

**PHYS 4011/5050:
Atomic and Molecular
Physics/Structure**

Lecture Notes

Tom Kirchner¹

Department of Physics and Astronomy
York University

March 2020

¹tomk@yorku.ca

Contents

1	Introduction: the field-free Schrödinger hydrogen atom	3
1.1	Reduction to an effective one-body problem	3
1.2	The central-field problem for the relative motion	5
1.3	Solution of the Coulomb problem	6
1.4	Assorted remarks	14
2	Atoms in electric fields: the Stark effect	17
2.1	Stationary perturbation theory for nondegenerate systems . . .	18
2.2	Degenerate perturbation theory	23
2.3	Electric field effects on excited states: the linear Stark effect .	25
3	Interaction of atoms with radiation	30
3.1	The semiclassical Hamiltonian	30
3.2	Time-dependent perturbation theory	33
3.3	Photoionization	42
3.4	Outlook on field quantization	47
4	Many-electron atoms	61
4.1	Systems of identical particles	62
4.2	The atomic shell model	67
4.3	The Hartree-Fock method	70
5	Molecules	77
5.1	The adiabatic (Born-Oppenheimer) approximation	78
5.2	Nuclear wave equation: rotations and vibrations	81
5.3	The hydrogen molecular ion H_2^+	84
5.4	Many-electron molecules	91

6	Brief introduction to relativistic QM	93
6.1	Klein-Gordon equation	93
6.2	Dirac equation	95
A	Incoming beam current in the photoionization problem	105

Chapter 1

Introduction: the field-free Schrödinger hydrogen atom

The starting point of the discussion is the stationary Schrödinger equation

$$\hat{H}\Psi = E\Psi \quad (1.1)$$

for the two-body problem consisting of a nucleus (n) and an electron (e). The Hamiltonian reads¹

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

with

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

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

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

¹Unless otherwise stated we will work in \mathbf{r} -space where $\hat{\mathbf{p}} = -i\hbar\nabla$ and $\hat{\mathbf{r}} = \mathbf{r}$. Accordingly, we will normally omit hats for operators which only depend on \mathbf{r} .

definitions :

$$\begin{aligned}
 M &= m_e + m_n \approx m_n \\
 \mu &= \frac{m_e m_n}{m_e + m_n} \approx m_e \\
 \mathbf{R} &= \frac{m_n \mathbf{r}_n + m_e \mathbf{r}_e}{M} \approx \mathbf{r}_n \\
 \mathbf{P} &= \mathbf{p}_e + \mathbf{p}_n = M \dot{\mathbf{R}} \approx \mathbf{p}_n \\
 \mathbf{r} &= \mathbf{r}_e - \mathbf{r}_n \\
 \mathbf{p} &= \mu \dot{\mathbf{r}} = \frac{m_n \mathbf{p}_e - m_e \mathbf{p}_n}{M} \approx \mathbf{p}_e
 \end{aligned}
 \left. \begin{array}{l} \\ \\ \\ \\ \end{array} \right\} \begin{array}{l} \text{centre - of - mass} \\ \text{motion} \\ \\ \text{relative} \\ \text{motion} \end{array}$$

- QM transformation analogously

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

insertion into Eq. (1.2) yields

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

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

$$\text{Ansatz : } \Psi(\mathbf{r}, \mathbf{R}) = \Phi_{CM}(\mathbf{R})\varphi_{\text{rel}}(\mathbf{r}) \quad (1.5)$$

\leftrightarrow Schrödinger equations (SEs)

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

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

$$\text{with } E = E_{CM} + E_{\text{rel}} \quad (1.8)$$

Equation (1.6) can be solved without difficulty:

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

Equation (1.7) can be solved analytically, but before we summarize these results 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
$$\hat{H}_{\text{rel}} = \frac{\hat{\mathbf{p}}^2}{2\mu} + V(r) \quad . \quad (1.9)$$

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

$$\hat{\mathbf{l}} = \hat{\mathbf{r}} \times \hat{\mathbf{p}}. \quad (1.10)$$

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

$$[\hat{H}_{\text{rel}}, \hat{\mathbf{l}}^2] = [\hat{H}_{\text{rel}}, \hat{l}_z] = [\hat{\mathbf{l}}^2, \hat{l}_z] = 0 \quad (1.11)$$

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

$$\hat{\mathbf{l}}^2 Y_{lm}(\theta, \varphi) = \hbar^2 l(l+1) Y_{lm}(\theta, \varphi), \quad l = 0, 1, 2, \dots \quad (1.12)$$

$$\hat{l}_z Y_{lm}(\theta, \varphi) = m\hbar Y_{lm}(\theta, \varphi), \quad m = -l, -l+1, \dots, l-1, l \quad (1.13)$$

$$\Leftrightarrow \text{Ansatz} \quad \varphi_{\text{rel}}(\mathbf{r}) = R_l(r) Y_{lm}(\theta, \varphi) \quad (1.14)$$

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

$$\left\{ \frac{\hat{p}_r^2}{2\mu} + \frac{\hbar^2 l(l+1)}{2\mu r^2} + V(r) - E_{\text{rel}} \right\} R_l(r) = 0 \quad (1.15)$$

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

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

(can be proven, e.g., in spherical coordinates in coordinate space)

Useful definition :
$$y_l(r) = r R_l(r) \quad (1.16)$$

$$\stackrel{(1.15)}{\hookrightarrow} \quad y_l''(r) + \left[\epsilon - U(r) - \frac{l(l+1)}{r^2} \right] y_l(r) = 0 \quad (1.17)$$

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

1.3 Solution of the Coulomb problem

The radial Eq. (1.17) is very similar to the one-dimensional SE. There are, however, two important differences. First, the total (effective) potential consists of two parts

$$U_l^{\text{eff}}(r) \equiv U(r) + \frac{l(l+1)}{r^2} \xrightarrow{r \rightarrow \infty} 0$$

↙ "angular momentum barrier"

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

a) Boundary conditions

- $r \rightarrow 0$
 $|\varphi_{\text{rel}}(\mathbf{r})|^2 = |R_l(r)|^2 |Y_{lm}(\theta, \varphi)|^2 < \infty$
 in particular for $\mathbf{r} = 0$
 \hookrightarrow 'regularity condition'
 $y_l(0) = 0$ (1.18)

- $r \rightarrow \infty$

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

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

(square integrable solutions required)

$$\hookrightarrow y_l(r) \xrightarrow{r \rightarrow \infty} 0 \quad (\text{strong boundary condition})$$

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

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

b) Bound-state solutions

definition :

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

\hookrightarrow radial Eq. (1.17):

$$\left(\frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} + \frac{2Z}{ar} - \kappa^2 \right) y_l(r) = 0 \quad (1.19)$$

transformation: $x = 2\kappa r$

$$\begin{aligned} \hookrightarrow \frac{d^2}{dx^2} &= \frac{1}{4\kappa^2} \frac{d^2}{dr^2} \\ \hookrightarrow \left(\frac{d^2}{dx^2} - \frac{l(l+1)}{x^2} + \frac{\lambda}{x} - \frac{1}{4} \right) y_l(x) &= 0 \end{aligned} \quad (1.20)$$

with $\lambda = \frac{Z}{\kappa a}$. Asymptotic solutions:

1. $x \rightarrow \infty$

$$\begin{aligned} \hookrightarrow \left(\frac{d^2}{dx^2} - \frac{1}{4} \right) y_l(x) &= 0 \\ \hookrightarrow y_l(x) &= Ae^{-\frac{x}{2}} + Be^{\frac{x}{2}} \end{aligned}$$

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

2. $x \rightarrow 0$

$$\begin{aligned} \hookrightarrow \left(\frac{d^2}{dx^2} - \frac{l(l+1)}{x^2} \right) y_l(x) &= 0 \\ \hookrightarrow y_l(x) &= \frac{A}{x^l} + Bx^{l+1} \end{aligned}$$

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

This consideration motivates the following ansatz

$$y_l(x) = x^{l+1} e^{-\frac{x}{2}} v_l(x). \quad (1.21)$$

Insertion into Eq. (1.20) yields a new differential equation for $v_l(x)$:

$$\hookrightarrow \left\{ x \frac{d^2}{dx^2} + (2l+2-x) \frac{d}{dx} - (l+1-\lambda) \right\} v_l(x) = 0. \quad (1.22)$$

The square integrable solutions of (1.22) (called Kummer's or Laplace's differential eq.) are known; they are the associated Laguerre polynomials²:

$$L_p^k(x) = \sum_{j=0}^p (-1)^j \frac{[(p+k)!]^2}{(p-j)!(k+j)!j!} x^j.$$

More specifically one finds

$$v_l(x) \rightarrow v_{n_r, l}(x) = L_{n-l-1}^{2l+1}(x), \quad \left(\begin{array}{l} n_r = n - l - 1 \geq 0 \\ \iff n - 1 \geq l \end{array} \right)$$

$$\text{with} \quad n \equiv \lambda_n = \frac{Z}{\kappa_n a}, \quad n = 1, 2, \dots \quad (1.23)$$

i.e., the integrability of the solutions requires λ to be a positive, integer number \rightarrow quantization of κ (i.e., quantization of the energy)³

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

²Other conventions regarding the normalization of the associated Laguerre polynomials are in use as well.

³One finds the square integrable solutions of (1.22) 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.

The properly normalized wave functions take the form

$$\begin{aligned}\varphi_{\text{rel}}(\mathbf{r}) \equiv \varphi_{nlm}(\mathbf{r}) &= \sqrt{\frac{(2\kappa_n)^3 (n-l-1)!}{2n[(n+l)!]^3}} (2\kappa_n)^l r^l e^{-\kappa_n r} L_{n-l-1}^{2l+1}(2\kappa_n r) Y_{lm}(\theta, \varphi) \\ &\equiv R_{nl}(r) Y_{lm}(\theta, \varphi) \quad \begin{array}{l} n \geq 0 \\ l \leq n-1 \\ -l \leq m \leq l \end{array} \end{aligned} \quad (1.24)$$

The quantization condition (1.23) yields

$$E_{\text{rel}} \equiv E_n = -\frac{\hbar^2}{2\mu a^2} \frac{Z^2}{n^2} \quad n = 1, 2, \dots \quad (1.25)$$

$$\approx -13.6 \text{ eV} \frac{Z^2}{n^2}. \quad (1.26)$$

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	2p 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	2p _{± 1} $\mp \frac{1}{8\sqrt{\pi}} \left(\frac{Z}{a}\right)^{\frac{3}{2}} \left(\frac{Zr}{a}\right) e^{-\frac{Zr}{2a}} \sin \theta e^{\pm i\varphi}$	$\frac{RZ^2}{4}$

with $R = 13.6 \text{ eV}$

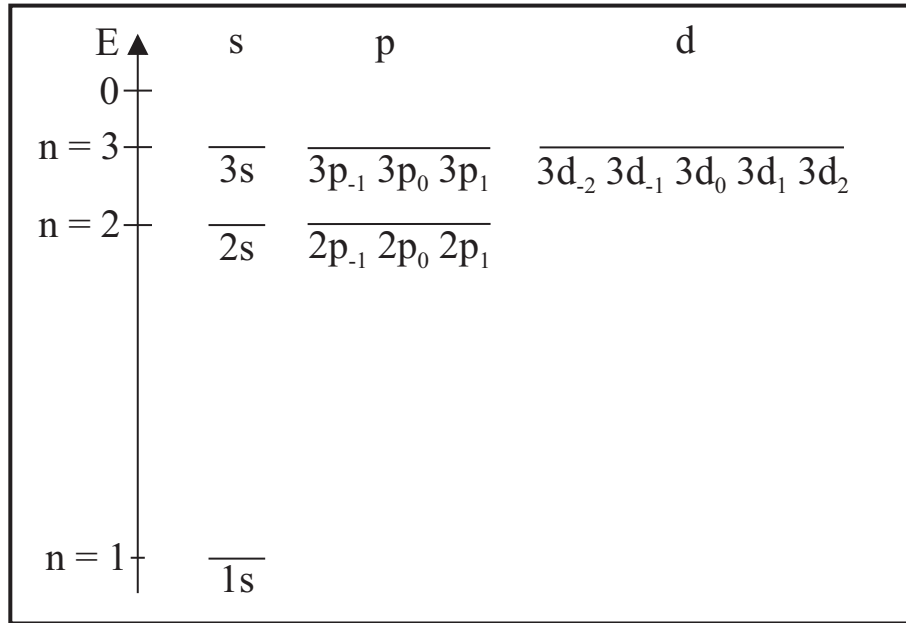


Figure 1.1: Energy spectrum of the Schrödinger-Coulomb problem. Note that the Coulomb potential supports infinitely many bound states ($E_n \xrightarrow{n \rightarrow \infty} 0$).

Degeneracy of energies (which depend only on n)

given n $l = 0, 1, \dots, n - 1$

given l $m = -l, \dots, l$

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

→ 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. The radial quantum number determines the number of nodes in the radial wave function).

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

$$\begin{aligned}\rho_{nlm}(\mathbf{r}) &= |\varphi_{nlm}(\mathbf{r})|^2 = R_{nl}^2 |Y_{lm}(\theta, \varphi)|^2 \\ &= \frac{y_{nl}^2(r)}{r^2} |Y_{lm}(\theta, \varphi)|^2.\end{aligned}\quad (1.27)$$

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 element $[\mathbf{r}, \mathbf{r} + d\mathbf{r}]$. For spherically symmetric potentials it is useful to also define a *radial* probability density by

$$\begin{aligned}\rho_{nl}(r) &= r^2 R_{nl}^2(r) \int |Y_{lm}(\theta, \varphi)|^2 d\Omega \\ &= y_{nl}^2(r)\end{aligned}\quad (1.28)$$

$\rho_{nl}(r) dr$ 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 represented by 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

$$\begin{aligned}\tilde{\varphi}_{nlm}(\mathbf{p}) &= \langle \mathbf{p} | \varphi_{nlm} \rangle = \int \langle \mathbf{p} | \mathbf{r} \rangle \langle \mathbf{r} | \varphi_{nlm} \rangle d^3r \\ &= \frac{1}{[2\pi\hbar]^{\frac{3}{2}}} \int e^{-\frac{i}{\hbar} \mathbf{p} \cdot \mathbf{r}} \varphi_{nlm}(\mathbf{r}) d^3r.\end{aligned}\quad (1.29)$$

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

$$e^{-i\mathbf{k} \cdot \mathbf{r}} = 4\pi \sum_{L=0}^{\infty} \sum_{M=-L}^L (-i)^L j_L(kr) Y_{LM}(\Omega_k) Y_{LM}^*(\Omega_r) \quad (1.30)$$

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

$$\begin{aligned}
\leftrightarrow \tilde{\varphi}_{nlm}(\mathbf{p}) &= 4\pi \frac{1}{[2\pi\hbar]^{\frac{3}{2}}} \sum_{L=0}^{\infty} \sum_{M=-L}^L (-i)^L \int_0^{\infty} r^2 j_L(kr) R_{nl}(r) dr \\
&\quad \times \int Y_{LM}^*(\Omega_r) Y_{lm}(\Omega_r) d\Omega_r Y_{LM}(\Omega_k) \\
&= 4\pi \frac{1}{[2\pi\hbar]^{\frac{3}{2}}} (-i)^l \int_0^{\infty} r^2 j_l(kr) R_{nl}(r) dr Y_{lm}(\Omega_k) \\
&=: P_{nl}(p) Y_{lm}(\Omega_k). \tag{1.31}
\end{aligned}$$

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

$$\begin{aligned}
\tilde{\rho}_{nlm}(\mathbf{p}) &= |\tilde{\varphi}_{nlm}(\mathbf{p})|^2 \\
\tilde{\rho}_{nl}(p) &= p^2 |P_{nl}(p)|^2. \tag{1.32}
\end{aligned}$$

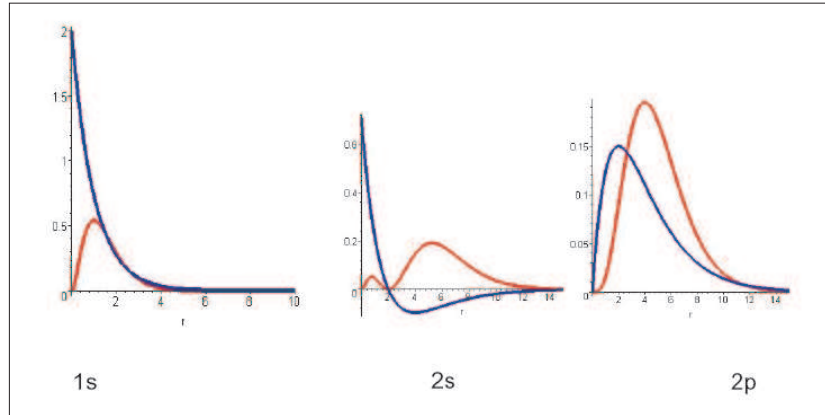


Figure 1.2: Radial hydrogen $1s$, $2s$, $2p$ wave functions (blue) and probability densities (red) in coordinate space (radial distance measured in Bohr radii).

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 (magnitude of the) potential energy is rather large as the nucleus is close. By contrast, the $2p$ state approaches zero for small distances (remember the angular momentum

barrier: only s states do not approach zero for $r \rightarrow 0$). 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.

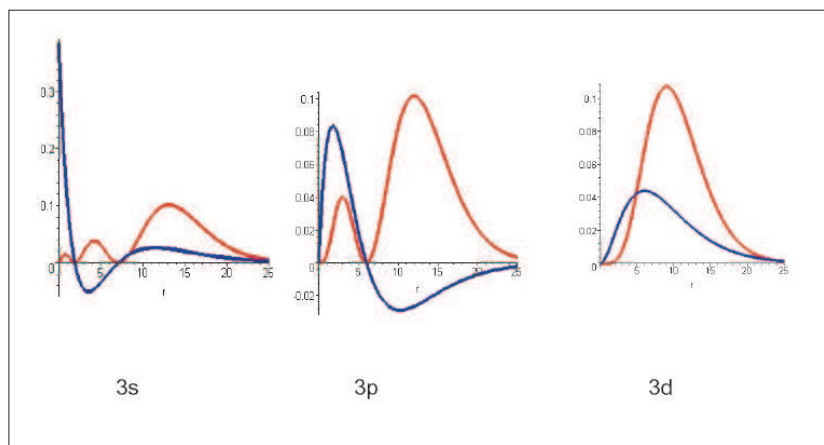


Figure 1.3: Radial hydrogen $3s$, $3p$, $3d$ wave functions (blue) and probability densities (red) in coordinate space (radial distance measured in Bohr radii).

