PHYS 4011, 5050: Atomic and Molecular Physics

Lecture Notes

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Contents

Chapter 1

Introduction: the field-free Schrödinger hydrogen atom

The starting point of the discussion is the stationary Schrödinger equation

$$\hat{H}\Psi = E\Psi \tag{1.1}$$

for the two-body problem consisting of a nucleus (n) and an electron (e). The Hamiltonian reads

$$\hat{H} = \frac{\hat{\mathbf{p}}_n^2}{2m_n} + \frac{\hat{\mathbf{p}}_e^2}{2m_e} - \frac{Ze^2}{4\pi\epsilon_0|\mathbf{r}_e - \mathbf{r}_n|} \tag{1.2}$$

with

$$m_n = N\,1836 m_e \ ; \quad m_e \approx 9.1 \times 10^{-31} \text{ kg}$$

and N being the number of nucleons ($N = 1$ for the hydrogen atom itself, where the nucleus is a single proton).

The first step is to separate this two-body problem into two effective one-body problems.

1.1 Reduction to an effective one-body problem

- Consider the (classical) coordinate transformation

$$(\mathbf{r}_e, \mathbf{p}_e, \mathbf{r}_n, \mathbf{p}_n) \quad \longrightarrow \quad (\mathbf{R}, \mathbf{P}, \mathbf{r}, \mathbf{p})$$

$$\text{definitions}: \qquad M = m_e + m_n \approx m_n$$
$$\mu = \frac{m_e m_n}{m_e + m_n} \approx m_e$$

$$\left.\begin{aligned} \mathbf{R} &= \tfrac{m_n \mathbf{r}_n + m_e \mathbf{r}_e}{M} && \approx \mathbf{r}_n \\ \mathbf{P} &= \mathbf{p}_e + \mathbf{p}_n = M\dot{\mathbf{R}} && \approx \mathbf{p}_n \end{aligned}\right\} \text{center} - \text{of} - \text{mass motion}$$

$$\left.\begin{aligned} \mathbf{r} &= \mathbf{r}_e - \mathbf{r}_n \\ \mathbf{p} &= \mu\dot{\mathbf{r}} = \tfrac{m_n \mathbf{p}_e - m_e \mathbf{p}_n}{M} \approx \mathbf{p}_e \end{aligned}\right\} \text{relative motion}$$

- QM transformation analogously

$$(\hat{\mathbf{r}}_e, \hat{\mathbf{p}}_e, \hat{\mathbf{r}}_n, \hat{\mathbf{p}}_n) \quad \longrightarrow \quad (\hat{\mathbf{R}}, \hat{\mathbf{P}}, \hat{\mathbf{r}}, \hat{\mathbf{p}}) \tag{1.3}$$

insertion into Eq. (1.2) yields

$$\begin{aligned} \hat{H} &= \frac{\hat{\mathbf{P}}^2}{2M} + \frac{\hat{\mathbf{p}}^2}{2\mu} + V(r) \ , \qquad \left(V(r) = \frac{-Ze^2}{4\pi\epsilon_0 r}\right) \\ &= \hat{H}_{CM} + \hat{H}_{rel} \end{aligned} \tag{1.4}$$

Eq. (1.4) is the Hamiltonian of a non-interacting two-(quasi-)particle system ↪ can be separated into two one-particle problems:

$$\text{ansatz}: \qquad \Psi(\mathbf{r}, \mathbf{R}) = \Phi_{CM}(\mathbf{R})\varphi_{rel}(\mathbf{r}) \tag{1.5}$$

↪ Schrödinger equations (SEs)

$$\hat{H}_{CM}\Phi_{CM}(\mathbf{R}) = -\frac{\hbar^2}{2M}\nabla_R^2 \Phi_{CM}(\mathbf{R}) = E_{CM}\Phi_{CM}(\mathbf{R}) \tag{1.6}$$

$$\hat{H}_{rel}\varphi_{rel}(\mathbf{r}) = \left(-\frac{\hbar^2}{2\mu}\nabla_r^2 - \frac{Ze^2}{4\pi\epsilon_0 r}\right)\phi_{rel}(\mathbf{r}) = E_{rel}\varphi_{rel}(\mathbf{r}) \tag{1.7}$$

$$\text{with} \qquad E = E_{CM} + E_{rel} \tag{1.8}$$

Equation (1.6) can be solved without difficulty:

$$\hookrightarrow \quad \left.\begin{aligned} \Phi_{CM}(\mathbf{R}) &= Ae^{i\mathbf{K}\mathbf{R}} \\ \mathbf{K} &= \tfrac{1}{\hbar}\mathbf{P} \\ E_{CM} &= \tfrac{\hbar^2\mathbf{K}^2}{2M} \end{aligned}\right\} \text{free} - \text{particle motion}$$

Equation (1.7) can be solved analytically, but before we sketch the solution we consider some general properties/features of the quantum central-field ($V(\mathbf{r}) = V(r)$) problem.

1.2 The central-field problem for the relative motion

Consider
$$\hat{H}_{rel} = \frac{\hat{\mathbf{p}}^2}{2\mu} + V(r) \quad . \tag{1.9}$$

One can show that $\hat{H}_{rel}$ is invariant with respect to rotations, and therefore commutes with the angular momentum operator

$$\hat{\mathbf{l}} = \hat{\mathbf{r}} \times \hat{\mathbf{p}}. \tag{1.10}$$

This is a manifestation of angular momentum conservation. In particular, the operators $\hat{H}_{rel}, \hat{\mathbf{l}}^2, \hat{l}_z$ form a complete set of *compatible* operators, i.e.,

$$[\hat{H}_{rel}, \hat{\mathbf{l}}^2] = [\hat{H}_{rel}, \hat{l}_z] = [\hat{\mathbf{l}}^2, \hat{l}_z] = 0 \tag{1.11}$$

$\hookrightarrow$ they have a common set of eigenstates. The eigenstates of $\hat{\mathbf{l}}^2, \hat{l}_z$ are the spherical harmonics Y_{lm}.

$\hookrightarrow$ ansatz
$$\varphi_{rel}(\mathbf{r}) = R_l(r) Y_{lm}(\theta, \varphi) \quad . \tag{1.12}$$

insertion into Eq. (1.7) for Hamiltonian (1.9) yields the radial SE

$$\left\{ \frac{\hat{p}_r^2}{2\mu} + \frac{\hbar^2 l(l+1)}{2\mu r^2} + V(r) - E_{rel} \right\} R_l(r) = 0 \tag{1.13}$$

with
$$\hat{p}_r^2 = -\frac{\hbar^2}{r^2}\partial_r(r^2\partial_r)$$

and operator identity
$$\hat{\mathbf{p}}^2 = \hat{p}_r^2 + \frac{\hat{\mathbf{l}}^2}{r^2}$$

(can be proven in spherical coordinates in coordinate space).

Useful definition :
$$y_l(r) = r R_l(r) \tag{1.14}$$

$$\stackrel{(1.13)}{\hookrightarrow} \qquad y_l''(r) + \left[\epsilon - U(r) - \frac{l(l+1)}{r^2}\right] y_l(r) = 0 \qquad (1.15)$$

$$\left(E_{rel} = \frac{\hbar^2}{2\mu}\epsilon \ , \quad V(r) = \frac{\hbar^2}{2\mu}U(r)\right)$$

1.3 Solution of the Coulomb problem

The radial Eq. (1.15) is very similar to the one-dimensional SE. There are, however, two important differences. First, the total (effective) potential consists of two parts

$$U_l^{eff}(r) \;=\; U(r) + \frac{l(l+1)}{r^2} \stackrel{r\to\infty}{\longrightarrow} 0$$

$\nwarrow$ "angular momentum barrier"

(cf. classical central-field problem) Second, the boundary conditions are different.

a) Boundary conditions

- $r \longrightarrow 0$
  $|\varphi_{rel}(\mathbf{r})|^2 = |R_l(r)|^2 |Y_{lm}(\theta,\varphi)|^2 < \infty$
  in particular for $\mathbf{r} = 0$
  $\hookrightarrow$ 'regularity condition'

$$y_l(0) = 0 \qquad (1.16)$$

- $r \longrightarrow \infty$

  1. $E_{rel} < 0$ (bound spectrum)

$$\int |\varphi_{rel}(\mathbf{r})|^2 \, d^3r \;=\; \int_0^\infty r^2 R_l^2(r)\, dr \int |Y_{lm}(\theta,\varphi)|^2 \, d\Omega \;=\; \int_0^\infty y_l^2(r)\, dr \;<\; \infty$$

(square integrable solutions required)

$$\hookrightarrow \quad y_l(r) \stackrel{r\to\infty}{\longrightarrow} 0 \qquad \text{('strong' boundary condition)}$$

2. $E_{rel} > 0$ (continuous spectrum)
   $\hookrightarrow$ oscillatory solutions $y_l(r)$ for $r \longrightarrow \infty$

(note: for $E_{rel} > 0$ the solution leads to Rutherford's scattering formula (which is identical in classical mechanics and QM))

b) Bound-state solutions

$$\begin{aligned} \text{definition :} \qquad \kappa^2 &= -\epsilon \; > \; 0 \\ a &= \frac{4\pi\epsilon_0\hbar^2}{\mu e^2} \; \approx \; 0.53 \cdot 10^{-10} \text{ m} \\ \text{for} \qquad \mu &\equiv m_e \; , \quad a \equiv a_0 \qquad \text{is the 'Bohr radius'} \end{aligned}$$

$\hookrightarrow$ radial Eq. (1.15):

$$\left(\frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} + \frac{2Z}{ar} - \kappa^2 \right) y_l(r) = 0 \tag{1.17}$$

transformation: $x = 2\kappa r$

$$\hookrightarrow \quad \frac{d^2}{dx^2} = \frac{1}{4\kappa^2} \frac{d^2}{dr^2}$$

$$\hookrightarrow \quad \left(\frac{d^2}{dx^2} - \frac{l(l+1)}{x^2} + \frac{\lambda}{x} - \frac{1}{4} \right) y_l(x) = 0 \tag{1.18}$$

asymptotic solutions:

1. $x \longrightarrow \infty$

$$\hookrightarrow \quad \left(\frac{d^2}{dx^2} - \frac{1}{4} \right) y_l(x) = 0$$

$$\hookrightarrow \quad y_l(x) = A e^{-\frac{x}{2}} + B e^{\frac{x}{2}}$$

   because of $y_l(x \to \infty) = 0 \quad \hookrightarrow \; B = 0$

2. $x \longrightarrow 0$

$$\hookrightarrow \quad \left(\frac{d^2}{dx^2} - \frac{l(l+1)}{x^2}\right) y_l(x) = 0$$

$$\hookrightarrow \quad y_l(x) = \frac{A}{x^l} + Bx^{l+1}$$

because of $y_l(0) = 0 \quad \hookrightarrow \; A = 0$.

This consideration motivates the following ansatz

$$y_l(x) = x^{l+1} e^{-\frac{x}{2}} v_l(x). \tag{1.19}$$

Insertion into Eq. (1.18) yields a new differential equation for $v_l(x)$:

$$\hookrightarrow \quad \left\{ x\frac{d^2}{dx^2} + (2l+2-x)\frac{d}{dx} - (l+1-\lambda)\right\} v_l(x) = 0. \tag{1.20}$$

The square integrable solution of (1.20) ('Kummer's' or 'Laplace's' differential eq.) are known; they are the associated Laguerre polynomials:

$$L_p^k(x) = \sum_{j=0}^{p} (-)^j \frac{\left[(p+k)!\right]^2}{(p-j)!(k+j)!j!} x^j .$$

More specifically:

$$v_l(x) = L_{n-l-1}^{2l+1}(x) \; , \qquad \left(\begin{array}{c} n_r = n-l-1 \geq 0 \\ \Longleftrightarrow \quad n-1 \geq l \end{array} \right)$$

$$\text{with} \qquad n \equiv \lambda_n = \frac{Z}{\kappa_n a} \; , \qquad n = 1, 2, ... \tag{1.21}$$

The detailed treatment shows that the integrability of the solutions requires $\lambda = \frac{Z}{\kappa a}$ to be positive, integer numbers $\longrightarrow$ quantization of κ (i.e. quantization of the energy)[1]

$$\hookrightarrow \quad y_{nl}(\mathbf{r}) = A_{nl} r^{l+1} e^{-\kappa_n r} L_{n-l-1}^{2l+1}(2\kappa_n r)$$

[1] One finds the square integrable solutions of (1.20) explicitly by using the ansatz $v_l(x) = \sum_i b_i^l x^i$ and by taking the boundary (and regularity) conditions into account.

and properly normalized wave functions take the form

$$\begin{aligned}
\varphi_{rel}(\mathbf{r}) \equiv \varphi_{nlm}(\mathbf{r}) &= \frac{(n-l-1)!}{\left[(n+l)!\right]^3} 2^{l+\frac{1}{2}} \kappa_n^{l+2} \sqrt{a} \\
&\quad \times r^l e^{-\kappa_n r} L_{n-l-1}^{2l+1}(2\kappa_n r) Y_{lm}(\theta,\varphi) \qquad (1.22) \\
&\equiv R_{nl}(r) Y_{lm}(\theta,\varphi) \qquad \begin{array}{l} n \geq 0 \\ l \leq n-1 \\ -l \leq m \leq l \end{array}
\end{aligned}$$

The quantization condition (1.21) yields

$$\begin{aligned}
E_{rel} \equiv E_n &= -\frac{\hbar^2}{2\mu a^2}\frac{Z^2}{n^2} \qquad n = 1, 2, ... \qquad (1.23) \\
&\approx -13.6 \text{ eV} \frac{Z^2}{n^2}. \qquad (1.24)
\end{aligned}$$

The lowest-lying hydrogen eigenfunctions ('orbitals'):

n	l	m	$n_r = n - l - 1$		$\varphi_{nlm}(\mathbf{r})$	$-E_n$
1	0	0	0	1s	$\frac{1}{\sqrt{\pi}}\left(\frac{Z}{a}\right)^{\frac{3}{2}} e^{-\frac{Zr}{a}}$	RZ^2
2	0	0	1	2s	$\frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a}\right)^{\frac{3}{2}}\left(2-\frac{Zr}{a}\right) e^{-\frac{Zr}{2a}}$	$\frac{RZ^2}{4}$
2	1	0	0	$2\mathrm{p}_0$	$\frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a}\right)^{\frac{3}{2}}\left(\frac{Zr}{a}\right) e^{-\frac{Zr}{2a}} \cos\theta$	$\frac{RZ^2}{4}$
2	1	±1	0	$2\mathrm{p}_{\pm1}$	$\mp\frac{1}{8\sqrt{\pi}}\left(\frac{Z}{a}\right)^{\frac{3}{2}}\left(\frac{Zr}{a}\right) e^{-\frac{Zr}{2a}} \sin\theta e^{\pm i\varphi}$	$\frac{RZ^2}{4}$

with $R = 13.6$ eV

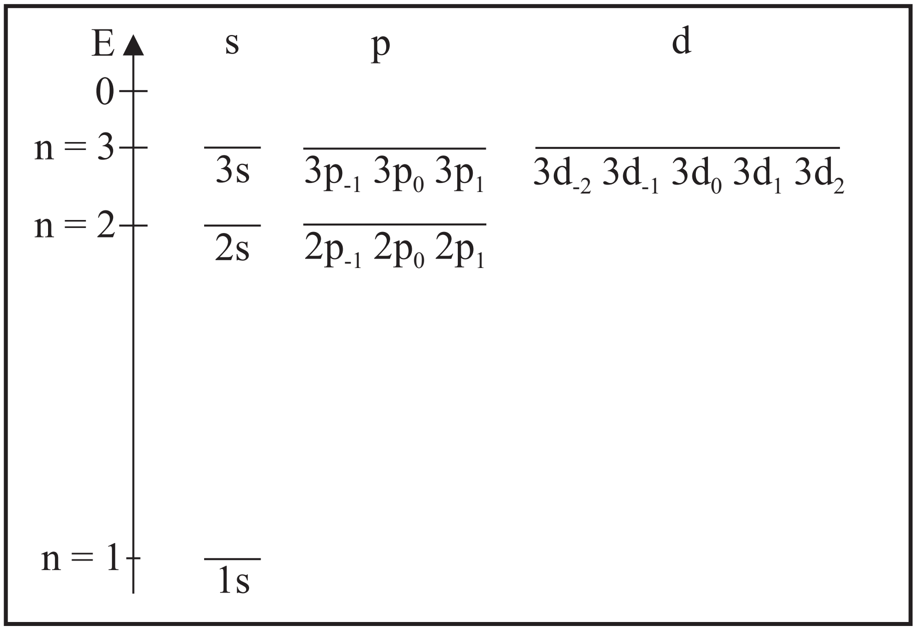


Figure 1.1: Energy spectrum of the Schrödinger-Coulomb problem. Note that the Coulomb potential supports infinitely many bound states ($E_n \overset{n\to\infty}{\longrightarrow} 0$).

<u>Degeneracy of energies (which depend only on n)</u>

given n $\quad l = 0, 1, ..., n-1$
given l $\quad m = -l, ..., l$

$$\hookrightarrow \quad \sum_{l=0}^{n-1}(2l+1) = n^2$$

$\longrightarrow$ each energy level E_n is n^2-fold degenerate. Note that all central-field problems share the $(2l+1)$-fold degeneracy which originates from rotational invariance. The fact that the energies do not depend on n_r, l separately, but only on $n = n_r + l + 1$ is specific to the Coulomb problem (one names n the principal quantum number and n_r the radial quantum number, which determines the number of nodes in the radial wave functions).

In QM, the wave functions themselves are (usually) not observable, but their absolute squares are

$$\begin{aligned}\rho_{nlm}(\mathbf{r}) &= |\varphi_{nlm}(\mathbf{r})|^2 = R_{nl}^2 |Y_{lm}(\theta,\varphi)|^2 \\ &= \frac{y_{nl}^2(r)}{r^2}|Y_{lm}(\theta,\varphi)|^2. \end{aligned} \tag{1.25}$$

If $\int \rho_{nlm}(\mathbf{r}) d^3r = 1$ one interpretes $\rho_{nlm}(\mathbf{r})d^3r$ as the probability to find the electron in the volume $[\mathbf{r}, \mathbf{r} + \mathbf{dr}]$. For spherically symmetric potentials it is useful to also define a *radial* probability density by

$$\begin{aligned}\rho_{nl}(r) &= r^2 R_{nl}^2(r) \int |Y_{lm}(\theta,\varphi)|^2 \, d\Omega \\ &= y_{nl}^2(r) \end{aligned} \tag{1.26}$$

$\rho_{nl}(r)dr$ is the probability to find the electron in the interval $[r, r + dr]$

Momentum space representation

So far we have worked in coordinate space, in which states are wave functions $\varphi(\mathbf{r})$. It is also possible — and insightful — to look at the problem in another, e.g., the momentum space representation, which is connected to the coordinate space representation by a (three-dimensional) Fourier transformation. Using the Dirac notation one can obtain momentum space wave functions by considering

$$\begin{aligned}\varphi_{nlm}(\mathbf{p}) &= \langle \mathbf{p}|\varphi_{nlm}\rangle = \int \langle \mathbf{p}|\mathbf{r}\rangle\langle \mathbf{r}|\varphi_{nlm}\rangle d^3r \\ &= \frac{1}{[2\pi\hbar]^{\frac{3}{2}}} \int \mathrm{e}^{-\frac{i}{\hbar}\mathbf{p}\cdot\mathbf{r}} \varphi_{nlm}(\mathbf{r}) d^3r. \end{aligned} \tag{1.27}$$

To work out the three-dimensional Fourier transform one uses the expansion of a plane wave in spherical coordinates

$$\mathrm{e}^{-i\mathbf{k}\cdot\mathbf{r}} = 4\pi \sum_{L=0}^{\infty} \sum_{M=-L}^{L} (-i)^L j_L(kr) Y_{LM}(\Omega_k) Y_{LM}^*(\Omega_r) \tag{1.28}$$

with $\mathbf{p} = \hbar\mathbf{k}$ and the spherical Bessel functions j_L.

$$\begin{aligned}
\hookrightarrow \varphi_{nlm}(\mathbf{p}) &= 4\pi \frac{1}{[2\pi\hbar]^{\frac{3}{2}}} \sum_{L=0}^{\infty} \sum_{M=-L}^{L} (-i)^L \int_0^\infty r^2 j_L(kr) R_{nl}(r) dr \\
&\quad \times \int Y_{LM}^*(\Omega_r) Y_{lm}^*(\Omega_r) d\Omega_r \, Y_{LM}(\Omega_k) \\
&= 4\pi \frac{1}{[2\pi\hbar]^{\frac{3}{2}}} (-i)^l \int_0^\infty r^2 j_l(kr) R_{nl}(r) dr \, Y_{lm}(\Omega_k) \\
&=: P_{nl}(p) Y_{lm}(\Omega_k). \qquad (1.29)
\end{aligned}$$

Probability densities can be defined in the same way as in coordinate space

$$\begin{aligned}
\rho_{nlm}(\mathbf{p}) &= |\varphi_{nlm}(\mathbf{p})|^2 \\
\rho_{nl}(p) &= p^2 P_{nl}^2(p). \qquad (1.30)
\end{aligned}$$

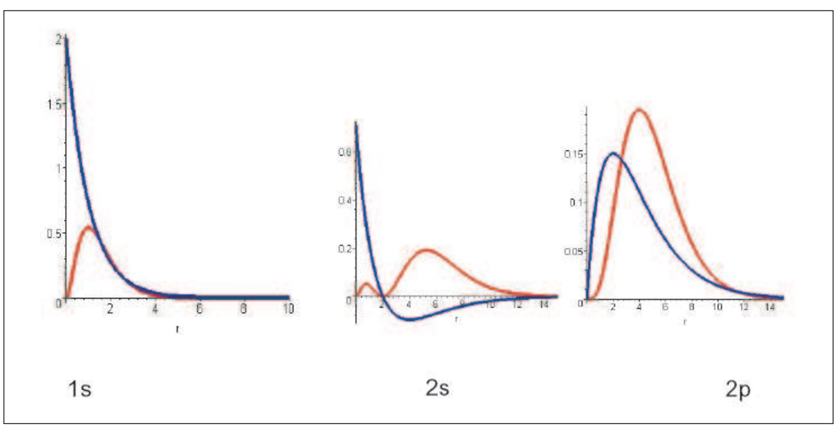


Figure 1.2: Radial hydrogen 1s, 2s, 2p wave functions (blue) and probability densities (red) in coordinate space.

