1}{2}$ au $= 13.6$ eV

photon wave length $\lambda = 800$ nm $\hat{=}\ \omega = 0.057$ a.u.
$\hbar\omega = 1.551$ eV

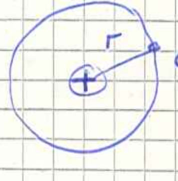
photon momentum $k = 1$ a.u. $\hat{=}\ E_\gamma = 3.7$ keV
$k\,[\text{a.u.}] = 2.7 \cdot 10^{-4}\, E_\gamma(\text{eV})$

ponderomotive energy $U_p = E^2/(4\omega^2)$
$= 9.33\, I\,[10^{14}\,\text{W/cm}^2]\, \lambda^2\,[\mu m]$

e.g. $\lambda = 800$ nm ; $I = 10^{14}$ W/cm²

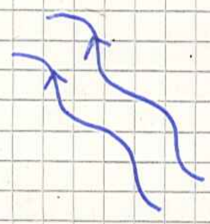
$\Rightarrow U_p = 6$ eV

I.A) One e^- atoms in e-m fields



atom : $V(r)$

e-m field : $\phi(\vec{r},t)$, $\vec{A}(\vec{r},t)$



Coulomb gauge, since no ext. sources:

$$\vec{\nabla}\cdot\vec{A} = 0 \quad , \quad \phi = 0$$

$$\nabla^2 \vec{A} = \frac{1}{c^2}\frac{\partial \vec{A}}{\partial t^2} \qquad c = 137.036\,\mathrm{au}$$

A.1 Weak cw fields

$$\vec{A} = \vec{A}_0(\omega)\cos(\vec{k}\cdot\vec{r} - \omega t) \quad , \quad \vec{A}_0 = \hat{\epsilon} A_0$$

$$\vec{k} = \frac{\omega}{c}\hat{k} \qquad \text{(wave number vector)}$$

$$\vec{k}\cdot\hat{\epsilon} = 0 \qquad \text{(tranverse wave)}$$

$$I(\omega) = \frac{c}{8\pi}\omega^2 A_0^2(\omega) \qquad \text{(spectral intensity)}$$

Hamiltonian

$$H = \frac{1}{2}(\vec{p} + \vec{A})^2 - \cancel{\phi} + V(r) \qquad \text{(a.u.)}$$

$$= \underbrace{-\frac{1}{2}\nabla^2 + V(r)}_{\substack{H_0 \text{ (field free} \\ \text{atom)}}} \underbrace{- i\vec{A}\cdot\vec{\nabla}}_{\substack{H_{int} \\ \text{(inter-} \\ \text{action)}}} + \underbrace{\frac{1}{2}A^2}_{\substack{\approx 0 \\ \text{(weak field)}}} \qquad \text{(Coul. gauge, } \phi = 0 \text{)}$$

Time-dependent Schrödinger equation

$$H\,\psi(\vec{r},t) = i\frac{\partial}{\partial t}\psi(\vec{r},t)$$

transition : $|a\rangle \xrightarrow{H_{int}} |b\rangle$

initial atomic state → final atomic state

atomic energies $E_a \longrightarrow E_b$

Transition probability in first order time-dependent perturbation theory

$$P_{a\to b}(t) = \left| \int^t dt' \, \langle b | H_{int}(t') | a \rangle \, e^{i\omega_{ba} t'} \right|^2$$

$$\omega_{ba} = E_b - E_a \quad \begin{cases} > 0 & \text{photo absorption} \\ < 0 & \text{" emission} \end{cases}$$

For absorption:

$$P_{a\to b}(t) = A_0^2(\omega) \, |\underbrace{\langle b| e^{i\vec{k}.\vec{r}} \, \hat{\epsilon}\cdot\vec{\nabla} | a\rangle}_{=: M_{ba}(\vec{k})}|^2$$

$$\times \underbrace{\frac{\sin^2[(\omega-\omega_{ba})t/2]}{(\omega-\omega_{ba})^2}}_{= \frac{\pi t}{2}\delta(\omega-\omega_{ba}) \text{ for } t\to\infty}$$

Transition rate (for $t \to \infty$)

$$W_{a\to b} = \int \lim_{t\to\infty} P_{a\to b}(t)/t \quad d\omega$$

$$= \underbrace{\frac{\pi}{2} A_0^2(\omega_{ba})}_{\frac{4\pi^2}{c\,\omega_{ba}^2} I(\omega_{ba})} |M_{ba}(\vec{k})|^2$$

Similarly, for (stimulated) emission

$$W_{a\to b} = \frac{4\pi^2}{c\,\omega_{ba}^2} I(|\omega_{ba}|) \, |M_{ba}(-\vec{k})|^2$$

$$= \text{absorption rate (detailed balance)}$$

Photoionization

= transition to (unbound) continuum states $|E\rangle$

$$\omega_{Ea} = E - E_a$$

$\rho(E)\, dE$: # states in $[E, E+dE]$

$\rho(E)$: density of states, to be included in $P_{a\to E}$, $W_{a\to E}$ since photo-electrons are always detected with finite energy (& momentum) resolution