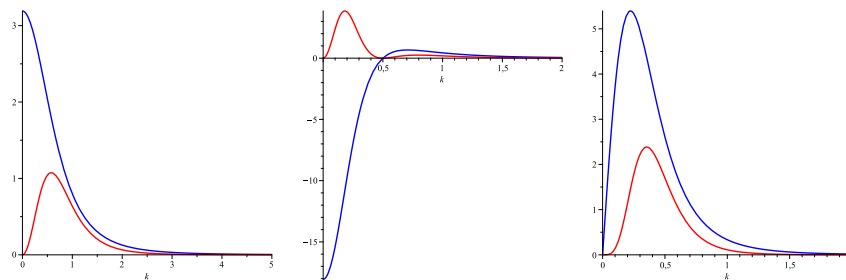


Figure 1.4: Radial hydrogen $1s$, $2s$, $2p$ wave functions (blue) and probability densities (red) in momentum space ($p = k$ measured in atomic units—see Sec. 1.4.e).

The number of nodes in momentum space and coordinate space is the same. Note that the momentum profile of $2s$ is mostly 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 broad range of momenta (and v.v.). However, 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.

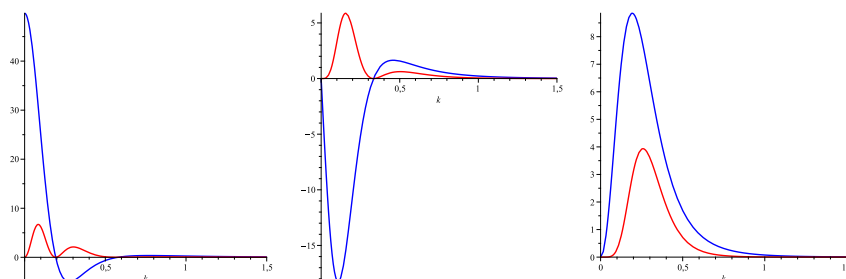


Figure 1.5: Radial hydrogen $3s$, $3p$, $3d$ wave functions (blue) and probability densities (red) in momentum space ($p = k$ measured in atomic units—see Sec. 1.4.e).

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 $Z = 2, 3, \dots$. 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 $E_n \propto \mu = \frac{m_1 m_2}{m_1 + m_2}$ and $\langle r \rangle \propto \mu^{-1}$, i.e., muonic hydrogen is much smaller than normal hydrogen (which is why it is well suited to probe the nuclear charge radius).

d) Corrections

The spectrum determined by Eq. (1.25) 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 (in Chap. 6).

e) Spin

A related item is that a full treatment of the hydrogen problem needs to include the spin degree of freedom. Assuming that you have seen discussions of this in previous courses, we skip this point here and just refer to the literature, e.g., [Gri], Chap. 4.4. Electron spin will naturally show up in the relativistic treatment of the hydrogen problem (Chap. 6). Until then, all we need to remember is that it is characterized by the quantum numbers $s = 1/2$ and $m_s = \pm 1/2$. One often writes $|m_s = +1/2\rangle = |\uparrow\rangle$ and $|m_s = -1/2\rangle = |\downarrow\rangle$ for the spin-up and spin-down states.

f) 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

$$\hat{H}_{\text{SI}} = -\frac{\hbar^2}{2m_e} \nabla_r^2 - \frac{e^2}{4\pi\epsilon_0 r} \quad (1.33)$$

(i.e., the one of Eq. (1.7) for $Z = 1$ and $\mu \rightarrow m_e$). 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

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

- 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

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

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

- 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:

$$\mathbf{E} = F\hat{z} \quad (2.1)$$

The associated electrostatic potential reads

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

↪ potential energy of an electron

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

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

$$\hat{H}|\varphi_\alpha\rangle = E_\alpha|\varphi_\alpha\rangle \quad (2.4)$$

for (using atomic units from now on)

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

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 non-degenerate systems

a) General formalism

Task: solve stationary SE

$$\hat{H}|\varphi_\alpha\rangle = E_\alpha|\varphi_\alpha\rangle \quad (2.6)$$

for Hermitian Hamiltonian ($\hat{H} = \hat{H}^\dagger$). Decompose

$$\hat{H} = \hat{H}_0 + \hat{W} \quad (2.7)$$

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

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

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 weak. Let’s introduce a smallness parameter λ :

$$\hat{W} \equiv \lambda\hat{w} \quad \text{with} \quad \lambda \ll 1 \quad (2.9)$$

$$\stackrel{(2.6)}{\longrightarrow} \quad \left(\hat{H}_0 + \lambda\hat{w}\right)|\varphi_\alpha(\lambda)\rangle = E_\alpha(\lambda)|\varphi_\alpha(\lambda)\rangle \quad (2.10)$$

Taylor expansions about $\lambda = 0$:

$$E_\alpha(\lambda) = E_\alpha^{(0)} + \left.\frac{dE_\alpha(\lambda)}{d\lambda}\right|_{\lambda=0} \lambda + \frac{1}{2} \left.\frac{d^2E_\alpha(\lambda)}{d\lambda^2}\right|_{\lambda=0} \lambda^2 + \dots \quad (2.11)$$

$$|\varphi_\alpha(\lambda)\rangle = |\varphi_\alpha^0\rangle + \left.\frac{d}{d\lambda}|\varphi_\alpha(\lambda)\rangle\right|_{\lambda=0} \lambda + \dots \quad (2.12)$$

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

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

$$\boxed{\text{i) } \alpha = \beta} \implies E'_\alpha(\lambda) = \langle \varphi_\alpha(\lambda) | \hat{w} | \varphi_\alpha(\lambda) \rangle \quad (2.13)$$

$$\boxed{\text{ii) } \alpha \neq \beta} \implies \langle \varphi_\beta(\lambda) | \varphi'_\alpha(\lambda) \rangle = \frac{\langle \varphi_\beta(\lambda) | \hat{w} | \varphi_\alpha(\lambda) \rangle}{E_\alpha(\lambda) - E_\beta(\lambda)} \quad (2.14)$$

In order to use Eq. (2.14) for an expansion of $|\varphi'_\alpha\rangle$ in terms of the orthonormal basis $\{|\varphi_\alpha\rangle\}$ 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

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

proof :

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

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

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

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

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):

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

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

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 (not sufficient) for convergence (cf. Eq. (2.18)):

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

3. In practice, ‘exact’ calculations for the energies beyond 1st order are often not feasible due to (infinite) sums over all basis states (cf. Eq. (2.17)).
4. Literature: [Gri], Chap. 6.1; [Lib], Chap. 13.1

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

Ingredients (in atomic units):

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

1st-order energy correction:

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

(with $x = \cos \theta$)

The 2nd-order energy correction

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

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 $E_{1s}^{(0)} - E_\beta^{(0)} < 0$, i.e., $\Delta E_{1s}^{(2)} < 0$.

Consider

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

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

$$|\Delta E_{1s}^{(2)}| < \frac{8}{3} F^2 \quad (2.21)$$

The exact result for the “quadratic Stark effect” (see [Sha], Chap. 17) is

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

Interpretation:

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

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

where d_z is the z -component of the electric dipole moment.

Link this to QM by recognizing that $\rho(\mathbf{r}) = -|\varphi(\mathbf{r})|^2$ (atomic units!).

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

Now use Eq. (2.18) to obtain

$$d_z = -2F \sum_{\beta \neq 1s} \frac{|\langle \varphi_{1s}^0 | z | \varphi_{\beta}^0 \rangle|^2}{E_{1s}^{(0)} - E_{\beta}^{(0)}} + O(\lambda^2) \approx -\frac{2}{F} \Delta E_{1s}^{(2)} = \frac{9}{2} F$$

Summary:

- $\Delta E_{1s}^{(1)} = 0$ expresses the fact that the unperturbed hydrogen ground state has no static electric 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:

$$\hat{H} = \hat{H}_0 + \lambda \hat{w} \quad (2.23)$$

with

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

where g_{α} is the degeneracy level. The set $\{|\varphi_{\alpha j}^0\rangle, j = 1, \dots, g_{\alpha}\}$ 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:

$$\hat{H} |\varphi_{\alpha j}\rangle = E_{\alpha j} |\varphi_{\alpha j}\rangle. \quad (2.25)$$

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

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

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

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

$$|\varphi_{\alpha j}\rangle = |\tilde{\varphi}_{\alpha j}^0\rangle + \lambda |\varphi_{\alpha j}^1\rangle + \dots \quad (2.28)$$

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

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

sort this in terms of powers of λ

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

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

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

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 $\det(\underline{w}^\alpha - E_\alpha^{(1)} \underline{1}) = 0 \rightarrow$ obtain eigenvalues $\{E_{\alpha j}^{(1)}, j = 1, \dots, g_\alpha\}$, which happen to be the first-order energy corrections, i.e., the quantities we are after!
- (ii) Find mixing coefficients $\{a_{kj}^\alpha, k, j = 1, \dots, g_\alpha\}$ by inserting eigenvalues into the matrix equations (2.29), i.e., obtain eigenvectors.
- (ii) Check that $\langle \tilde{\varphi}_{\alpha l}^0 | \hat{w} | \tilde{\varphi}_{\alpha k}^0 \rangle = E_{\alpha j}^{(1)} \delta_{lk}$ (i.e., perturbation matrix is diagonal with respect to the states $\{|\tilde{\varphi}_{\alpha k}^0\rangle\}$).

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

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

with (cf. Eq. (1.24))

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

$$\hookrightarrow \langle \varphi_{nlm}^0 | z | \varphi_{nl'm'}^0 \rangle = \sqrt{\frac{4\pi}{3}} \int_0^\infty r^3 R_{nl}(r) R_{nl'}(r) dr \int Y_{lm}^*(\Omega) Y_{10}(\Omega) Y_{l'm'}(\Omega) d\Omega \quad (2.30)$$

The angular integral is a special case of a more general integral over three spherical harmonics, the result of which is known (“Wigner-Eckart theorem”, see, e.g., [SN], Chap. 3.11):

$$\begin{aligned} &\sqrt{\frac{4\pi}{2L+1}} \int Y_{lm}^*(\Omega) Y_{LM}(\Omega) Y_{l'm'}(\Omega) d\Omega \\ &= (-1)^m \sqrt{(2l+1)(2l'+1)} \begin{pmatrix} l & L & l' \\ -m & M & m' \end{pmatrix} \begin{pmatrix} l & L & l' \\ 0 & 0 & 0 \end{pmatrix} \quad (2.31) \end{aligned}$$

with

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \in \mathcal{R} \quad \text{“Wigner’s } 3j\text{-symbol”}$$

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:

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

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

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

$$m = m' \quad \text{and} \quad \Delta l \equiv l - l' = \pm 1 \quad (2.32)$$

These conditions are called *electric dipole selection rules*.

Further literature on angular momentum operators, 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 enumerated from one to four in the following order: $\{\varphi_{2s}^0, \varphi_{2p_0}^0, \varphi_{2p_{-1}}^0, \varphi_{2p_{+1}}^0\}$

- matrix elements:
due to the dipole selection rules (2.32) there is only one nonzero matrix element we need to calculate:

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

→ 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:

$$\det \begin{pmatrix} -E^{(1)} & w_{12} & 0 & 0 \\ w_{12} & -E^{(1)} & 0 & 0 \\ 0 & 0 & -E^{(1)} & 0 \\ 0 & 0 & 0 & -E^{(1)} \end{pmatrix} = 0 \quad (2.33)$$

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

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

- mixing coefficients

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

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

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

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

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

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

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

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

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

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

\hookrightarrow normalized ‘Stark’ states:

$$|\tilde{\varphi}_{E_3}^0\rangle = \frac{1}{\sqrt{2}} (|\varphi_{2s}^0\rangle + |\varphi_{2p_0}^0\rangle) \quad (2.34)$$

$$|\tilde{\varphi}_{E_4}^0\rangle = \frac{1}{\sqrt{2}} (|\varphi_{2s}^0\rangle - |\varphi_{2p_0}^0\rangle) \quad (2.35)$$

Summary and interpretation

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

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

3. The Stark states (2.34), (2.35) do have nonzero static dipole moments which is why they acquire energy in an applied electric field (calculate the dipole moments!).

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 :

$$\det \begin{pmatrix} A_1 & 0 & 0 \\ 0 & A_2 & 0 \\ 0 & 0 & A_3 \end{pmatrix} = 0$$

$$\Leftrightarrow \det A = 0 \Leftrightarrow \det A_i = 0 \quad \text{for } i = 1, \dots, 3$$

The only nontrivial secular equation for the L -shell problem then is (cf. Eq. (2.33)):

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

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

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

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

$$\mathbf{B} = \nabla \times \mathbf{A} \quad (3.1)$$

$$\mathbf{E} = -\nabla\Phi - \frac{\partial\mathbf{A}}{\partial t} \quad (3.2)$$

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

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

- Generalized potential energy

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

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

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

i.e.,

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

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

- Lagrangian

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

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

- Hamiltonian

$$H = \mathbf{p} \cdot \mathbf{v} - L \quad (3.7)$$

with the generalized momentum

$$\mathbf{p} = \nabla_v L = m\mathbf{v} + q\mathbf{A} \quad (3.8)$$

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

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

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

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

b) Semiclassical Hamiltonian for an electron in an EM field

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

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

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

$$\nabla^2 \mathbf{A} - \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \mathbf{A} = 0 \quad (3.12)$$

$$\nabla^2 \Phi = 0 \quad (3.13)$$

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

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

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

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

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 formalism

The Hamiltonian under discussion is of the generic form

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

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

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

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

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

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

$$\equiv \sum_j c_j(t) |\psi_j(t)\rangle \quad (3.20)$$

Substituting Eq. (3.19) into Eq. (3.17) yields

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

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

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

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

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

$$\hookrightarrow \text{transition probabilities } \varphi_0 \longrightarrow \varphi_k$$

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

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

Using this ansatz in Eq. (3.21) results in

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

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

These equation can be solved successively:

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

$$\begin{aligned}
\hookrightarrow \quad & c_k^{(1)}(t) - \underbrace{c_k^{(1)}(t_0)}_{=0} = -\frac{i}{\hbar} \int_{t_0}^t e^{\frac{i}{\hbar}(\epsilon_k - \epsilon_0)t'} \langle \varphi_k | \hat{w}(t') | \varphi_0 \rangle dt' \quad (3.25) \\
& (\text{as } \lambda = 0 \text{ at } t = t_0)
\end{aligned}$$

accordingly:

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

Comments:

(i) “Exact” calculations beyond 1st order are in general impossible due to infinite sums

(ii) “Closure approximation”: $\epsilon_j \approx \bar{\epsilon}$

$$\hookrightarrow c_k^{(2)}(t) = -\frac{1}{\hbar^2} \int_{t_0}^t dt' \int_{t_0}^{t'} dt'' e^{\frac{i}{\hbar}\bar{\epsilon}(t'' - t')} e^{\frac{i}{\hbar}\epsilon_k t'} e^{-\frac{i}{\hbar}\epsilon_0 t''} \langle \varphi_k | \hat{w}(t') \hat{w}(t'') | \varphi_0 \rangle$$

(iii) Interpretation

$$\begin{array}{ccccccc}
& & t_0 & & t & & \\
1^{\text{st}} \text{ order} & & |\varphi_0\rangle & \xrightarrow{\hat{W}} & |\varphi_k\rangle & & \text{direct (one-step) transition} \\
2^{\text{nd}} \text{ order} & & |\varphi_0\rangle & \xrightarrow{\hat{W}} & |\varphi_j\rangle & \xrightarrow{\hat{W}} & |\varphi_k\rangle \\
& & \text{transition via 'virtual' intermediate states} & & & & \text{(two steps)}
\end{array}$$

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

b) Discussion of the 1st-order result

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

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

$$\text{with} \quad \omega_{k0} = \omega_k - \omega_0 = \frac{\epsilon_k - \epsilon_0}{\hbar}$$

transition frequency

$$W_{k0}(t') = \langle \varphi_k | \hat{W}(t') | \varphi_0 \rangle = \lambda \langle \varphi_k | \hat{w}(t') | \varphi_0 \rangle$$

transition matrix element

$$p_{0 \rightarrow k}^{\text{1st order}} = \frac{1}{\hbar^2} \left| \int_{t_0}^t e^{i\omega_{k0}t'} W_{k0}(t') dt' \right|^2, \quad k \neq 0$$

transition probability

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

$$\begin{aligned} p_{0 \rightarrow 0} &= |c_0^{(0)} + \lambda c_0^{(1)} + \lambda^2 c_0^{(2)} + \dots|^2 \\ &= 1 + \lambda(c_0^{(1)} + c_0^{(1)*}) + \lambda^2(c_0^{(2)} + c_0^{(2)*} + |c_0^{(1)}|^2) + O(\lambda^3) \\ &= 1 + \lambda^2(2\text{Re}(c_0^{(2)}) + |c_0^{(1)}|^2) + O(\lambda^3) \\ &= \dots \approx 1 - \sum_{k \neq 0} p_{0 \rightarrow k}^{\text{1st order}} \end{aligned} \quad (3.28)$$

The latter result can be worked out explicitly and is not surprising: it expresses probability conservation (which is automatically fulfilled if the TDSE is solved exactly).

Examples

(i) Slowly varying perturbation

Let's assume that the perturbation is turned on very gently at $t = t_0$. 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.

$$\boxed{k \neq 0}$$

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

This implies that $p_k^{\text{1st order}} = 0$, i.e., there are no transitions. Let's sub the result for the first-order coefficients into the time-dependent state vector:

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

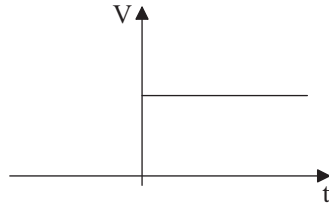
The amplitude c_0 can be set equal to one. This introduces at most a small phase error (up to first order).

$$\begin{aligned} \hookrightarrow |\psi(t)\rangle &\approx \left(|\varphi_0\rangle + \sum_{k \neq 0} \frac{\langle \varphi_k | \hat{W}(t) | \varphi_0 \rangle}{\epsilon_0 - \epsilon_k} |\varphi_k\rangle \right) e^{-\frac{i}{\hbar} \epsilon_0 t} \\ &\equiv |\tilde{\varphi}_0(t)\rangle e^{-\frac{i}{\hbar} \epsilon_0 t} \end{aligned} \tag{3.29}$$

Comparing this to the general results of *stationary* PT one can interpret $|\tilde{\varphi}_0(t)\rangle$ 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*.