The maximum of the 2p probability density is shifted to smaller r compared to the 2s state. We can understand this qualitatively in the following way. Both states 2s,2p correspond to the same eigenenergy. The 2s state has a contribution at small r (the first lobe), for which the potential energy is rather large as the nucleus is close. By contrast, the 2p state approaches 0 for small distances (remember the angular momentum barrier: only s states do not approach zero for $r \to 0$). To compensate for the stronger binding energy of the 2s state at small r the 2p state has to have its only maximum at smaller r compared to the second maximum of the 2s state.

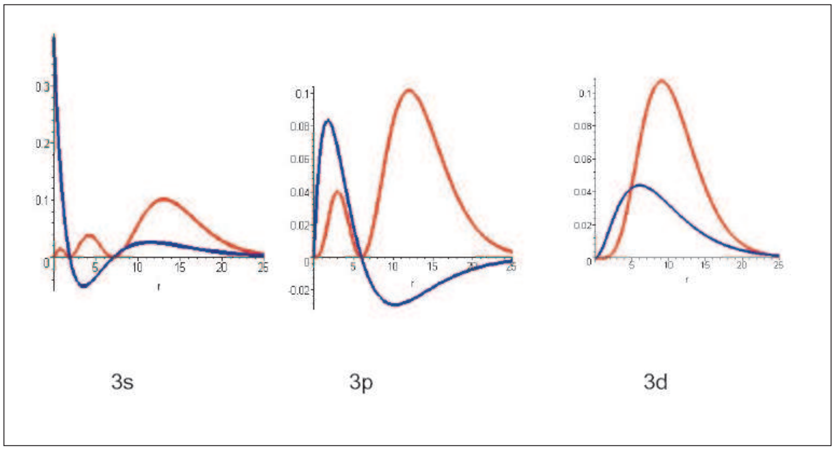


Figure 1.3: Radial hydrogen 3s, 3p, 3d wave functions (blue) and probability densities (red) in coordinate space.

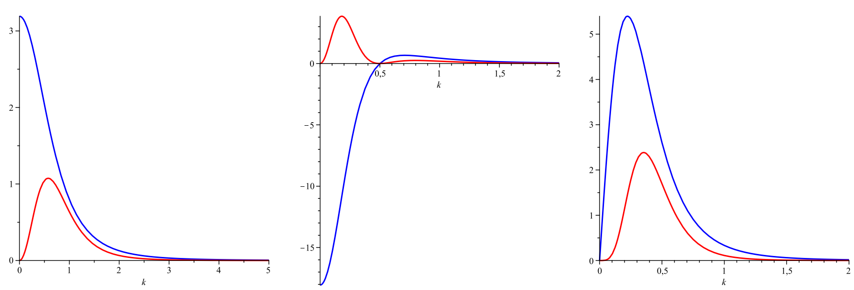


Figure 1.4: Radial hydrogen 1s, 2s, 2p wave functions (blue) and probability densities (red) in momentum space.

The number of nodes in momentum space and coordinate space is the same. Note that the momentum profile of 2s is restricted to rather small momenta. Loosely speaking, the inner lobe of the momentum distribution corresponds to the outer lobe of the distribution in coordinate space: When the electron is far away from the nucleus the momentum is relatively small (and vice versa). This phenomenon is related to the uncertainty principle. The inner lobe in coordinate space is rather sharp, whereas the outer lobe in momentum space extends over a relatively wide range of momenta (and v.v.). But note that this is not a rigorous argument, because the radial momentum is NOT the canonical momentum of the radial coordinate, i.e., they do not fulfill standard commutation and uncertainty relations.

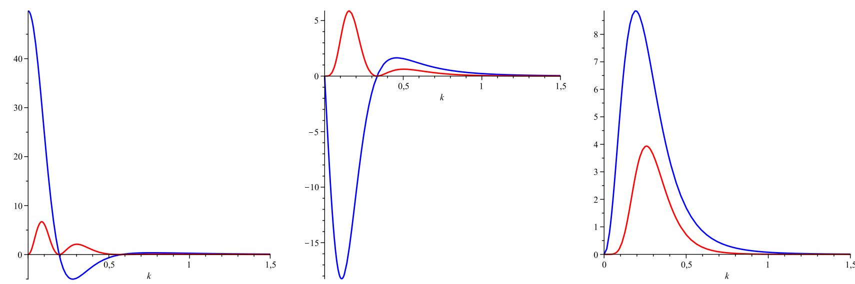


Figure 1.5: Radial hydrogen 3s, 3p, 3d wave functions (blue) and probability densities (red) in momentum space.

Check the Maple file `hydrogen.mw` for more details!

1.4 Assorted remarks

a) More (mathematical) details about the Coulomb problem can be found in any QM textbook, in particular in [Gri], Chap. 4.1–4.3.

b) Hydrogen-like ions

   We have solved not only the (Schrödinger) hydrogen problem ($Z = 1$), but also the bound-state problems of all one-electron atomic ions (e.g. He^+, Li^{2+},...) for $Z = 2, 3, \ldots$ Note that $E_n \propto Z^2$.

c) Exotic systems

   ... are also solved

   (a) positronium (e^+e^-)
   (b) muonium (μ^+e^-)
   (c) muonic atom ($p\mu^-$)

In these cases one has to take care of the different masses compared to the hydrogen problem. Note that $E_n \propto \mu = \frac{m_1 m_2}{m_1+m_2}$.

d) Corrections

The spectrum determined by Eq. (1.23) is the exact solution of the Schrödinger-Coulomb problem, but not exactly what one sees experimentally. The reason is that the Schrödinger equation is not the ultimate answer, e.g., it has to be modified to meet the requirements of the theory of special relativity. Therefore, corrections show up, which lead to a (partial) lifting of the degeneracy. This will be discussed later on.

e) Atomic units

So far, we have used SI units (as we are supposed to). In atomic and molecular physics another set of units is more convenient and widely used: atomic units. The starting point for their definition is the Hamiltonian

$$\hat{H}_{SI} = -\frac{\hbar^2}{2m_e}\nabla_r^2 - \frac{e^2}{4\pi\epsilon_0 r} \tag{1.31}$$

(i.e., the one of Eq. (1.7) for $Z = 1$ and $\mu \to m_e$). Four constants show up in this Hamiltonian — way too many — and so they are all made to disappear!

Recipe

- measure mass in units of m_e
- measure charge in units of e
- measure angular momentum in units of $\hbar$
- measure permittivity of the vacuum in units of $4\pi\epsilon_0$

In other words, atomic units (a.u.) are defined by setting $m_e = e = \hbar = 4\pi\epsilon_0 = 1$.

Consequences

- $\hat{H}_{a.u.} = -\frac{1}{2}\nabla_r^2 - \frac{1}{r}$

- length: let's look at Bohr's radius

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} = 0.53 \cdot 10^{-10} m = 1 \text{a.u.}$$

- energy: let's look at the hydrogen ground state H(1s)

$$E_{1s} = -\frac{\hbar^2}{2m_e a_0^2} = -13.6\,\text{eV} = -0.5\,\text{a.u.} = -0.5\,\text{hartree} = -1\,\text{Rydberg}$$

- time: let's do a dimensional analysis

$$\text{time} = \frac{\text{distance}}{\text{speed}} = \frac{\text{distance} \times \text{mass}}{\text{momentum}} = \frac{\text{distance}^2 \times \text{mass}}{\text{angular momentum}}$$

$\hookrightarrow t_0 := \frac{a_0^2 m_e}{\hbar} = 2.4 \cdot 10^{-17} s = 1$ a.u.

- fine structure constant (dimensionless)

$$\alpha = \frac{e^2}{4\pi\epsilon_0\hbar c} \approx \frac{1}{137}.$$

In atomic units we have $\alpha = 1/c$, i.e. $c \approx 137$ a.u. Thus, one atomic unit of velocity corresponds to $2.2 \cdot 10^6$ m/s. This is also obtained by using $v_0 = a_0/t_0$.

Chapter 2

Atoms in electric fields: the Stark effect

What happens if we place an atom in a uniform electric field? One observes a splitting and shifting of energy levels (spectral lines). This was first discovered by Johannes Stark in 1913, i.e. in the same year, in which Bohr developed his model of the hydrogen atom. Later on, this problem was one of the first treated by Schrödinger shortly after the discovery of his wave equation. Schrödinger used perturbation theory, and this is what we will do in this chapter.

The first step is to figure out what kind of modification a classical electric field brings about. Let's assume the field $\mathbf{E}$ is oriented in positive z-direction:

$$\mathbf{E} = F\hat{k} \tag{2.1}$$

The associated electrostatic potential reads

$$\Phi(\mathbf{r}) = -\mathbf{E} \cdot \mathbf{r} = -Fz \tag{2.2}$$

$\hookrightarrow$ potential energy of an electron

$$W(\mathbf{r}) = -e\Phi(\mathbf{r}) = eFz \tag{2.3}$$

has to be added to the Hamiltonian. The task then is to solve

$$\hat{H}|\varphi_\alpha\rangle = E_\alpha|\varphi_\alpha\rangle \tag{2.4}$$

for (using atomic units from now on)

$$\hat{H} = -\frac{1}{2}\nabla^2 - \frac{1}{r} + Fz \tag{2.5}$$

Taking a look at the total potential (Coulomb + Stark) one finds that tunnelling is possible — i.e. in a strict sense the Hamiltonian (2.5) does not support stationary states. Eventually, a bound electron will tunnel through the barrier and escape from the atom. In practice, however, the Stark potential is weak compared to the Coulomb potential and the tunnel effect is unimportant unless one studies highly-excited states. This is why we can apply stationary perturbation theory (PT).

2.1 Stationary perturbation theory for nondegenerate systems

a) General formalism

Task: solve stationary SE

$$\hat{H}|\varphi_\alpha\rangle = E_\alpha|\varphi_\alpha\rangle \tag{2.6}$$

decompose

$$\hat{H} = \hat{H}_0 + \hat{W} \tag{2.7}$$

and assume that the eigenvalue problem of $\hat{H}_0$ is known

$$\hat{H}_0|\varphi_\alpha^0\rangle = E_\alpha^{(0)}|\varphi_\alpha^0\rangle, \qquad \langle\varphi_\alpha^0|\varphi_\beta^0\rangle = \delta_{\alpha\beta} \tag{2.8}$$

We seek solutions of. Eq. (2.6) in terms of a Taylor (like) expansion based on the (nondegenerate) eigenvalues and eigenstates of the 'unperturbed problem' Eq. (2.8). Therefore, we require that the 'perturbation' $\hat{W}$ be small. Let's introduce a smallness parameter λ:

$$\hat{W} \equiv \lambda\hat{w} \qquad \text{with} \quad \lambda \ll 1 \tag{2.9}$$

$$\stackrel{(2.6)}{\longrightarrow} \qquad \Big(\hat{H}_0 + \lambda\hat{w}\Big)|\varphi_\alpha(\lambda)\rangle = E_\alpha(\lambda)|\varphi_\alpha(\lambda)\rangle \tag{2.10}$$

Taylor expansions about $\lambda = 0$:

$$E_\alpha(\lambda) = E_\alpha^{(0)} + \frac{dE_\alpha(\lambda)}{d\lambda}\bigg|_{\lambda=0} \lambda + \frac{1}{2}\frac{d^2E_\alpha(\lambda)}{d\lambda^2}\bigg|_{\lambda=0} \lambda^2 + \ldots \tag{2.11}$$

$$|\varphi_\alpha(\lambda)\rangle = |\varphi_\alpha^0\rangle + \frac{d}{d\lambda}\,|\varphi_\alpha(\lambda)\rangle|_{\lambda=0}\,\lambda + \ldots \tag{2.12}$$

We need to find expressions for the derivatives in Eqs. (2.11), (2.12): consider derivative of. Eq. (2.10):

$$\begin{aligned}
&\frac{d}{d\lambda}\Big(\hat{H}_0 + \lambda\hat{w} - E_\alpha(\lambda)\Big)|\varphi_\alpha(\lambda)\rangle = 0 \\
\Longleftrightarrow\quad &\Big(\hat{H}_0 + \lambda\hat{w} - E_\alpha(\lambda)\Big)|\varphi'_\alpha(\lambda)\rangle + \Big(\hat{w} - E'_\alpha(\lambda)\Big)|\varphi_\alpha(\lambda)\rangle = 0 \\
&\qquad (E'_\alpha = \frac{dE_\alpha}{d\lambda} \quad \text{etc.}) \\
\hookrightarrow\quad &\langle\varphi_\beta(\lambda)|\hat{H}(\lambda) - E_\alpha(\lambda)|\varphi'_\alpha(\lambda)\rangle + \langle\varphi_\beta(\lambda)|\hat{w} - E'_\alpha(\lambda)|\varphi_\alpha(\lambda)\rangle = 0
\end{aligned}$$

i) $\alpha = \beta$

$$\Longrightarrow \quad E'_\alpha(\lambda) = \langle\varphi_\alpha(\lambda)|\hat{w}|\varphi_\alpha(\lambda)\rangle \tag{2.13}$$

ii) $\alpha \neq \beta$

$$\Longrightarrow \quad \langle\varphi_\beta(\lambda)|\varphi'_\alpha(\lambda)\rangle = \frac{\langle\varphi_\beta(\lambda)|\hat{w}|\varphi_\alpha(\lambda)\rangle}{E_\alpha(\lambda) - E_\beta(\lambda)} \tag{2.14}$$

In order to use Eq. (2.14) for an expansion of $|\varphi'_\alpha\rangle$ in terms of the orthonormal basis $\big\{|\varphi_\alpha\rangle\big\}$ we have to consider the coefficient $\langle\varphi_\alpha(\lambda)|\varphi'_\alpha(\lambda)\rangle$ in addition. If we assume that $\langle\varphi_\alpha(\lambda)|\varphi'_\alpha(\lambda)\rangle = \langle\varphi'_\alpha(\lambda)|\varphi_\alpha(\lambda)\rangle$ (i.e. we choose real states which is not a restriction) we can show that

$$\langle\varphi_\alpha(\lambda)|\varphi'_\alpha(\lambda)\rangle = 0$$

<u>proof :</u>

$$\begin{aligned}
\frac{d}{d\lambda}\underbrace{\langle\varphi_\alpha(\lambda)|\varphi_\alpha(\lambda)\rangle}_{=1} &= \langle\varphi'_\alpha(\lambda)|\varphi_\alpha(\lambda)\rangle + \langle\varphi_\alpha(\lambda)|\varphi'_\alpha(\lambda)\rangle \\
&= 2\langle\varphi_\alpha(\lambda)|\varphi'_\alpha(\lambda)\rangle \;=\; 0
\end{aligned}$$

$$\begin{aligned}
\hookrightarrow\quad |\varphi'_\alpha(\lambda)\rangle &= \sum_\beta |\varphi_\beta(\lambda)\rangle\langle\varphi_\beta(\lambda)|\varphi'_\alpha(\lambda)\rangle \\
&= \sum_{\beta\neq\alpha} \frac{\langle\varphi_\beta(\lambda)|\hat{w}|\varphi_\alpha(\lambda)\rangle}{E_\alpha(\lambda) - E_\beta(\lambda)}|\varphi_\beta(\lambda)\rangle
\end{aligned} \tag{2.15}$$

Let's also consider the 2^{nd} derivative term in Eq. (2.11):

$$\begin{aligned} \frac{d^2}{d\lambda^2}E_\alpha(\lambda) &= \frac{d}{d\lambda}E'_\alpha(\lambda) \overset{(2.13)}{=} \frac{d}{d\lambda}\langle\varphi_\alpha(\lambda)|\hat{w}|\varphi_\alpha(\lambda)\rangle \\ &= \langle\varphi'_\alpha(\lambda)|\hat{w}|\varphi_\alpha(\lambda)\rangle + \langle\varphi_\alpha(\lambda)|\hat{w}|\varphi'_\alpha(\lambda)\rangle \\ &\overset{(2.15)}{=} 2\sum_{\beta\neq\alpha}\frac{|\langle\varphi_\alpha(\lambda)|\hat{w}|\varphi_\beta(\lambda)\rangle|^2}{E_\alpha(\lambda)-E_\beta(\lambda)} \end{aligned} \tag{2.16}$$

Higher order terms can be calculated by differentiating expressions (2.15), (2.16) successively. We stop here and insert (2.13)–(2.16) in the Taylor expansions (2.11), (2.12):

$$\begin{aligned} E_\alpha(\lambda) &= E_\alpha^{(0)} + \lambda\langle\varphi_\alpha(0)|\hat{w}|\varphi_\alpha(0)\rangle \\ &\quad + \lambda^2\sum_{\beta\neq\alpha}\frac{|\langle\varphi_\alpha(0)|\hat{w}|\varphi_\beta(0)\rangle|^2}{E_\alpha(0)-E_\beta(0)} + \ldots \\ &= E_\alpha^{(0)} + \langle\varphi_\alpha^0|\hat{W}|\varphi_\alpha^0\rangle + \sum_{\beta\neq\alpha}\frac{|\langle\varphi_\alpha^0|\hat{W}|\varphi_\beta^0\rangle|^2}{E_\alpha^{(0)}-E_\beta^{(0)}} + \ldots \end{aligned} \tag{2.17}$$

$$|\varphi_\alpha(\lambda)\rangle = |\varphi_\alpha^0\rangle + \sum_{\beta\neq\alpha}\frac{\langle\varphi_\beta^0|\hat{W}|\varphi_\alpha^0\rangle}{E_\alpha^{(0)}-E_\beta^{(0)}}|\varphi_\beta^0\rangle + \ldots \tag{2.18}$$

Eqs. (2.17), (2.18) are the standard expressions for the lowest-order corrections — the glorious result of this section!

Remarks:

1. Derivation and result are valid only if $E_\alpha^{(0)} \neq E_\beta^{(0)}$ (i.e. no degeneracies)

2. Convergence of perturbation series?
   This cannot be answered in general. In some cases, perturbation expansions do converge, in some they do not, and in some other cases the perturbation series turns out to be a so-called semi-convergent (asymptotic) series.

   Consistency criterion for convergence (cf. Eq. (2.18))

$$\left|\frac{\langle\varphi_\beta^0|\hat{W}|\varphi_\alpha^0\rangle}{E_\alpha^{(0)}-E_\beta^{(0)}}\right| \ll 1\ , \qquad (\text{for } \alpha\neq\beta)$$

3. In practice, 'exact' calculations beyond 1^{st} order in the energy are often not feasible due to (infinite) sums over all basis states (cf. Eq. (2.17)).

4. <u>Literature:</u> [Gri], Chap. 6.1; [Lib], Chap. 13.1

b) Application to H($1s$) in an electric field

Ingredients (in atomic units):

$$\begin{aligned}
\varphi^0_{1s}(r) &= \frac{1}{\sqrt{\pi}}e^{-r} \\
E^{(0)}_{1s} &= -0.5 \text{ a.u.} \\
W &= Fz
\end{aligned}$$

1^{st}-order energy correction:

$$\begin{aligned}
\Delta E^{(1)}_{1s} &= \langle \varphi^0_{1s}|W|\varphi^0_{1s}\rangle && (2.19) \\
&= \frac{F}{\pi}\int e^{-2r} r\cos\theta d^3r \\
&= \frac{F}{\pi}\int_0^\infty r^3 e^{-2r}dr \int_{-1}^{1}\cos\theta d\cos\theta \int_0^{2\pi} d\varphi \\
&= F\int_0^\infty r^3e^{-2r}drx^2\Big|_{-1}^{1} = 0 && (2.20)
\end{aligned}$$

(with $x = \cos\theta$)

The 2^{nd}-order energy correction

$$\Delta E^{(2)}_{1s} = \sum_{\beta\neq 1s}\frac{|\langle\varphi^0_{1s}|Fz|\varphi^0_\beta\rangle|^2}{E^{(0)}_{1s} - E^{(0)}_\beta}$$

is hard to calculate due to the infinite sum (which actually also involves an integral over the continuum states). Let us content ourselves with an estimate.

Note that $E^{(0)}_{1s} - E^{(0)}_\beta < 0$, i.e., $\Delta E^{(2)}_{1s} < 0$.

Consider

$$\begin{aligned}
|\Delta E_{1s}^{(2)}| &= F^2 \sum_{\beta\neq 1s} \frac{|\langle \varphi_{1s}^0|z|\varphi_\beta^0\rangle|^2}{E_\beta^{(0)} - E_{1s}^{(0)}} < \frac{F^2}{E_{n=2}^{(0)} - E_{1s}^{(0)}} \sum_{\beta\neq 1s} \langle \varphi_{1s}^0|z|\varphi_\beta^0\rangle\langle \varphi_\beta^0|z|\varphi_{1s}^0\rangle \\
&= \frac{F^2}{E_{n=2}^{(0)} - E_{1s}^{(0)}} \left(\langle \varphi_{1s}^0|z \sum_\beta |\varphi_\beta^0\rangle\langle\varphi_\beta^0|z|\varphi_{1s}^0\rangle - \langle \varphi_{1s}^0|z|\varphi_{1s}^0\rangle\langle \varphi_{1s}^0|z|\varphi_{1s}^0\rangle \right) \\
&= \frac{8F^2}{3}(\langle \varphi_{1s}^0|z^2|\varphi_{1s}^0\rangle - \langle \varphi_{1s}^0|z|\varphi_{1s}^0\rangle^2) \overset{(2.20)}{=} \frac{8F^2}{3}\langle \varphi_{1s}^0|z^2|\varphi_{1s}^0\rangle
\end{aligned}$$

One finds $\langle \varphi_{1s}^0|z^2|\varphi_{1s}^0\rangle = 1$ and obtains

$$|\Delta E_{1s}^{(2)}| < \frac{8}{3}F^2 \qquad \text{quadratic Stark effect} \tag{2.21}$$

The exact result (see [Sha], Chap. 17) is

$$\Delta E_{1s}^{(2)} = -\frac{9}{4}F^2 \tag{2.22}$$

Interpretation:
Consider a classical charge distribution ρ in an electric field. The associated potential energy is

$$\begin{aligned}
W &= \int \rho(\mathbf{r})\Phi(\mathbf{r})d^3r = -F\int \rho(\mathbf{r})zd^3r \\
&= -Fd_z
\end{aligned}$$

where d_z is the z-component of the dipole moment.
Link this to QM by recognizing that $\rho(\mathbf{r}) = -|\varphi(\mathbf{r})|^2$ (atomic units!).

$$\hookrightarrow d_z = -\int |\varphi_{1s}(\mathbf{r})|^2 zd^3r = -\langle\varphi_{1s}|z|\varphi_{1s}\rangle$$

Now use Eq. (2.18) to obtain

$$d_z = -2F\sum_{\beta\neq 1s} \frac{|\langle \varphi_{1s}^0|z|\varphi_\beta^0\rangle|^2}{E_{1s}^{(0)} - E_\beta^{(0)}} + O(\lambda^2) \approx -\frac{2}{F}\Delta E_{1s}^{(2)} < \frac{16}{3}F$$

Summary:

- $\Delta E_{1s}^{(1)} = 0$ expresses the fact that the unperturbed hydrogen ground state has no static dipole moment $d_z^{(0)}$ (this is in fact true for any spherically symmetric charge distribution).
- $\Delta E_{1s}^{(2)} \neq 0$ expresses the fact that it has a nonzero induced dipole moment $d_z^{(1)}$, i.e., a nonzero dipole polarizability $\alpha_D := d_z^{(1)}/F$. We have found $\alpha_D < 16/3$ a.u. (the exact result being $\alpha_D = 9/2$ a.u.)