Photoionization rate

take absorption rate $W_{a\to b}$, replace $b \to E$, integrate over $\rho(E)\, dE$:

$$\frac{dW_{a\to E}}{dE} = \frac{4\pi^2}{c\,\omega_{Ea}^2}\, I(\omega_{Ea})\, \underbrace{|M_{Ea}(\vec{k})|^2}_{M_{Ea}(\omega_{Ea})}\, \rho(E)$$

Photoionization cross section

$$\frac{d\sigma_{a\to E}}{dE} = \frac{1}{I(\omega_{Ea})}\, \underbrace{\omega_{Ea}\,\frac{dW_{a\to E}}{dE}}_{\text{rate of energy absorption}}$$

Notes:

i) extension to incident light pulses by superposition of plane waves $\vec{A}(\vec{r}, t)$

ii) energy normalization $\langle E | E' \rangle \overset{!}{=} \delta(E-E')$

$$\Rightarrow \rho(E) = 1$$

Dipole approximation

$$M_{ba} = \langle b | e^{i\vec{k}\cdot\vec{r}} \, \hat{\varepsilon}\cdot\vec{\nabla} | a \rangle$$

$$\int d^3r \ldots \qquad e^{i\vec{k}\cdot\vec{r}} \to 1 + \underbrace{i\vec{k}\vec{r} - \frac{1}{2}(\vec{k}\cdot\vec{r})^2 + \ldots}_{\text{neglect if } kr \ll 1 \ (*)}$$

(*) means $\frac{2\pi}{\lambda} r \ll 1$ or $r \ll \lambda$

If $|\langle \vec{r} | a \rangle|^2$ or $|\langle \vec{r} | b \rangle|^2$ are strongly concentrated in a sphere of radius $\ll \lambda$, then all terms in the expansion, exept for 1, can be neglected. The external electric field and vector potential are then only time (not $\vec{r}$) dependent and the magnetic-field component vanishes:

$$M^{dip}_{ba} = \hat{\varepsilon}\cdot\langle b | \vec{\nabla} | a \rangle = i\,\hat{\varepsilon}\cdot\langle b | \vec{p} | a \rangle$$

$$= -\omega_{ba}\,\hat{\varepsilon}\cdot\langle b | \vec{r} | a \rangle \quad \text{using } \vec{p} = -i[\vec{r}, H_0]$$

$$= \omega_{ba}\,\hat{\varepsilon}\cdot\begin{cases} \vec{D}^L, & \vec{D}^L = -\langle b | \vec{r} | a \rangle \\ \vec{D}^V, & \vec{D}^V = i\langle b | \vec{v} | a \rangle / \omega_{ba} \\ \vec{D}^A, & \vec{D}^A = \langle b | \vec{\nabla} V | a \rangle / \omega_{ba}^2 \end{cases}$$

$D^{L,V,A}$: Length, Velocity, Acceleration form

- ✓ same M^{dip}_{ba} for exact states $|a\rangle$, $|b\rangle$
- ✓ discrepancies indicate quality of states used

Dipole selection rules (drop indices a, b)

$$\vec{D}^L = \underbrace{(D^L_x, D^L_y, D^L_z)}_{\text{cartesian repr.}} \hat{=} \underbrace{(D^L_0, D^L_{-1}, D^L_1)}_{\text{spherical repr.}}$$

✓ switch to spherical representation

$$q=0 \quad : \quad z = r\cos\Theta = \sqrt{\frac{4\pi}{3}}\; r\; Y_{1,0}(\Theta,\varphi)$$

$$q=\pm 1 \quad : \quad \mp\frac{1}{\sqrt{2}}(x \pm iy) = \mp\frac{1}{\sqrt{2}} r\sin\Theta\, e^{\pm i\varphi}$$

$$= \sqrt{\frac{4\pi}{3}}\; r\; Y_{1,\pm 1}(\Theta,\varphi)$$

note: $|\vec{D}^L|^2 = \sum_{i=x,y,z} |D^L_i|^2 = \sum_{q=-1}^{1} |D^L_q|^2$

✓ central potential eigenstates

$$|a\rangle = |n, \ell, m\rangle \;, \quad |b\rangle = |E, \ell', m'\rangle$$

The dipole matrix elements now read

$$D^L_q = \sqrt{\frac{4\pi}{3}}\; \underbrace{\langle E, \ell', m' |\, r\, Y_{1,q}\, | n \ell m\rangle}$$

$$\langle E \ell' | r | n\ell\rangle \;\; \langle Y_{\ell' m'} | Y_{1q} | Y_{\ell m}\rangle$$

$\int dr\, r^2 \ldots$ radial wfs $\int d\cos\Theta\, d\varphi$

$$\sqrt{\frac{3(2\ell+1)}{4\pi(2\ell'+1)}}\; \underbrace{\langle \ell 1 0 0 | \ell' 0\rangle}_{0 \text{ unless } \ell'=\ell\pm 1} \underbrace{\langle \ell 1 m q | \ell' m'\rangle}_{0 \text{ unless } m'=m+q}$$