Comments:

- (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 a so-called quasimolecular state during the collision and back in the initial atomic state thereafter.
 - (iii) Further reading: [Boh], Chap. 20; [Gri], Chap. 10; [SN], Chap. 5.6
- (ii) Sudden perturbation



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

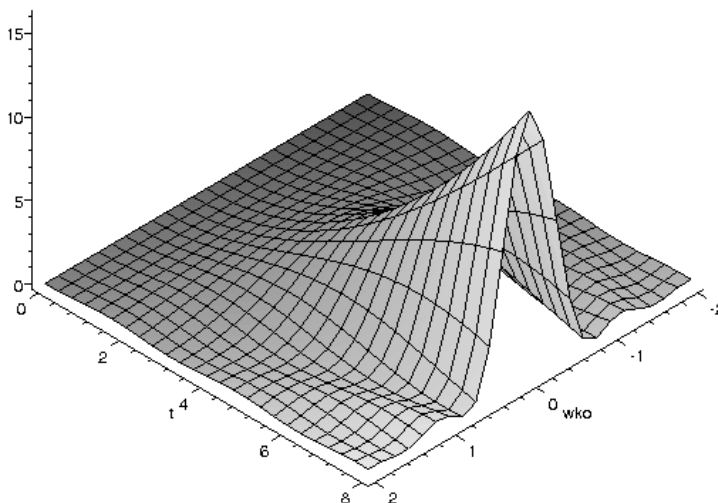
$$\boxed{k \neq 0}$$

$$\begin{aligned} \hookrightarrow c_k^{\text{1st order}}(t) &= -\frac{i}{\hbar} \int_0^t e^{i\omega_{k0}t'} W_{k0}(t') dt' \\ &= \frac{\langle \varphi_k | \hat{W} | \varphi_0 \rangle}{i\hbar} \int_0^t e^{i\omega_{k0}t'} dt' \\ &= -\frac{\langle \varphi_k | \hat{W} | \varphi_0 \rangle}{\hbar\omega_{k0}} (e^{i\omega_{k0}t} - 1) \end{aligned}$$

\hookrightarrow transition probability

$$p_{0 \rightarrow k}^{\text{1st order}}(t) = |c_k^{\text{1st order}}(t)|^2 = \frac{4|W_{k0}|^2}{\hbar^2} f(t, \omega_{k0}) \quad (3.30)$$

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

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 $t \rightarrow \infty$:

$$f(t, \omega_{k0}) \xrightarrow{t \rightarrow \infty} \frac{\pi t}{2} \delta(\omega_k - \omega_0) \quad (3.32)$$

$$\hookrightarrow p_{0 \rightarrow k}^{\text{1st order}} \xrightarrow{t \rightarrow \infty} \frac{2\pi t}{\hbar} |W_{k0}|^2 \delta(\omega_k - \omega_0)$$

The sudden perturbation sounds academic, but it prepares us for the next example and has in fact an important application (see later).

(iii) Periodic perturbation

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

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

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

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

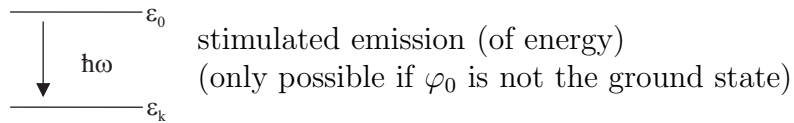
$$\begin{aligned} p_{0 \rightarrow k}^{\text{1st order}}(t) &= \frac{4|B_{k0}|^2}{\hbar^2} \left\{ f(t, \omega_{k0} + \omega) + f(t, \omega_{k0} - \omega) \right\} \quad (3.34) \\ &\xrightarrow{t \rightarrow \infty} \frac{2\pi t}{\hbar} |B_{k0}|^2 \left\{ \delta(\omega_k - \omega_0 + \omega) + \delta(\omega_k - \omega_0 - \omega) \right\} \end{aligned}$$

with $B_{k0} = \langle \varphi_k | \hat{B} | \varphi_0 \rangle$ and Eqs. (3.31) and (3.32).

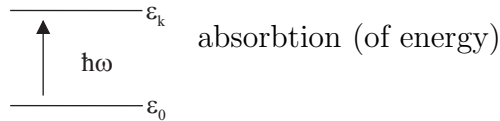
Comments:

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

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



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



- (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

$$\hat{W} = \frac{e}{m} \mathbf{A} \cdot \hat{\mathbf{p}} \quad (3.35)$$

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

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

with

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

(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 at resonance

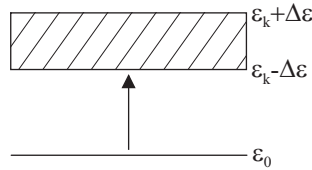
$$\begin{aligned} p_{i \rightarrow f}^{\text{1st order}} &= \frac{4|B_{fi}|^2}{\hbar^2} f(t, \omega_{fi} \pm \omega = 0) = \frac{|B_{fi}|^2}{\hbar^2} t^2 \ll 1 \\ \Leftrightarrow \quad t &\ll \frac{\hbar}{|B_{fi}|} \end{aligned}$$

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

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 $p_{i \rightarrow f} = |\langle \varphi_f | \psi(t) \rangle|^2$ is a probability density rather than a probability. A proper probability is obtained if one integrates over an interval of final states.

a) Transitions to the continuum: Fermi's Golden Rule



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

The weight factor in the integral, $\rho(\epsilon'_f)$, is called density of states (in the interval $\Delta\epsilon_f \equiv [\epsilon_f - \Delta\epsilon; \epsilon_f + \Delta\epsilon]$). Let's try to understand why we need it. We will be specific and consider free-particle continuum states, i.e., momentum eigenstates (= eigenstates of $\hat{H}_0 = \hat{\mathbf{p}}^2/(2m)$)

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

For a normalized solution of the TDSE the probability to find the system in the (3D) momentum region $\Delta\mathbf{p}_f$ is:

$$P_{i \rightarrow \Delta\mathbf{p}_f} = \int_{\Delta\mathbf{p}_f} \langle \psi(t) | \mathbf{p}_f \rangle \langle \mathbf{p}_f | \psi(t) \rangle d^3p_f = \int_{\Delta\mathbf{p}_f} |\tilde{\psi}(\mathbf{p}_f, t)|^2 d^3p_f.$$

We need to transform this from momentum to energy, because we are interested in transitions into a certain energy interval. For free particles we have the simple relation $\epsilon_f = \mathbf{p}_f^2/2m$ such that

$$\begin{aligned} \hookrightarrow d^3p_f &= p_f^2 dp_f d\Omega_p = p_f^2 \frac{dp_f}{d\epsilon_f} d\epsilon_f d\Omega_p \\ &= \sqrt{2m^3\epsilon_f} d\epsilon_f d\Omega_p \\ \hookrightarrow P_{i \rightarrow \Delta\epsilon_f} &= \int_{\Delta\mathbf{p}_f} |\tilde{\psi}(\mathbf{p}_f)|^2 d^3p_f = \int \sqrt{2m^3\epsilon_f} \left(\int |\tilde{\psi}(\mathbf{p}_f)|^2 d\Omega_p \right) d\epsilon_f \\ &\equiv \int_{\Delta\epsilon_f} \rho(\epsilon_f) p_{i \rightarrow f}(\epsilon_f) d\epsilon_f \end{aligned}$$

with

$$\rho(\epsilon_f) = \sqrt{2m^3\epsilon_f} \quad (3.38)$$

i.e., the density of states is a weight factor that originates in the transformation of the Jacobian.

Let's go back to our example of a time-periodic perturbation and calculate the probability for a transition into the energy interval $\Delta\epsilon_f = [\epsilon_f - \Delta\epsilon; \epsilon_f + \Delta\epsilon]$. Because the probability density (3.34) we want to use depends on the emission angle¹ we write

$$P_{i \rightarrow f} \equiv \frac{dP_{i \rightarrow \Delta\epsilon_f}}{d\Omega_p} = \int_{\epsilon_f - \Delta\epsilon}^{\epsilon_f + \Delta\epsilon} \rho(\epsilon'_f) p_{i \rightarrow f}(\epsilon'_f, \Omega_p) d\epsilon'_f$$

and obtain

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

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 $w_{i \rightarrow f} = \frac{d}{dt} P_{i \rightarrow f}$ to obtain

Fermi's Golden Rule (FGR)

$$w_{i \rightarrow f}^{e,a} = \frac{2\pi}{\hbar} |B_{fi}|^2 \rho(\epsilon_f) \Big|_{\epsilon_f = \epsilon_i \pm \hbar\omega} \quad (3.39)$$

¹The angular dependence is hidden in the matrix element B_{fi} .

b) The photoionization cross section

Let's start with a general definition of a cross section for a transition $i \rightarrow f$:

$$\sigma_{i \rightarrow f} := \frac{\text{rate}_{i \rightarrow f}}{\text{incoming beam current}} = \frac{W_{i \rightarrow f}}{j_{\text{inc}}} \quad (3.40)$$

Dimensionally, $\sigma_{i \rightarrow f}$ is an area. We can picture it as the cross sectional area (of the atom) that the incoming beam (of photons or massive particles) has to 'hit' in order to induce a transition. Collecting all relevant previous results the total photoionization cross section can be written as:

$$\sigma_{\text{tot}}^{\text{ion}} = \int \frac{d\sigma_{\text{ion}}}{d\Omega} d\Omega = \frac{2\pi e^2 |A_0|^2}{4\hbar m^2 j_{\text{inc}}} \rho(\epsilon_f = \epsilon_i + \hbar\omega) \int |T_{fi}(\Omega)|^2 d\Omega \quad (3.41)$$

with the "T-matrix element"

$$T_{fi}(\Omega) = \langle \varphi_f | e^{-i\mathbf{k}\cdot\mathbf{r}} \hat{\pi} \cdot \hat{\mathbf{p}} | \varphi_i \rangle. \quad (3.42)$$

One finds for the incoming beam current for the photoionization problem $j_{\text{inc}} = \epsilon_0 c \omega |A_0|^2 / (2\hbar)$ (see Appendix A) such that

$$\frac{|A_0|^2}{j_{\text{inc}}} = \frac{8\pi\hbar^2\alpha}{e^2\omega} \quad (3.43)$$

and the differential cross section (DCS) becomes

$$\frac{d\sigma_{\text{ion}}}{d\Omega} = \frac{4\pi^2\alpha}{\omega} \frac{\hbar}{m^2} |T_{fi}(\Omega)|^2 \rho(\epsilon_f) \quad (3.44)$$

c) 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:

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

$$\stackrel{(3.42)}{\hookrightarrow} T_{fi}^{\text{dip}} = \langle \varphi_f | \hat{\pi} \cdot \hat{\mathbf{p}} | \varphi_i \rangle$$

The T-matrix element can be rewritten using

$$\hat{\mathbf{p}} = \frac{im}{\hbar} [\hat{H}_0, \mathbf{r}] \quad (3.45)$$

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

$$\begin{aligned} \hookrightarrow T_{fi}^{\text{dip}} &= \frac{im}{\hbar} \langle \varphi_f | \hat{H}_0 \hat{\boldsymbol{\pi}} \cdot \hat{\mathbf{r}} - \hat{\boldsymbol{\pi}} \cdot \hat{\mathbf{r}} \hat{H}_0 | \varphi_i \rangle \\ &= \frac{im}{\hbar} (\epsilon_f - \epsilon_i) \hat{\boldsymbol{\pi}} \cdot \langle \varphi_f | \mathbf{r} | \varphi_i \rangle = im\omega \hat{\boldsymbol{\pi}} \cdot \langle \varphi_f | \mathbf{r} | \varphi_i \rangle \end{aligned}$$

The remaining matrix elements are the well-known dipole matrix elements (cf. Chap. 2). The DCS in dipole approximation reads

$$\frac{d\sigma_{\text{ion}}^{\text{dip}}}{d\Omega} = 4\pi^2 \hbar \omega \alpha |\langle \varphi_f | \hat{\boldsymbol{\pi}} \cdot \hat{\mathbf{r}} | \varphi_i \rangle|^2 \rho(\epsilon_f) \quad (3.46)$$

Evaluation of the cross section for hydrogen

Assumptions

1. $\hat{\boldsymbol{\pi}} = \hat{\mathbf{z}} \Rightarrow$ standard selection rules apply²: $\Delta m = 0, \Delta l = \pm 1$
2. Initial and final states (in atomic units)

$$\begin{aligned} \varphi_i &= \varphi_{1s}(r) = \frac{1}{\sqrt{\pi}} e^{-r} \\ \varphi_f &= \langle \mathbf{r} | \mathbf{p} \rangle = \frac{1}{(2\pi)^{3/2}} e^{i\mathbf{p} \cdot \mathbf{r}} \end{aligned}$$

One finds

$$|\langle \varphi_f | \hat{\boldsymbol{\pi}} \cdot \hat{\mathbf{r}} | \varphi_i \rangle|^2 = |\langle \varphi_f | z | \varphi_i \rangle|^2 = \frac{128p^2}{\pi^2(1+p^2)^6} \cos^2 \theta \quad (3.47)$$

and for the DCS [using Eq. (3.38) and the dipole approximation]

$$\frac{d\sigma_{\text{ion}}^{\text{dip}}}{d\Omega} = 1024\omega\alpha\sqrt{2\epsilon_f} \frac{\epsilon_f}{(1+2\epsilon_f)^6} \cos^2 \theta \quad (3.48)$$

where $\epsilon_f = -0.5 + \omega$. Note the characteristic dipole ($\cos^2 \theta$) dependence of the DCS. The total cross section is

$$\sigma_{\text{tot}}^{\text{dip}} = \int \frac{d\sigma_{\text{ion}}^{\text{dip}}}{d\Omega} d\Omega = \frac{4096\pi}{3} \frac{\omega\alpha\sqrt{2\epsilon_f}\epsilon_f}{(1+2\epsilon_f)^6}$$

²For other polarizations the m -selection rule changes, but the l -selection rule does not.

For large ϵ_f we have $\omega \approx \epsilon_f$ and $1 + 2\epsilon_f \approx 2\epsilon_f$ and obtain the approximate result

$$\sigma_{\text{tot}}^{\text{dip}} \approx \frac{64\pi\sqrt{2}}{3}\alpha\omega^{-7/2} \quad (3.49)$$

which shows that the cross section decreases rapidly with increasing energy (frequency).

Final comments:

- (i) A calculation beyond the dipole approximation is feasible for the hydrogen problem.
- (ii) Literature on photoionization [BS], Chap. IV b
- (iii) Literature on semiclassical atom-radiation interactions [CT], Chap. XIII; [Lib], Chap. 13.5-13.9
- (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 expressions for stimulated emission and absorption, but it makes it possible to also describe the process of *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}, Φ) , which act on the wave function of the electron(s). Now, we want to construct a Hamiltonian that acts on the electron(s) and the EM field. Accordingly, we need state vectors which include the degrees of freedom of the field.

Let's begin 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:

$$\begin{aligned}\hat{H} &= \hat{H}_1 + \hat{H}_2 + \hat{W} \\ \hat{H} &= \underbrace{\hat{H}_A + \hat{H}_F}_{=\hat{H}_0} + \hat{W}\end{aligned}\tag{3.50}$$

\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 towards a first-order perturbation theory treatment

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

- solve eigenvalue problem of \hat{H}_0

$$\begin{aligned}
 \hat{H}_A|\varphi_j\rangle &= \epsilon_j |\varphi_j\rangle \checkmark \\
 \hat{H}_F|\xi_k\rangle &= \epsilon_k |\xi_k\rangle ? \\
 \hookrightarrow \hat{H}_0|\Phi_{jk}\rangle &= \left(\hat{H}_A + \hat{H}_F\right) |\varphi_j\rangle|\xi_k\rangle \\
 &= (\epsilon_j + \epsilon_k) |\varphi_j\rangle|\xi_k\rangle \\
 &= (\epsilon_j + \epsilon_k) |\Phi_{jk}\rangle \\
 \Leftrightarrow \hat{H}_0|\Phi_l\rangle &= E_l|\Phi_l\rangle, \quad l \rightarrow (j, k)
 \end{aligned} \tag{3.51a}$$

$$\Leftrightarrow \hat{H}_0|\Phi_l\rangle = E_l|\Phi_l\rangle, \quad l \rightarrow (j, k) \tag{3.51b}$$

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

$$\hat{W} = \frac{e}{m} \hat{\mathbf{A}} \cdot \hat{\mathbf{p}} \tag{3.52}$$

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

$$W_{fi} = \langle \Phi_f | \hat{W} | \Phi_i \rangle \tag{3.53}$$

a) Construction of \hat{H}_F

Loosely speaking, Hamiltonians are the quantum analogs of classical energy expressions. Let's start from the energy of a classical EM field in a (vacuum) cube of volume L^3

$$\begin{aligned}
 W_{\text{EM}} &= \frac{1}{2} \int_{L^3} (\mathbf{E} \cdot \mathbf{D} + \mathbf{B} \cdot \mathbf{H}) d^3r \\
 &= \frac{\epsilon_0}{2} \int_{L^3} (\mathbf{E}^2 + c^2 \mathbf{B}^2) d^3r \quad c^2 = \frac{1}{\mu_0 \epsilon_0}
 \end{aligned} \tag{3.54}$$

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:

$$\mathbf{A}(\mathbf{r}, t) = \sum_{\lambda} \mathbf{A}_{\lambda}(\mathbf{r}, t) \quad (3.55a)$$

$$\mathfrak{R}^3 \ni \mathbf{A}_{\lambda}(\mathbf{r}, t) = \frac{\hat{\pi}_{\lambda}}{L^{\frac{3}{2}}} \{q_{\lambda} e^{i(\mathbf{k}_{\lambda} \mathbf{r} - \omega_{\lambda} t)} + q_{\lambda}^* e^{-i(\mathbf{k}_{\lambda} \mathbf{r} - \omega_{\lambda} t)}\} \quad (3.55b)$$

λ mode index

$\hat{\pi}_{\lambda}$ unit polarization vectors $|\hat{\pi}_{\lambda}| = 1$

$\mathbf{k}_{\lambda} = \frac{2\pi}{L}(n_x^{\lambda}, n_y^{\lambda}, n_z^{\lambda})$ $n_i^{\lambda} \in \mathcal{Z}$ wave vectors and numbers

$\omega_{\lambda} = ck_{\lambda}$ dispersion relations \rightarrow field frequencies

$\hat{\pi}_{\lambda} \cdot \mathbf{k}_{\lambda} = 0$ transverse wave requirement

Each mode is thus defined by a wave vector (with three components) and a polarization direction³. 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 subs this into Eq. (3.54) one arrives (after some calculation) at

$$W_{\text{EM}} = 2\epsilon_0 \sum_{\lambda} \omega_{\lambda}^2 q_{\lambda}^* q_{\lambda} \quad (3.56)$$

³This is to say that λ is actually a quadruple index. Note that for the general solution of the wave equation we actually need two linearly independent polarizations per wave vector, consistent with the transverse wave condition. 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:

$$Q_\lambda := \sqrt{\epsilon_0} (q_\lambda^* + q_\lambda) \quad (3.57)$$

$$P_\lambda := i\sqrt{\epsilon_0} \omega_\lambda (q_\lambda^* - q_\lambda) \quad (3.58)$$

$$\Leftrightarrow q_\lambda = \frac{1}{2\sqrt{\epsilon_0}} \left(Q_\lambda + i\frac{P_\lambda}{\omega_\lambda} \right) \quad (3.59)$$

$$q_\lambda^* = \frac{1}{2\sqrt{\epsilon_0}} \left(Q_\lambda - i\frac{P_\lambda}{\omega_\lambda} \right) \quad (3.60)$$

$$\hookrightarrow W_{\text{EM}} = \frac{1}{2} \sum_\lambda \omega_\lambda^2 \left(Q_\lambda - i\frac{P_\lambda}{\omega_\lambda} \right) \left(Q_\lambda + i\frac{P_\lambda}{\omega_\lambda} \right) \quad (3.61)$$

$$= \frac{1}{2} \sum_\lambda (P_\lambda^2 + \omega_\lambda^2 Q_\lambda^2) \quad (3.62)$$

Doesn't this look familiar? The EM field has the algebraic form of a collection of harmonic oscillators⁴. We know how to quantize the harmonic oscillator, so here is the quantization recipe:

$$P_\lambda \rightarrow \hat{P}_\lambda = \hat{P}_\lambda^\dagger \quad (3.63)$$

$$Q_\lambda \rightarrow \hat{Q}_\lambda = \hat{Q}_\lambda^\dagger \quad (3.64)$$

$$\text{with } [\hat{Q}_\lambda, \hat{P}_{\lambda'}] = i\hbar\delta_{\lambda\lambda'} \quad (3.65)$$

$$\hookrightarrow W_{\text{EM}} \rightarrow \hat{H}_F = \frac{1}{2} \sum_\lambda \left(\hat{P}_\lambda^2 + \omega_\lambda^2 \hat{Q}_\lambda^2 \right) = \hat{H}_F^\dagger \quad (3.66)$$

The algebraic form of \hat{H}_F together with the commutation relations (3.65) determine its spectrum:

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

⁴One obtains the standard form if one substitutes $p_\lambda = \sqrt{m_\lambda} P_\lambda, x_\lambda = Q_\lambda / \sqrt{m_\lambda}$

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’⁵, 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 accommodate (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:

$$\text{zero-point energy} \quad E_0 = \sum_\lambda \frac{\hbar \omega_\lambda}{2} \rightarrow \infty \quad (3.67)$$

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 significance⁶. These are always finite since the zero-point energies cancel out.