2.2 Degenerate perturbation theory

Problem:

$$\hat{H} = \hat{H}_0 + \lambda \hat{w} \tag{2.23}$$

with

$$\hat{H}_0 |\varphi_{\alpha j}^0\rangle = E_\alpha^{(0)} |\varphi_{\alpha j}^0\rangle, \quad j = 1, \ldots, g_\alpha \tag{2.24}$$

where g_α is the degeneracy level. The set $\{|\varphi_{\alpha j}^0\rangle, j = 1, \ldots, g_\alpha\}$ spans a g_α-dimensional subspace of Hilbert space associated with the eigenvalue $E_\alpha^{(0)}$. This implies that any linear combination of these states is an eigenstate of $\hat{H}_0$ for $E_\alpha^{(0)}$. When the perturbation is turned on, the degeneracy is (normally) lifted:

$$\hat{H} |\varphi_{\alpha j}\rangle = E_{\alpha j} |\varphi_{\alpha j}\rangle. \tag{2.25}$$

The question arises which of the degenrate states is approached by a given state $|\varphi_{\alpha j}\rangle$ in the limit $\lambda \to 0$. At this point we can't say more than that it can be any linear combination, i.e.

$$|\varphi_{\alpha j}\rangle \xrightarrow{\lambda \to 0} |\tilde{\varphi}_{\alpha j}^0\rangle = \sum_{k=1}^{g_\alpha} a_{kj}^\alpha |\varphi_{\alpha k}^0\rangle. \tag{2.26}$$

The unknown states $|\tilde{\varphi}_{\alpha j}^0\rangle$ are the 0^{th}-order states of the pertubation expansion:

$$E_{\alpha j} = E_\alpha^{(0)} + \lambda E_{\alpha j}^{(1)} + \cdots \tag{2.27}$$

$$|\varphi_{\alpha j}\rangle = |\tilde{\varphi}_{\alpha j}^0\rangle + \lambda |\varphi_{\alpha j}^1\rangle + \cdots \tag{2.28}$$

Note that this expansion is of the same type as the previous Taylor series of Eqs. (2.11), (2.12) if one identifies

$$\Delta E_\alpha^{(1)} = \lambda E_\alpha^{(1)} = \left. \frac{dE_\alpha(\lambda)}{d\lambda} \right|_{\lambda=0} \lambda \quad \text{etc.}$$

Now proceed as follows: Insert (2.27), (2.28) into the Schrödinger equation (2.25) to obtain

$$\begin{aligned} (\hat{H}_0 \;\; &+ \;\; \lambda\hat{w}) \left(|\tilde{\varphi}^0_{\alpha j}\rangle + \lambda|\varphi^1_{\alpha j}\rangle + \cdots\right) \\ &= \;\; (E_\alpha^{(0)} + \lambda E_{\alpha j}^{(1)} + \cdots) \left(|\tilde{\varphi}^0_{\alpha j}\rangle + \lambda|\varphi^1_{\alpha j}\rangle + \cdots\right), \end{aligned}$$

sort this in terms of powers of λ

$$\begin{aligned} \lambda^0: \qquad & \hat{H}_0|\tilde{\varphi}^0_{\alpha j}\rangle \;\; = \;\; E_\alpha^{(0)}|\tilde{\varphi}^0_{\alpha j}\rangle \\ \lambda^1: \qquad & \hat{H}_0|\varphi^1_{\alpha j}\rangle \;\; + \;\; \hat{w}|\tilde{\varphi}^0_{\alpha j}\rangle = E_\alpha^{(0)}|\varphi^1_{\alpha j}\rangle + E_{\alpha j}^{(1)}|\tilde{\varphi}^0_{\alpha j}\rangle, \end{aligned}$$

and project the second equation onto an undisturbed eigenstate of the same subspace:

$$\begin{aligned} 0 \;\; &= \;\; \langle\varphi^0_{\alpha l}|\hat{H}_0 - E_\alpha^{(0)}|\varphi^1_{\alpha j}\rangle + \langle\varphi^0_{\alpha l}|\hat{w} - E_{\alpha j}^{(1)}|\tilde{\varphi}^0_{\alpha j}\rangle \\ \Leftrightarrow \qquad 0 \;\; &= \;\; \langle\varphi^0_{\alpha l}|\hat{w} - E_{\alpha j}^{(1)}|\tilde{\varphi}^0_{\alpha j}\rangle \\ \Leftrightarrow \qquad 0 \;\; &= \;\; \sum_{k=1}^{g_\alpha}\langle\varphi^0_{\alpha l}|\hat{w} - E_{\alpha j}^{(1)}|\varphi^0_{\alpha k}\rangle a^\alpha_{kj} \qquad l = 1,\ldots,g_\alpha \qquad (2.29) \end{aligned}$$

Eq. (2.29) is a standard matrix eigenvalue problem of size $g_\alpha \times g_\alpha$. Its solution is what (lowest-order) degenerate perturbation theory boils down to in practice. Here is how to do it:

(i) Solve secular (characteristic) equation $\det(\underline{\underline{w}}^\alpha - E_\alpha^{(1)}\underline{\underline{1}}) = 0 \rightarrow$ obtain eigenvalues $\{E_{\alpha j}^{(1)}, j = 1,\ldots,g\alpha\}$, which happen to be the first-order energy corrections, i.e. the quantities we are after!

(ii) Find mixing coefficients $\{a^\alpha_{kj}, k, j = 1,\ldots,g_\alpha\}$ by inserting eigenvalues into the matrix equations (2.29).

(ii) Check that $\langle\tilde{\varphi}^0_{\alpha l}|\hat{w}|\tilde{\varphi}^0_{\alpha k}\rangle = E_{\alpha j}^{(1)}\delta_{lk}$ (i.e. perturbation matrix is diagonal with respect to the states $\{|\tilde{\varphi}^0_{\alpha k}\rangle\}$).

Note that higher-order calculations are possible, but tedious and not discussed in our textbooks. Refs. [Gri], Chap. 6.2 and [Lib], Chap. 13.2, (13.3) merely paraphrase the material provided in this section.

2.3 Electric field effects on excited states: the linear Stark effect

Let us now apply degenerate perturbation theory to the problem of the excited hydrogen states in a uniform electric field. To this end we have to set up and diagonalize the perturbation matrix. Let's first look at

a) Matrix elements and selection rules

$$w_{lk}^{\alpha} = \langle\varphi_{\alpha l}^{0}|\hat{w}|\varphi_{\alpha k}^{0}\rangle \stackrel{\text{explicitly}}{\longrightarrow} \langle\varphi_{nlm}^{0}|z|\varphi_{nl'm'}^{0}\rangle$$

with (cf. Eq. (1.22))

$$\begin{aligned} \lambda &\equiv F \qquad \text{(smallness parameter)} \\ \varphi_{nlm}(\mathbf{r}) &= R_{nl}(r)Y_{lm}(\Omega) \\ z &= r\cos\theta = \sqrt{\frac{4\pi}{3}}rY_{10}(\Omega) \end{aligned}$$

$$\hookrightarrow \langle\varphi_{nlm}^{0}|z|\varphi_{nl'm'}^{0}\rangle = \sqrt{\frac{4\pi}{3}}\int_0^\infty r^3 R_{nl}(r)R_{nl'}(r)dr \int Y_{lm}^{*}(\Omega)Y_{10}(\Omega)Y_{l'm'}(\Omega)d\Omega$$

The angular integral is a special case of a more general integral over three (arbitrary) spherical harmonics, the result of which is known ("Wigner-Eckart theorem"):

$$\begin{aligned} &\sqrt{\frac{4\pi}{2L+1}}\int Y_{lm}^{*}(\Omega)Y_{LM}(\Omega)Y_{l'm'}(\Omega)d\Omega \\ &= (-1)^m\sqrt{(2l+1)(2l'+1)}\begin{pmatrix} l & L & l' \\ -m & M & m' \end{pmatrix}\begin{pmatrix} l & L & l' \\ 0 & 0 & 0 \end{pmatrix} \end{aligned} \qquad (2.30)$$

with

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \in \Re \qquad \text{"Wigner's } 3j\text{-symbol"}$$

The $3j$-symbols are closely related to the Clebsch-Gordan coefficients. We don't need to know much detail here other than that they fulfill certain selection rules, i.e., they are zero in many cases:

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \neq 0 \quad \text{iff} \quad m_1 + m_2 + m_3 = 0 \ \wedge \ |j_1 - j_2| \leq j_3 \leq j_1 + j_2$$

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ 0 & 0 & 0 \end{pmatrix} \neq 0 \quad \text{iff} \quad j_1 + j_2 + j_3 = \text{even} \ \wedge \ |j_1 - j_2| \leq j_3 \leq j_1 + j_2$$

These relations imply that Eq. (2.30) is nonzero only if

$$m = m' \quad \text{and} \quad \Delta l = l - l' = \pm 1 \tag{2.31}$$

These conditions are called *electric dipole selection rules.*

Literature on angular momentum, Clebsch-Gordan coefficients, and $3j$-symbols: [Lib], Chap. 9; [Mes], Vol II, Chap. 13 (and appendix); [CT], Chaps. 6, 10 (and complements)

b) Linear Stark effect for H($n = 2$)

Let's do an explicit calculation for the four degenerate states of the hydrogen L shell: $\{\varphi^0_{2s}, \varphi^0_{2p_0}\varphi^0_{2p_{-1}}\varphi^0_{2p_{+1}}\}$

- matrix elements:
  due to the dipole selection rules (2.31) there is only one nonzero matrix element we need to calculate:

$$\begin{aligned} w_{12} &= \langle\varphi^0_{2s}|r\cos\theta|\varphi^0_{2p_0}\rangle = \frac{1}{32\pi}\int_0^\infty (2-r)r^4 e^{-r}dr \int_{-1}^1 \cos^2\theta \, d\cos\theta \int_0^{2\pi} d\varphi \\ &= \frac{1}{24}\left(2\int_0^\infty r^4 e^{-r}dr - \int_0^\infty r^5 e^{-r}dr\right) = \frac{1}{24}(2\times 4! - 5!) = -3 \text{ (a.u.)} \\ &= w_{21} \end{aligned}$$

  $\rightarrow$ perturbation matrix:

$$\underline{\underline{w}} = \begin{pmatrix} 0 & w_{12} & 0 & 0 \\ w_{12} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}$$

- secular equation:

$$\det\begin{pmatrix} -E^{(1)} & w_{12} & 0 & 0 \\ w_{12} & -E^{(1)} & 0 & 0 \\ 0 & 0 & -E^{(1)} & 0 \\ 0 & 0 & 0 & -E^{(1)} \end{pmatrix} = 0 \tag{2.32}$$

$$\Leftrightarrow (E^{(1)})^4 - (E^{(1)})^2 w_{12}^2 = 0$$

$$\hookrightarrow E^{(1)} = \{0, 0, w_{12}, -w_{12}\}$$

- mixing coefficients
  (i) $E_{1,2}^{(1)} = 0$:

$$\begin{pmatrix} 0 & w_{12} & 0 & 0 \\ w_{12} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} a_{2s}^{(1,2)} \\ a_{2p_0}^{(1,2)} \\ a_{2p_{-1}}^{(1,2)} \\ a_{2p_{+1}}^{(1,2)} \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \end{pmatrix}$$

$$\Leftrightarrow a_{2s}^{(1,2)} = a_{2p_0}^{(1,2)} = 0$$

$$\hookrightarrow |\tilde{\varphi}^0_{E_{1,2}^{(1)}}\rangle = a_{2p_{-1}}^{(1,2)} |\varphi^0_{2p_{-1}}\rangle + a_{2p_{+1}}^{(1,2)} |\varphi^0_{2p_{+1}}\rangle$$

We can choose the nonzero coefficients as we please — so let's pick

$$|\tilde{\varphi}^0_{E_1^{(1)}}\rangle \equiv |\varphi^0_{2p_{-1}}\rangle$$

$$|\tilde{\varphi}^0_{E_2^{(1)}}\rangle \equiv |\varphi^0_{2p_{+1}}\rangle$$

(ii) $E_3^{(1)} = w_{12}$:

$$\begin{pmatrix} -w_{12} & w_{12} & 0 & 0 \\ w_{12} & -w_{12} & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} a_{2s}^{(3)} \\ a_{2p_0}^{(3)} \\ a_{2p_{-1}}^{(3)} \\ a_{2p_{+1}}^{(3)} \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \end{pmatrix}$$

$$\Leftrightarrow a_{2s}^{(3)} = a_{2p_0}^{(3)}\,,\ a_{2p_{-1}}^{(3)} = a_{2p_{+1}}^{(3)} = 0$$

(iii) $E_4^{(1)} = -w_{12}$:

$$\begin{pmatrix} w_{12} & w_{12} & 0 & 0 \\ w_{12} & w_{12} & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} a_{2s}^{(4)} \\ a_{2p_0}^{(4)} \\ a_{2p_{-1}}^{(4)} \\ a_{2p_{+1}}^{(4)} \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \end{pmatrix}$$

$$\Leftrightarrow a_{2s}^{(4)} = -a_{2p_0}^{(4)}\,,\ a_{2p_{-1}}^{(4)} = a_{2p_{+1}}^{(4)} = 0$$

$\hookrightarrow$ normalized 'Stark' states:

$$|\tilde{\varphi}^0_{E_3^{(1)}}\rangle = \frac{1}{\sqrt{2}}\left(|\varphi^0_{2s}\rangle + |\varphi^0_{2p_0}\rangle\right) \qquad (2.33)$$

$$|\tilde{\varphi}^0_{E_4^{(1)}}\rangle = \frac{1}{\sqrt{2}}\left(|\varphi^0_{2s}\rangle - |\varphi^0_{2p_0}\rangle\right) \qquad (2.34)$$

Summary

1. The (weak) electric field results in a *splitting* of the energy level — the degeneracy is (partly) lifted. The energy shifts are linear in the electric field strength:

$$\begin{aligned} \Delta E_{1,2}^{(1)} &= 0 \\ \Delta E_3^{(1)} &= \lambda w_{12} = -3F \\ \Delta E_4^{(1)} &= -\lambda w_{12} = 3F \end{aligned}$$

2. Note that the 'original' L-shell states have no static dipole moment since

$$\langle \varphi^0_{nlm}|z|\varphi^0_{nlm}\rangle = 0$$

3. The Stark states (2.33), (2.34) do have nonzero static dipole moments (calculate them!). Check the Maple worksheet `starkstates.mw` to see how these states look like.

4. Cylindrical symmetry is preserved by the Stark potential $W = Fz$, since

$$[\hat{l}_z, W] = 0,$$

i.e., m is still a good quantum number, but l is not.

5. The diagonalization procedure can be simplified by recognizing that the perturbation matrix is of block-diagonal structure (with three blocks corresponding to the magnetic quantum numbers $m = 0, m = -1, m = +1$. Consider three blocks A_i:

$$\det \begin{pmatrix} A_1 & 0 & 0 \\ 0 & A_2 & 0 \\ 0 & 0 & A_3 \end{pmatrix} = 0$$
$$\hookrightarrow \det A = 0 \Leftrightarrow \det A_i = 0 \quad \text{for } i = 1, \ldots, 3$$

   The only nontrivial secular equation for the L-shell problem then is (cf. Eq. (2.32)):

$$\det \begin{pmatrix} -E^{(1)} & w_{12} \\ w_{12} & -E^{(1)} \end{pmatrix} = 0$$

   In a similar fashion, one can study the Stark problem for the nine M shell states. The perturbation matrix can be decomposed into five blocks corresponding to the states with magnetic quantum numbers $m = -2$ to $m = 2$.

Chapter 3

Interaction of atoms with radiation

The first question to be addressed when discussing the interaction of atoms with radiation concerns the level on which the electromagnetic (EM) field shall be described. It seems natural to aim at a quantum theory. It is only on this level that photons come into the picture. We will take a look at them a bit later, but start off with coupling the *classical* EM field to our quantal description of the (hydrogen) atom. It turns out that this is sufficient for the description of a number of processes including the photoelectric effect, which prompted Einstein to introduce the notion of photons in the first place.

3.1 The semiclassical Hamiltonian

The goal is to derive a Hamiltonian, which accounts for the interaction of an atom with a classical EM field. Let's start completely classically.

a) Classical particle in an EM field

- The action of a classical EM field on a classical particle is described by the Lorentzian force

$$\mathbf{F}_L = q\big(\mathbf{E} + (\mathbf{v} \times \mathbf{B})\big)$$

where q and $\mathbf{v}$ are the charge and the velocity of the particle and $\mathbf{E}$ and $\mathbf{B}$ the electric and magnetic fields. However, if we want to construct a Hamiltonian we need EM potentials instead of EM fields:

- EM potentials
  the scalar potential Φ and the vector potential $\mathbf{A}$ are defined via

$$\mathbf{B} = \nabla \times \mathbf{A} \tag{3.1}$$

$$\mathbf{E} = -\nabla\Phi - \frac{\partial \mathbf{A}}{\partial t} \tag{3.2}$$

$$\hookrightarrow \quad \mathbf{F}_L = q\left(-\nabla\Phi - \frac{\partial \mathbf{A}}{\partial t} + (\mathbf{v} \times (\nabla \times \mathbf{A}))\right) \tag{3.3}$$

  this equation can be rewritten by introducing a generalized (i.e., velocity-dependent) potential energy:

- Generalized potential energy

$$U := q(\Phi - \mathbf{A} \cdot \mathbf{v}) \tag{3.4}$$

  one can show that Eq. (3.3) can be written as

$$\mathbf{F}_L = -\nabla U + \frac{d}{dt}\nabla_v U \tag{3.5}$$

  i.e.,

$$F_L^i = -\left(\frac{\partial U}{\partial x_i} - \frac{d}{dt}\frac{\partial U}{\partial \dot{x}_i}\right) \qquad i = 1, 2, 3$$

  the generalized potential paves the way to set up the Lagrangian:

- Lagrangian

$$L = T - U = \frac{m}{2}\mathbf{v}^2 - q\Phi + q\mathbf{A} \cdot \mathbf{v} \tag{3.6}$$

  if one works out the Lagrangian equations of motion one finds $m\mathbf{a} = \mathbf{F}_L$, i.e., Newton's equation of motion with the Lorentzian force. This shows that the construction is consistent. Now we are only one step away from the Hamiltonian:

- Hamiltonian

$$H = \mathbf{p} \cdot \mathbf{v} - L \tag{3.7}$$

with the generalized momentum

$$\mathbf{p} = \nabla_v L = m\mathbf{v} + q\mathbf{A} \tag{3.8}$$

$$\mathbf{v} = \frac{1}{m}(\mathbf{p} - q\mathbf{A}) \tag{3.9}$$

if one uses Eq. (3.9) in Eq. (3.7) one arrives at

$$H = \frac{1}{2m}(\mathbf{p} - q\mathbf{A})^2 + q\Phi \tag{3.10}$$

for details see [GPS], Chaps. 1.5 and 8.1

b) Quantum mechanical Hamiltonian for an electron

- add a scalar potential V (to account, e.g., for the Coulomb potential of the atomic nucleus)
- $q = -e$
- quantization: $\mathbf{p} \to \hat{\mathbf{p}} = -i\hbar\nabla$

$$\begin{aligned}
\hookrightarrow \hat{H} &= \frac{1}{2m}(\hat{\mathbf{p}} + e\mathbf{A})^2 - e\Phi + V \\
&= \frac{1}{2m}(-\hbar^2\nabla^2 - i\hbar e\nabla\cdot\mathbf{A}(\mathbf{r},t) - i\hbar e\mathbf{A}(\mathbf{r},\mathbf{t})\cdot\nabla + e^2\mathbf{A}^2(\mathbf{r},t)) \\
&\quad - e\Phi(\mathbf{r},t) + V(\mathbf{r}) \\
&= -\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}) + \frac{e\hbar}{mi}\mathbf{A}(\mathbf{r},t)\cdot\nabla + \frac{e\hbar}{2mi}(\nabla\cdot\mathbf{A}(\mathbf{r},\mathbf{t})) \\
&\quad + \frac{e^2}{2m}\mathbf{A}^2(\mathbf{r},t) - e\Phi(\mathbf{r},t) \\
&\equiv \hat{H}_0 + \hat{W}(t)
\end{aligned} \tag{3.11}$$

question: how do $\mathbf{A}$ and Φ look like?
$\hookrightarrow$ assume EM field without sources (neither charges nor currents). The homogeneous Maxwell equations for $\mathbf{A}$ and Φ take a simple form if one uses

the so-called Coulomb gauge defined by the requirement $\nabla \cdot \mathbf{A} = 0$. One is then left with

$$\begin{aligned} \nabla^2 \mathbf{A} - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\mathbf{A} &= 0 \qquad (3.12) \\ \nabla^2 \Phi &= 0 \qquad (3.13) \end{aligned}$$

The only solution to Eq. (3.13) which is compatible with the requirement that free EM waves are transverse is the trivial one $\Phi = 0$. A monochromatic (real) solution of Eq. (3.12) reads

$$\mathbf{A}(\mathbf{r}, t) = \hat{\pi}|A_0| \cos(\mathbf{k} \cdot \mathbf{r} - \omega t + \alpha) \qquad (3.14)$$

with the unit vector $\hat{\pi}$ being orthogonal to the wave vector $\mathbf{k}$. This ensures that indeed $\nabla \cdot \mathbf{A} = 0$. If one inserts (3.14) into (3.12) one obtains the dispersion relation $\omega = ck$. For details on the solutions of the free Maxwell equations see [Jac], Chap 6.5.