Clebsch-Gordan coeffs

$\Downarrow$

$|a\rangle, |b\rangle$ need to have opposite parity $\sim (-1)^\ell$

Photoelectron angular distributions

From p. 4; assuming energy normalization

$$\frac{d\sigma_{a\to E}}{dE} = \frac{4\pi^2}{c\,\omega_{Ea}} \left| M_{Ea}(\omega_{Ea}) \right|^2$$

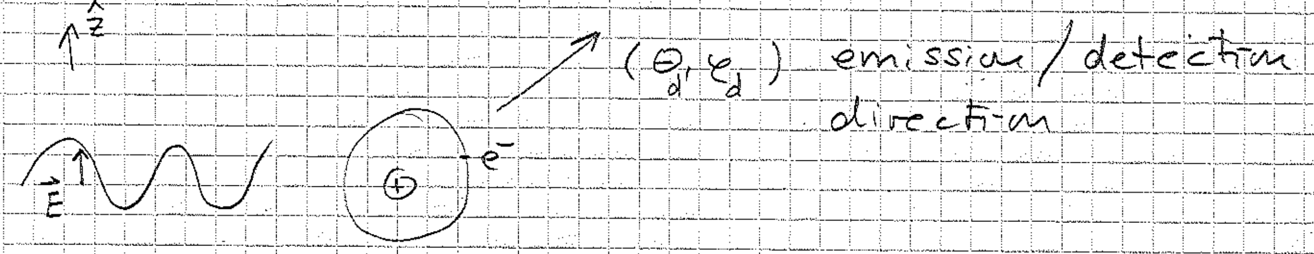
$$= \frac{4\pi^2}{c}\,\omega_{Ea} \left| D^{L}_{q=0} \right|^2 \quad \text{for } \hat{\epsilon} = \hat{z}$$

($\vec{E}$ polarized linearly along z axis)

Use spherical coordinates for initial & final state,

$$\langle \vec{r} \,|\, a \rangle = \langle \vec{r} \,|\, n\ell m \rangle = \frac{R_{n\ell}(r)}{r}\, Y_{\ell m}(\theta,\varphi)$$

$$\langle \vec{r} \,|\, b \rangle = \langle \vec{r} \,|\, E\ell' m' \rangle = \frac{R_{E\ell'}(r)}{r}\, Y_{\ell' m'}(\theta,\varphi)$$



Partial-wave composition of final state with asymptotic momentum in direction (θ_d, φ_d)

$$\langle \vec{r} \,|\, E, \theta_d, \varphi_d \rangle = \sum_{\ell'=0}^{\infty} \sum_{m'=-\ell'}^{\ell'} \underbrace{i^{\ell'} e^{-i\eta_{E\ell'}}\, Y_{\ell' m'}(\theta_d,\varphi_d)}_{} \,\frac{u_{E\ell'}}{r}\, Y_{\ell m}(\theta,\varphi)$$

coeff.s of partial wave expansion: $C_{E\ell' m'}(\theta_d, \varphi_d)$

$\eta_{E\ell'}$: asymptotic phase shift

$\left(= \arg \Gamma\left(\ell'+1 - i\,Z/\sqrt{2E}\right) \text{ for } V = -\frac{Z}{r}\right)$

To get the photoemission cross section for emission to (asympt.) direction (θ_d, φ_d), we need dipole matrix elements with partial-wave contributions, given as D_q^L on page 6.

Then, we need to coherently add them up with coefficients $c_{E'\ell' m'}(\theta_d, \varphi_d)$.

From the second equation on page 7 we now obtain the energy- and emission-angle differential photoelectron-emission cross section:

$$\frac{d^2\sigma_{a \to E, \theta_d, \varphi_d}}{dE\, d\Omega_d} = \frac{16\pi^3}{3c}\, \omega_{Ea}$$

$\int d\cos\theta\, d\varphi$

$$\times \left| \sum_{\ell' m'} a^{*}_{\ell' m'} f_{\ell'} \langle Y_{\ell' m'} | Y_{10} | Y_{\ell m} \rangle \right|^2$$

using dipole selection rules and some tedious algebra:

$$= \frac{\sigma_{tot}}{4\pi} \left[1 + \beta\, \frac{3\cos^2\theta - 1}{2} \right],$$

where

$$a_{\ell' m'} := i^{\ell'} e^{-i\eta_{E\ell'}} Y_{\ell' m'}(\theta, \varphi), \quad f_{\ell'} := \langle R_{E\ell'} | r | R_{n\ell} \rangle$$

$$\beta = \frac{\ell(\ell-1) f_{\ell-1}^2 + (\ell+1)(\ell+2) f_{\ell+1}^2 - 6\ell(\ell+1) f_{\ell+1} f_{\ell-1} \cos(\Delta_{E\ell})}{(2\ell+1)\left[\ell f_{\ell-1}^2 + (\ell+1) f_{\ell+1}^2\right]}$$

$$\Delta_{E,\ell} := \eta_{E,\ell+1} - \eta_{E,\ell-1}.$$

σ_{tot} is the total, angle-integrated cross section.