⁵You may say particles instead of quanta, but these particles turn out to have an odd property: zero rest mass.

⁶In fact, renormalization is not much more than a more formal way of adopting this viewpoint.

b) Creation and annihilation operators

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

$$\hat{b}_\lambda^\dagger = \frac{1}{\sqrt{2\hbar \omega_\lambda}} (\omega_\lambda \hat{Q}_\lambda - i\hat{P}_\lambda) \quad \text{creation op.} \quad (3.68)$$

$$\hat{b}_\lambda = \frac{1}{\sqrt{2\hbar \omega_\lambda}} (\omega_\lambda \hat{Q}_\lambda + i\hat{P}_\lambda) \quad \text{annihilation op.} \quad (3.69)$$

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

$$\begin{aligned} \triangleleft \quad [\hat{b}_\lambda, \hat{b}_{\lambda'}^\dagger] &= \frac{1}{2\hbar \omega_\lambda} [\omega_\lambda \hat{Q}_\lambda + i\hat{P}_\lambda, \omega_\lambda \hat{Q}_\lambda - i\hat{P}_\lambda] \\ &= \frac{1}{2\hbar \omega_\lambda} \left\{ -i\omega_\lambda \underbrace{[\hat{Q}_\lambda, \hat{P}_\lambda]}_{i\hbar} + i\omega_\lambda \underbrace{[\hat{P}_\lambda, \hat{Q}_\lambda]}_{-i\hbar} \right\} \\ &= \frac{1}{2\hbar \omega_\lambda} \{ \hbar \omega_\lambda + \hbar \omega_\lambda \} = 1 \\ &\Rightarrow [\hat{b}_\lambda, \hat{b}_{\lambda'}^\dagger] = \delta_{\lambda\lambda'} \end{aligned} \quad (3.70)$$

$$[\hat{b}_\lambda, \hat{b}_{\lambda'}] = 0 \quad (3.71)$$

$$[\hat{b}_\lambda^\dagger, \hat{b}_{\lambda'}^\dagger] = 0 \quad (3.72)$$

↔ rewrite the Hamiltonian

$$\begin{aligned} \hat{H}_F &= \frac{1}{2} \sum_\lambda (\hat{P}_\lambda^2 + \omega_\lambda^2 \hat{Q}_\lambda^2) \\ &= \frac{1}{2} \sum_\lambda \left\{ -\frac{\hbar \omega_\lambda}{2} (\hat{b}_\lambda^\dagger - \hat{b}_\lambda)^2 + \frac{\hbar \omega_\lambda}{2} (\hat{b}_\lambda^\dagger + \hat{b}_\lambda)^2 \right\} \\ &= \frac{1}{2} \sum_\lambda \hbar \omega_\lambda (\hat{b}_\lambda^\dagger \hat{b}_\lambda + \hat{b}_\lambda \hat{b}_\lambda^\dagger) \end{aligned} \quad (3.73)$$

$$\begin{aligned} &= \sum_\lambda \hbar \omega_\lambda (\hat{b}_\lambda^\dagger \hat{b}_\lambda + \frac{1}{2}) \\ &= \sum_\lambda \hbar \omega_\lambda (\hat{n}_\lambda + \frac{1}{2}) \end{aligned} \quad (3.74)$$

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

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

$$\begin{aligned} \hat{H}_F &= \sum_{\lambda} \hat{H}_F^{\lambda} \\ \hat{H}_F^{\lambda} |\psi_{n_\lambda}\rangle &= \hbar \omega_\lambda \left(n_\lambda + \frac{1}{2}\right) |\psi_{n_\lambda}\rangle \\ &\text{with } n_\lambda \in N_0 \end{aligned} \quad (3.75)$$

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 $|\psi_{0_\lambda}\rangle \equiv |0_\lambda\rangle$ is not a vector of zero length, but the (ground) state associated with the statement that there are no photons in the λ th mode (but energy $E_0 = \hbar\omega_\lambda/2$). As eigenstates of a Hermitian operator the $|n_\lambda\rangle$ fulfill an orthonormality relation

$$\langle n_\lambda | n'_\lambda \rangle = \delta_{n_\lambda n'_\lambda} \quad (3.76)$$

$$\Leftrightarrow \hat{n}_\lambda |n_\lambda\rangle = n_\lambda |n_\lambda\rangle \quad \left(\hat{n}_\lambda = \frac{\hat{H}_F^{\lambda} - \frac{1}{2}}{\hbar \omega_\lambda} \right) \quad (3.77)$$

$$\hat{n}_\lambda |0_\lambda\rangle = 0 |0_\lambda\rangle = 0 \quad \text{this is a real zero!} \quad (3.78)$$

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

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.

$$[\hat{b}_\lambda, \hat{n}_{\lambda'}] = \hat{b}_\lambda \delta_{\lambda\lambda'} \quad (3.79)$$

$$[\hat{b}_\lambda^\dagger, \hat{n}_{\lambda'}] = -\hat{b}_\lambda^\dagger \delta_{\lambda\lambda'} \quad (3.80)$$

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

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:

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

\leftrightarrow combine:

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

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

$$\leftrightarrow \hat{b}_\lambda^\dagger |n_\lambda\rangle = \sqrt{n_\lambda + 1} |n_\lambda + 1\rangle \quad (3.81)$$

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

$$\hat{b}_\lambda |n_\lambda\rangle = \sqrt{n_\lambda} |n_\lambda - 1\rangle \quad (3.82)$$

to be consistent with Eq. (3.78) we stipulate

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

Generalization:

$$\hat{H}_F |n_1, n_2, \dots\rangle = E |n_1, n_2, \dots\rangle \quad (3.83)$$

$$E = \sum_\lambda \hbar \omega_\lambda \left(n_\lambda + \frac{1}{2} \right) = \sum_\lambda \hbar \omega_\lambda n_\lambda + E_0 \quad (3.84)$$

$$|n_1, n_2, \dots\rangle = |n_1\rangle |n_2\rangle \dots \quad \text{product states} \quad (3.85)$$

$$\hat{n}_\lambda | \dots n_\lambda \dots \rangle = n_\lambda | \dots n_\lambda \dots \rangle \quad (3.86)$$

$$\hat{b}_\lambda^\dagger | \dots n_\lambda \dots \rangle = \sqrt{n_\lambda + 1} | \dots n_\lambda + 1 \dots \rangle \quad (3.87)$$

$$\hat{b}_\lambda | \dots n_\lambda \dots \rangle = \sqrt{n_\lambda} | \dots n_\lambda - 1 \dots \rangle \quad (3.88)$$

c) Interaction between electron(s) and photons

We start from Eq. (3.52) 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:

$$q_\lambda \rightarrow \hat{q}_\lambda = \frac{1}{2\sqrt{\epsilon_0}} \left(\hat{Q}_\lambda + i \frac{\hat{P}_\lambda}{\omega_\lambda} \right) = \sqrt{\frac{\hbar}{2\epsilon_0\omega_\lambda}} \hat{b}_\lambda \quad (3.89)$$

which yields

$$\hat{\mathbf{A}}(\mathbf{r}, t) = \sum_\lambda \hat{\pi}_\lambda \sqrt{\frac{\hbar}{2\omega_\lambda\epsilon_0 L^3}} \left(\hat{b}_\lambda e^{i(\mathbf{k}_\lambda \cdot \mathbf{r} - \omega_\lambda t)} + \hat{b}_\lambda^\dagger e^{-i(\mathbf{k}_\lambda \cdot \mathbf{r} - \omega_\lambda t)} \right) \quad (3.90)$$

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

$$\hat{\mathbf{A}}^S(\mathbf{r}) = \sum_\lambda \hat{\pi}_\lambda \sqrt{\frac{\hbar}{2\omega_\lambda\epsilon_0 L^3}} \left(\hat{b}_\lambda e^{i\mathbf{k}_\lambda \cdot \mathbf{r}} + \hat{b}_\lambda^\dagger e^{-i\mathbf{k}_\lambda \cdot \mathbf{r}} \right) \quad (3.91)$$

The latter is used in the quantized interaction:

$$\begin{aligned} \hat{W} &= \frac{e}{m} \hat{\mathbf{A}}^S \cdot \hat{\mathbf{p}} \\ &= -i \sum_\lambda \sqrt{\frac{e^2 \hbar^3}{2\omega_\lambda \epsilon_0 m^2 L^3}} \hat{\pi}_\lambda \cdot \left\{ \hat{b}_\lambda e^{i\mathbf{k}_\lambda \cdot \mathbf{r}} \nabla + \hat{b}_\lambda^\dagger e^{-i\mathbf{k}_\lambda \cdot \mathbf{r}} \nabla \right\} \end{aligned} \quad (3.92)$$

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

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

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

$$\langle n_1^f \dots n_\lambda^f \dots | \hat{b}_\lambda | n_1^i \dots n_\lambda^i \dots \rangle = \sqrt{n_\lambda^i} \langle n_1^f \dots n_\lambda^f \dots | n_1^i \dots n_\lambda^i - 1 \dots \rangle \quad (3.93)$$

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

$$\langle n_1^f \dots n_\lambda^f \dots | \hat{b}_\lambda | n_1^i \dots n_\lambda^i \dots \rangle = \sqrt{n_\lambda^i} \delta_{n_1^f n_1^i} \delta_{n_2^f n_2^i} \dots \delta_{n_\lambda^f n_\lambda^i - 1} \dots \quad (3.94)$$

and similarly

$$\langle n_1^f \dots n_\lambda^f \dots | \hat{b}_\lambda^\dagger | n_1^i \dots n_\lambda^i \dots \rangle = \sqrt{n_\lambda^i + 1} \delta_{n_1^f n_1^i} \delta_{n_2^f n_2^i} \dots \delta_{n_\lambda^f n_\lambda^i + 1} \dots \quad (3.95)$$

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 (3.94) corresponds to photon absorption (one photon less in the final state than in the initial state) and the creation process (3.95) to photon emission (one photon more in the final state than in the initial state).

Summary:

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

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 Chap. 3.2 b)).

Elaborate on energy conservation: noting that the energy eigenvalues of electronic and photonic parts add (cf. Eq. (3.51b)) we find

$$E_i = \epsilon_i + \sum_{\lambda'} \hbar\omega_{\lambda'} \left(n_{\lambda'}^i + \frac{1}{2} \right) \quad (3.96)$$

$$E_f = \epsilon_f + \sum_{\lambda'} \hbar\omega_{\lambda'} \left(n_{\lambda'}^f + \frac{1}{2} \right) \quad (3.97)$$

$$E_i = E_f \Leftrightarrow \epsilon_f = \epsilon_i \pm \hbar\omega_{\lambda} \quad (3.98)$$

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

e) Spontaneous emission

$$\langle \Phi_i | = \langle \varphi_i | 0, 0, \dots \rangle$$

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 $|0, 0, \dots\rangle$. 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 discussion of the quantitative aspects of spontaneous emission one uses FGR (3.39). The transition rate can be written as

$$w_{i \rightarrow f}^{s.e.} = \frac{2\pi}{\hbar} |W_{fi}|^2 \rho(E_f = E_i) \quad (3.99)$$

$$W_{fi} = -i \sqrt{\frac{e^2 \hbar^3}{2\omega \epsilon_0 m^2 L^3}} \langle \varphi_f | e^{-i\mathbf{k}\lambda \cdot \mathbf{r}} \hat{\pi}_\lambda \cdot \nabla | \varphi_i \rangle \quad (3.100)$$

$$\text{with } \omega \equiv \omega_\lambda = \frac{\epsilon_f - \epsilon_i}{\hbar}$$

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

$$\mathbf{k}_\lambda = \frac{2\pi}{L} (n_x^\lambda, n_y^\lambda, n_z^\lambda) \quad n_i^\lambda \in \mathcal{Z}$$

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

We need to transform this to energy space:

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

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

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

Inserting this into Eq. (3.99) one obtains for the (differential) spontaneous emission rate (for a given polarization $\hat{\pi}$):

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

In dipole approximation (using once again Eq. (3.45)) this reduces to

$$\frac{dw_{i \rightarrow f}^{s.e., \hat{\pi}}}{d\Omega_k} = \frac{e^2 \omega^3}{8\pi^2 \epsilon_0 \hbar c^3} |\hat{\pi} \cdot \mathbf{r}_{fi}|^2 \quad (3.101)$$

$$\mathbf{r}_{fi} = \langle \varphi_f | \mathbf{r} | \varphi_i \rangle \quad (3.102)$$

The total rate is obtained by integrating (3.101) over $d\Omega_k$ and summing over two perpendicular (transverse) polarizations. The final result for the inverse lifetime $1/\tau_{i \rightarrow f} = w_{i \rightarrow f}^{s.e.}$ is

$$\left(\frac{1}{\tau}\right)_{i \rightarrow f}^{\text{dip}} = \frac{e^2 \omega^3}{3\pi \epsilon_0 \hbar c^3} |\mathbf{r}_{fi}|^2. \quad (3.103)$$

Examples:

- Lifetime of $H(2p)$

$$\tau_{2p \rightarrow 1s}^{\text{dip}} \approx 1.6 \cdot 10^{-9} \text{ s}$$

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

- $\tau_{2s \rightarrow 1s}^{\text{1st order}} \rightarrow \infty$

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

This expresses a general pattern: an N -photon process corresponds to an N -th order transition 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

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

using similar arguments as for elevating W_{EM} to \hat{H}_f one obtains

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

and

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

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

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

using similar arguments as for elevating 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!
According to the spin-statistics theorem (see Chap. 4.1) 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 haven't 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. The electron creation and annihilation operators fulfill anticommutation relations instead of Eq. (3.70).

- 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

Many-electron atoms

So far, we have focused on the hydrogen atom and its interactions with fields (and photons). Two issues need to be addressed to extend the discussion to atoms with more than one electron¹:

- Electrons interact with each other.
- Electrons are fermions \rightarrow N -electron wave functions must be antisymmetric with respect to particle exchange.

The first item in particular makes an exact treatment of many-electron atoms impossible, i.e., we need models and approximate treatments. The second one sounds more formal, but this should not be mistaken for it being of little physical relevance. It's quite the opposite (as we will see).

Let's begin with writing down a (somewhat simplified, but still intractable) Hamiltonian for an N -electron atom (in atomic units)². This Hamiltonian

¹Plus some formalities associated with the description of composite systems.

²The assumptions made to obtain this Hamiltonian are that (i) the nucleus is infinitely heavy, (ii) a nonrelativistic treatment with Coulomb interactions only suffices.

will form the basis of the discussion in this chapter:

$$\hat{H} = \hat{T}_e + V_{\text{nuc}} + V_{ee} \quad (4.1)$$

$$\hat{T}_e = \sum_{i=1}^N \left(-\frac{1}{2} \nabla_i^2 \right) \equiv \sum_{i=1}^N \hat{t}^{(i)} \quad (4.2)$$

$$V_{\text{nuc}} = \sum_{i=1}^N \left(-\frac{Z}{r_i} \right) \equiv \sum_{i=1}^N v_{\text{nuc}}^{(i)} \quad (4.3)$$

$$V_{ee} = \frac{1}{2} \sum_{i \neq j}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \equiv \frac{1}{2} \sum_{i \neq j}^N v_{ee}^{(ij)} \quad (4.4)$$

The Hamiltonian can be written as

$$\hat{H} = \sum_{i=1}^N \hat{h}^{(i)} + \frac{1}{2} \sum_{i \neq j}^N v_{ee}^{(ij)} \quad (4.5)$$

with

$$\hat{h}^{(i)} = \hat{t}^{(i)} + v_{\text{nuc}}^{(i)} \quad \text{one-particle operators} \quad (4.6)$$

$$v_{ee}^{(ij)} = \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \quad \text{two-particle operators} \quad (4.7)$$

Both the one-particle and the two-particle operators are Hermitian. Equation (4.5) has the standard form of a Hamiltonian of an interacting particle system implying that the general aspects of the following discussion are of relevance beyond atomic physics.

4.1 Systems of identical particles

The problem of identical-particle systems in quantum mechanics is discussed in all QM textbooks, in particular in [Gri], Chap. 5. This section summarizes the salient points.

a) N -particle systems and product states

Let's pretend the electron-electron interaction doesn't exist. The Hamiltonian would then be non-interacting (NI) and of the form

$$\hat{H}_{\text{NI}} = \sum_i \hat{h}^{(i)} \quad (4.8)$$

- The one-particle operators $\hat{h}^{(i)}$ have eigenvectors and (real) eigenvalues:

$$\hat{h}^{(i)} |k^{(i)}\rangle = \epsilon_k |k^{(i)}\rangle$$

Note that we are using a short-hand notation for the eigenkets ($|k^{(i)}\rangle \equiv |\varphi_k^{(i)}\rangle$) and that the eigenvalues are numbers, i.e., they don't depend on the particle index.