Using the gauge conditions we arrive at the perturbation

$$\hat{W}(t) = \frac{e}{m}\mathbf{A}(t) \cdot \hat{\mathbf{p}} + \frac{e^2}{2m}\mathbf{A}^2 \qquad (3.15)$$

For weak fields one can neglect the $\mathbf{A}^2$ term. $\hat{W} = \frac{e}{m}\mathbf{A} \cdot \hat{\mathbf{p}}$ is the usual starting point for a perturbative treatment of atom-radiation interactions in the semiclassical framework. The perturbation depends on time. We need a time-dependent version of perturbation theory to deal with it.

3.2 Time-dependent perturbation theory

a) General formulation

The Hamiltonian under discussion is of the generic form

$$\begin{aligned} \hat{H}(t) &= \hat{H}_0 + \hat{W}(t) \\ &\equiv \hat{H}_0 + \lambda \hat{w}(t) \qquad (3.16) \end{aligned}$$

task: solve the time-dependent Schrödinger equation (TDSE)

$$i\hbar \partial_t |\psi(t)\rangle = \hat{H}(t)|\psi(t)\rangle \qquad (3.17)$$

assume that $\hat{W}(t \leq t_0) = 0$

$$\begin{aligned} \hookrightarrow \quad t \leq t_0 : \quad & \hat{H}_0|\varphi_j\rangle &=& \ \epsilon_j|\varphi_j\rangle \qquad j = 0, 1, \ldots \\ \text{assume} \quad & |\psi(t_0)\rangle &=& \ |\varphi_0\rangle\ , \qquad \text{(initial state)} \end{aligned} \tag{3.18}$$

$$\text{ansatz :} \qquad |\psi(t)\rangle = \sum_j c_j(t) e^{-\frac{i}{\hbar}\epsilon_j t}|\varphi_j\rangle \tag{3.19}$$

$$= \sum_j c_j(t)|\psi_j(t)\rangle \tag{3.20}$$

insertion of Eq. (3.19) into Eq. (3.17):

$$\hookrightarrow \quad \sum_j \Big(i\hbar\dot{c}_j + \epsilon_j\Big) e^{-\frac{i}{\hbar}\epsilon_j t}|\varphi_j\rangle = \sum_j c_j e^{-\frac{i}{\hbar}\epsilon_j t}\hat{H}(t)|\varphi_j\rangle \qquad |\ \langle\psi_k(t)|$$

$$\boxed{\hookrightarrow \quad i\hbar\dot{c}_k = \lambda \sum_j e^{\frac{i}{\hbar}(\epsilon_k - \epsilon_j)t} c_j \langle\varphi_k|\hat{w}(t)|\varphi_j\rangle} \tag{3.21}$$

'coupled-channel' equations. (still exact if basis is complete)

If $\hat{W}(t > T) = 0 \qquad \hookrightarrow \quad c_k(t > T) = \text{const}$ and

$$p_k = |c_k|^2\Big|_{t>T} = |\langle\psi_k|\psi\rangle|^2\Big|_{t>T} = |\langle\varphi_k|\psi\rangle|^2\Big|_{t>T} = \text{const} \tag{3.22}$$

$\hookrightarrow$ transition probabilities $\varphi_0 \longrightarrow \varphi_k$

note that

$$\sum_k p_k = \sum_k \langle\psi|\varphi_k\rangle\langle\varphi_k|\psi\rangle = \langle\psi|\psi\rangle = 1$$

as it should.

Ansatz for solution of Eq. (3.21): power series expansion

$$c_k(t) = c_k^{(0)}(t) + \lambda c_k^{(1)}(t) + \lambda^2 c_k^{(2)}(t) + \ldots \tag{3.23}$$

insertion into Eq. (3.21) yields

$$i\hbar\Big(\dot{c}_k^{(0)} + \lambda\dot{c}_k^{(1)} + \lambda^2\dot{c}_k^{(2)} + \ldots\Big) = \lambda \sum_j \Big(c_j^{(0)} + \lambda c_j^{(1)} + \lambda^2 c_j^{(2)} + \ldots\Big) e^{\frac{i}{\hbar}(\epsilon_k - \epsilon_j)t}\langle\varphi_k|\hat{w}(t)|\varphi_j\rangle$$

$\hookrightarrow$

$$
\begin{aligned}
\lambda^0 : &\qquad i\hbar\dot{c}_k^{(0)} = 0 \\
\lambda^1 : &\qquad i\hbar\dot{c}_k^{(1)} = \sum_j c_j^{(0)} e^{\frac{i}{\hbar}(\epsilon_k-\epsilon_j)t}\langle\varphi_k|\hat{w}(t)|\varphi_j\rangle \\
\lambda^2 : &\qquad i\hbar\dot{c}_k^{(2)} = \sum_j c_j^{(1)} e^{\frac{i}{\hbar}(\epsilon_k-\epsilon_j)t}\langle\varphi_k|\hat{w}(t)|\varphi_j\rangle
\end{aligned}
$$

these equation can be solved successively:

$$
\begin{aligned}
\lambda^0 : &\qquad c_k^{(0)}(t) &=& \ \text{const} \ = \ \delta_{k0} \qquad \text{(cf. Eq. (3.18))} \qquad (3.24)\\
\lambda^1 : &\qquad i\hbar\dot{c}_k^{(1)} &=& \ \sum_j \delta_{j0} e^{\frac{i}{\hbar}(\epsilon_k-\epsilon_j)t}\langle\varphi_k|\hat{w}(t)|\varphi_j\rangle \\
& &=& \ e^{\frac{i}{\hbar}(\epsilon_k-\epsilon_0)t}\langle\varphi_k|\hat{w}(t)|\varphi_0\rangle
\end{aligned}
$$

$$
\hookrightarrow \quad c_k^{(1)}(t) - \underbrace{c_k^{(1)}(t_0)}_{=0} \ = \ -\frac{i}{\hbar}\int_{t_0}^{t} e^{\frac{i}{\hbar}(\epsilon_k-\epsilon_0)t'}\langle\varphi_k|\hat{w}(t')|\varphi_0\rangle\, dt' \qquad (3.25)
$$

(as $\lambda = 0$ at $t = t_0$)

accordingly:

$$
\begin{aligned}
\lambda^2 : \qquad c_k^{(2)}(t) = -\frac{1}{\hbar^2}\sum_j \int_{t_0}^{t} dt' \int_{t_0}^{t'} dt'' e^{\frac{i}{\hbar}(\epsilon_k-\epsilon_j)t'} e^{\frac{i}{\hbar}(\epsilon_j-\epsilon_0)t''} \\
\times\ \langle\varphi_k|\hat{w}(t')|\varphi_j\rangle\langle\varphi_j|\hat{w}(t'')|\varphi_0\rangle \qquad (3.26)
\end{aligned}
$$

Comments:

(i) "exact" calculations beyond 1^{st} order are in general impossible due to infinite sums

(ii) interpretation

	t_0				t	
1^{st} order	$\|\varphi_0\rangle$		$\xrightarrow{\hat{W}}$		$\|\varphi_k\rangle$	'direct transition'
2^{nd} order	$\|\varphi_0\rangle$	$\xrightarrow{\hat{W}}$	$\|\varphi_j\rangle$	$\xrightarrow{\hat{W}}$	$\|\varphi_k\rangle$	

transition via 'virtual' intermediate states (two steps)

(iii) further reading (and better visualization in terms of generic diagrams): [Mes] II, Chap. 17

b) Discussion of the 1^{st}-order result

To 1^{st} order time-dependent perturbation theory we have (cf. Eqs. (3.24) and (3.25)):

$$c_k(t) \approx \delta_{k0} - \frac{i}{\hbar}\int_{t_0}^{t} e^{i\omega_{k0}t'} W_{k0}(t')\, dt' \tag{3.27}$$

with

$$\begin{aligned} \omega_{k0} &= \omega_k - \omega_0 \;=\; \frac{\epsilon_k - \epsilon_0}{\hbar} \\ &\quad \text{transition frequency} \\ W_{k0} &= \langle \varphi_k | \hat{W} | \varphi_0 \rangle \;=\; \lambda \langle \varphi_k | \hat{w} | \varphi_0 \rangle \\ &\quad \text{transition matrix element} \\ p_{0\to k} &= \frac{1}{\hbar^2} \left| \int_{t_0}^{t} e^{i\omega_{k0}t'} W_{k0}(t')\, dt' \right|^2 \\ &\quad \text{transition probability} \end{aligned}$$

What about the 'elastic channel' ($k = 0$)?
the calculation of the probability that the system remains in the initial state is a bit trickier due to the occurrence of the '1' in c_0. To be consistent in the orders of the smallness parameter λ one has to consider

$$\begin{aligned} p_{0\to 0} &= |c_0^{(0)} + \lambda c_0^{(1)} + \lambda^2 c_0^{(2)} + \ldots |^2 \\ &= 1 + \lambda(c_0^{(1)} + c_0^{(1)*}) + \lambda^2(c_0^{(2)} + c_0^{(2)*} + |c_0^{(1)}|^2) + O(\lambda^3) \\ &= 1 + \lambda^2(2Re(c_0^{(2)}) + |c_0^{(1)}|^2) + O(\lambda^3) \\ &= \ldots = 1 - \sum_{k\neq 0} p_{0\to k} \end{aligned} \tag{3.28}$$

the latter result can be worked out explicitly and is not surprising: it expresses probability conservation.

Examples

(i) Slowly varying perturbation
Let's assume that the perturbation is turned on very gently after $t = t_0$. It might then stay constant for a while and/or is turned off equally gently. This is to say that the time derivative of $\hat{W}$ is a very small quantity for all times.

$\boxed{k \neq 0}$

$$\begin{aligned}
\hookrightarrow \quad c_k(t) &= -\frac{i}{\hbar}\int_{t_0}^{t} e^{i\omega_{k0}t'} W_{k0}(t')\, dt' \\
&= -\frac{i}{\hbar}\Big[\frac{1}{i\omega_{k0}} e^{i\omega_{k0}t'} W_{k0}(t')\Big|_{t_0}^{t} - \frac{1}{i\omega_{k0}}\int_{t_0}^{t} e^{i\omega_{k0}t'} \dot{W}_{k0}(t')\, dt'\Big] \\
&\overset{\dot{W}_{k0}\approx 0}{\equiv} -\frac{\langle\varphi_k|\hat{W}(t)|\varphi_0\rangle}{\epsilon_k - \epsilon_0} e^{i\omega_{k0}t}
\end{aligned}$$

let's plug this into the time-dependent state vector:

$$\begin{aligned}
|\psi(t)\rangle &= \sum_k c_k(t) e^{-\frac{i}{\hbar}\epsilon_k t}|\varphi_k\rangle \\
&= c_0(t) e^{-\frac{i}{\hbar}\epsilon_0 t}|\varphi_0\rangle + \sum_{k\neq 0} \frac{\langle\varphi_k|\hat{W}(t)|\varphi_0\rangle}{\epsilon_0 - \epsilon_k} e^{-\frac{i}{\hbar}\epsilon_0 t}|\varphi_k\rangle
\end{aligned}$$

the amplitude c_0 can be set equal to 1. This introduces at most a small phase error (up to first order)

$$\begin{aligned}
\hookrightarrow \quad |\psi(t)\rangle &= \Big(|\varphi_0\rangle + \sum_{k\neq 0} \frac{\langle\varphi_k|\hat{W}(t)|\varphi_0\rangle}{\epsilon_0 - \epsilon_k}|\varphi_k\rangle\Big) e^{-\frac{i}{\hbar}\epsilon_0 t} \\
&\equiv |\varphi_0(t)\rangle e^{-\frac{i}{\hbar}\epsilon_0 t} \qquad (3.29)
\end{aligned}$$

comparing this to the general results of *stationary* PT one can interpret $|\varphi_0(t)\rangle$ as the first-order eigenstate of $\hat{H}(t) = \hat{H}_0 + \hat{W}(t)$ with eigenenergy $\epsilon_0^{(1)}(t) = \epsilon_0 + \langle\varphi_0|\hat{W}(t)|\varphi_0\rangle$. The system is in the ground state of the instantaneous Hamiltonian $\hat{H}(t)$ at all times. This situation is called *adiabatic*.

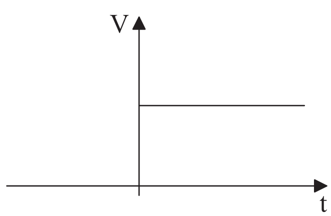
<u>Comments</u>:

(i) The argument can be generalized to strong perturbations. The general *adiabatic approximation* then results in the statement: if the perturbation varies slowly with time, the system is found in an eigenstate of $\hat{H}(t)$ at all times.

(ii) Adiabatic conditions are realized, e.g., if atom beams are directed through slowly varying magnetic fields ($\rightarrow$ Stern-Gerlach experiment) and in slow atomic collisions. In the latter case the electrons adapt to the slowly varying Coulomb potentials of the (classically) moving nuclei and do not undergo transitions. They are in so-called quasimolecular states during the collision and back in their initial atomic states thereafter.

(iii) further reading: [Boh], Chap. 20; [Gri], Chap. 10

(ii) Sudden perturbation



$$\hat{W}(t) = \begin{cases} 0 & t \leq t_0 \equiv 0 \\ \hat{W} & t > t_0 \end{cases}$$

$\boxed{k \neq 0}$

$$\hookrightarrow \quad c_k(t) = -\frac{i}{\hbar}\int_0^t e^{i\omega_{k0}t'} W_{k0}(t')\,dt' = \frac{\langle\varphi_k|\hat{W}|\varphi_0\rangle}{i\hbar}\int_0^t e^{i\omega_{k0}t'}\,dt' = -\frac{\langle\varphi_k|\hat{W}|\varphi_0\rangle}{\hbar\omega_{k0}}\left(e^{i\omega_{k0}t}-1\right)$$

$\hookrightarrow$ transition probability

$$p_{0\rightarrow k}(t) = |c_k(t)|^2 = \frac{4|W_{k0}|^2}{\hbar^2} f(t,\omega_{k0}) \tag{3.30}$$

$$f(t,\omega_{k0}) = \frac{\sin^2\frac{\omega_{k0}t}{2}}{\omega_{k0}^2} \overset{\omega_{k0}\rightarrow 0}{\longrightarrow} \frac{t^2}{4} \tag{3.31}$$

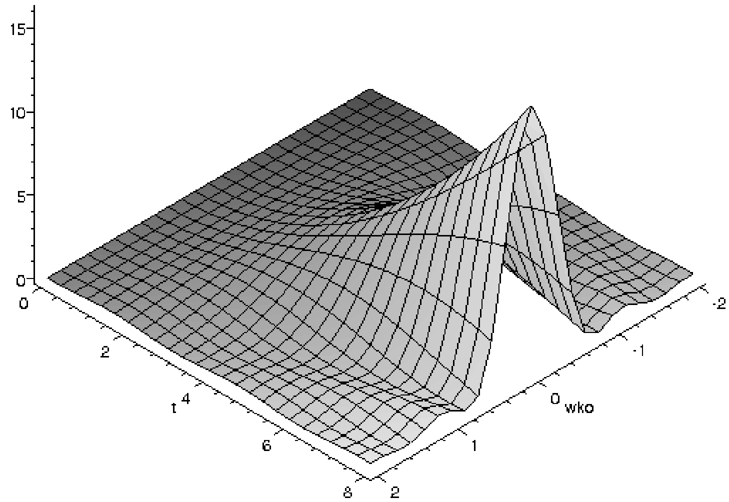


Figure 3.1: $y = f(t, \omega_{k0})$

Significant transitions occur only around $\omega_{k0} = 0$ within the width $\Delta\omega = \frac{2\pi}{t}$. This is a manifestation of the energy-time uncertainty relation: if one waits long enough, transitions can only occur into states that have the same energy as the initial state. One can state this more precisely (mathematically) by considering the limit $t \longrightarrow \infty$:

$$f(t, \omega_{k0}) \quad \stackrel{t\to\infty}{\longrightarrow} \quad \frac{\pi t}{2}\delta(\omega_k - \omega_0) \tag{3.32}$$

$$\hookrightarrow \quad p_{0\to k} \quad \stackrel{t\to\infty}{\longrightarrow} \quad \frac{2\pi t}{\hbar}|W_{k0}|^2\delta(\omega_k - \omega_0)$$

The sudden perturbation sounds academic, but it has an important application (see later).

(iii) Periodic perturbation

$$\hat{W}(t) = \begin{cases} 0 & t \leq t_0 = 0 \\ \hat{B}e^{i\omega t} + \hat{B}^\dagger e^{-i\omega t} & t > t_0 \end{cases} \tag{3.33}$$

(note that $\hat{W} = \hat{W}^\dagger$)

$$\hookrightarrow \quad c_k(t) = \frac{1}{i\hbar}\int_0^t e^{i\omega_{k0}t'} W_{k0}(t')\, dt'$$
$$= -\frac{1}{\hbar}\left\{ \frac{\langle\varphi_k|\hat{B}|\varphi_0\rangle}{\omega_{k0}+\omega}\left(e^{i(\omega_{k0}+\omega)t} - 1\right) + \frac{\langle\varphi_k|\hat{B}^\dagger|\varphi_0\rangle}{\omega_{k0}-\omega}\left(e^{i(\omega_{k0}-\omega)t} - 1\right)\right\}$$

if $t \gg \frac{2\pi}{\omega}$ (i.e. $\Delta\omega \ll \omega$):

$$p_{0\to k}(t) = \frac{4|B_{k0}|^2}{\hbar^2}\left\{ f(t,\omega_{k0}+\omega) + f(t,\omega_{k0}-\omega)\right\} \tag{3.34}$$

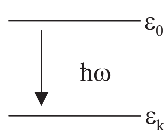
$$\xrightarrow{t\to\infty} \quad \frac{2\pi t}{\hbar}|B_{k0}|^2\left\{\delta(\omega_k - \omega_0 + \omega) + \delta(\omega_k - \omega_0 - \omega)\right\}$$

with $B_{k0} = \langle\varphi_k|\hat{B}|\varphi_0\rangle$ and Eq. (3.31)

Comments:

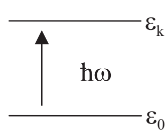
(i) 'Resonances' at $\omega_{k0} = \pm\omega$: significant transitions occur only around these frequencies

- $\omega_{k0} = -\omega \iff \epsilon_k = \epsilon_0 - \hbar\omega$



stimulated emission (of energy)
(only possible if φ_0 is not the ground state)

- $\omega_{k0} = +\omega \iff \epsilon_k = \epsilon_0 + \hbar\omega$



absorbtion (of energy)

(ii) Since φ_0 is not the ground state in the case of stimulated emission it makes sense to change the notation and use φ_i for the initial and φ_f for the final state. Transition frequencies are then denoted as ω_{fi} etc.

(iii) We were careful enough to write that energy is emitted or absorbed if the resonance conditions are met. We can't tell in which form this happens. Later we will see that the energy is carried by photons if the perturbation is exerted on the atom by the *quantized* radiation field. The perturbation derived in Sec. 3.1 corresponds to a classical radiation field. Let's stick to this case first and convince ourselves that it can be written in the form (3.33).