- $\{|k^{(i)}\rangle, k = 1, \dots\}$ is an orthonormal basis (ONB) in the one-particle Hilbert space $\mathcal{H}^{(i)}$:

$$\begin{aligned} \sum_k |k^{(i)}\rangle \langle k^{(i)}| &= \hat{1} \\ \langle k^{(i)} | j^{(i)} \rangle &= \langle k | j \rangle = \delta_{kj} \end{aligned}$$

- Now define direct product states

$$\begin{aligned} |\Psi\rangle &\equiv |k_1^{(1)} k_2^{(2)} \dots k_i^{(i)} \dots k_j^{(j)} \dots k_N^{(N)}\rangle := |k_1^{(1)}\rangle |k_2^{(2)}\rangle \dots |k_i^{(i)}\rangle \dots |k_j^{(j)}\rangle \dots |k_N^{(N)}\rangle \\ &\in \mathcal{H}_N = \mathcal{H}^{(1)} \times \mathcal{H}^{(2)} \times \dots \times \mathcal{H}^{(i)} \times \dots \times \mathcal{H}^{(j)} \times \dots \times \mathcal{H}^{(N)} \end{aligned}$$

\mathcal{H}_N is called a (tensor) product space. Note the interpretation of $|\Psi\rangle$: particle #1 is in state k_1 , particle #2 is in state k_2 etc, i.e., $|\Psi\rangle$ describes *distinguishable*, non-interacting particles. It is an eigenstate of the Hamiltonian (4.8) with the eigenvalue $E_{\text{NI}} = \sum_i \epsilon_{k_i}$.

- The direct product states form an ONB in \mathcal{H}_N . Therefore, we can use them to expand any element of \mathcal{H}_N :

$$|\Lambda\rangle = \sum_{k_1 \dots k_N} |k_1^{(1)} \dots k_N^{(N)}\rangle \langle k_1^{(1)} \dots k_N^{(N)} | \Lambda \rangle = \sum_{k_1 \dots k_N} c_{k_1 \dots k_N} |k_1^{(1)} \dots k_N^{(N)}\rangle$$

Orthonormality relation for product states:

$$\langle k_1^{(1)} \dots k_N^{(N)} | l_1^{(1)} \dots l_N^{(N)} \rangle = \langle k_1 | l_1 \rangle \dots \langle k_N | l_N \rangle = \delta_{k_1 l_1} \dots \delta_{k_N l_N}$$

b) Exchange degeneracy, permutations and the symmetrization postulate

$N = 2$ Let's consider two different (in fact, orthogonal) states:

$$\begin{aligned} |\Psi\rangle &\equiv |k_1^{(1)}k_2^{(2)}\rangle = |k_1^{(1)}\rangle|k_2^{(2)}\rangle = |k_2^{(2)}\rangle|k_1^{(1)}\rangle \\ |\Phi\rangle &\equiv |k_2^{(1)}k_1^{(2)}\rangle = |k_2^{(1)}\rangle|k_1^{(2)}\rangle = |k_1^{(2)}\rangle|k_2^{(1)}\rangle \end{aligned}$$

They are related via the exchange operator \hat{P}_{12} which, as the name suggests, exchanges (swaps) the states of the two particles:

$$\hat{P}_{12}|\Psi\rangle = |\Phi\rangle, \quad \hat{P}_{12}|\Phi\rangle = |\Psi\rangle$$

Obviously we have

$$\hat{P}_{12}^2 = \hat{1} \Leftrightarrow \hat{P}_{12}^{-1} = \hat{P}_{12}$$

Both $|\Psi\rangle$ and $|\Phi\rangle$ are eigenstates of the Hamiltonian (4.8)

$$\begin{aligned} \hat{H}_{\text{NI}}|\Psi\rangle &= (\hat{h}^{(1)} + \hat{h}^{(2)})|k_1^{(1)}k_2^{(2)}\rangle = (\hat{h}^{(1)}|k_1^{(1)}\rangle)|k_2^{(2)}\rangle + |k_1^{(1)}\rangle(\hat{h}^{(2)}|k_2^{(2)}\rangle) \\ &= \epsilon_{k_1}|k_1^{(1)}\rangle|k_2^{(2)}\rangle + \epsilon_{k_2}|k_1^{(1)}\rangle|k_2^{(2)}\rangle = (\epsilon_{k_1} + \epsilon_{k_2})|k_1^{(1)}k_2^{(2)}\rangle \\ &= E_{\text{NI}}|\Psi\rangle \\ \hat{H}_{\text{NI}}|\Phi\rangle &= (\hat{h}^{(1)} + \hat{h}^{(2)})|k_2^{(1)}k_1^{(2)}\rangle = (\hat{h}^{(1)}|k_2^{(1)}\rangle)|k_1^{(2)}\rangle + |k_2^{(1)}\rangle(\hat{h}^{(2)}|k_1^{(2)}\rangle) \\ &= \epsilon_{k_2}|k_2^{(1)}\rangle|k_1^{(2)}\rangle + \epsilon_{k_1}|k_2^{(1)}\rangle|k_1^{(2)}\rangle = (\epsilon_{k_1} + \epsilon_{k_2})|k_2^{(1)}k_1^{(2)}\rangle \\ &= E_{\text{NI}}|\Phi\rangle \end{aligned}$$

for the same eigenvalue E_{NI} —this is called exchange degeneracy. It implies that

$$[\hat{H}_{\text{NI}}, \hat{P}_{12}] = 0$$

and generalizes straightforwardly to $N > 2$, except that we have now more possibilities to interchange particles without changing the eigenvalues of direct product states, i.e., the degeneracy level increases. The situation can be characterized by introducing a set of $N!$ permutation operators \hat{P}_ρ (which can be shown to form a group). All permutation operators commute with the non-interacting Hamiltonian (4.8).

At this point we take a leap and postulate that *all* observables \hat{O} commute with *all* $N!$ permutation operators \hat{P}_ρ for a system of N identical particles (i.e., a system of particles which share all their properties).

symmetrization postulate for identical particles

$$[\hat{P}_\rho, \hat{O}] = 0, \quad \forall \hat{O}, \hat{P}_\rho$$

This implies that there is no way to distinguish identical particles in QM, since no observable is sensitive to the particle identity. In other words, identical particles in QM are indistinguishable.

Consequences

- (i) Exchange symmetry can never be broken (more formally: all permutation operators commute with the time-evolution operator).
- (ii) States of identical particle systems are either (totally) symmetric (+) or (totally) antisymmetric (−) under particle exchange, i.e.,

$$\begin{aligned} \text{either} \quad \hat{P}_{ij}|\Psi^+\rangle &= +|\Psi^+\rangle && \text{for all } i, j : \quad \text{“bosons”} \\ \text{or} \quad \hat{P}_{ij}|\Psi^-\rangle &= -|\Psi^-\rangle && \text{for all } i, j : \quad \text{“fermions”} \end{aligned}$$

The totally symmetric and totally antisymmetric states are orthogonal, i.e., $\langle \Psi^+ | \Psi^- \rangle = 0$. This implies that we never need the whole N -particle Hilbert space \mathcal{H}_N to represent the state of a system of identical particles. In fact, one can show:

- (iii) $\mathcal{H}_N =$ orthogonal sum of \mathcal{H}_N^+ , \mathcal{H}_N^- , $\mathcal{H}_N^{\text{ort}}$, with $|\Psi^+\rangle \in \mathcal{H}_N^+$ and $|\Psi^-\rangle \in \mathcal{H}_N^-$. Note that $\mathcal{H}_N^{\text{ort}}$ is not empty, but it is irrelevant for *identical* particles, i.e., it cannot be accessed.
- (iv) Exchange degeneracy is completely lifted by the symmetrization postulate i.e., \hat{H}_{NI} has exactly one totally symmetric and one totally antisymmetric eigenstate for a given E_{NI} .
- (v) Spin-statistics theorem (Pauli, 1940)

$$\begin{aligned} \text{bosons} &\longrightarrow \text{spin} = 0, 1, 2, \dots \\ &\quad \quad \quad (\text{photons, mesons, } \dots) \end{aligned}$$

$$\begin{aligned} \text{fermions} &\longrightarrow \text{spin} = \frac{1}{2}, \frac{3}{2}, \dots \\ &\quad \quad \quad (e^-, p, n, \text{quarks, } \dots) \end{aligned}$$

The spin-statistics theorem connects the exchange symmetry of identical particles with their spin—a rather nonobvious statement, but it can be proven.

c) Fermions

In atomic physics we are interested in electrons—fermions. The so-called Slater determinants

$$|k_1 \cdots k_N^-\rangle := \frac{1}{\sqrt{N!}} \begin{vmatrix} |k_1^{(1)}\rangle & \cdots & |k_1^{(N)}\rangle \\ \vdots & & \\ |k_N^{(1)}\rangle & \cdots & |k_N^{(N)}\rangle \end{vmatrix} \quad (4.9)$$

can be shown to form an ONB of \mathcal{H}_N^- :

$$\sum_{k_1 < k_2 < \cdots < k_N} |k_1 \cdots k_N^-\rangle \langle k_1 \cdots k_N^-| = \hat{1} \quad (4.10)$$

where the ordered summation is necessary to ensure that each linearly independent state is counted only once. Equation (4.10) implies that any antisymmetrical state can be expanded according to

$$|\Psi^-\rangle = \sum_{k_1 < k_2 < \cdots < k_N} c_{k_1 \cdots k_N} |k_1 \cdots k_N^-\rangle \quad (4.11)$$

which suggests that Slater determinants provide a convenient starting point for the discussion of *interacting* many-fermion systems (such as atoms), whose eigenstates are not direct product states.

Recall that a determinant is zero if two rows or two columns are identical. The implication of this is

Pauli's exclusion principle (for fermions)	two identical fermions cannot occupy the same single-particle state
---	---

The shell structure of atoms is an immediate consequence of the Pauli principle.

4.2 The atomic shell model

a) Non-interacting electrons

Let's elaborate on our previous assumption that the electron-electron interaction wouldn't exist, i.e., we consider a model atom which is described by the Hamiltonian (4.8). For the single-particle Hamiltonians we have [cf. Eq. (4.6)]

$$\hat{h} = -\frac{1}{2}\nabla^2 - \frac{Z}{r}$$

We know the eigenvectors and eigenvalues of \hat{h} (see Chap. 1):

$$\begin{aligned} \hat{h}|k\rangle &\longrightarrow \hat{h}|nlmm_s\rangle = -\frac{Z^2}{2n^2}|nlm\rangle|m_s\rangle \\ \langle \mathbf{r}|nlm\rangle|m_s\rangle &= \varphi_{nlm}(\mathbf{r})|m_s\rangle \end{aligned} \quad (4.12)$$

with $|m_s = +\frac{1}{2}\rangle = |\uparrow\rangle$ and $|m_s = -\frac{1}{2}\rangle = |\downarrow\rangle$ ³. One may simplify the notation and write $\varphi_{nlmm_s}(\mathbf{r})$ for the *spin orbitals* (4.12).

Let's consider an atom with $N = Z$ electrons. The ground state is the state with the lowest possible energy. It is described by a Slater determinant (because electrons are fermions). In order to produce a nonzero determinant that corresponds to the lowest possible energy we need to fill up the spin orbitals starting with the lowest-energy orbitals. This is

Pauli's "Aufbau" (building-up) principle	build N -electron atom by adding electrons one by one into lowest unfilled 'shells'
--	---

³An alternative, more compact, notation for the k th orbital is $|k\rangle = |\tilde{k}\rangle|\sigma_k\rangle$ where $|\tilde{k}\rangle$ accounts for the spatial degrees of freedom and $|\sigma_k\rangle = |\pm\frac{1}{2}\rangle$ for the spin.

Example (i): helium ($N = Z = 2$)

$$\begin{aligned}
 |k_1 k_2^-\rangle &\equiv |1s \uparrow 1s \downarrow^-\rangle = \frac{1}{\sqrt{2}} \begin{vmatrix} |1s \uparrow^{(1)}\rangle & |1s \uparrow^{(2)}\rangle \\ |1s \downarrow^{(1)}\rangle & |1s \downarrow^{(2)}\rangle \end{vmatrix} \\
 &= \frac{1}{\sqrt{2}} (|1s \uparrow^{(1)}\rangle |1s \downarrow^{(2)}\rangle - |1s \downarrow^{(1)}\rangle |1s \uparrow^{(2)}\rangle) \\
 &= |1s^{(1)}\rangle |1s^{(2)}\rangle \underbrace{\frac{1}{\sqrt{2}} (|\uparrow^{(1)}\rangle |\downarrow^{(2)}\rangle - |\downarrow^{(1)}\rangle |\uparrow^{(2)}\rangle)}_{\text{spin singlet state with } s=M_s=0}
 \end{aligned}$$

This state is called the “ $1s^2$ configuration”. Projected on r -space the (radially symmetric) spatial part has the simple product form $\Phi(r_1, r_2) = \varphi_{1s}(r_1)\varphi_{1s}(r_2)$.

Example (ii): lithium ($N = Z = 3$)

$$|k_1 k_2 k_3^-\rangle \equiv |1s \uparrow 1s \downarrow 2s \uparrow^-\rangle = \frac{1}{\sqrt{6}} \begin{vmatrix} |1s \uparrow^{(1)}\rangle & |1s \uparrow^{(2)}\rangle & |1s \uparrow^{(3)}\rangle \\ |1s \downarrow^{(1)}\rangle & |1s \downarrow^{(2)}\rangle & |1s \downarrow^{(3)}\rangle \\ |2s \uparrow^{(1)}\rangle & |2s \uparrow^{(2)}\rangle & |2s \uparrow^{(3)}\rangle \end{vmatrix}$$

This looks right, but instead of $2s$ we could have chosen any of the $2p$ orbitals, because they are degenerate (and we could fill the $|2l \downarrow\rangle$ state first). The $2s, 2p$ degeneracy is lifted by going beyond the non-interacting electron model.

b) Independent electrons: the central-field approximation

Let’s look at the full Hamiltonian (4.5) and let’s write

$$\hat{H} = \sum_i \hat{h}_{\text{eff}}^{(i)} + V_{\text{residual}} \equiv \hat{H}_{\text{IEM}} + V_{\text{residual}} \quad (4.13)$$

with

$$\hat{h}_{\text{eff}} = -\frac{1}{2}\nabla^2 - \frac{Z}{r} + v_{\text{eff}}(r) \quad (4.14)$$

and

$$V_{\text{residual}} = \frac{1}{2} \sum_{i \neq j}^N v_{ee}^{(ij)} - \sum_i v_{\text{eff}}^{(i)} \quad (4.15)$$

The term ‘central-field’ approximation derives from the fact that the effective potential v_{eff} is chosen to be spherically symmetric. Whatever detailed form

is chosen (and there are several options), the independent-electron-model (IEM) Hamiltonian \hat{H}_{IEM} is of single-particle form and its eigenstates are Slater determinants

$$\hat{H}_{\text{IEM}}|k_1 \cdots k_N^-\rangle = \sum_i \varepsilon_{k_i} |k_1 \cdots k_N^-\rangle \quad (4.16)$$

with $\hat{h}_{\text{eff}}|k\rangle = \varepsilon_k|k\rangle$ and single-particle eigenstates whose spatial representation can be written as products of radial wave functions and spherical harmonics (because of the spherical symmetry of v_{eff}). It turns out that the l -degeneracy of the Coulomb problem is lifted (but the m -degeneracy is not)

$$\begin{aligned} |k\rangle &\longrightarrow \varphi_{nlm}(\mathbf{r})|m_s\rangle = R_{nl}(r)Y_{lm}(\theta, \varphi)|m_s\rangle \\ \varepsilon_k &\longrightarrow \varepsilon_{nl} \end{aligned}$$

The spatial wave functions $\varphi_{nlm}(\mathbf{r})$ are called atomic orbitals (AOs).

One can understand the ordering of the ε_{nl} by looking at the effective atomic potential. A reasonable choice for a neutral atom ($Z = N$) would interpolate between $-N/r$ at small distances and $-1/r$ at large distances (i.e., for any of the atomic electrons the nuclear Coulomb potential appears totally unscreened at small distances, but screened by $N - 1$ electrons at large distances).

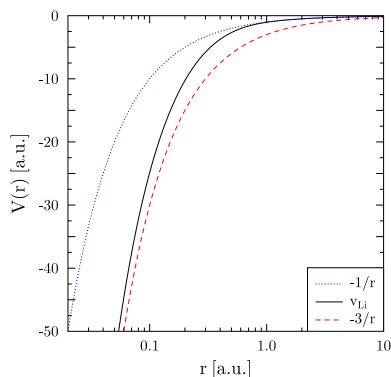


Figure 4.1: Coulomb potentials and atomic potential for the lithium atom $v_{\text{Li}}(r) = -3/r + v_{\text{eff}}(r)$.

Since “angular momentum tends to throw the electron outward” [Gri] an electron in a high l -state experiences mostly the $-1/r$ asymptotic tail while lower l electrons (electrons in s -states in particular) experience a stronger potential, which increases their binding. As a consequence, $|\varepsilon_{nl}|$ for given n decreases with increasing l (in particular, $|\varepsilon_{2p}| < |\varepsilon_{2s}|$ and the ground-state configuration of lithium is $1s^2 2s$).

The effect described above becomes so strong that for higher n the principal shells overlap. More on the “Aufbau” principle and the atomic-shell structure can be found, e.g., in [Gri], Chap. 5.2; [Fri], Chap. 2.2.3; [Fox], Chap. 4.

4.3 The Hartree-Fock method

Question: What would be the “best” IEM, i.e., the optimal \hat{h}_{eff} ?

Answer: The best IEM is the one that results in the lowest possible ground-state energy!

Comments and program

- (i) This answer is based on Ritz’s variational principle (see, e.g., [Gri], Chap. 7.1 for a proof and simple applications), which establishes that

$$E_{\text{gs}} \leq \frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle} \quad (4.17)$$

i.e., the true ground-state energy E_{gs} for a given Hamiltonian \hat{H} is lower or equal than the expectation value of \hat{H} with respect to *any* state vector $|\psi\rangle$. The RHS of the inequality (4.17) is sometimes called the energy functional $E[\psi]$ ⁴.