(iv) Connection to atom-radiation interaction
In Sec. 3.1 we found that for weak EM fields the perturbation takes the form

$$\hat{W} = \frac{e}{m}\mathbf{A}\cdot\hat{\mathbf{p}} \tag{3.35}$$

If we use Eq. (3.14) for a monochromatic field we obtain

$$\begin{aligned}\hat{W} &= \frac{e}{2m}\left(A_0 e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)}\hat{\pi}\cdot\hat{\mathbf{p}} + A_0^* e^{-i(\mathbf{k}\cdot\mathbf{r}-\omega t)}\hat{\pi}\cdot\hat{\mathbf{p}}\right)\\ &= \hat{B}e^{i\omega t} + \hat{B}^\dagger e^{-i\omega t}\end{aligned}$$

with

$$\hat{B} = \frac{e}{2m}A_0^* e^{-i\mathbf{k}\cdot\mathbf{r}}\hat{\pi}\cdot\hat{\mathbf{p}} \tag{3.36}$$

(v) Validity of first-order time-dependent perturbation theory
We have two conditions to fulfill to be able to apply our results for the periodic perturbation:

- criterion to avoid overlap of the resonances

$$\Delta\omega = \frac{2\pi}{t} \ll \omega \quad \Leftrightarrow \quad t \gg \frac{2\pi}{\omega}$$

- validity criterion on resonance

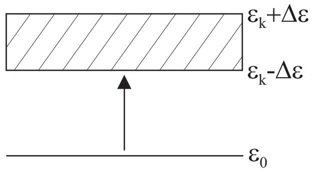
$$\begin{aligned}p_{i\to f} &= \frac{4|B_{fi}|^2}{\hbar^2}f(t,\omega_{fi}\pm\omega=0) = \frac{|B_{fi}|^2}{\hbar^2}t^2 \ll 1\\ \Leftrightarrow \quad t &\ll \frac{\hbar}{|B_{fi}|}\end{aligned}$$

$$\begin{aligned}\xrightarrow{\text{combine}} \quad \frac{2\pi}{\omega} &= \frac{2\pi}{|\omega_{fi}|} \ll \frac{\hbar}{|B_{fi}|}\\ \Leftrightarrow \quad |\Delta\epsilon_{fi}| &\gg |B_{fi}|\end{aligned}$$

3.3 Photoionization

Let us elaborate on the case of absorption. If the energy, i.e., the field frequency ω is high enough, the atom will be ionized. The final state of the electron will then be a continuum state and this requires some additional considerations, since such a state is not normalizable. This implies that $p_{i\to f} = |\langle\varphi_f||\psi(t)\rangle|^2$ is a probability density rather than a probability. A proper probability is obtained if one integrates over an interval of final states

a) Transitions into the continuum[1].



$$P_{i\to f} := \int_{\epsilon_f-\Delta\epsilon}^{\epsilon_f+\Delta\epsilon} p_{i\to f}(\epsilon_{f'})\rho(\epsilon_{f'})\; d\epsilon_{f'} \quad (3.37)$$

with $\rho(\epsilon_{f'})$: density of states $\Big($in interval $[\epsilon_f - \Delta\epsilon; \epsilon_f + \Delta\epsilon]\Big)$

Let's be a bit more specific and calculate the density of states for free-particle continuum states

$$\varphi_f(\mathbf{r}) = \langle\mathbf{r}|\mathbf{p}\rangle = \frac{1}{[2\pi\hbar]^{3/2}}\exp(\frac{i}{\hbar}\mathbf{p}\cdot\mathbf{r})$$

These states are 'normalized' with respect to δ-functions:

$$\langle\mathbf{p}|\mathbf{p}'\rangle = \int\langle\mathbf{p}|\mathbf{r}\rangle\langle\mathbf{r}|\mathbf{p}'\rangle\, d^3r = \frac{1}{[2\pi\hbar]^{3/2}}\int\exp[\frac{i}{\hbar}(\mathbf{p}'-\mathbf{p})\cdot\mathbf{r}]d^3r = \delta(\mathbf{p}'-\mathbf{p})$$

Nevertheless, they fulfill a completeness relation (like the position eigenstates $|\mathbf{r}\rangle$) such that for any (normalized) state $|\psi\rangle$

$$1 = \langle\psi|\psi\rangle = \int\langle\psi|\mathbf{p}\rangle\langle\mathbf{p}|\psi\rangle\, d^3p = \int|\psi(\mathbf{p})|^2\, d^3p$$

and the density of states with respect to momentum is simply $\rho(\mathbf{p}) = 1$. We need to transform this from momentum to energy. For free particles we have

[1]Unfortunately, the figure doesn't correspond to the $i \to f$ notation, but I cannot change it easily!

the simple relation $\epsilon_f = \mathbf{p}^2/2m$ such that

$$\begin{aligned}
\hookrightarrow \quad d^3p &= p^2 dp d\Omega_p = p^2 \frac{dp}{d\epsilon_f} d\epsilon_f d\Omega_p \\
&= \sqrt{2m^3\epsilon_f}\, d\epsilon_f d\Omega_p \\
\hookrightarrow \quad 1 &= \int |\psi(\mathbf{p})|^2\, d^3p = \int \sqrt{2m^3\epsilon_f} \Big(\int |\psi(\mathbf{p})|^2 d\Omega_p \Big) d\epsilon_f \\
&= \int \rho(\epsilon_f) p_{i\to f}(\epsilon_f) d\epsilon_f
\end{aligned}$$

with

$$\rho(\epsilon_f) = \sqrt{2m^3\epsilon_f}$$

Let's go back to the probability (3.37) and insert the first-order result (3.34):

$$\begin{aligned}
P_{i\to f} &= \frac{4}{\hbar^2} \int_{\epsilon_f-\Delta\epsilon}^{\epsilon_f+\Delta\epsilon} |B_{f'i}|^2 \rho(\epsilon_{f'}) \Big\{ f(t, \omega_{f'i}+\omega) + f(t, \omega_{f'i}-\omega) \Big\} d\epsilon_{f'} \\
P^{\text{abs}}_{i\to f} &\approx \frac{4}{\hbar^2} |B_{fi}|^2 \rho(\epsilon_f) \int_{\epsilon_f-\Delta\epsilon}^{\epsilon_f+\Delta\epsilon} f(t, \omega_{f'i}-\omega) d\epsilon_{f'} \\
&\approx \frac{4}{\hbar} |B_{fi}|^2 \rho(\epsilon_f) \int_{-\infty}^{\infty} \frac{\sin^2(\frac{\tilde\omega t}{2})}{\tilde\omega^2} d\tilde\omega \\
&= \frac{2\pi}{\hbar} |B_{fi}|^2 \rho(\epsilon_f) t
\end{aligned}$$

where we have used $\int_{-\infty}^{\infty} \frac{\sin^2(\frac{\tilde\omega t}{2})}{\tilde\omega^2} d\tilde\omega = \frac{\pi t}{2}$. A similar result is obtained for the case of emission. One defines a transition rate $\mathrm{w}_{i\to f} = \frac{d}{dt} P_{i\to f}$ to obtain

Fermi's Golden Rule (FGR)

$$\mathrm{w}^{e,a}_{i\longrightarrow f} = \frac{2\pi}{\hbar} |B_{fi}|^2 \rho(\epsilon_f) \Big|_{\epsilon_f = \epsilon_i \pm \hbar\omega} \tag{3.38}$$

b) Dipole approximation

In a typical photoionization experiment the wavelength of the applied EM field is large compared to the size of the atom. This allows for a simplification, which is called the dipole approximation:

$$\text{if } \lambda = \frac{2\pi}{k} \gg a_0 \qquad \Rightarrow e^{i\mathbf{k}\cdot\mathbf{r}} \approx 1$$

$$\overset{(3.36)}{\hookrightarrow} \qquad B_{fi}^{\text{dip}} = \frac{e}{2m} A_0^* \langle \varphi_f | \hat{\pi} \cdot \hat{\mathbf{p}} | \varphi_i \rangle$$

this can be rewritten by using

$$\hat{\mathbf{p}} = \frac{im}{\hbar} [\hat{H}_0, \mathbf{r}] \tag{3.39}$$

for $\hat{H}_0 = \frac{\mathbf{p}^2}{2m} + V(\mathbf{r})$

$$\begin{aligned} \hookrightarrow \qquad \langle \varphi_f | \hat{\pi} \cdot \hat{\mathbf{p}} | \varphi_i \rangle &= \frac{im}{\hbar} \langle \varphi_f | \hat{H}_0 \hat{\pi} \cdot \hat{\mathbf{r}} - \hat{\pi} \cdot \hat{\mathbf{r}} \hat{H}_0 | \varphi_i \rangle \\ &= \frac{im}{\hbar} (\epsilon_f - \epsilon_i) \hat{\pi} \cdot \langle \varphi_f | \mathbf{r} | \varphi_i \rangle \end{aligned}$$

The matrix elements in questions are the well-known dipole matrix elements (cf. Sec. 2). For $\hat{\pi} = \hat{z}$ we have the standard selection rules $\Delta m = 0, \Delta l = \pm 1$[2]. They result in characteristic angular dependencies of photoionized electrons, e.g., (see assignment # 3)

$$\begin{aligned} \mathrm{w}_{i \longrightarrow f}^{\text{dip},\hat{z}} &= \frac{\pi e^2}{2\hbar^3} |A_0|^2 (\epsilon_f - \epsilon_i)^2 \rho(\epsilon_f) |\langle \varphi_f | z | \varphi_i \rangle|^2 \\ &\propto \cos^2 \theta \end{aligned}$$

if the initital state is an s-state ($l = 0$).

Literature: [CT], Chap. XIII; [Lib], Chap. 13.5-13.9; [Sch], Chap. 11; [BS], Chap. IV

Note that the notion of photons for the interpretation of photoionization (and stimulated emission) has no significance as long as the analysis is based on *classical* EM fields. From a theoretical point of view photons come into the picture only if the EM field is quantized. This does not change the final

[2] for other polarizations the m-selection rule changes, but the l-selection rule does not.

expressions for stimulated emission and absorbtion, but it shows that there is another process which cannot be described in our semiclassical framework: *spontaneous* emission, i.e., the emission of a photon (and transition to a lower-lying state) without any external EM field. So, let's take a look at field quantization.

3.4 Outlook on field quantization

In the semiclassical framework we represented the EM field by classical potentials $(\mathbf{A}, \Phi)$, which act on the wave function of the electron(s). Now, we want to derive a Hamiltonian that acts on the electron(s) and the EM field. Accordingly, we need a wave function that includes the degrees of freedom of the field.

Let's start with the Hamiltonian. The generic ansatz for a system that consists of two subsystems (atom and EM field in our case) which may interact is as follows:

$$\begin{aligned} \hat{H} &= \hat{H}_1 + \hat{H}_2 + \hat{W} \\ \hat{H} &= \underbrace{\hat{H}_A + \hat{H}_F}_{=\hat{H}_0} + \hat{W} \end{aligned} \tag{3.40}$$

$\hat{H}_A$ is the Hamiltonian of the atom, $\hat{H}_F$ the (yet unknown) Hamiltonian of the field, and $\hat{W}$ the interaction. We aim at a description of the problem within first-order perturbation theory. So we know which steps we have to take:

Steps for a first-order TDPT treatment

- determine $\hat{H}_0$
  (a) $\hat{H}_A = \frac{\hat{\mathbf{p}}^2}{2m} + V$ $\surd$
  (b) $\hat{H}_F = ?$

- solve eigenvalue problem of $\hat{H}_0$

$$\begin{aligned}
\hat{H}_A|\varphi_j\rangle &= \epsilon_j \; |\varphi_j\rangle \; \checkmark \\
\hat{H}_F|\xi_k\rangle &= \varepsilon_k \; |\xi_k\rangle \; ? \qquad (3.41a) \\
\hookrightarrow \hat{H}_0|\Phi_{jk}\rangle &= \left(\hat{H}_A + \hat{H}_F\right) \; |\varphi_j\rangle|\xi_k\rangle \\
&= (\epsilon_j + \varepsilon_k) \; |\varphi_j\rangle|\xi_k\rangle \\
&= (\epsilon_j + \varepsilon_k) \; |\Phi_{jk}\rangle \qquad (3.41b)
\end{aligned}$$

While the first step (determining $\hat{H}_0$) is a physics problem, the second one (solving $\hat{H}_0$'s eigenvalue problem) is a math problem.

- determine $\hat{W}$
here it seems natural to start from the semiclassical expression (3.35) and replace the classical vector potential by an operator that acts on the degrees of freedom of the EM field

$$\hat{W} = \frac{e}{m}\hat{\mathbf{A}} \cdot \hat{\mathbf{p}} \qquad (3.42)$$

Not surprisingly, it turns out that consistency with the form of $\hat{H}_F$ determines the form of $\hat{\mathbf{A}}$

- apply FGR
the main issue here is to calculate the transition matrix elements

$$W_{if} = \langle\Phi_f|\hat{W}|\Phi_i\rangle \qquad (3.43)$$

a) Construction of $\hat{H}_F$

Loosely speaking, Hamiltonians are the quantum analogs of classical energy expressions. Let's look at the energy of a classical EM field in a cube of volume L^3

$$\begin{aligned}
W_{\mathrm{EM}} &= \frac{1}{2}\int_{L^3} (\mathbf{E}\cdot\mathbf{D} + \mathbf{B}\cdot\mathbf{H}) d^3r \\
&= \frac{\epsilon_0}{2}\int_{L^3} (\mathbf{E}^2 + c^2 \; \mathbf{B}^2) d^3r \qquad c^2 = \frac{1}{\mu_0\epsilon_0} \qquad (3.44)
\end{aligned}$$

Recall that free EM waves within Coulomb gauge ($\nabla \cdot \mathbf{A} = 0$) are obtained from

$$\begin{aligned} \nabla^2 \mathbf{A} - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\mathbf{A} &= 0 \\ \Phi &= 0 \end{aligned}$$

Instead of a monochromatic solution of the wave equation we consider the full solution in L^3 for periodic boundary conditions $\mathbf{A}(x, y, z = 0) = \mathbf{A}(x, y, z = L)$ etc. The latter are a convenient means to obtain a set of discrete *modes* and discrete sums in all expressions instead of integrals:

$$\mathbf{A}(\mathbf{r}, t) = \sum_\lambda \mathbf{A}_\lambda(\mathbf{r}, t) \tag{3.45a}$$

$$\Re^3 \ni \mathbf{A}_\lambda(\mathbf{r}, t) = \frac{\hat{\pi}_\lambda}{L^{\frac{3}{2}}} \left\{ q_\lambda e^{i(\mathbf{k}_\lambda \mathbf{r} - \omega_\lambda t)} + q_\lambda^* e^{-i(\mathbf{k}_\lambda \mathbf{r} - \omega_\lambda t)} \right\} \tag{3.45b}$$

λ		mode index	
$\hat{\pi}_\lambda$		unit polarization vectors	$\lvert\hat{\pi}_\lambda\rvert = 1$
$\mathbf{k}_\lambda = \frac{2\pi}{L}(n_x^\lambda, n_y^\lambda, n_z^\lambda)$	$n_i^\lambda \in \mathcal{Z}$	wave vectors and numbers	
$\omega_\lambda = ck_\lambda$		field frequencies	
$\hat{\pi}_\lambda \cdot \mathbf{k}_\lambda = 0$		$\rightarrow$ transverse waves	

Each mode is thus defined by a wave vector (with three components) and a polarization direction[3]. If one uses this explicit form of $\mathbf{A}$ to calculate

$$\begin{aligned} \mathbf{E}(\mathbf{r}, t) &= -\partial_t \mathbf{A}(\mathbf{r}, t) \\ \mathbf{B}(\mathbf{r}, t) &= \nabla \times \mathbf{A}(\mathbf{r}, t) \end{aligned}$$

and plugs this into Eq. (3.44) one arrives at

$$W_{\text{EM}} = 2\epsilon_0 \sum_\lambda \omega_\lambda^2 q_\lambda^* q_\lambda \tag{3.46}$$

[3]this is to say that λ is actually a quadruple index. Note that for the general solution of the wave equation we need two linearly independent polarizations per wave vector. This can be made more explicit by a somewhat more elaborate notation, see, e.g. [Sch], Chap. 14.

Obviously, the EM energy doesn't change with time—this is another (convenient) consequence of using periodic boundary conditions.

The next step is a transformation to real amplitudes:

$$\begin{aligned} Q_\lambda &:= \sqrt{\epsilon_0}\ (q_\lambda^* + q_\lambda) && (3.47)\\ P_\lambda &:= i\sqrt{\epsilon_0}\ \omega_\lambda\ (q_\lambda^* - q_\lambda) && (3.48)\end{aligned}$$

$$\begin{aligned} \Leftrightarrow q_\lambda &= \frac{1}{2\sqrt{\epsilon_0}}\left(Q_\lambda + i\frac{P_\lambda}{\omega_\lambda}\right) && (3.49)\\ q_\lambda^* &= \frac{1}{2\sqrt{\epsilon_0}}\left(Q_\lambda - i\frac{P_\lambda}{\omega_\lambda}\right) && (3.50)\end{aligned}$$

$$\begin{aligned} \hookrightarrow\ W_{\mathrm{EM}} &= \frac{1}{2}\sum_\lambda \omega_\lambda^2 (Q_\lambda + i\frac{P_\lambda}{\omega_\lambda})\left(Q_\lambda - i\frac{P_\lambda}{\omega_\lambda}\right) && (3.51)\\ &= \frac{1}{2}\sum_\lambda \left(P_\lambda^2 + \omega_\lambda^2\ Q_\lambda^2\right) && (3.52)\end{aligned}$$

Doesn't this look familiar? The EM field has the algebraic form of a collection of harmonic oscillators. We know how to quantize the harmonic oscillator, so here is the quantization recipe:

$$\begin{aligned} P_\lambda &\quad\rightarrow\quad \hat{P}_\lambda = \hat{P}_\lambda^\dagger && (3.53)\\ Q_\lambda &\quad\rightarrow\quad \hat{Q}_\lambda = \hat{Q}_\lambda^\dagger && (3.54)\\ \text{with}\quad [\hat{Q}_\lambda, \hat{P}_{\lambda'}] &= i\hbar\delta_{\lambda\lambda'} && (3.55)\end{aligned}$$

$$\hookrightarrow \quad W_{\mathrm{EM}} \rightarrow \hat{H}_F = \frac{1}{2}\sum_\lambda \left(\hat{P}_\lambda^2 + \omega^2\ \hat{Q}_\lambda^2\right) = \hat{H}_F^\dagger \qquad (3.56)$$

The algebraic form of $\hat{H}_F$ together with the commutation relations (3.55) determine its spectrum:

$$E_{n_1,n_2,\ldots} = \sum_\lambda \hbar\,\omega_\lambda\left(n_\lambda + \frac{1}{2}\right) \qquad n_\lambda = 0, 1, 2, \ldots$$

The standard QM interpretation would be to associate each mode with a particle trapped in a parabolic potential. The energies $E_{n_\lambda} = \hbar\,\omega_\lambda\ (n_\lambda + \frac{1}{2})$

would then correspond to the ground- and the excited-state levels of that particle. However, it is not clear what kind of particle this should be, since Q_λ and P_λ do not correspond to usual position and momentum variables (and actually there is no parabolic potential around).

The fact that the spectrum is equidistant allows for an alternate interpretation, in which each mode is associated with n_λ 'quanta' [4], each of which carries the energy $\hbar\omega_\lambda$. In this interpretation a mode does not have a ground state and excited states, but is more like a (structureless) container that can accomodate (any number of) quanta of a given energy. The quanta are called **photons**. At this point their only property is that they carry energy, but we will see later that there is more in store. Note that the photon interpretation is only possible because the spectrum of the harmonic oscillator is equidistant!

n_λ : occupation number of mode λ

$N = \sum_\lambda n_\lambda$: total number of photons in the field

However, even without any photon around there is energy, unfortunately even an infinite amount:

$$\text{zero-point energy} \qquad E_0 = \sum_\lambda \frac{\hbar\,\omega_\lambda}{2} \;\rightarrow\; \infty \tag{3.57}$$

A proper treatment of this infinite zero-point energy requires a so-called renormalization procedure. We will not dwell on this issue, but (try to) put our minds at ease with the remark that normally only energy differences have physical significance[5]. These are always finite since the zero-point energies cancel.

b) Creation and annihilation operators

For the further development it is useful to introduce creation and annihilation operators:

$$\hat{b}_\lambda = \frac{1}{\sqrt{2\hbar\,\omega_\lambda}}\,(\omega_\lambda\,\hat{Q}_\lambda + i\hat{P}_\lambda) \quad \text{anniliation op.} \tag{3.58}$$

$$\hat{b}^\dagger_\lambda = \frac{1}{\sqrt{2\hbar\,\omega_\lambda}}\,(\omega_\lambda\,\hat{Q}_\lambda - i\hat{P}_\lambda) \quad \text{creation op.} \tag{3.59}$$

[4] you may say particles instead of quanta, but these particles turn out to have an odd property: zero rest mass.

[5] In fact, renormalization is not much more than a more formal way of adopting this viewpoint.

Let's play with them and look at their commutators, e.g.

$$\sphericalangle \qquad \left[\hat{b}_\lambda\ ,\ \hat{b}^\dagger_\lambda\right] = \frac{1}{2\hbar\ \omega_\lambda}\left[\omega_\lambda\ \hat{Q}_\lambda + i\hat{P}_\lambda\ ,\ \omega_\lambda\ \hat{Q}_\lambda - i\hat{P}_\lambda\right]$$

$$= \frac{1}{2\hbar\ \omega_\lambda}\left\{-i\omega_\lambda\ \underbrace{\left[\hat{Q}_\lambda\ ,\ \hat{P}_\lambda\right]}_{i\hbar} + i\omega_\lambda\ \underbrace{\left[\hat{P}_\lambda, \hat{Q}_\lambda\right]}_{-i\hbar}\right\}$$

$$= \frac{1}{2\hbar\ \omega_\lambda}\left\{\hbar\ \omega_\lambda\ + \hbar\ \omega_\lambda\ \right\} = 1$$

$$\Rightarrow \qquad \left[\hat{b}_\lambda, \hat{b}^\dagger_{\lambda'}\right] = \delta_{\lambda\lambda'} \tag{3.60}$$

$$\left[\hat{b}_\lambda\ , \hat{b}_{\lambda'}\right] = 0 \tag{3.61}$$

$$\left[\hat{b}^\dagger_\lambda\ , \hat{b}^\dagger_{\lambda'}\right] = 0 \tag{3.62}$$

$\hookrightarrow$ rewrite the Hamiltonian

$$\hat{H}_F = \frac{1}{2}\sum_\lambda\ \left(\hat{P}^2_\lambda + \omega^2\ \hat{Q}^2_\lambda\right)$$

$$= \frac{1}{2}\sum_\lambda\ \left\{-\frac{\hbar\ \omega_\lambda}{2}(\hat{b}^\dagger_\lambda - \hat{b}_\lambda)^2 + \frac{\hbar\ \omega_\lambda}{2}(\hat{b}^\dagger_\lambda + \hat{b}_\lambda)^2\right\}$$

$$= \frac{1}{2}\sum_\lambda\ \hbar\ \omega_\lambda\ \left(\hat{b}^\dagger_\lambda\ \hat{b}_\lambda + \hat{b}_\lambda\ \hat{b}^\dagger_\lambda\right) \tag{3.63}$$

$$= \sum_\lambda\ \hbar\ \omega_\lambda\ (\hat{b}^\dagger_\lambda\ \hat{b}_\lambda + \frac{1}{2})$$

$$= \sum_\lambda\ \hbar\ \omega_\lambda\ (\hat{n}_\lambda + \frac{1}{2}) \tag{3.64}$$

$\hat{n}_\lambda = \hat{b}^\dagger_\lambda\ \hat{b}_\lambda$ is called occupation number operator.

Obviously $\left[\hat{H}_F, \hat{n}_\lambda\right] = 0 \quad \forall\ \lambda$, i.e., they have the same eigenstates. Let's first consider a single mode only:

$$\begin{aligned}\hat{H}_F &= \sum_\lambda \hat{H}_F^\lambda \\ \hat{H}_F^\lambda \, |\psi_{n_\lambda}\rangle &= \hbar\,\omega_\lambda (n_\lambda + \frac{1}{2}) \, |\psi_{n_\lambda}\rangle \\ &\quad \text{with} \quad n_\lambda \in N_0\end{aligned} \tag{3.65}$$

Usually, one uses a short-hand notation for the eigenstates and writes $|\psi_{n_\lambda}\rangle \equiv |n_\lambda\rangle$. These states are called (photon) number or Fock states. Note that $|\psi_0\rangle \equiv |0\rangle$ is not a vector of zero length, but the (ground) state associated with the statement that there are no photons in the mode (but energy $E_0 = \hbar\omega_\lambda/2$). As eigenstates of a hermitian operator the $|n_\lambda\rangle$ fulfill an orthonormality relation

$$\langle n_\lambda | n'_\lambda \rangle = \delta_{n_\lambda n'_\lambda} \tag{3.66}$$

$$\hookrightarrow \quad \hat{n_\lambda}\, |n_\lambda\rangle \;=\; n_\lambda \, |n_\lambda\rangle \qquad \left(\hat{n}_\lambda = \frac{\hat{H}_F^\lambda - \frac{1}{2}}{\hbar\,\omega_\lambda} \right) \tag{3.67}$$

$$\hat{n_\lambda}\, |0\rangle \;=\; 0|0\rangle = 0 \qquad \text{this is a real zero!} \tag{3.68}$$

The eigenvalue n_λ is the number of photons in the mode. This justifies the name occupation number operator for $\hat{n}_\lambda$.

Let's operate with creation and annihilation operators on these photon number states. To do this we need a few relations that can be proven without difficulty.

$$\left[\hat{b}_\lambda, \hat{n}_{\lambda'}\right] = \hat{b}_\lambda \, \delta_{\lambda\lambda'} \tag{3.69}$$

$$\left[\hat{b}_\lambda^\dagger, \hat{n}_{\lambda'}\right] = -\hat{b}_\lambda^\dagger \, \delta_{\lambda\lambda'} \tag{3.70}$$

$$\begin{aligned}\lessdot \qquad \hat{n}_\lambda \left(\hat{b}_\lambda^\dagger \, |n_\lambda\rangle\right) &= \hat{b}_\lambda^\dagger \, \hat{n}_\lambda \, |n_\lambda\rangle + \hat{b}_\lambda^\dagger \, |n_\lambda\rangle \\ &= (n_\lambda + 1) \left(\hat{b}_\lambda^\dagger \, |n_\lambda\rangle\right)\end{aligned}$$

obviously, the vector $\hat{b}_\lambda^\dagger \; |n_\lambda\rangle$ is an eigenstate of n_λ with the eigenvalue $(n_\lambda + 1)$. On the other hand:

$$\hat{n}_\lambda \; |n_\lambda + 1\rangle = (n_\lambda + 1) \; |n_\lambda + 1\rangle$$

$\hookrightarrow$ combine:

$$\begin{aligned} \hat{b}_\lambda^\dagger \; |n_\lambda\rangle &= \alpha \; |n_\lambda + 1\rangle \\ \Rightarrow \qquad |\alpha|^2 \; \underbrace{\langle n_\lambda + 1 | n_\lambda + 1\rangle}_{=1} &= \langle n_\lambda| \; \hat{b}_\lambda \; \hat{b}_\lambda^\dagger \; |n_\lambda\rangle \\ &= \langle n_\lambda| \; \hat{n}_\lambda + 1 \; |n_\lambda\rangle \\ &= n_\lambda + 1 \end{aligned}$$

$$\Leftrightarrow \qquad \alpha = \sqrt{n_\lambda + 1}$$

$$\hookrightarrow \qquad \hat{b}_\lambda^\dagger \; |n_\lambda\rangle = \sqrt{n_\lambda + 1} \; |n_\lambda + 1\rangle \tag{3.71}$$

This justifies the notion creation operator: operating with it on a number state creates one additional photon. Similarly one finds

$$\hat{b}_\lambda \; |n_\lambda\rangle = \sqrt{n_\lambda} \; |n_\lambda - 1\rangle \tag{3.72}$$

to be consistent with Eq. (3.68) we stipulate

$$\hat{b}_\lambda \; |0\rangle = 0$$

Generalization:

$$\hat{H}_F \; |n_1, n_2, ...\rangle = E \; |n_1, n_2, ...\rangle \tag{3.73}$$

$$E = \sum_\lambda \hbar \, \omega_\lambda \left(n_\lambda + \frac{1}{2} \right) = \sum_\lambda \hbar \, \omega_\lambda \; n_\lambda + E_0 \tag{3.74}$$

$$|n_1, n_2, ...\rangle = |n_1\rangle \; |n_2\rangle ... \qquad \text{product states} \tag{3.75}$$

$$\hat{n_\lambda} \; |... \; n_\lambda \; ...\rangle = n_\lambda \; |... \; n_\lambda \; ...\rangle \tag{3.76}$$

$$\hat{b}_\lambda^\dagger \; |... \; n_\lambda \; ...\rangle = \sqrt{n_\lambda + 1} \; |... \; n_\lambda + 1 \; ...\rangle \tag{3.77}$$

$$\hat{b}_\lambda \; |... \; n_\lambda \; ...\rangle = \sqrt{n_\lambda} \; |... \; n_\lambda - 1 \; ...\rangle \tag{3.78}$$

c) Interaction between electron(s) and photons

We start from Eq. (3.42) and require that the quantization of the vector potential be consistent with the quantization of the EM energy. The latter implies the following quantization rule for the amplitudes:

$$q_\lambda \quad \rightarrow \quad \hat{q}_\lambda = \frac{1}{2\sqrt{\epsilon_0}}\left(\hat{Q}_\lambda + i\frac{\hat{P}_\lambda}{\omega_\lambda}\right) = \sqrt{\frac{\hbar}{2\epsilon_0\omega_\lambda}}\hat{b}_\lambda \tag{3.79}$$

which yields

$$\hat{\mathbf{A}}(\mathbf{r},t) = \sum_\lambda \ \hat{\pi}_\lambda \sqrt{\frac{\hbar}{2\omega_\lambda\epsilon_0 L^3}} \left(\hat{b}_\lambda e^{i(\mathbf{k}_\lambda\cdot\mathbf{r}-\omega_\lambda t)} + \hat{b}_\lambda^\dagger e^{-i(\mathbf{k}_\lambda\cdot\mathbf{r}-\omega_\lambda t)}\right) \tag{3.80}$$

The time dependence of $\hat{\mathbf{A}}$ is the time dependence of an operator in the Heisenberg picture. The corresponding Schrödinger operator reads

$$\hat{\mathbf{A}}(\mathbf{r}) = \sum_\lambda \ \hat{\pi}_\lambda \sqrt{\frac{\hbar}{2\omega_\lambda\epsilon_0 L^3}} \left(\hat{b}_\lambda e^{i\mathbf{k}_\lambda\cdot\mathbf{r}} + \hat{b}_\lambda^\dagger e^{-i\mathbf{k}_\lambda\cdot\mathbf{r}}\right) \tag{3.81}$$

The latter is used in the interaction potential:

$$\begin{aligned}\hat{W} &= \frac{e}{m}\hat{\mathbf{A}}\cdot\hat{\mathbf{p}} \\ &= -i\sum_\lambda \sqrt{\frac{e^2\hbar^3}{2\omega_\lambda\epsilon_0 m^2 L^3}}\ \hat{\pi}_\lambda \left\{\hat{b}_\lambda e^{i\mathbf{k}_\lambda\cdot\mathbf{r}}\ \nabla\ + \hat{b}_\lambda^\dagger e^{-i\mathbf{k}_\lambda\cdot\mathbf{r}}\ \nabla\ \right\} \end{aligned} \tag{3.82}$$

Not surprisingly, the interaction has a part that acts on the electron and a part that acts on the photons. The electronic part is the same as in the semi-classical treatment. The photonic part involves the creation or annihilation of a photon in the mode λ.

d) Transitions matrix elements

We need

$$\begin{aligned} W_{if} &= \langle\Phi_f|\hat{W}|\Phi_i\rangle = \sum_\lambda \langle\Phi_f|\hat{W}_\lambda|\Phi_i\rangle \\ \langle\Phi_f|\hat{W}_\lambda|\Phi_i\rangle &= -i\sqrt{\frac{e^2\hbar^3}{2\omega_\lambda\epsilon_0 m^2 L^3}} \\ &\quad \times \{\langle\varphi_f|\ e^{i\mathbf{k}_\lambda\cdot\mathbf{r}}\ \hat{\pi}_\lambda\cdot\nabla\ |\varphi_i\rangle\ \langle n_1^f\ ...\ n_\lambda^f\ ...|\ \hat{b}_\lambda\ |n_1^i\ ...\ n_\lambda^i\ ...\rangle \\ &\quad + \langle\varphi_f|\ e^{-i\mathbf{k}_\lambda\cdot\mathbf{r}}\ \hat{\pi}_\lambda\cdot\nabla\ |\varphi_i\rangle\ \langle n_1^f\ ...\ n_\lambda^f\ ...|\ \hat{b}_\lambda^\dagger\ |n_1^i\ ...\ n_\lambda^i\ ...\rangle\} \end{aligned}$$

The electronic matrix elements are the same as in the semiclassical framework. We have discussed them in dipole approximation in Sec. 3.3. Let's look at the photonic matrix elements. Basically, they result in selection rules:

$$\langle n_1^f \ ... \ n_\lambda^f \ ...| \ \hat{b}_\lambda \ |n_1^i \ ... \ n_\lambda^i \ ...\rangle = \sqrt{n_\lambda^i} \ \langle n_1^f \ ... \ n_\lambda^f \ ...|n_1^i \ ... \ n_\lambda^i - 1 \ ...\rangle \quad (3.83)$$

noting that $\langle n_f | n_i \rangle = \delta_{fi}$ in each mode one obtains

$$\langle n_1^f \ ... \ n_\lambda^f \ ...| \ \hat{b}_\lambda \ |n_1^i \ ... \ n_\lambda^i \ ...\rangle = \sqrt{n_\lambda^i} \ \delta_{n_1^f n_1^i} \ \delta_{n_2^f n_2^i} ... \delta_{n_\lambda^f n_\lambda^i - 1} ... \quad (3.84)$$

and similarly

$$\langle n_1^f \ ... \ n_\lambda^f \ ...| \ \hat{b}_\lambda^\dagger \ |n_1^i \ ... \ n_\lambda^i \ ...\rangle = \sqrt{n_\lambda^i + 1} \ \delta_{n_1^f n_1^i} \ \delta_{n_2^f n_2^i} ... \delta_{n_\lambda^f n_\lambda^i + 1} ... \quad (3.85)$$

We obtain a nonvanishing contribution only if the number of photons in one mode λ differs by one in the initial and final states, but is the same in all other modes. Obviously, the annihilation process (3.84) corresponds to photon absorption (one photon less in the final state than in the initial state) and the creation process (3.85) to photon emission (one photon more in the final state than in the initial state).

Summary:

$$\langle \Phi_f | \hat{W} | \Phi_i \rangle \neq 0 \qquad \text{iff}$$

1. the photon numbers in $|\Phi_i\rangle$ and $|\Phi_f\rangle$ differ exactly by one in one single mode. Otherwise orthogonality will kill the transition amplitude. This is to say that first-order perturbation theory accounts for one-photon processes only.

2. dipole selection rules are fulfilled for the crucial mode (assuming that $e^{i\mathbf{k}_\lambda \cdot \mathbf{r}} \approx 1$).

3. energy conservation is fulfilled: $E_i = E_f$. This follows from the fact that the total Hamiltonian is time independent and is also consistent with the application of TDPT for a time-independent perturbation (cf. example (ii) of Sec. 3.2 b)).

Elaborate on energy conservation: noting that the energy eigenvalues of electronic and photonic parts add (cf. Eq. (3.41b)) we find

$$E_i = \epsilon_i + \sum_{\lambda'} \hbar\omega_{\lambda'} \left(n^i_{\lambda'} + \frac{1}{2} \right) \tag{3.86}$$

$$E_f = \epsilon_f + \sum_{\lambda'} \hbar\omega_{\lambda'} \left(n^f_{\lambda'} + \frac{1}{2} \right) \tag{3.87}$$

$$E_i = E_f \quad \Leftrightarrow \quad \epsilon_f = \epsilon_i \pm \hbar\omega_\lambda \tag{3.88}$$

with the plus sign for absorption and the minus sign for emission.

e) Spontaneous emission

$\triangleleft \qquad |\Phi_i\rangle = |\varphi_i\rangle|0, 0, \ldots\rangle$

Even if there is no photon around in the initial state we can obtain a nonvanishing transition matrix element by operating with a creation operator on the vacuum state $|0, 0, \ldots\rangle$. This corresponds to the process of *spontaneous emission*: an excited electronic state decays by (one-) photon emission even though no external radiation field is present. One may say that it is the zero-point energy in the given mode that triggers the transition.

For the investigation of the quantitative aspects of spontaneous emission one uses FGR (3.38). The transition rate can be written as

$$\mathrm{w}^{s.e.}_{i\longrightarrow f} = \frac{2\pi}{\hbar}|W_{fi}|^2\rho(e_f) \tag{3.89}$$

$$W_{fi} = -i\sqrt{\frac{e^2\hbar^3}{2\omega\epsilon_0 m^2 L^3}}\langle\varphi_f|e^{-i\mathbf{k}_\lambda\cdot\mathbf{r}}\hat{\pi}_\lambda\cdot\nabla|\varphi_i\rangle \tag{3.90}$$

$$\text{with} \quad \omega = \frac{\epsilon_f - \epsilon_i}{\hbar}$$

The density of states in FGR refers to the photon density in the final states. To calculate it recall

$$\mathbf{k}_\lambda = \frac{2\pi}{L}(n^\lambda_x, n^\lambda_y, n^\lambda_z) \qquad n^\lambda_i \in \mathcal{Z}$$

$$\hookrightarrow \rho(\mathbf{k}) = \frac{\Delta N}{\Delta V} = \frac{\Delta n_x \Delta n_y \Delta n_z}{\Delta k_x \Delta k_y \Delta k_z} = \left(\frac{L}{2\pi}\right)^3$$

We need $\rho = \rho(e_f)$, i.e., we need to transform to energy space:

$$dV = d^3k = k^2 dk d\Omega_k = k^2 \frac{dk}{de_f} de_f d\Omega_k$$

$$\text{photons:} \quad e_f = \hbar\omega = \hbar c k \quad \rightarrow \frac{dk}{de_f} = \frac{1}{\hbar c}$$

$$\hookrightarrow dN = \rho(\mathbf{k}) d^3k = \left(\frac{L}{2\pi}\right)^3 \frac{k^2}{\hbar c} de_f d\Omega_k = \left(\frac{L}{2\pi}\right)^3 \frac{\omega^2}{\hbar c^3} de_f d\Omega_k \equiv \rho(e_f) de_f d\Omega_k$$

Inserting this into Eq. (3.89) one obtains for the (differential) spontaneous emission rate (for a given polarization $\hat{\pi}$):

$$\frac{d\mathrm{w}^{s.e.,\hat{\pi}}_{i\longrightarrow f}}{d\Omega_k} = \frac{e^2\hbar\omega}{8\pi^2\epsilon_0 m^2 c^3} |\langle\varphi_f|e^{-i\mathbf{k}_\lambda\cdot\mathbf{r}}\hat{\pi}_\lambda \cdot \nabla|\varphi_i\rangle|^2$$

In dipole approximation (using once again Eq. (3.39)) this reduces to

$$\frac{d\mathrm{w}^{s.e.,\hat{\pi}}_{i\longrightarrow f}}{d\Omega_k} = \frac{e^2\omega^3}{8\pi^2\epsilon_0\hbar c^3} |\hat{\pi}\cdot\mathbf{r}_{if}|^2 \tag{3.91}$$

$$\mathbf{r}_{if} = \langle\varphi_f|\mathbf{r}|\varphi_i\rangle \tag{3.92}$$

The total rate is obtained by integrating (3.91) over $d\Omega_k$ and summing over two perpendicular (transverse) polarizations. The final result for the inverse lifetime $1/\tau_{i\to f} = \mathrm{w}^{s.e.}_{i\longrightarrow f}$ is

$$\left(\frac{1}{\tau}\right)^{dip}_{i\to f} = \frac{e^2\omega^3}{3\pi\epsilon_0\hbar c^3} \mid \mathbf{r}_{if} \mid^2. \tag{3.93}$$

Examples:

- Lifetime of $H(2p)$

  $$\tau^{dip}_{2p\to 1s} \approx 1.6\cdot 10^{-9}s$$

  This looks like a short lifetime, but compare it to the classical revolution time of an electron in the hydrogen ground state!

- $\tau^{1^{st}\text{order}}_{2s\to 1s} \;\rightarrow\; \infty$
  For the transition rate $2s \to 1s$ one finds a strict zero for the first-order rate even beyond the dipole approximation. Experimentally one finds $\tau_{2s\to 1s} \approx 0.12s$. Theoretically, one obtains this number in a second-order calculation, in which *two-photon* processes are taken into account.

This expresses to a general pattern: an N-photon process corresponds to an N-th order TDPT amplitude.

f) Concluding remarks on photons

What have we learned about photons (associated with a given mode)?

- they can be created and annihilated (i.e. they don't last forever)
- they carry energy $\hbar\omega_\lambda$
- they carry momentum $\hbar\mathbf{k}_\lambda$
  this can be shown by starting from the classical expression for the total momentum of the free electromagnetic field

$$\mathbf{P}_{\mathrm{EM}} = \epsilon_0 \int_{L^3} \mathbf{E} \times \mathbf{B} \; d^3r$$

  using similar arguments as for the translation of W_{EM} to $\hat{H}_f$ one obtains

$$\hat{P}_F = \sum_\lambda \hbar\mathbf{k}_\lambda \hat{n}_\lambda$$

  and

$$\hat{P}_F|n_1, n_2, \ldots\rangle = \sum_\lambda \hbar\mathbf{k}_\lambda n_\lambda |n_1, n_2, \ldots\rangle$$

- they carry angular momentum (called spin) $\pm\hbar$
  this can be shown by starting from the classical expression for the total angular momentum of the free electromagnetic field

$$\mathbf{L}_{\mathrm{EM}} = \epsilon_0 \int_{L^3} \mathbf{r} \times \mathbf{E} \times \mathbf{B} \; d^3r$$

  using similar arguments as for the translation of W_{EM} to $\hat{H}_f$. However, this calculation requires a more explicit consideration of different possible polarization directions (which are not obvious in our condensed λ-notation).

- photons are bosons!
  The spin-statistics theorem shows that particles with integer spin fulfill Bose-Einstein statistics. There is no restriction on the number of

bosons (photons) which can occupy a given state (mode)—we have'nt encountered an upper limit for the occupation numbers n_λ. One can set up a similar (occupation number) formalism for many-electron systems and finds that in this case the occupation numbers can only be 0 or 1 due to the Pauli principle for fermions.

- Finally, we add that photons travel with $v = c$ (because free EM waves do) and thus must have zero mass (to avoid conflicts with Einstein's theory of relativity).

- literature on field quantization:
  relatively simple accounts on the quantization of the EM field can be found in [Fri], Chap. 2.4 and [SN], Chap. 7.6
  'higher formulations': [Sch], Chap. 14; [Mes], Chap. 21 (and, of course, QED textbooks)

Chapter 4

Brief introduction to relativistic QM

<u>Literature:</u> [BD]; [BS], Chap. 1.b; [Mes], Chap. 20; [Sch], Chap. 13; [Lib], Chap. 15; [SN], Chap. 8
The first reference is a classic textbook. The latter book chapters provide condensed accounts on relativistic quantum mechanics.

4.1 Klein-Gordon equation

a) Setting up a relativistic wave equation

- starting point: classical relativistic energy-momentum relation[1]

$$E^2 = \mathbf{p}^2 c^2 + m^2 c^4 \tag{4.1}$$

- quantization : (standard rules)

$$\begin{aligned} E &\longrightarrow i\hbar\partial_t \\ \mathbf{p} &\longrightarrow \frac{\hbar}{i}\boldsymbol{\nabla} \\ \hookrightarrow \quad \mathbf{p}^2 &\longrightarrow -\hbar^2\nabla^2 \\ \hookrightarrow \quad E^2 &\longrightarrow -\hbar^2\partial_t \end{aligned}$$

[1] In the following, m always denotes the rest mass m_0.

- obtain (free) wave equation (Klein-Gordon equation (KGE))

$$-\hbar^2\partial_{t^2}\psi(\mathbf{r},t) = -\hbar^2c^2\Delta\psi(\mathbf{r},t) + m^2c^4\psi(\mathbf{r},t) \tag{4.2}$$

  The KGE was first obtained by Schrödinger in the winter of 1925/26, but abandoned due to problems. Schrödinger then concentrated on the nonrelativistic case and found his equation, while the KGE was rediscovered a bit later by Klein and (independently) by Gordon.

b) Discussion

1. KGE is second-order PDE wrt. space and time
2. KGE is Lorentz covariant
3. Time development is determined from initial conditions $\psi(t_0)$, $\frac{\partial\psi}{\partial t}(t_0)$, which is at odds with evolution postulate of QM
4. Continuity equation?
   $\longrightarrow$ one can derive $\partial_t\rho + div\mathbf{j} = 0$
   with standard current $\mathbf{j} = \frac{i\hbar}{2m}(\psi\boldsymbol{\nabla}\psi^* - \psi^*\boldsymbol{\nabla}\psi)$

   but :
   $$\rho = \frac{i\hbar}{2mc^2}(\psi^*\partial_t\psi - \psi\partial_t\psi^*) \tag{4.3}$$

   problem: $\rho(\mathbf{r}t) \gtrless 0$ (i.e. not positive definite)
   $\longrightarrow$ probabilistic interpretation is not possible (or at least not obvious)
5. Ansatz (i)
   $$\psi(\mathbf{r},t) = Ae^{i(\mathbf{kr}-\omega t)}$$

   $\longrightarrow$ insertion into Eq. (4.2) yields together with de Broglie relations

   $$E = \hbar\omega = \pm\sqrt{c^2\hbar^2\mathbf{k}^2 + m^2c^4} \lesseqgtr 0 \tag{4.4}$$

   ρ and $\mathbf{j}$ are okay (check!), but what does $E < 0$ signify?
   Ansatz (ii)
   $$\psi(\mathbf{r},t) = Ae^{-i(\mathbf{kr}-\omega t)}$$

   results in the same expression for E, but corresponds to $\rho < 0$ (check!).
   Ansatz (iii)
   $$\psi(\mathbf{r},t) = A\sin(\mathbf{kr} - \omega t)$$

also results in the same expression for E, but corresponds to $\rho = 0$, $\mathbf{j} = 0$ (check!).

6. Add Coulomb potential to free KGE and solve it (in spherical coordinates)
   $\longrightarrow$ yields wrong fine structure of hydrogen spectrum (i.e., contradicts experimental findings)

7. In 1934, the KGE was recognized as the correct wave equation for spin-zero particles (mesons).

4.2 Dirac equation

In 1928, Dirac found a new wave equation which is suitable for electrons (spin $\frac{1}{2}$-particles): the Dirac equation (DE)

a) Free particles

$$\text{ansatz}: \qquad i\hbar\partial_t \Psi = \hat{H}_D \Psi \tag{4.5}$$

i.e. stick to the form of the TDSE; a PDE of 1^{st} order in t such that $\Psi(t_0)$ is the only initial condition

<u>requirements (Dirac's wish list):</u>

1. DE must be compatible with energy-momentum relation (4.1)
2. DE must be Lorentz-covariant
3. Obtain continuity equation with probabilistic interpretation
4. Stick to the usual quantization rules!