- (ii) Any IEM corresponds to determinantal N -electron states. Hence, in order to apply Ritz’s principle we need to consider energy expectation values of the many-electron Hamiltonian (4.5) with respect to Slater determinants. Deriving those expressions is not a simple exercise and we won’t do it, but merely state and use them. Details can be found in [Fri], Chap. 2.2.2.
- (iii) Variation of $E[\Psi]$, where Ψ are Slater determinants, yields a set of single-particle equations for the ‘optimal’ orbitals. These equations are called **Hartree-Fock (HF) equations** and have to be solved iteratively (self-consistently). We will derive and discuss them below.
- (iv) The HF method, i.e., the execution of the idea to find that Slater determinant that yields the lowest possible energy expectation value, provides a quantitative foundation of the atomic shell model.
- (v) The solutions of the HF equations have to be interpreted carefully.
- (vi) The HF method can also be used, e.g., to describe the electronic structure of molecules (cf. Chap. 5).
- (vii) Literature on the HF method: [Fri], Chap. 2.3.1; [Mes], Chap. 18; Levine, Chap. 11.1.

⁴A functional is a linear map of a (state) vector on a number.

a) Energy expectation value with respect to Slater determinants

$$\begin{aligned}
\langle \hat{H} \rangle &= \langle k_1 \cdots k_N^- | \hat{H} | k_1 \cdots k_N^- \rangle \\
&\stackrel{(4.5)}{=} \langle k_1 \cdots k_N^- | \sum_{i=1}^N \hat{h}^{(i)} | k_1 \cdots k_N^- \rangle + \langle k_1 \cdots k_N^- | \frac{1}{2} \sum_{i \neq j}^N v_{ee}^{(ij)} | k_1 \cdots k_N^- \rangle \\
&= \dots\dots\dots = \sum_{k=1}^N \langle k | \hat{h} | k \rangle \\
&\quad + \underbrace{\frac{1}{2} \sum_{k,l=1}^N \langle k^{(1)} l^{(2)} | v_{ee}^{(12)} | k^{(1)} l^{(2)} \rangle}_{\text{Coulomb energy}} - \underbrace{\frac{1}{2} \sum_{k,l=1}^N \langle k^{(1)} l^{(2)} | v_{ee}^{(12)} | l^{(1)} k^{(2)} \rangle}_{\text{exchange energy}}
\end{aligned} \tag{4.18}$$

Let's make this more explicit by using $|k\rangle = |\tilde{k}\rangle |\sigma_k\rangle$ with $\langle \mathbf{r} | \tilde{k} \rangle = \varphi_k(\mathbf{r})$, $|\sigma_k\rangle = |\uparrow\rangle$ or $|\sigma_k\rangle = |\downarrow\rangle$, and the electron density $\rho(\mathbf{r}) = \sum_{k=1}^N |\varphi_k(\mathbf{r})|^2$

- $$\begin{aligned}
\bullet \quad & \sum_{k=1}^N \langle k | \hat{h} | k \rangle = \sum_{k=1}^N \langle \tilde{k} | \hat{h} | \tilde{k} \rangle \underbrace{\langle \sigma_k | \sigma_k \rangle}_{=1} \\
&= \sum_{k=1}^N \int d^3 r \int d^3 r' \langle \tilde{k} | \mathbf{r} \rangle \underbrace{\langle \mathbf{r} | \hat{h} | \mathbf{r}' \rangle}_{=\delta(\mathbf{r}-\mathbf{r}')(-\frac{1}{2}\nabla^2 - \frac{Z}{r})} \langle \mathbf{r}' | \tilde{k} \rangle \\
&= \sum_{k=1}^N \int \varphi_k^*(\mathbf{r}) \left(-\frac{1}{2} \nabla^2 \varphi_k(\mathbf{r}) \right) d^3 r - \int \frac{Z}{r} \rho(\mathbf{r}) d^3 r
\end{aligned} \tag{4.19}$$
- $$\begin{aligned}
\bullet \quad & \frac{1}{2} \sum_{k,l=1}^N \langle k^{(1)} l^{(2)} | v_{ee}^{(12)} | k^{(1)} l^{(2)} \rangle = \frac{1}{2} \sum_{k,l=1}^N \langle \sigma_k | \sigma_k \rangle \langle \sigma_l | \sigma_l \rangle \langle \tilde{k}^{(1)} \tilde{l}^{(2)} | v_{ee}^{(12)} | \tilde{k}^{(1)} \tilde{l}^{(2)} \rangle \\
&= \frac{1}{2} \sum_{k,l=1}^N \int d^3 r \int d^3 r' \varphi_k^*(\mathbf{r}) \varphi_l^*(\mathbf{r}') v_{ee}(\mathbf{r}, \mathbf{r}') \varphi_k(\mathbf{r}) \varphi_l(\mathbf{r}') \\
&= \frac{1}{2} \int d^3 r \int d^3 r' \frac{\rho(\mathbf{r}) \rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}
\end{aligned} \tag{4.20}$$

The last expression can be interpreted as the (classical) Coulomb energy stored in the charge distribution ρ . However, there seems to be a problem:

An electron in the orbital φ_k doesn't interact with itself; nevertheless self-interaction contributions are included in Eq. (4.20). This is rectified by subtracting the exchange term

$$\begin{aligned} \bullet \quad & \frac{1}{2} \sum_{k,l=1}^N \langle k^{(1)}l^{(2)} | v_{ee}^{(12)} | l^{(1)}k^{(2)} \rangle = \frac{1}{2} \sum_{k,l=1}^N \langle \sigma_k | \sigma_l \rangle \langle \sigma_l | \sigma_k \rangle \langle \tilde{k}^{(1)}\tilde{l}^{(2)} | v_{ee}^{(12)} | \tilde{l}^{(1)}\tilde{k}^{(2)} \rangle \\ & = \frac{1}{2} \sum_{k,l=1}^N \delta_{\sigma_k \sigma_l} \int d^3r \int d^3r' \varphi_k^*(\mathbf{r}) \varphi_l^*(\mathbf{r}') v_{ee}(\mathbf{r}, \mathbf{r}') \varphi_l(\mathbf{r}) \varphi_k(\mathbf{r}') \end{aligned} \quad (4.21)$$

For $k = l$ the unphysical self-interaction terms in the Coulomb energy (4.20) are cancelled. For $k \neq l$ the exchange term has further nonzero contributions if $\sigma_k = \sigma_l$, i.e., for parallel spins. This is a consequence of the antisymmetrical structure of $|k_1 \cdots k_N^-\rangle$ and is sometimes referred to as Pauli correlation. Note that these Pauli correlations are absent in the helium $1s^2$ ground-state configuration.

b) Derivation of the HF equations

Task: Vary

$$\begin{aligned} E[\Psi] = & \sum_{k=1}^N \langle k | \hat{h} | k \rangle + \frac{1}{2} \sum_{k,l=1}^N (\langle k^{(1)}l^{(2)} | v_{ee}^{(12)} | k^{(1)}l^{(2)} \rangle \\ & - \langle k^{(1)}l^{(2)} | v_{ee}^{(12)} | l^{(1)}k^{(2)} \rangle) \end{aligned} \quad (4.22)$$

subject to the orthonormality constraints⁵

$$\langle k | l \rangle \equiv \langle \varphi_k | \varphi_l \rangle = \delta_{kl}$$

i.e., solve the variational problem

$$\delta \{ E[\{\varphi_k\}] - \sum_{k,l=1}^N \lambda_{kl} \langle \varphi_k | \varphi_l \rangle \} = 0 \quad (4.23)$$

with the N^2 Lagrange multipliers λ_{kl} .

⁵We go back to the more elaborate notation $|k\rangle \equiv |\varphi_k\rangle$ in the following to make the subsequent operations more transparent.

$$\begin{aligned}
4.23 \Leftrightarrow & \sum_{k=1}^N \langle \delta\varphi_k | \hat{h} | \varphi_k \rangle + \frac{1}{2} \sum_{k,l=1}^N \left(\langle \delta\varphi_k^{(1)} \varphi_l^{(2)} | v_{ee}^{(12)} | \varphi_k^{(1)} \varphi_l^{(2)} - \varphi_l^{(1)} \varphi_k^{(2)} \rangle \right. \\
& \left. + \langle \varphi_k^{(1)} \delta\varphi_l^{(2)} | v_{ee}^{(12)} | \varphi_k^{(1)} \varphi_l^{(2)} - \varphi_l^{(1)} \varphi_k^{(2)} \rangle \right) - \sum_{k,l=1}^N \lambda_{kl} \langle \delta\varphi_k | \varphi_l \rangle \\
= & \sum_{k=1}^N \langle \delta\varphi_k | \hat{h} | \varphi_k \rangle + \sum_{k,l=1}^N \left(\langle \delta\varphi_k^{(1)} \varphi_l^{(2)} | v_{ee}^{(12)} | \varphi_k^{(1)} \varphi_l^{(2)} - \varphi_l^{(1)} \varphi_k^{(2)} \rangle \right) \\
& - \sum_{k,l=1}^N \lambda_{kl} \langle \delta\varphi_k | \varphi_l \rangle = 0 \tag{4.24}
\end{aligned}$$

This equation has the form

$$\sum_{k=1}^N \langle \delta\varphi_k | \{ \dots \} \rangle = 0 \tag{4.25}$$

Since the $k = 1, \dots, N$ variations are independent, Eq. (4.25) is fulfilled iff

$$\{ \dots \} = 0 \quad \forall k$$

i.e., iff

$$\begin{aligned}
\hat{h}^{\text{HF}} | \varphi_k \rangle & \equiv \hat{h} | \varphi_k \rangle + \sum_{l=1}^N \langle \varphi_l^{(2)} | v_{ee}^{(12)} | \varphi_l^{(2)} \rangle | \varphi_k^{(1)} \rangle - \sum_{l=1}^N \langle \varphi_l^{(2)} | v_{ee}^{(12)} | \varphi_k^{(2)} \rangle | \varphi_l^{(1)} \rangle \\
& = \sum_{l=1}^N \lambda_{kl} | \varphi_l \rangle, \quad k = 1, \dots, N \tag{4.26}
\end{aligned}$$

The **HF equations** (4.26) are the Euler equations of the variational problem (4.23). They can be brought into their standard form

$$\boxed{\hat{h}^{\text{HF}} | \psi_k \rangle = \varepsilon_k | \psi_k \rangle, \quad \text{with } \varepsilon_k \in \mathbb{R} \tag{4.27}}$$

by noting that $\hat{h}^{\text{HF}} = (\hat{h}^{\text{HF}})^\dagger$ and inferring that the Hermitian matrix $\underline{h}^{\text{HF}}$ with elements $\langle \varphi_j | \hat{h}^{\text{HF}} | \varphi_k \rangle = \lambda_{kj}$ can be diagonalized. The orbitals $\{ \varphi_k \}$ and

$\{\psi_k\}$ are related by a unitary transformation (which leaves their orthonormality intact).

c) Discussion of the HF equations

It is useful⁶ to write the HF equations (4.27) out in r -space:

$$\begin{aligned} \left(-\frac{1}{2}\nabla^2 - \frac{Z}{r}\right) \psi_k(\mathbf{r}) + \int d^3r' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \psi_k(\mathbf{r}) - \sum_{l=1}^N \delta_{\sigma_l \sigma_k} \int d^3r' \frac{\psi_l^*(\mathbf{r}') \psi_k(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \psi_l(\mathbf{r}) \\ = \varepsilon_k \psi_k(\mathbf{r}) \end{aligned} \quad (4.28)$$

- The first term on the LHS of Eq. (4.28) has single-particle character.
- The second (“direct” or “Hartree”) term describes the action of the electrostatic potential of the charge distribution ρ on the orbital ψ_k . It includes the unphysical self-interaction term discussed above.
- The third (“exchange” or “Fock”) term has a nonlocal structure (which makes it difficult to evaluate). It corrects for the self-interaction contribution in the Hartree term and accounts for Pauli correlations of spin-parallel electrons.
- The HF equations (4.28) have a nonlinear structure and are solved by an iterative procedure. One usually starts with a trial set of orbitals $\{\psi_k^{(0)}\}$ and calculates the Hartree and exchange potentials based on them. With these potentials, one solves (numerically) the HF equations to obtain ‘new’ orbitals $\{\psi_k^{(1)}\}$. These new orbitals are used to re-calculate the Hartree and exchange potentials, which are then fed again into the HF equations for the next iteration. The process is continued until self-consistency is reached, i.e., until the orbitals obtained in the last step are identical to those of the previous step (within a pre-defined numerical accuracy). The ‘final’ orbitals are then substituted into Eq. (4.22) to calculate the total energy E_{HF} .

d) Total energy, orbital energies, electron correlation

It seems natural to interpret the orbital eigenvalue ε_k in Eq. (4.28) as the binding energy of the k th electron. Indeed, there is a formal argument that supports this interpretation (“Koopmans’ theorem”, see, e.g., [Lev], problem

⁶and also a good exercise!

15.17), but one nevertheless needs to be careful. To appreciate the subtleties associated with the HF energies, let's project Eq. (4.27) onto ψ_k :

$$\begin{aligned} \text{RHS} &= \varepsilon_k = \text{LHS} = \langle \psi_k | \hat{h}^{\text{HF}} | \psi_k \rangle \\ &\stackrel{(4.26)}{=} \langle \psi_k | \hat{h} | \psi_k \rangle + \sum_{l=1}^N \langle \psi_k^{(1)} \psi_l^{(2)} | v_{ee}^{(12)} | \psi_k^{(1)} \psi_l^{(2)} - \psi_l^{(1)} \psi_k^{(2)} \rangle \end{aligned}$$

If we sum over k we obtain

$$\begin{aligned} \sum_{k=1}^N \varepsilon_k &= \sum_{k=1}^N \langle \psi_k | \hat{h} | \psi_k \rangle + \frac{1}{2} \sum_{k,l=1}^N \langle \psi_k^{(1)} \psi_l^{(2)} | v_{ee}^{(12)} | \psi_k^{(1)} \psi_l^{(2)} - \psi_l^{(1)} \psi_k^{(2)} \rangle \\ &+ \frac{1}{2} \sum_{k,l=1}^N \langle \psi_k^{(1)} \psi_l^{(2)} | v_{ee}^{(12)} | \psi_k^{(1)} \psi_l^{(2)} - \psi_l^{(1)} \psi_k^{(2)} \rangle \\ &= E_{\text{HF}} + \langle \Psi_{\text{HF}} | V_{ee} | \Psi_{\text{HF}} \rangle \\ \Leftrightarrow E_{\text{HF}} &= \sum_{k=1}^N \varepsilon_k - \langle \Psi_{\text{HF}} | V_{ee} | \Psi_{\text{HF}} \rangle \end{aligned} \quad (4.29)$$

where $|\Psi_{\text{HF}}\rangle = |\psi_1 \cdots \psi_N^-\rangle$ is the Slater determinant built from the HF orbitals. Equation (4.29) expresses the fact that the total energy is NOT simply the sum over the orbital energies as one might expect because of some double counting of terms in the latter.

Given that the HF method determines the 'best' IEM one refers to effects beyond the HF solution as electron correlation effects; in particular one defines the correlation energy E_{corr} as

$$E_{\text{corr}} = |E_{\text{exact}} - E_{\text{HF}}| \quad (4.30)$$

If one wants to capture electron correlation effects in a calculation one needs an ansatz for the many-electron wave function that goes beyond the one-determinantal form of the IEM (see [Fri], Chap. 2.3.2 and [Lev], Chap. 11.3). The same is true for *molecular* structure calculations briefly discussed in the next chapter.

	non-interacting electrons	simple varia- tional ansatz	HF	exact
total energy [eV]	-108.8	-77.5	-77.9	-79.0
ionization energy [eV]	54.4		25.0	24.6

Table 4.1: Some numbers for the He($1s^2$) atom. The non-interacting electron and HF ionization potentials are calculated as the negative orbital energy eigenvalues. The simple variational ansatz corresponds to the trial wave function $\Psi(r_1, r_2) = (\beta^3/\pi) \exp[-\beta(r_1 + r_2)]$ with $\beta = 27/16$. The HF results are taken from [FF] and the exact values from [KYRa19].

Chapter 5

Molecules

A simple man's definition of a molecule goes like this: A molecule is an aggregate of atoms which cling together by bonds. The 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 nuclei 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 (we start in SI units):

$$\hat{H} = \hat{T}_{\text{nuc}} + \hat{T}_e + V \quad (5.1)$$

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

$$\hat{T}_e = \sum_{i=1}^N \frac{\hat{\mathbf{p}}_i^2}{2m_e} = -\frac{\hbar^2}{2m_e} \sum_{i=1}^N \nabla_{r_i}^2 \quad (5.3)$$

$$V = V_{nn} + V_{ne} + V_{ee} \quad (5.4)$$

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

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

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

The task is to solve the stationary Schrödinger equation

$$\hat{H} |\Phi\rangle = E |\Phi\rangle \quad (5.8)$$

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:

$$M_\alpha \rightarrow \infty \Rightarrow \hat{T}_{\text{nuc}} \rightarrow 0.$$

We are left with the simpler "electronic" SE

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

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

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., $\mathbf{r} \rightarrow x = (\mathbf{r}_1 s_1, \dots, \mathbf{r}_N s_N)$, 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.,

$$\begin{aligned} \langle \Psi_m | \Psi_n \rangle_{\mathbf{r}} &= \langle \Psi_m(\mathbf{R}) | \Psi_n(\mathbf{R}) \rangle_{\mathbf{r}} \\ &= \int \Psi_m^*(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, \mathbf{R}) \Psi_n(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, \mathbf{R}) d^3 r_1 d^3 r_2 \dots d^3 r_N \\ &= \delta_{mn} \end{aligned}$$

b) Adiabatic approximation: separation of electronic and nuclear motion

Back to the full problem.

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

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

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

to obtain

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

with definitions

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

The adiabatic approximation consists in neglecting all the coupling terms:

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

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

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

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

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

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.

Discussion

- “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 (see Fig. 5.1 for an illustration for $M = 2$ where a PES is actually a potential energy curve (PEC).)