Dirac recognized that these requirements cannot be satisfied by a single scalar equation, but by a matrix equation for a spinor wave function with N components.

$$\text{ansatz}: \qquad \begin{aligned} \hat{H}_D &= c\boldsymbol{\alpha} \cdot \hat{\mathbf{p}} + \beta mc^2 \\ &= \frac{c\hbar}{i} \sum_{j=1}^{3} \alpha_i \partial_{x_i} + \beta mc^2 \end{aligned} \tag{4.6}$$

with $N \times N$ matrices $\alpha_x, \alpha_y, \alpha_z, \beta$ and spinor wave function

$$\Psi = \begin{pmatrix} \psi_1(\mathbf{r}, t) \\ \vdots \\ \psi_N(\mathbf{r}, t) \end{pmatrix} \qquad \text{as solution of (4.5)}$$

$\hookrightarrow$ requirement (1) is met if each component ψ_i solves KGE (4.2)
$\longrightarrow$ iterate Eq. (4.5):

$$i\hbar\partial_t(i\hbar\partial_t\Psi) = \hat{H}_D(\hat{H}_D\Psi)$$

$$\begin{aligned} \hookrightarrow \quad -\hbar^2\partial_{t^2}\Psi &= \Big(\frac{c\hbar}{i}\sum_j \alpha_j\partial_{x_j} + \beta mc^2\Big)\Big(\frac{c\hbar}{i}\sum_k \alpha_k\partial_{x_k} + \beta mc^2\Big)\Psi \\ &= \Big\{ -\hbar^2c^2\sum_{jk}\alpha_j\alpha_k\partial_{x_j}\partial_{x_k} + \frac{\hbar}{i}mc^3\sum_j \big(\alpha_j\beta + \beta\alpha_j\big)\partial_{x_j} + \beta^2m^2c^4\Big\}\Psi \\ &= -\hbar^2c^2\sum_{jk}\frac{\alpha_j\alpha_k + \alpha_k\alpha_j}{2}\partial^2_{x_jx_k}\Psi + \beta^2m^2c^4\Psi + \frac{\hbar mc^3}{i}\sum_j(\alpha_j\beta + \beta\alpha_j)\partial_{x_j}\Psi \end{aligned}$$

comparison with KGE yields conditions for α_i, β:

$$\alpha_j\alpha_k + \alpha_k\alpha_j = 2\delta_{jk} \tag{4.7}$$
$$\alpha_j\beta + \beta\alpha_j = 0 \tag{4.8}$$
$$\alpha_j^2 = \beta^2 = 1 \tag{4.9}$$

further conditions and consequences:

- α_j, β hermitian (because $\hat{H}_D$ shall be hermitian)
  $\Longrightarrow$ real eigenvalues
  $\overset{4.9}{\Longrightarrow}$ eigenvalues are ± 1
- from (4.7)-(4.9) it follows that α_j, β are 'traceless', i.e.
  $tr\ \alpha_j = tr\ \beta = 0$[2]
- together with eigenvalues ± 1 this implies that dimension N is even

[2] The trace of a matrix $\underline{\underline{A}}$ is defined as the sum over the diagonal elements. The trace does not change when $\underline{\underline{A}}$ is diagonalized. Hence $tr\ \underline{\underline{A}} = \sum$ eigenvalues.

- $N = 2$ is too small as there are only three 'anti-commuting' (Eqs. (4.7) and (4.8)) matrices for $N = 2$ (the Pauli matrices). Dirac needs four!
- try $N = 4$
- derive explicit representations from these conditions

$$\hookrightarrow \quad \alpha_i = \begin{pmatrix} 0 & \sigma_i \\ \sigma_i & 0 \end{pmatrix} , \qquad \beta = \begin{pmatrix} 1 & & & 0 \\ & 1 & & \\ & & -1 & \\ 0 & & & -1 \end{pmatrix} \tag{4.10}$$

with Pauli matrices σ_i

$$\underline{\underline{\sigma}}_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} , \quad \underline{\underline{\sigma}}_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} , \quad \underline{\underline{\sigma}}_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$\Longrightarrow$ free DE takes the form

$$i\hbar\partial_t \begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{pmatrix} = (c\boldsymbol{\alpha} \cdot \hat{\mathbf{p}} + \beta mc^2) \begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{pmatrix} \tag{4.11}$$

and one can derive a meaningful continuity equation:

$$\partial_t \rho + div\mathbf{j} = 0$$

with $$\rho = \Psi^\dagger \Psi = \sum_{i=1}^{4} \psi^*(\mathbf{r},t)\psi(\mathbf{r},t)$$

and $$\mathbf{j} = c\Psi^\dagger \boldsymbol{\alpha} \Psi$$

$$(\text{ i.e. } \quad j_k = c(\psi_1^*, \psi_2^*, \psi_3^*, \psi_4^*) \begin{pmatrix} 0 & \sigma_k \\ \sigma_k & 0 \end{pmatrix} \begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{pmatrix})$$

b) Solutions of the free DE

Ansatz : $$\psi_j(\mathbf{r},t) = u_j e^{i(\mathbf{kr}-\omega t)} , \qquad j = 1, ..., 4$$

after some calculation one finds:

- there are 4 linear independent solutions.

$$\begin{aligned} \text{Two correspond to} \qquad E &= +\sqrt{\mathbf{p}^2c^2 + m^2c^4} \\ \text{and two to} \qquad E &= -\sqrt{\mathbf{p}^2c^2 + m^2c^4} \end{aligned}$$

- they have the form ($E > 0$):

$$u^{(1)} = \begin{pmatrix} 1 \\ 0 \\ \chi_1 \\ \chi_2 \end{pmatrix}, \qquad u^{(2)} = \begin{pmatrix} 0 \\ 1 \\ \chi_1' \\ \chi_2' \end{pmatrix}$$

and for $E < 0$:

$$u^{(3)} = \begin{pmatrix} \varphi_1 \\ \varphi_2 \\ 1 \\ 0 \end{pmatrix}, \qquad u^{(4)} = \begin{pmatrix} \varphi_1' \\ \varphi_2' \\ 0 \\ 1 \end{pmatrix}$$

with

$$\chi_1 = \frac{cp_z}{E + mc^2}, \quad \chi_2 = \frac{c(p_x + ip_y)}{E + mc^2}, \quad \chi_1' = \frac{c(p_x - ip_y)}{E + mc^2}, \quad \chi_2' = -\chi_1$$

$$\varphi_1 = \frac{cp_z}{E - mc^2}, \quad \varphi_2 = \frac{c(p_x + ip_y)}{E - mc^2}, \quad \varphi_1' = \frac{c(p_x - ip_y)}{E - mc^2}, \quad \varphi_2' = -\varphi_1$$

note that all these 'small components' approach zero for $v \ll c$.
$u^{(1)}, u^{(3)}$ are interpreted as 'spin up'
$u^{(2)}, u^{(4)}$ are interpreted as 'spin down' solutions

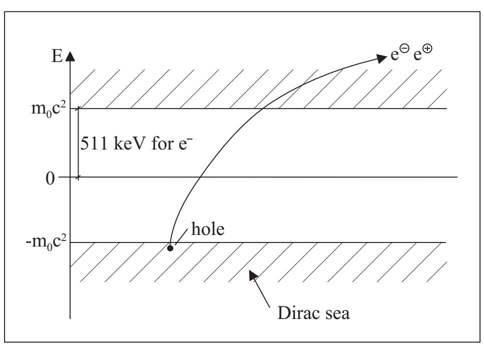


Figure 4.1: Energy spectrum of the free DE

Dirac's interpretation(1930):

In the vacuum all negative energy states (in the Dirac sea) are occupied. Hence, if electrons are present at $E > mc^2$ they cannot "fall down" into the Dirac sea because of the Pauli principle (electrons are fermions).

On the other hand, one can imagine that it is possible to excite one electron from the Dirac sea to $E > mc^2$. Such an excitation corresponds to a hole in the Dirac sea, which can be interpreted as the presence of a positively charged particle — an anti-particle (i.e. a positron). This process — electron-positron pair creation — has indeed been observed, and also the reversed process — destruction of electron-positron pairs and γ-ray emission (the latter to balance the total energy).

In fact, the first experimental detection of positrons in 1932 was considered a strong proof of Dirac's theory.

c) Throw in (classical) EM potentials

use the 'minimal coupling prescription'

$$\begin{aligned} \mathbf{p} &\longrightarrow \frac{\hbar}{i}\boldsymbol{\nabla} + e\mathbf{A} = \hat{\mathbf{p}} + e\mathbf{A} \\ E &\longrightarrow i\hbar\partial_t + e\phi \end{aligned}$$

$$\stackrel{(4.11)}{\hookrightarrow} \quad i\hbar\partial_t\Psi = \left\{c\hat{\boldsymbol{\alpha}}\cdot(\hat{\mathbf{p}} + e\mathbf{A}) - e\phi + \beta mc^2\right\}\Psi \tag{4.12}$$

one can show that Eq. (4.12) is Lorentz-covariant.

d) The relativistic hydrogen problem

Consider Eq. (4.12) with $\mathbf{A} = 0$ and

$$\phi = \frac{Ze}{4\pi\epsilon_0 r}$$

ansatz : $$\Psi(\mathbf{r}, t) = \Phi(\mathbf{r})e^{-\frac{i}{\hbar}Et} \tag{4.13}$$

$$\stackrel{\text{yields}}{\longrightarrow} \quad \left\{c\hat{\boldsymbol{\alpha}}\cdot\hat{\mathbf{p}} + \beta mc^2 - \frac{Ze^2}{4\pi\epsilon_0 r}\right\}\Phi(\mathbf{r}) = E\Phi(\mathbf{r}) \tag{4.14}$$

this stationary DE can be solved analytically!

Result for the bound spectrum ($\longrightarrow$ fine structure):

$$E_{nj} = mc^2\left[1+\frac{(Z\alpha)^2}{(n-\delta_j)^2}\right]^{-\frac{1}{2}} \qquad n = 1, 2, ... \tag{4.15}$$

$$\delta_j = j+\frac{1}{2}-\sqrt{\left(j+\frac{1}{2}\right)^2-(Z\alpha)^2}\ , \qquad j=\frac{1}{2},\frac{3}{2},...n-\frac{1}{2} \tag{4.16}$$

n (still) is the principal quantum number, while j can be identified as quantum number of total angular momentum.

$$\alpha = \frac{\hbar}{mca_0} = \frac{e^2}{4\pi\epsilon_0\hbar c} \approx \frac{1}{137} \tag{4.17}$$

fine-structure constant

expansion of Eq. (4.15) in powers of $(Z\alpha)^2 \ll 1$:

$$E_{nj} = mc^2\left[1-\frac{(Z\alpha)^2}{2n^2}-\frac{(Z\alpha)^4}{2n^3}\left(\frac{1}{j+\frac{1}{2}}-\frac{3}{4n}\right)\pm ...\right] \tag{4.18}$$

1^{st} term: rest energy
2^{nd} term: non-relativistic binding energy (1.23)
3^{rd} term: lowest order relativistic corrections $\longrightarrow$ fine structure splitting of energy levels

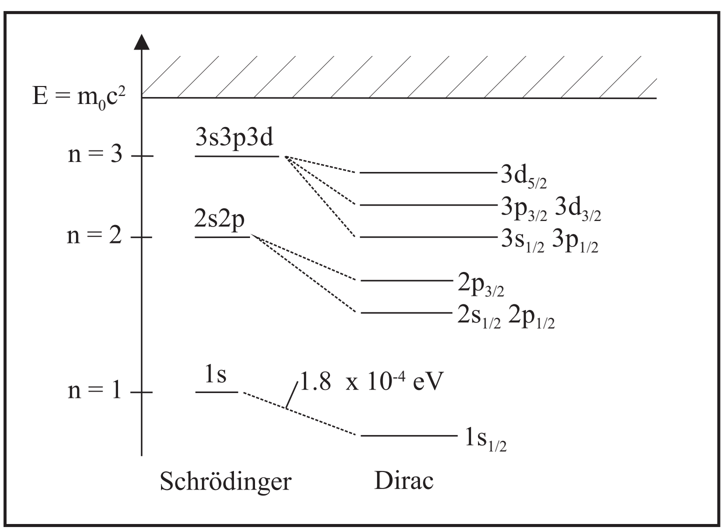


Figure 4.2: Energy spectrum of the Coulomb problem

Further corrections (beyond DE)[3]:

- hyperfine structure (coupling of magnetic moments of electron(s) and nucleus)
  $\sim 10^{-6}$ eV
- QED effects (Lamb shift): further splitting of levels with same j, but different l quantum numbers
  $\sim 10^{-6}$ eV

e) Nonrelativistic limit of the DE

Instead of solving Eq. (4.14) exactly and subsequently expanding the exact eigenvalues (4.15) it is useful to consider the non- (or rather: weak-) relativistic limit of the stationary DE (4.14) and to account for the lowest-order relativistic corrections obtained in this way in 1^{st}-order perturbation theory. This procedure yields the same result (4.18) once again, but this time it comes with an interpretation regarding the nature of the relativistic corrections.

Starting point: stationary DE

$$\left\{c\hat{\boldsymbol{\alpha}}\cdot\hat{\mathbf{p}}+\beta mc^2+V(r)\right\}\Phi(\mathbf{r})=E\Phi(\mathbf{r}) \tag{4.19}$$

group the 4-component spinor according to

$$\Phi=\begin{pmatrix}\varphi\\ \chi\end{pmatrix}\ ,\quad \text{with }\ \varphi=\begin{pmatrix}\varphi_1\\ \varphi_2\end{pmatrix},\ \chi=\begin{pmatrix}\chi_1\\ \chi_2\end{pmatrix}$$

insert into (4.19) (using similar groupings of the Dirac matrices in terms of Pauli matrices):

$$\hookrightarrow c\begin{pmatrix}0&\boldsymbol{\sigma}\\ \boldsymbol{\sigma}&0\end{pmatrix}\cdot\hat{\mathbf{p}}\begin{pmatrix}\varphi\\ \chi\end{pmatrix}=\left\{E-V(r)-mc^2\begin{pmatrix}1&0\\0&1\end{pmatrix}\right\}\begin{pmatrix}\varphi\\ \chi\end{pmatrix} \tag{4.20}$$

$$\Longleftrightarrow$$

$$c\boldsymbol{\sigma}\cdot\hat{\mathbf{p}}\,\chi = (E-V(r)-mc^2)\varphi \tag{4.21}$$
$$c\boldsymbol{\sigma}\cdot\hat{\mathbf{p}}\,\varphi = (E-V(r)+mc^2)\chi \tag{4.22}$$

[3]for details see [BS]

Solve (4.22) for χ and insert into (4.21):

$$\hookrightarrow \boldsymbol{\sigma}\cdot\hat{\mathbf{p}}\frac{c^2}{E-V(r)+mc^2}\boldsymbol{\sigma}\cdot\hat{\mathbf{p}}\,\varphi=(E-V(r)-mc^2)\varphi \tag{4.23}$$

- define $\varepsilon = E - mc^2 \ll mc^2$
- assume $V(r) \ll mc^2$
- expand

$$\frac{c^2}{E-V(r)+mc^2}=\frac{c^2}{\varepsilon+2mc^2-V(r)}=\frac{1}{2m(1+\frac{\varepsilon-V(r)}{2mc^2})}\approx\frac{1}{2m}\left(1-\frac{\varepsilon-V(r)}{2mc^2}\right)$$

use all this in (4.23) to obtain

$$\frac{1}{2m}\left[\boldsymbol{\sigma}\cdot\hat{\mathbf{p}}\left(1-\frac{\varepsilon-V(r)}{2mc^2}\right)\boldsymbol{\sigma}\cdot\hat{\mathbf{p}}\right]\varphi=(\varepsilon-V(r))\varphi$$

- apply the product rule for $\hat{\mathbf{p}}[V(r)\varphi]$
- use the following identity for Pauli matrices and arbitrary vector operators $\hat{\mathbf{A}}, \hat{\mathbf{B}}$

$$(\boldsymbol{\sigma}\cdot\hat{\mathbf{A}})(\boldsymbol{\sigma}\cdot\hat{\mathbf{B}})=\hat{\mathbf{A}}\cdot\hat{\mathbf{B}}+i\boldsymbol{\sigma}\cdot(\hat{\mathbf{A}}\times\hat{\mathbf{B}})$$

- use for a central potential

$$\boldsymbol{\nabla}V(r)=\frac{1}{r}\frac{dV}{dr}\mathbf{r}$$

to obtain

$$(T_1+T_2+T_3)\varphi=(\varepsilon-V(r))\varphi$$

with

$$T_1 = \left(1-\frac{\varepsilon-V(r)}{2mc^2}\right)\frac{\hat{\mathbf{p}}^2}{2m} \tag{4.24}$$

$$T_2 = \frac{\hbar}{4m^2c^2}\frac{1}{r}\frac{dV}{dr}(\boldsymbol{\sigma}\cdot\hat{\mathbf{l}}) \tag{4.25}$$

$$T_3 = \frac{\hbar}{i}\frac{1}{4m^2c^2}\frac{1}{r}\frac{dV}{dr}(\mathbf{r}\cdot\hat{\mathbf{p}}) \tag{4.26}$$

Interpretation of terms

- For the interpretation of T_1 note that

$$(\varepsilon - V(r))\varphi \approx \frac{\hat{\mathbf{p}}^2}{2m}\varphi$$

$$\hookrightarrow T_1 = \frac{\hat{\mathbf{p}}^2}{2m} - \frac{\hat{\mathbf{p}}^4}{8m^3c^2} \equiv \hat{T}_{NR} + \hat{H}_{KE} \tag{4.27}$$

  $\hat{H}_{KE}$ represents the lowest-order relativistic correction to the kinetic energy (as it appears — without hats — in a classical treatment).

- Introducing the spin operator $\hat{\mathbf{s}} = \frac{\hbar}{2}\boldsymbol{\sigma}$, which due to the properties of the Pauli matrices fulfills the standard commutation relations of an angular momentum operator[4], T_2 is identified as the spin-orbit coupling term

$$T_2 \equiv \hat{H}_{SO}.$$

  Hence, spin and spin-orbit coupling are automatically included in a relativistic treatment (which is why some authors insist that electron spin is a relativistic property).

- T_3 is not hermitian. Consider its hermitian average

$$\begin{aligned} \bar{T}_3 &= \frac{T_3 + T_3^\dagger}{2} = \frac{1}{8m^2c^2}\left(\frac{\hbar}{i}\frac{1}{r}\frac{dV}{dr}(\mathbf{r}\cdot\hat{\mathbf{p}}) - \frac{\hbar}{i}(\hat{\mathbf{p}}\cdot\mathbf{r})\frac{1}{r}\frac{dV}{dr}\right) \\ &= \frac{\hbar^2}{8m^2c^2}\nabla^2 V(r) \equiv \hat{H}_{\text{Darwin}}. \end{aligned}$$

  The Darwin term doesn't have a nonrelativistic or classical counterpart. It is usually associated with the "Zitterbewegung" (trembling motion) of the electron due to the nonzero coupling of electrons and positions (or: large and small components of the Dirac spinor) [BD].

Now apply perturbation theory to the problem

$$\hat{H} = \hat{H}_0 + \hat{W} \tag{4.28}$$

$$\hat{H}_0 = \hat{T}_{NR} + V(r) = \frac{\hat{\mathbf{p}}^2}{2m} - \frac{Ze^2}{4\pi\epsilon_0 r} \tag{4.29}$$

$$\hat{W} = \hat{H}_{KE} + \hat{H}_{SO} + \hat{H}_{\text{Darwin}} \tag{4.30}$$

[4]for a recap of angular momentum and spin operators consult a QM textbook, e.g. [Gri], Chaps. 4.3, 4.4

One obtains for the first-order energy correction

$$\Delta E^{(1)} = -\frac{mc^2}{2n^3}(Z\alpha)^4\left(\frac{1}{j+\frac{1}{2}} - \frac{3}{4n}\right), \tag{4.31}$$

i.e., the same results as in Eq. (4.18), which shows the consistency of the approach.

Chapter 5

Molecules

A simple man's definition of a molecule says that it is an aggregate of atoms which cling together by bonds. The big question then is: why are the atoms doing this, i.e., what is the nature of the chemical bond? It turns out that this can only be answered satisfactorily by quantum mechanics.

We should thus start by insisting that molecules are quantum-mechanical many-body systems consisting of $M \geq 2$ atomic nulcei and $N \geq 1$ electrons, which interact with each other (mainly) by Coulomb forces. Let's assume that the Coulomb force is the only force present and that everything can be described nonrelativistically.

Hamiltonian:

$$\hat{H} = \hat{T}_{\rm nuc} + \hat{T}_{el} + V \tag{5.1}$$

$$\hat{T}_{\rm nuc} = \sum_{\alpha=1}^{M} \frac{\hat{\mathbf{P}}_\alpha^2}{2M_\alpha} = -\frac{\hbar^2}{2} \sum_{\alpha=1}^{M} \frac{1}{M_\alpha} \nabla_{R_\alpha}^2 \tag{5.2}$$

$$\hat{T}_{el} = \sum_{i=1}^{M} \frac{\hat{\mathbf{p}}^2}{2m_e} = -\frac{\hbar^2}{2m_e} \sum_{i=1}^{N} \nabla_{r_i}^2 \tag{5.3}$$

$$V = V_{nn} + V_{ne} + V_{ee} \tag{5.4}$$

$$V_{nn} = \sum_{\alpha<\beta}^{M} \frac{Z_\alpha Z_\beta e^2}{4\pi\epsilon_0 \left|\mathbf{R}_\alpha - \mathbf{R}_\beta\right|} \tag{5.5}$$

$$V_{ne} = -\sum_{\alpha=1}^{M} \sum_{i=1}^{N} \frac{Z_\alpha e^2}{4\pi\epsilon_0 \left|\mathbf{R}_\alpha - \mathbf{r}_i\right|} \tag{5.6}$$

$$V_{ee} = \sum_{i<j}^{N} \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_i - \mathbf{r}_j|} \tag{5.7}$$

The task is to solve the stationary Schrödinger equation

$$\hat{H} |\Phi\rangle = E |\Phi\rangle \tag{5.8}$$

for this Hamiltonian. This would be a complicated problem, but one doesn't really have to do it in most situations of interest.