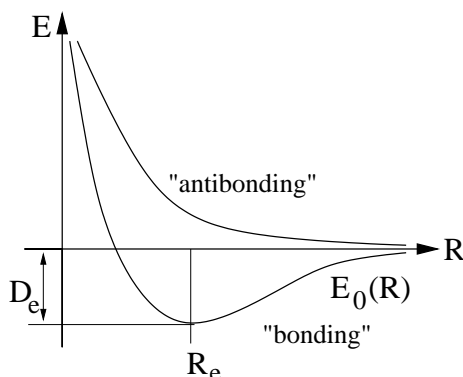


Figure 5.1: Typical PECs for $M = 2$ ($E_m(\mathbf{R}) = E_m(R)$) as functions of the internuclear distance R . For $R \rightarrow \infty$ all PECs become horizontal (vanishing Coulomb forces), for $R \rightarrow 0$ all PECs increase like $\frac{1}{R}$ because V_{nn} dominates. The minimum of the lower (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

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

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

$$E_{\text{rot}}\phi_{JM}(\theta, \varphi) = \frac{\hat{\mathbf{J}}^2}{2\mu R_e^2}\phi_{JM}(\theta, \varphi) \quad (5.17)$$

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

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

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

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

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

↪ radial equation:

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

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

$$\begin{aligned} U_0(R) &\approx U_0(R_e) + U'_0(R_e)(R - R_e) + \frac{1}{2} U''_0(R_e)(R - R_e)^2 + \dots \\ &= U_0(R_e) + \frac{k_e}{2} x^2 \end{aligned} \quad (5.22)$$

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

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

which is the SE of the harmonic oscillator with eigenenergies

$$\begin{aligned} E_{\text{vib}} &= \hbar \omega_e \left(\nu + \frac{1}{2} \right) \quad \nu = 0, 1, 2, \dots \\ \text{and } \omega_e &= \sqrt{\frac{k_e}{\mu}} = \sqrt{\frac{U''_0(R_e)}{\mu}} \end{aligned}$$

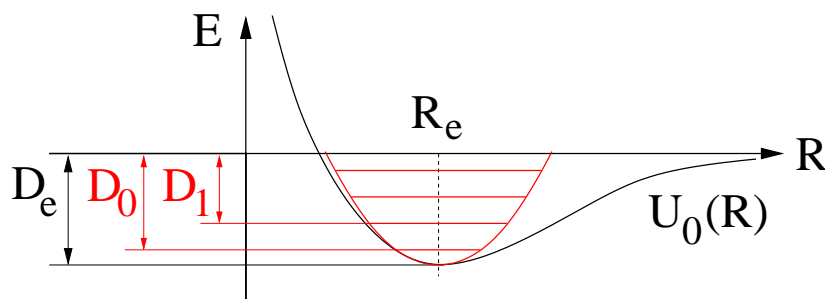


Figure 5.2: Typical ground-state PEC and harmonic oscillator model of vibrational motion. $D_e = U_0(R_e)$ is the binding energy and $D_0 = D_e - \frac{\hbar\omega_e}{2}$ the dissociation energy of the molecule.

Summary:

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

with

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

note that

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

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, albeit not in closed analytical form. We won't go into any technical detail of the exact solution, but we will look at some exact results and compare them with results obtained from a simple approximate treatment.

a) General aspects and exact solution

The electronic SE (in atomic units)

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

where r_a and r_b are the distances between the electron and nucleus 'a' and nucleus 'b', respectively, is separable in confocal-elliptical coordinates (ξ, η, φ) :

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

with the standard azimuthal angle φ :

$$\psi(\xi, \eta, \varphi) = M(\xi)N(\eta)\phi(\varphi) \quad (5.25)$$

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:

$$\begin{aligned} \phi(\varphi) &= \phi(\varphi + 2\pi) \\ &= \underbrace{e^{i\lambda 2\pi}}_1 e^{i\lambda\varphi} \Rightarrow \lambda = 0, \pm 1, \pm 2, \dots \end{aligned}$$

$$\begin{aligned} \hookrightarrow \hat{l}_z \phi_\lambda(\varphi) &= -i \frac{\partial}{\partial \varphi} \phi_\lambda(\varphi) = \lambda \phi_\lambda(\varphi) \\ &\Rightarrow [\hat{H}, \hat{l}_z] = 0 \end{aligned}$$

However:

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

\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 \triangleleft point reflections:

$$\mathbf{r} \rightarrow -\mathbf{r} \implies \begin{cases} \xi \rightarrow \xi \\ \eta \rightarrow -\eta \\ \varphi \rightarrow \varphi + \pi \end{cases}$$

\rightarrow two types of solutions

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

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

→ classification of molecular orbitals (MOs)

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

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

Note that

$$\begin{aligned}
 E_n^{el}(R \rightarrow 0) &= -\frac{2}{n^2} && \text{”united-atom limit”} \\
 E_n^{el}(R \rightarrow \infty) &= -\frac{1}{2n^2} && \text{”separated-atom limit”}
 \end{aligned}$$

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. $\sigma_g(1s)$).

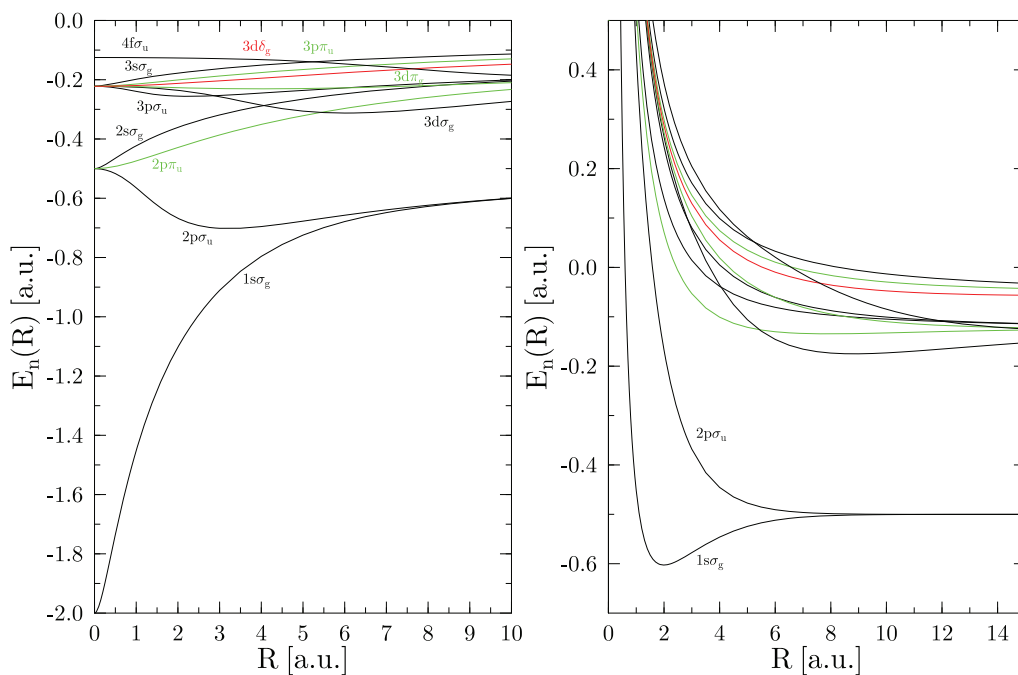


Figure 5.3: Calculated correlation diagram (left) and PECs (right) of H_2^+ .

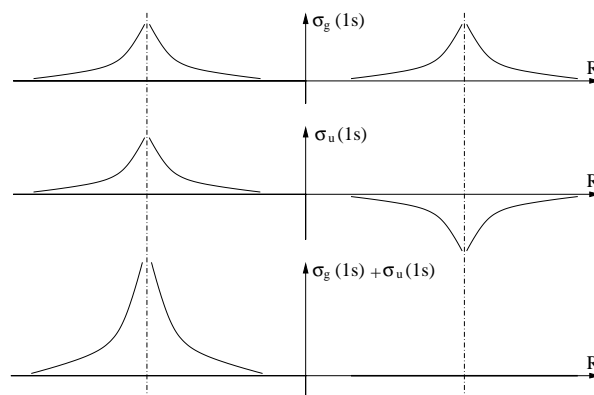


Figure 5.4: Schematic plots of the electron density distributions of the lowest states of gerade and ungerade parity in the separated-atom limit and how they add to form an atomic state, e.g., on the left center.

$E_n^{el}(R \rightarrow 0)$	AO	MO	AO	$E_n^{el}(R \rightarrow \infty)$
-2.0	1s	1 σ_g	1s	-0.5
-0.5	2p ₀	1 σ_u	1s	-0.5
-0.5	2p ₁	1 π_u	2p ₁	-0.125
-0.5	2s	2 σ_g	2s	-0.125
-0.222	3p ₀	2 σ_u	2s	-0.125
-0.222	3d ₀	3 σ_g	2p ₀	-0.125
-0.222	3d ₁	1 π_g	2p ₁	-0.125
-0.222	3d ₂	1 δ_g	3d ₂	-0.056
-0.222	3p ₁	3 π_u	3p ₁	-0.056
-0.222	3s	4 σ_g	3s	-0.056
-0.125	4f ₀	3 σ_u	2p ₀	-0.125

Table 5.2: Energies (in atomic units) and united- and separated-atom limits of a few MOs of H₂⁺.

b) Simplified solution and discussion

Approximate (but insightful) solutions of the H₂⁺ problem can be based on the variational principle (4.17) used in the following way:

- Ansatz:

$$|\psi\rangle = \sum_j c_j |\varphi_j\rangle \quad (5.26)$$

We do not require the set $\{|\varphi_j\rangle\}$ to be orthogonal or complete¹.

- Substitution into the RHS of Eq. (4.17) yields

$$E[\psi] = \frac{\langle\psi|\hat{H}|\psi\rangle}{\langle\psi|\psi\rangle} = \frac{\sum_{j,k} c_k^* c_j H_{kj}}{\sum_{j,k} c_k^* c_j S_{kj}} \quad (5.27)$$

with the interaction and overlap matrix elements

$$H_{kj} = \langle\varphi_k|\hat{H}|\varphi_j\rangle, \quad S_{kj} = \langle\varphi_k|\varphi_j\rangle$$

- We have to equate the partial derivatives of E with respect to the expansion coefficients with zero to determine the minimum of $E[\psi]$. Assuming that we use n states in the expansion we find (after some calculation) the system of n homogeneous linear equations

$$\sum_{j=1}^n c_j H_{lj} - E \sum_{j=1}^n c_j S_{lj} = 0, \quad l = 1, \dots, n \quad (5.28)$$

- The condition for a nontrivial solution of (5.28) is (cf. Chap. 2.2) that the determinant of the matrix $(\underline{\underline{H}} - E\underline{\underline{S}})$ be zero (characteristic equation of the matrix eigenvalue problem).
- Solving the characteristic equation yields n (real) eigenvalues E_1, \dots, E_n , which we take as approximations for the n lowest exact eigenvalues of the Hamiltonian².

¹If the $\{|\varphi_j\rangle\}$ would form a complete set, the variational treatment would yield the exact solution, but since completeness usually implies that infinitely many states are required, this wouldn't be practical.

²The Ritz theorem tells us that the lowest algebraic eigenvalue is an upper bound to the exact ground-state energy. The interpretation of the other $n - 1$ eigenvalues as approximate eigenvalues of the $n - 1$ lowest excited states is based on the *Hylleraas-Undheim theorem* [HU30], which establishes that these roots of the algebraic eigenvalue problem are upper bounds to the exact energies provided that the spectrum is bounded from below (which it is).

- Substituting the eigenvalues E_1, \dots, E_n back into the matrix equations (5.28) yields the expansion coefficients, i.e., the representations of the n lowest-energy states in terms of the set $\{|\varphi_j\rangle\}$ (cf. Eq. (5.26)).

This ‘linear’ version of the variational method is also used to construct approximate solutions of interacting many-electron problems (see Chap. 5.4). But let’s not jump ahead of ourselves and apply it to the H_2^+ problem first by using the ansatz

$$\psi(\mathbf{r}, R) = c_a \varphi_{1s}(r_a) + c_b \varphi_{1s}(r_b) \quad (5.29)$$

$$\varphi_{1s}(r_{a,b}) = \frac{1}{\sqrt{\pi}} e^{-r_{a,b}} \quad (5.30)$$

i.e., we represent the state of the molecule as a linear combination of one atomic hydrogen ground-state orbital on each center. This is the simplest form of the so-called linear-combination-of-atomic-orbitals (LCAO) ansatz. The solution is straightforward³ and yields

$$\psi_g(\mathbf{r}, R) = \frac{\varphi_{1s}(r_a) + \varphi_{1s}(r_b)}{\sqrt{2(1 + S_{ab}(R))}} \quad (5.31)$$

$$E_g(R) = \frac{H_{aa}(R) + H_{ab}(R)}{1 + S_{ab}(R)} \quad (5.32)$$

$$\psi_u(\mathbf{r}, R) = \frac{\varphi_{1s}(r_a) - \varphi_{1s}(r_b)}{\sqrt{2(1 - S_{ab}(R))}} \quad (5.33)$$

$$E_u(R) = \frac{H_{aa}(R) - H_{ab}(R)}{1 - S_{ab}(R)} \quad (5.34)$$

where we have used the subscripts ‘g’ and ‘u’ to indicate the parity of the states. One finds for the matrix elements

$$\begin{aligned} S_{ab}(R) &= \langle \varphi_a | \varphi_b \rangle = e^{-R} \left(1 + R + \frac{R^2}{3} \right) \\ H_{aa}(R) &= \langle \varphi_a | \hat{H} | \varphi_a \rangle = -\frac{1}{2} + e^{-2R} \left(1 + \frac{1}{R} \right) = H_{bb}(R) \\ H_{ab}(R) &= \langle \varphi_a | \hat{H} | \varphi_b \rangle = e^{-R} \left(\frac{1}{R} - \frac{1}{2} - \frac{7}{6}R - \frac{R^2}{6} \right) \end{aligned}$$

³Try it!

It is instructive to plot them [and also the energies (5.32) and (5.34)] as functions of the internuclear distance R .

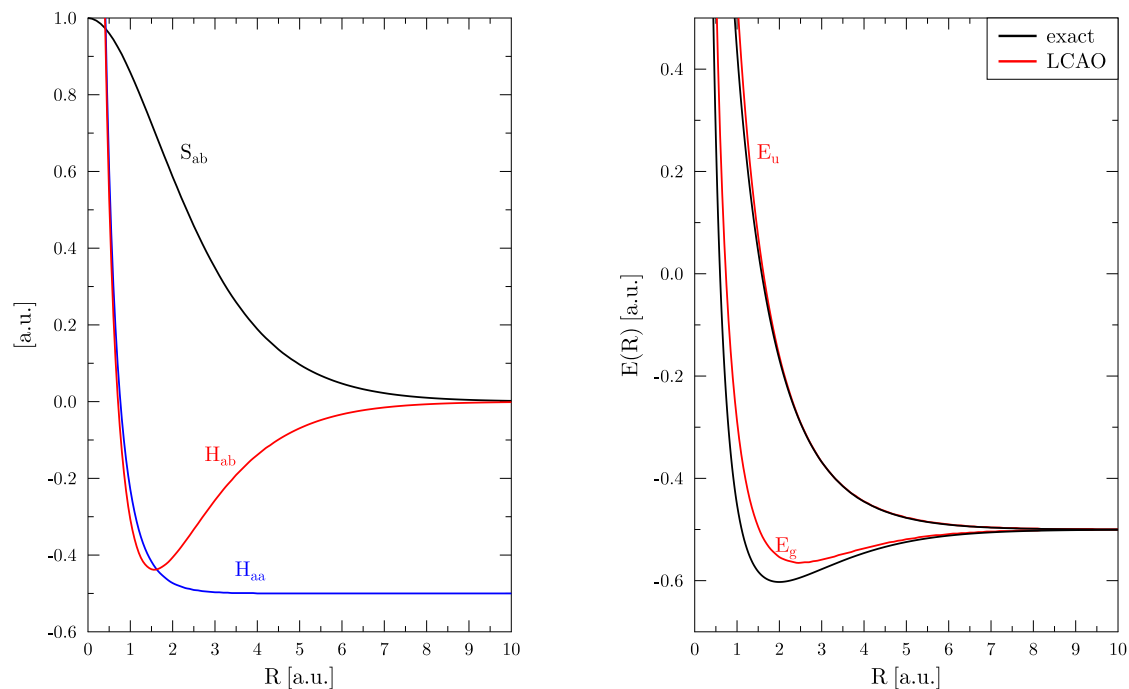


Figure 5.5: LCAO matrix elements (left) and PECs (right) for the two lowest states compared to the exact results.

One can see that H_{ab} is crucial for achieving a stable bond in the ground state. In fact, one can argue that $E_{\text{mod}} \equiv H_{aa} = \frac{1}{2}(H_{aa} + H_{bb})$ corresponds to the ground-state energy of a quasiclassical model in which one takes the electronic probability distribution of the molecule as the average of two atomic probability distributions. Since $E_{\text{mod}}(R)$ doesn't produce a minimum this model cannot explain the existence of the chemical bond. One may say that the occurrence of H_{ab} in the LCAO energy (5.32) reflects the ability of the atomic orbitals to interfere (otherwise, H_{ab} wouldn't be there), thereby accumulating enough negative charge between the two protons to prevent them from flying apart. In other words, quantum-mechanical interference effects are needed to explain the phenomenon of chemical binding in the hydrogen molecular ion.

The simple LCAO ansatz (5.29) can be improved by introducing a scale parameter in Eq. (5.30), i.e., an effective charge, and/or by adding more AOs

on both centers.

	LCAO	exact
R_e (a.u.)	2.49	2.00
D_e (a.u.)	-0.065	-0.103
D_e (eV)	-1.76	-2.79

Table 5.3: Ground state properties (equilibrium internuclear distance R_e and binding energy D_e) of H_2^+ obtained from the simple LCAO model and the exact calculation.

Literature: [Lev], Chap. 13

5.4 Many-electron molecules

We conclude this chapter with a few short comments on the description of many-electron molecules within the BOA, a field that is usually referred to as quantum chemistry. More information can be found in [Lev], Chaps. 15 and 17. The Nobel lectures from the 1998 Nobel Prize in Chemistry (awarded to Walter Kohn and John Pople) are also interesting (and rather non-technical) reads, including historical perspectives on the development of quantum chemistry [Pop99] and density functional theory [Koh99].

- (i) The Born-Oppenheimer Hamiltonian (5.13) is of the general form (4.5) if one disregards the internuclear repulsion term V_{nn} ⁴.
- (ii) As a consequence, like for atoms, the independent electron model and the Hartree-Fock method in particular are standard approaches for molecular structure calculations. They are usually good enough to explain the occurrence of chemical bonds.
- (iii) More refined, *correlated*, calculations are usually needed to achieve what is called chemical accuracy, roughly defined as a target accuracy of 1 kcal/mol for energy quantities such as heats of formation or ionization potentials [Pop99]⁵. Roughly speaking, one distinguishes so-called

⁴Given that V_{nn} does not depend on the electronic coordinates it does not affect the solutions of the Born-Oppenheimer eigenvalue problem.

⁵1 kcal/mol corresponds to 43 meV.

conventional **ab-initio approaches** and **density-functional theory methods**⁶.

- (iv) **Ab-initio approaches** are often based on HF as a “0th-order” calculation. One then improves on this in various ways, e.g., by applying perturbation theory or by assuming that the many-electron wave function is a linear combination of Slater determinants (cf. Eq. (4.11)) consisting of occupied and unoccupied HF orbitals, and determining the expansion coefficients of this linear combination by using the version of Ritz’s principle described in Sec. 5.3. The latter method is called the “configuration-interaction” approach.
- (v) **Density functional theory (DFT) methods** do not attempt to represent the many-electron wave function as a single or a combination of Slater determinants. In fact, the basic theorems of DFT establish that one does not need that wave function (the state vector) to solve the problem and obtain, in principle exact, results for observables such as the ground-state energy of the system. Rather, the electron density distribution suffices and assumes the role of the basic quantity in DFT. In practice, DFT calculations bear some similarity to HF, although there are important differences regarding the interpretation of the results (and some empirical parameters are often involved in the former as well). DFT methods have become highly popular in quantum chemistry since the 1990s and are nowadays included in most computational chemistry packages (some of which are freely available).

⁶Semi-empirical methods have played a big role as well in the development of computational chemistry, see, e.g. [Lev], Chap. 16.

Chapter 6

Brief introduction to relativistic QM

Literature: [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.

6.1 Klein-Gordon equation

a) Setting up a relativistic wave equation

- starting point: classical relativistic energy-momentum relation¹

$$E^2 = \mathbf{p}^2 c^2 + m^2 c^4 \quad (6.1)$$

- quantization :
(standard rules)

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

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

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

$$-\hbar^2 \partial_t^2 \psi(\mathbf{r}, t) = -\hbar^2 c^2 \Delta \psi(\mathbf{r}, t) + m^2 c^4 \psi(\mathbf{r}, t) \quad (6.2)$$

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?

→ one can derive $\partial_t \rho + \text{div} \mathbf{j} = 0$

with standard current $\mathbf{j} = \frac{i\hbar}{2m} (\psi \nabla \psi^* - \psi^* \nabla \psi)$

$$\text{but :} \quad \rho = \frac{i\hbar}{2mc^2} (\psi^* \partial_t \psi - \psi \partial_t \psi^*) \quad (6.3)$$

problem: $\rho(\mathbf{r}t) \geq 0$ (i.e. not positive definite)

→ probabilistic interpretation is not possible (or at least not obvious)

5. Ansatz (i)

$$\psi(\mathbf{r}, t) = A e^{i(\mathbf{k}\mathbf{r} - \omega t)}$$

→ insertion into Eq. (6.2) yields together with de Broglie relations

$$E = \hbar\omega = \pm \sqrt{c^2 \hbar^2 \mathbf{k}^2 + m^2 c^4} \leq 0 \quad (6.4)$$

ρ and \mathbf{j} are okay (check!), but what does $E < 0$ signify?

Ansatz (ii)

$$\psi(\mathbf{r}, t) = A e^{-i(\mathbf{k}\mathbf{r} - \omega t)}$$

results in the same expression for E , but corresponds to $\rho < 0$ (check!).

Ansatz (iii)

$$\psi(\mathbf{r}, t) = A \sin(\mathbf{k}\mathbf{r} - \omega t)$$

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)
 - 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).

6.2 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

$$\text{ansatz :} \quad i\hbar\partial_t\Psi = \hat{H}_D\Psi \quad (6.5)$$

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

requirements (Dirac's wish list):

1. DE must be compatible with energy-momentum relation (6.1)
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.

$$\begin{aligned} \text{ansatz :} \quad \hat{H}_D &= c\boldsymbol{\alpha} \cdot \hat{\mathbf{p}} + \beta mc^2 \\ &= \frac{c\hbar}{i} \sum_{j=1}^3 \alpha_j \partial_{x_j} + \beta mc^2 \end{aligned} \quad (6.6)$$

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

$$\Psi = \begin{pmatrix} \psi_1(\mathbf{r}, t) \\ \vdots \\ \psi_N(\mathbf{r}, t) \end{pmatrix} \quad \text{as solution of (6.5)}$$

↪ requirement (1) is met if each component ψ_i solves KGE (6.2)

→ iterate Eq. (6.5):

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

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

comparison with KGE yields conditions for α_i, β :

$$\alpha_j\alpha_k + \alpha_k\alpha_j = 2\delta_{jk} \quad (6.7)$$

$$\alpha_j\beta + \beta\alpha_j = 0 \quad (6.8)$$

$$\alpha_j^2 = \beta^2 = 1 \quad (6.9)$$

further conditions and consequences:

- α_j, β hermitian (because \hat{H}_D shall be hermitian)
 \implies real eigenvalues
 $\stackrel{6.9}{\implies}$ eigenvalues are ± 1
- from (6.7)-(6.9) 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

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

- $N = 2$ is too small as there are only three 'anti-commuting' (Eqs. (6.7) and (6.8)) matrices for $N = 2$ (the Pauli matrices). Dirac needs four!
- try $N = 4$
- derive explicit representations from these conditions

$$\hookrightarrow \alpha_i = \begin{pmatrix} 0 & \sigma_i \\ \sigma_i & 0 \end{pmatrix}, \quad \beta = \begin{pmatrix} 1 & & & 0 \\ & 1 & & \\ & & -1 & \\ 0 & & & -1 \end{pmatrix} \quad (6.10)$$

with Pauli matrices σ_i

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

\Rightarrow free DE takes the form

$$i\hbar\partial_t \begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{pmatrix} = (c\boldsymbol{\alpha} \cdot \hat{\mathbf{p}} + \beta mc^2) \begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{pmatrix} \quad (6.11)$$

and one can derive a meaningful continuity equation:

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

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

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

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

b) Solutions of the free DE

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

after some calculation one finds:

- there are 4 linear independent solutions.

Two correspond to $E = +\sqrt{\mathbf{p}^2 c^2 + m^2 c^4}$
 and two to $E = -\sqrt{\mathbf{p}^2 c^2 + m^2 c^4}$

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

$$u^{(1)} = \begin{pmatrix} 1 \\ 0 \\ \chi_1 \\ \chi_2 \end{pmatrix}, \quad u^{(2)} = \begin{pmatrix} 0 \\ 1 \\ \chi'_1 \\ \chi'_2 \end{pmatrix}$$

and for $E < 0$:

$$u^{(3)} = \begin{pmatrix} \varphi_1 \\ \varphi_2 \\ 1 \\ 0 \end{pmatrix}, \quad u^{(4)} = \begin{pmatrix} \varphi'_1 \\ \varphi'_2 \\ 0 \\ 1 \end{pmatrix}$$

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

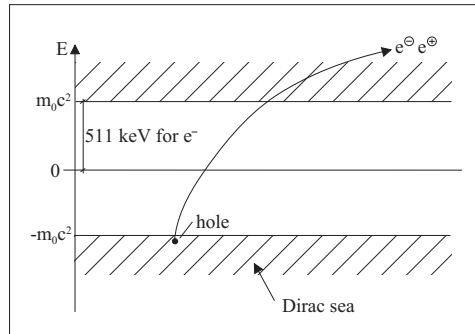


Figure 6.1: Energy spectrum of the free DE

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'

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

$$\stackrel{(6.11)}{\hookrightarrow} i\hbar\partial_t\Psi = \left\{ c\hat{\boldsymbol{\alpha}} \cdot (\hat{\mathbf{p}} + e\mathbf{A}) - e\phi + \beta mc^2 \right\} \Psi \quad (6.12)$$

one can show that Eq. (6.12) is Lorentz-covariant.

d) The relativistic hydrogen problem

Consider Eq. (6.12) with $\mathbf{A} = 0$ and

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

ansatz :

$$\Psi(\mathbf{r}, t) = \Phi(\mathbf{r})e^{-\frac{i}{\hbar}Et} \quad (6.13)$$

$$\xrightarrow{\text{yields}} \left\{ c\hat{\boldsymbol{\alpha}} \cdot \hat{\mathbf{p}} + \beta mc^2 - \frac{Ze^2}{4\pi\epsilon_0 r} \right\} \Phi(\mathbf{r}) = E\Phi(\mathbf{r}) \quad (6.14)$$

this stationary DE can be solved analytically!

Result for the bound spectrum (\rightarrow fine structure):

$$E_{nj} = mc^2 \left[1 + \frac{(Z\alpha)^2}{(n - \delta_j)^2} \right]^{-\frac{1}{2}} \quad n = 1, 2, \dots \quad (6.15)$$

$$\delta_j = j + \frac{1}{2} - \sqrt{\left(j + \frac{1}{2}\right)^2 - (Z\alpha)^2}, \quad j = \frac{1}{2}, \frac{3}{2}, \dots, n - \frac{1}{2} \quad (6.16)$$

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

$$\alpha = \frac{\hbar}{mca_0} = \frac{e^2}{4\pi\epsilon_0\hbar c} \approx \frac{1}{137} \quad (6.17)$$

fine-structure constant

expansion of Eq. (6.15) in powers of $(Z\alpha)^2 \ll 1$:

$$E_{nj} = mc^2 \left[1 - \frac{(Z\alpha)^2}{2n^2} - \frac{(Z\alpha)^4}{2n^3} \left(\frac{1}{j + \frac{1}{2}} - \frac{3}{4n} \right) \pm \dots \right] \quad (6.18)$$

1st term: rest energy

2nd term: non-relativistic binding energy (1.25)

3rd term: lowest order relativistic corrections \rightarrow fine structure splitting of energy levels

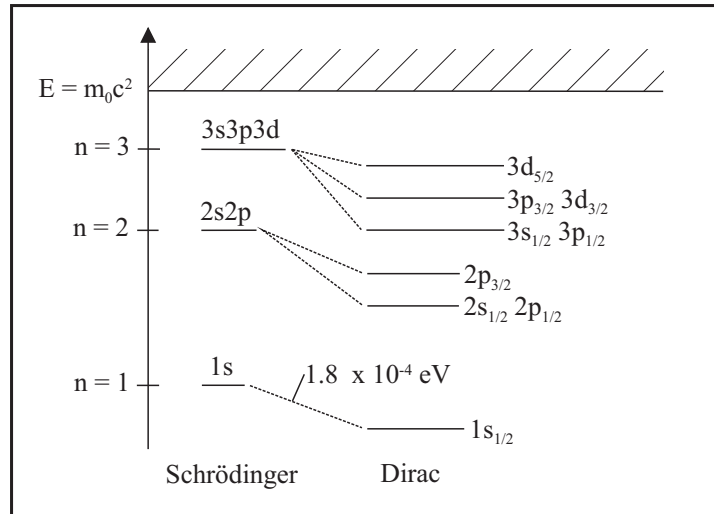


Figure 6.2: Energy spectrum of the Coulomb problem

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. (6.14) exactly and subsequently expanding the exact eigenvalues (6.15) it is useful to consider the non- (or rather: weak-) relativistic limit of the stationary DE (6.14) and to account for the lowest-order relativistic corrections obtained in this way in 1st-order perturbation theory. This procedure yields the same result (6.18) once again, but this time it comes with an interpretation regarding the nature of the relativistic corrections.

Starting point: stationary DE

$$\left\{ c\hat{\boldsymbol{\alpha}} \cdot \hat{\mathbf{p}} + \beta mc^2 + V(r) \right\} \Phi(\mathbf{r}) = E\Phi(\mathbf{r}) \quad (6.19)$$

group the 4-component spinor according to

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

insert into (6.19) (using similar groupings of the Dirac matrices in terms of Pauli matrices):

$$\hookrightarrow c \begin{pmatrix} 0 & \boldsymbol{\sigma} \\ \boldsymbol{\sigma} & 0 \end{pmatrix} \cdot \hat{\mathbf{p}} \begin{pmatrix} \varphi \\ \chi \end{pmatrix} = \left\{ E - V(r) - mc^2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \right\} \begin{pmatrix} \varphi \\ \chi \end{pmatrix} \quad (6.20)$$

\Leftrightarrow

$$c\boldsymbol{\sigma} \cdot \hat{\mathbf{p}}\chi = (E - V(r) - mc^2)\varphi \quad (6.21)$$

$$c\boldsymbol{\sigma} \cdot \hat{\mathbf{p}}\varphi = (E - V(r) + mc^2)\chi \quad (6.22)$$

³for details see [BS]

Solve (6.22) for χ and insert into (6.21):

$$\hookrightarrow \boldsymbol{\sigma} \cdot \hat{\mathbf{p}} \frac{c^2}{E - V(r) + mc^2} \boldsymbol{\sigma} \cdot \hat{\mathbf{p}} \varphi = (E - V(r) - mc^2) \varphi \quad (6.23)$$

- 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 (6.23) 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

$$T_1 = \left(1 - \frac{\varepsilon - V(r)}{2mc^2} \right) \frac{\hat{\mathbf{p}}^2}{2m} \quad (6.24)$$

$$T_2 = \frac{\hbar}{4m^2 c^2} \frac{1}{r} \frac{dV}{dr} (\boldsymbol{\sigma} \cdot \hat{\mathbf{1}}) \quad (6.25)$$

$$T_3 = \frac{\hbar}{i} \frac{1}{4m^2 c^2} \frac{1}{r} \frac{dV}{dr} (\mathbf{r} \cdot \hat{\mathbf{p}}) \quad (6.26)$$

Interpretation of terms

- For the interpretation of T_1 note that

$$\begin{aligned} (\varepsilon - V(r))\varphi &\approx \frac{\hat{\mathbf{p}}^2}{2m}\varphi \\ \Leftrightarrow T_1 &= \frac{\hat{\mathbf{p}}^2}{2m} - \frac{\hat{\mathbf{p}}^4}{8m^3c^2} \equiv \hat{T}_{NR} + \hat{H}_{KE} \end{aligned} \quad (6.27)$$

\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 operator⁴, 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 positrons (or: large and small components of the Dirac spinor) [BD].

Now apply perturbation theory to the problem

$$\hat{H} = \hat{H}_0 + \hat{W} \quad (6.28)$$

$$\hat{H}_0 = \hat{T}_{NR} + V(r) = \frac{\hat{\mathbf{p}}^2}{2m} - \frac{Ze^2}{4\pi\epsilon_0 r} \quad (6.29)$$

$$\hat{W} = \hat{H}_{KE} + \hat{H}_{SO} + \hat{H}_{\text{Darwin}} \quad (6.30)$$

⁴for 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

$$\Delta E^{(1)} = -\frac{mc^2}{2n^3}(Z\alpha)^4\left(\frac{1}{j + \frac{1}{2}} - \frac{3}{4n}\right), \quad (6.31)$$

i.e., the same results as in Eq. (6.18), which shows the consistency of the approach.

Appendix A

Incoming beam current in the photoionization problem

- Recall

$$\begin{aligned}\mathbf{A}(\mathbf{r}, t) &= \hat{\pi}|A_0| \cos(\mathbf{k} \cdot \mathbf{r} - \omega t + \alpha) \\ &= \frac{\hat{\pi}}{2} (A_0 e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)} + A_0^* e^{-i(\mathbf{k} \cdot \mathbf{r} - \omega t)}) \\ \hookrightarrow \mathbf{E}(\mathbf{r}, t) &= -\frac{\partial \mathbf{A}(\mathbf{r}, t)}{\partial t} = i\omega \frac{\hat{\pi}}{2} (A_0 e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)} - A_0^* e^{-i(\mathbf{k} \cdot \mathbf{r} - \omega t)}) \\ \mathbf{B}(\mathbf{r}, t) &= \nabla \times \mathbf{A}(\mathbf{r}, t) = \frac{i}{2} (\mathbf{k} \times \hat{\pi}) (A_0 e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)} - A_0^* e^{-i(\mathbf{k} \cdot \mathbf{r} - \omega t)})\end{aligned}$$

- Calculate Poynting vector

$$\begin{aligned}\mathbf{S}(\mathbf{r}, t) &= \frac{1}{\mu_0} \mathbf{E}(\mathbf{r}, t) \times \mathbf{B}(\mathbf{r}, t) = c^2 \epsilon_0 \mathbf{E}(\mathbf{r}, t) \times \mathbf{B}(\mathbf{r}, t) \\ &= -\frac{c\epsilon_0 \omega^2}{4} (\hat{\pi} \times (\hat{\mathbf{k}} \times \hat{\pi})) (A_0 e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)} - A_0^* e^{-i(\mathbf{k} \cdot \mathbf{r} - \omega t)})^2\end{aligned}$$

- Average \mathbf{S} over $T = 2\pi/\omega$ and use $\int_0^T \exp[\pm 2i\omega t] dt = 0$ to arrive at

$$S_{\text{ave}} = \left| \frac{1}{T} \int_0^T \mathbf{S}(\mathbf{r}, t) dt \right| = \frac{\epsilon_0}{2} c \omega^2 |A_0|^2$$

- Obtain

$$j_{\text{inc}} = \frac{S_{\text{ave}}}{\hbar \omega} = \frac{\epsilon_0}{2\hbar} c \omega |A_0|^2 \quad (\text{A.1})$$

Bibliography

- [BD] BJØRKEN, J.D. and DRELL, S.D.: *Relativistic Quantum Mechanics*. McGraw-Hill.
- [Boh] BOHM, D.: *Quantum Theory*. Prentice Hall.
- [BS] BETHE, H. A. and SALPETER, E. E.: *Quantum Mechanics of one- and two-electron atoms*. Plenum.
- [CT] COHEN-TANNOUJI, C.: *Quantum Mechanics I, II*. Wiley Interscience.
- [FF] FROESE FISCHER, C.: *The Hartree-Fock Method For Atoms: A Numerical Approach*. John Wiley & Sons.
- [Fox] FOX, M.: *A Student's Guide to Atomic Physics*. Cambridge University Press.
- [Fri] FRIEDRICH, H.: *Theoretical Atomic Physics*. Springer.
- [GPS] GOLDSTEIN, H., C. POOLE and J. SAFKO: *Classical Mechanics*. Addison Wesley.
- [Gri] GRIFFITHS, D. J.: *Introduction to Quantum Mechanics*. Prentice Hall.
- [HU30] HYLLERAAS, E. A. and B. UNDHEIM. *Z. Phys.*, 65:759, 1930.
- [Hur] HURLEY, A. C.: *Introduction to the Electron Theory of Small Molecules*. Academic Press.
- [Jac] JACKSON, J. D.: *Classical Electrodynamics*. John Wiley & Sons.

- [Koh99] KOHN, W. *Rev. Mod. Phys.*, 71:1253, 1999.
- [KYRa19] KRAMIDA, A., YU. RALCHENKO, J. READER and AND NIST ASD TEAM. NIST Atomic Spectra Database (ver. 5.7.1), [Online]. Available: <https://physics.nist.gov/asd> [2020, January 2]. National Institute of Standards and Technology, Gaithersburg, MD., 2019.
- [Lev] LEVINE, I. N.: *Quantum Chemistry*. Prentice Hall.
- [Lib] LIBOFF, R. L.: *Introductory Quantum Mechanics*. Addison-Wesley.
- [Mes] MESSIAH, A.: *Quantum Mechanics I, II*. Dover Publications.
- [Pop99] POPLE, J. A. *Rev. Mod. Phys.*, 71:1267, 1999.
- [Sch] SCHIFF, L. L.: *Quantum Mechanics*. McGraw-Hill.
- [Sha] SHANKAR, R.: *Principles of Qunatum Mechanics*. Kluwer Academic.
- [SN] SAKURAI, J. J. and J. NAPOLITANO: *Modern Quantum Mechanics*. Addison-Wesley.