5.1 The adiabatic (Born-Oppenheimer) approximation

The adiabatic (or: Born-Oppenheimer) approximation forms the basis for the discussion of molecular structure and properties. It exploits the large mass difference between electrons and nuclei.

a) Prelude

Let's consider the (drastic) approximation of infinitely heavy nuclei which cannot move:

$$M_\alpha \to \infty \;\Rightarrow\; \hat{T}_{\text{nuc}} \to 0\,.$$

We are left with the simpler "electronic" SE

$$\left(\hat{T}_{el} + V(\mathbf{R})\right) \Psi_n(\mathbf{r}, \mathbf{R}) = E_n(\mathbf{R}) \Psi_n(\mathbf{r}, \mathbf{R}) \tag{5.9}$$

with $\mathbf{r} = (\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N)$ and $\mathbf{R} = (\mathbf{R}_1, \mathbf{R}_2, ..., \mathbf{R}_M)$.

Remarks

1. The nuclear coordinates $\mathbf{R}$ are now 'external' parameters (no independent variables). The electronic wave functions Ψ_n and the energy eigenvalues depend parametrically on $\mathbf{R}$.
2. Actually, we should use a better notation that accounts for the electrons' spins, e.g., $\mathbf{r} \to x = (\mathbf{r}_1 s_1, ... \mathbf{r}_N s_N)$, since the spin coordinates play a role for the permutation symmetry of many-electron systems (even though spin-dependent interactions are neglected). We don't do it for the sake of simplicity, since the arguments used in this section are independent of symmetry and spin.

3. Since $\hat{T}_{el}+V(\mathbf{R})$ is hermitian, the Ψ_n form a complete (and orthogonal) basis for any configuration $\{\mathbf{R}\}$ of the nuclei. We can write, e.g.,

$$\begin{aligned}\langle \Psi_m | \Psi_n \rangle_{\mathbf{r}} &= \langle \Psi_m(\mathbf{R}) | \Psi_n(\mathbf{R}) \rangle_{\mathbf{r}} \\ &= \int \Psi_m^*(\mathbf{r}_1, \mathbf{r}_{,2}, ...\mathbf{r}_N, \mathbf{R}) \Psi_n(\mathbf{r}_1, \mathbf{r}_{,2}, ...\mathbf{r}_N, \mathbf{R}) d^3r_1 d^3r_2 ... d^3r_N \\ &= \delta_{mn}\end{aligned}$$

b) Adiabatic approximation: separation of electronic and nuclear motion

Back to the full problem.

$$\text{Ansatz:} \qquad \Phi(\mathbf{r}, \mathbf{R}) = \sum_n \phi_n(\mathbf{R}) \Psi_n(\mathbf{r}, \mathbf{R}) \tag{5.10}$$

Sub into Eq. (5.8), multiply everything by $\Psi_n^*(\mathbf{r}, \mathbf{R})$, use Eq. (5.9) and integrate over electronic coordinates choosing $\Psi_n^*(\mathbf{r}, \mathbf{R}) = \Psi_n(\mathbf{r}, \mathbf{R})$ such that

$$\begin{aligned}\boldsymbol{\nabla}_{R_\alpha} \langle \Psi_m | \Psi_m \rangle_{\mathbf{r}} &= \langle \boldsymbol{\nabla}_{R_\alpha} \Psi_m | \Psi_m \rangle_{\mathbf{r}} + \langle \Psi_m | \boldsymbol{\nabla}_{R_\alpha} | \Psi_m \rangle_{\mathbf{r}} \\ \Leftrightarrow\ 0 &= 2 \langle \Psi_m | \boldsymbol{\nabla}_{R_\alpha} | \Psi_m \rangle_{\mathbf{r}}\end{aligned}$$

to obtain

$$\left(\hat{T}_{\text{nuc}} + E_m(\mathbf{R}) + \Delta_m(\mathbf{R}) - E)\right) \phi_m(\mathbf{R}) = \sum_{n \neq m} \hat{C}_{mn}(\mathbf{R}) \phi_n(\mathbf{R}) \tag{5.11}$$

with definitions

$$\begin{aligned}\Delta_m(\mathbf{R}) &= \left\langle \Psi_m(\mathbf{R}) \middle| \hat{T}_{\text{nuc}} \middle| \Psi_m(\mathbf{R}) \right\rangle_{\mathbf{r}} \\ \hat{C}_{mn}(\mathbf{R}) &= \sum_\alpha \frac{\hbar^2}{M_\alpha} \left(\mathbf{A}_{mn}^\alpha(\mathbf{R}) \cdot \boldsymbol{\nabla}_{R_\alpha} + B_{mn}^\alpha(\mathbf{R}) \right) \\ \mathbf{A}_{mn}^\alpha(\mathbf{R}) &= \langle \Psi_m | \boldsymbol{\nabla}_{R_\alpha} | \Psi_n \rangle_{\mathbf{r}} \\ B_{mn}^\alpha(\mathbf{R}) &= \frac{1}{2} \langle \Psi_m | \nabla_{R_\alpha}^2 | \Psi_n \rangle_{\mathbf{r}}\end{aligned}$$

The adiabatic approximation consists in neglecting all the coupling terms:

$$\sum_{m \neq n} \hat{C}_{mn}(\mathbf{R}) \phi_n(\mathbf{R}) \approx 0\ . \tag{5.12}$$

Hence, we arrive at two SEs; one for the electronic and one for the nuclear motion:

$$\left(\hat{T}_{el} + V(\mathbf{R})\right)\Psi_m(\mathbf{r},\mathbf{R}) = E_m(\mathbf{R})\Psi_m(\mathbf{r},\mathbf{R}) \quad (5.13)$$

$$\left(\hat{T}_{\text{nuc}} + U_m(\mathbf{R})\right)\phi_m(\mathbf{R}) = E\phi_m(\mathbf{R}) \quad (5.14)$$

$$U_m(\mathbf{R}) = E_m(\mathbf{R}) + \Delta_m(\mathbf{R})\,. \quad (5.15)$$

The third equation provides the connection of the two SEs. This set of equations is the standard framework for the discussion of molecular structure and properties.

<u>Discussion</u>

- „Born-Oppenheimer approximation" (BOA): adiabatic approximation plus assumption $\Delta_m(\mathbf{R}) \approx 0$.
  → "potential energy surfaces" (PES) $E_m(\mathbf{R})$ determine nuclear motion:

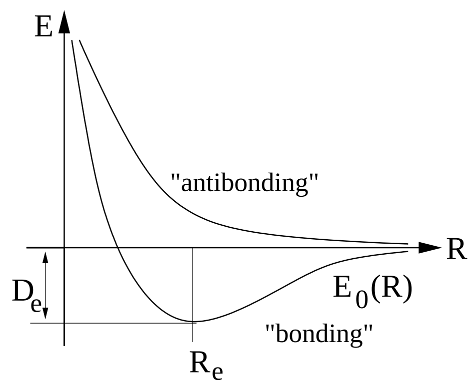


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Figure 5.1: Typical PESs for $M = 2$ ($E_m(\mathbf{R}) = E_m(R)$) as functions of the internuclear distance R.

  For $R \to \infty$ all PESs become horizontal (vanishing Coulomb forces), for $R \to 0$ all PESs increase like $\frac{1}{R}$ because V_{nn} dominates. The minimum of the lower (ground-state) curve corresponds to the equilibrium distance (bond length) of the molecule.

- Gist and justification of BOA: $\frac{m_e}{M_\alpha} \approx 10^{-4}$
  The nuclei are so slow that they feel only an average electronic field

(via the PESs). The fast electrons follow the slow nuclear motion adiabatically, i.e., without undergoing transitions.

A closer inspection of the BOA shows that the neglected terms $\Delta_m(\mathbf{R})$ and $\hat{C}_{mn}(\mathbf{R})$ are proportional to the smallness parameter $1/M_\alpha$.

5.2 Nuclear wave equation: rotations and vibrations

Let's consider a diatomic molecule ($M = 2$). The structure of the problem is that of a two-body central-field problem. Hence, we can reduce it to an effective one-body problem using CM and relative coordinates (cf. Chaps. 1.1 and 1.2). The nontrivial SE for the relative (internal) motion reads

$$\begin{aligned} E\phi_n(\mathbf{R}) &= \left(\frac{\hat{\boldsymbol{P}}_R^2}{2\mu} + U_n(R) \right) \phi_n(\mathbf{R}) \\ &= \left(\frac{\hat{P}_R^2}{2\mu} + \frac{\hat{\boldsymbol{J}}^2}{2\mu R^2} + U_n(R) \right) \phi_n(\mathbf{R}) \end{aligned} \tag{5.16}$$

with the reduced mass $\mu = \frac{M_1 M_2}{M_1 + M_2}$.

- Simplest model: rigid rotor
  The rigid rotor is defined by setting $R = R_e$, i.e., by assuming that the internuclear distance is held fixed at the equilibrium distance. In this model, ϕ_n depend only on angular coordinates and Eq. (5.16) reduces to

$$E_{\mathrm{rot}}\phi_{JM}(\theta,\varphi) = \frac{\hat{\boldsymbol{J}}^2}{2\mu R_e^2}\phi_{JM}(\theta,\varphi) \tag{5.17}$$

$$E_{\mathrm{rot}} = \frac{\hbar^2 J(J+1)}{2\mu R_e^2} = \frac{\hbar^2 J(J+1)}{2I} \quad J = 0, 1, \ldots \tag{5.18}$$

$$I = \mu R_e^2 \quad \text{moment of inertia} \tag{5.19}$$

$$\phi_{JM}(\theta,\varphi) = Y_{JM}(\theta,\varphi) \tag{5.20}$$

  Measurement of rotational absorption spectra (typically in the microwave regime) give information on I, i.e., on R_e.

- Allow for radial motion: vibrations
  Equation (5.16) can be separated by using the ansatz

$$\phi_n(\mathbf{R}) = \frac{P_{nJ}(R)}{R} Y_{JM}(\theta, \varphi)$$

  $\hookrightarrow$ radial equation:

$$\left(-\frac{\hbar^2}{2\mu}\frac{d^2}{dR^2} + U_n(R) + \frac{\hbar^2 J(J+1)}{2\mu R^2}\right) P_{nJ}(R) = E P_{nJ}(R) \qquad (5.21)$$

- Taylor-expand bonding ground-state PES about equilibrium distance:

$$\begin{aligned} U_0(R) &\approx U_0(R_e) + U_0'(R_e)(R-R_e) + \frac{1}{2}U_0''(R_e)(R-R_e)^2 + ... \\ &= U_0(R_e) + \frac{k_e}{2}x^2 \qquad (5.22) \end{aligned}$$

  with

$$\begin{aligned} k_e &= U_0''(R_e) \quad \text{molecular force constant} \\ x &= R - R_e \end{aligned}$$

  use this to obtain the approximate radial equation

$$\begin{aligned} -\frac{\hbar^2}{2\mu}P_{nJ}''(x) + \frac{1}{2}k_e x^2 P_{nJ}(x) &= \left(E - U_0(R) - \frac{\hbar^2 J(J+1)}{2\mu R_e^2}\right) P_{nJ}(x) \\ &\equiv E_{\text{vib}} P_{nJ}(x) \qquad (5.23) \end{aligned}$$

  which is the SE of the harmonic oscillator with eigenenergies

$$\begin{aligned} E_{\text{vib}} &= \hbar\omega_e \left(\nu + \frac{1}{2}\right) \quad \nu = 0, 1, 2, ... \\ \text{and } \omega_e &= \sqrt{\frac{k_e}{\mu}} = \sqrt{\frac{U_0''(R_e)}{\mu}} \end{aligned}$$

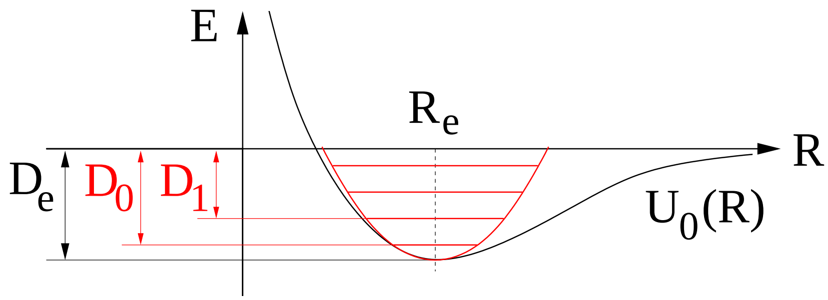

Figure 5.2: Typical ground-state PES and harmonic oscillator model of vibrational motion. $D_e = U_0(R_e)$ is the binding energy and $D_0 = D_e - \frac{\hbar\omega_e}{2}$ the dissociation energy of the molecule.

Summary:

$$E = U_0(R_e) + E_{\text{vib}} + E_{\text{rot}}$$

with

$$\begin{aligned} E_{el} &= U_0(R_e) = E_0(R_e) + \Delta_0(R_e) \\ E_{\text{vib}} &= \hbar\omega_e\left(\nu + \frac{1}{2}\right) \\ E_{\text{rot}} &= \frac{\hbar^2 J(J+1)}{2I} \end{aligned}$$

note that

- $E_0(R_e)$ is independent of μ
- $E_{vib} \propto \frac{1}{\sqrt{\mu}}$
- $E_{rot} \propto \frac{1}{\mu}$
- $\hookrightarrow E_{rot} \ll E_{vib} \ll E_{el}$

Literature: [Lev], Chaps. 4.3 and 6.4; [Hur], Chap. 1

5.3 The hydrogen molecular ion H_2^+

The hydrogen molecular ion is the simplest molecular system and plays a similar role in molecular physics as the hydrogen atom in atomic physics. The electronic SE can be solved exactly (but not in closed analytical form). Let's just take a look (without going into technical details).

The electronic SE (atomic units)

$$\left(-\frac{1}{2}\nabla^2 - \frac{1}{r_a} - \frac{1}{r_b} + \frac{1}{R}\right)\Psi_n(\mathbf{r},R) \quad = \quad E_n(R)\Psi_n(\mathbf{r},R) \tag{5.24}$$

is separable in confocal-elliptical coordinates (ξ, η, φ):

$$\begin{aligned} \xi &= \frac{1}{R}(r_a + r_b) \quad 1 \leq \xi < \infty \\ \eta &= \frac{1}{R}(r_a - r_b) \quad -1 \leq \eta \leq 1 \\ \varphi &= \arctan\frac{y}{x} \quad 0 \leq \varphi < 2\pi \end{aligned}$$

with the standard azimuthal angle φ:

$$\Psi(\xi,\eta,\varphi) = M(\xi)N(\eta)\phi(\varphi) \tag{5.25}$$

for $\Phi(\varphi)$ one obtains

$$\begin{aligned} \left(\frac{d^2}{d\varphi^2} + \lambda^2\right)\phi(\varphi) &= 0 \\ \Rightarrow \phi(\varphi) &= e^{i\lambda\varphi} \end{aligned}$$

require uniqueness:

$$\begin{aligned} \phi(\varphi) &= \phi(\varphi + 2\pi) \\ &= \underbrace{e^{i\lambda 2\pi}}_{1} e^{i\lambda\varphi} \Rightarrow \lambda = 0, \pm 1, \pm 2, ... \end{aligned}$$

$$\hookrightarrow \hat{l}_z\phi_\lambda(\varphi) = -i\frac{\partial}{\partial\varphi}\phi_\lambda(\varphi) = \lambda\phi_\lambda(\varphi)$$

$$\Rightarrow \left[\hat{H}, \hat{l}_z\right] = 0$$

However:

$$\left[\hat{H}, \hat{\boldsymbol{l}}^2\right] \neq 0$$

$\Rightarrow$ use λ to classify states

H atom	$l =$	0	1	2	3
notation		s	p	d	f
H_2^+	$\lambda =$	0	± 1	± 2	± 3
notation		σ	π	δ	φ

Table 5.1: Classification of atomic vs. molecular one-electron states

Eigenfunctions $\Psi(\xi, \eta, \varphi)$ of Eq. (5.25) are also parity eigenstates $\sphericalangle$ point reflections:

$$\mathbf{r} \to -\mathbf{r} \quad \Longrightarrow \quad \begin{cases} \xi & \to & \xi \\ \eta & \to & -\eta \\ \varphi & \to & \varphi + \pi \end{cases}$$

$\rightarrow$ two types of solutions

$$\begin{aligned} \psi(\mathbf{r}) &= \psi(\xi, \eta, \varphi) \\ &= \psi(\xi, -\eta, \varphi + \pi) \\ &= \psi(-\mathbf{r}) \\ &= \psi_g(\mathbf{r}) \qquad \text{gerade (even) parity} \end{aligned}$$

$$\begin{aligned} \psi(\mathbf{r}) &= \psi(\xi, \eta, \varphi) \\ &= -\psi(\xi, -\eta, \varphi + \pi) \\ &= -\psi(-\mathbf{r}) \\ &= \psi_u(\mathbf{r}) \qquad \text{ungerade (odd) parity} \end{aligned}$$

$\rightarrow$ classification of molecular orbitals (MOs)

$$\begin{aligned} &1\sigma_g,\ 1\sigma_u,\ 2\sigma_g,\ 2\sigma_u,\ 3\sigma_g,\ 3\sigma_u,\ \ldots \\ &1\pi_g,\ 1\pi_u,\ 2\pi_g,\ 2\pi_u,\ 3\pi_g,\ 3\pi_u,\ \ldots \\ &\vdots \end{aligned}$$

Discussion of exact PESs $E_n(R)$ and "correlation diagrams" $E_n^{el}(R) = E_n(R) - \frac{1}{R}$

Note that

$$E_n^{el}(R \to 0) \;=\; -\frac{2}{n^2} \qquad \text{"united-atom limit"}$$
$$E_n^{el}(R \to \infty) \;=\; -\frac{1}{2n^2} \qquad \text{"separated-atom limit"}$$

Since the E_n^{el} are continuous functions of R, each united-atom state (e.g. $1s\sigma_g$) is correlated with a separated-atom state (e.g. $\sigma_g(1s)$).

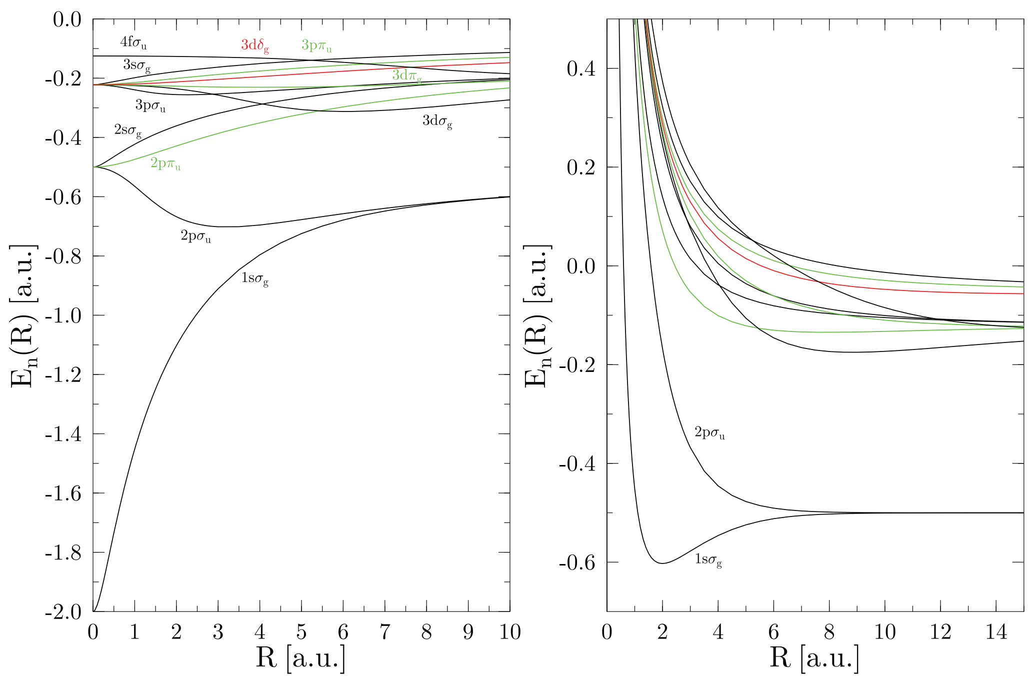

Figure 5.3: Calculated correlation diagram (left) and PESs (right) of H_2^+

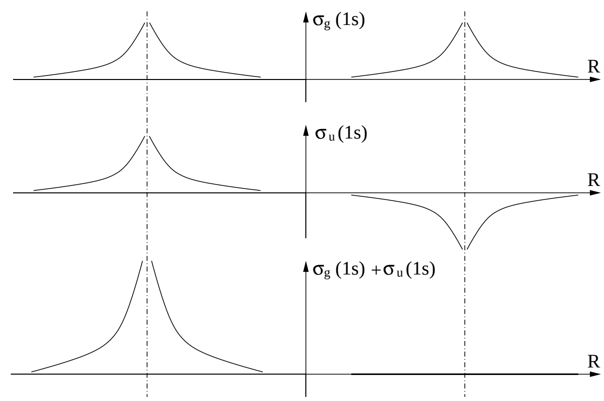

Figure 5.4: Sketch of the electron density distributions of the lowest states of gerade and ungerade parity in the separated-atom limit and how they add to form an atomic state, e.g., on the left centre

$E_n^{el}(R \to 0)$	AO	MO	AO	$E_n^{el}(R \to \infty)$
-2.0	$1s$	$1\sigma_g$	$1s$	-0.5
-0.5	$2p_0$	$1\sigma_u$	$1s$	-0.5
-0.5	$2p_1$	$1\pi_u$	$2p_1$	-0.125
-0.5	$2s$	$2\sigma_g$	$2s$	-0.125
-0.222	$3p_0$	$2\sigma_u$	$2s$	-0.125
-0.222	$3d_0$	$3\sigma_g$	$2p_0$	-0.125
-0.222	$3d_1$	$1\pi_g$	$2p_1$	-0.125
-0.222	$3d_2$	$1\delta_g$	$3d_2$	-0.056
-0.222	$3p_1$	$3\pi_u$	$3p_1$	-0.056
-0.222	$3s$	$4\sigma_g$	$3s$	-0.056
-0.125	$4f_0$	$3\sigma_u$	$2p_0$	-0.125

Table 5.2: Energies (in atomic units) and united- and separated-atom limits of a few MOs of H_2^+

bond length	R_e	1.9972
	$E_0(R_e)$	-0.6026
	$E_0^{el}(R_e)$	-1.1033
binding energy	D_e	-0.1026

Table 5.3: Ground state properties of H_2^+

Literature: [Lev], Chap. 13

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