

# Week 0 / 1

PHY 402 Atomic and Molecular Physics

*Instructor: Sebastian Wüster, IISER Bhopal, 2018*

*These notes are provided for the students of the class above only. There is no warranty for correctness, please contact me if you spot a mistake.*

## 0 Administrative affairs

(i) Office: AB1 - 014

Phone: 1213

Email: [sebastian@iiserb.ac.in](mailto:sebastian@iiserb.ac.in)

Office hours: Tue 3-6 p.m.

webpage: <http://home.iiserb.ac.in/~sebastian/teaching.html>

(ii) Literature:

- Demtröder, *"Atoms, Molecules and Photons"* [DT]
- Brandsen and Joachain, *"Physics of Atoms and Molecules"* [B&J]
- Atkins, Friedman, *"Molecular quantum mechanics"*
- Shankar, *"Principles of quantum mechanics"* [Shankar]
- Griffiths, *"Introduction to quantum mechanics"*
- Sakurai, *"Modern quantum mechanics"*

There is no primary text-book, I collect material from wherever I find it best covered case-by-case.

(iii) Assessment:

- **Surprise Quizzes: 10%** These are "open notes" quizzes, so please always bring yours. Times are random. These will be simple questions on material of maybe the last week's lecture to motivate attendance and continuously keeping on top of the material.
- **Assignments: 20%** I don't mind you working in groups. However, every student must hand in one separate personally handwritten solution. It should be tidy and with commented steps. TA is authorised to deduct marks for messy presentation and blatant copying.
- **Mid-Sem exam: 20%**
- **Final exam: 50%** The exam will try to test understanding of the essential *physics* concepts taught, not maths. For guidance regarding what are the most important concepts look at the quizzes and assignments of this and last year. All exams will be designed to give a significant advantage to those students that solved all assignments by *themselves*.

# Contents

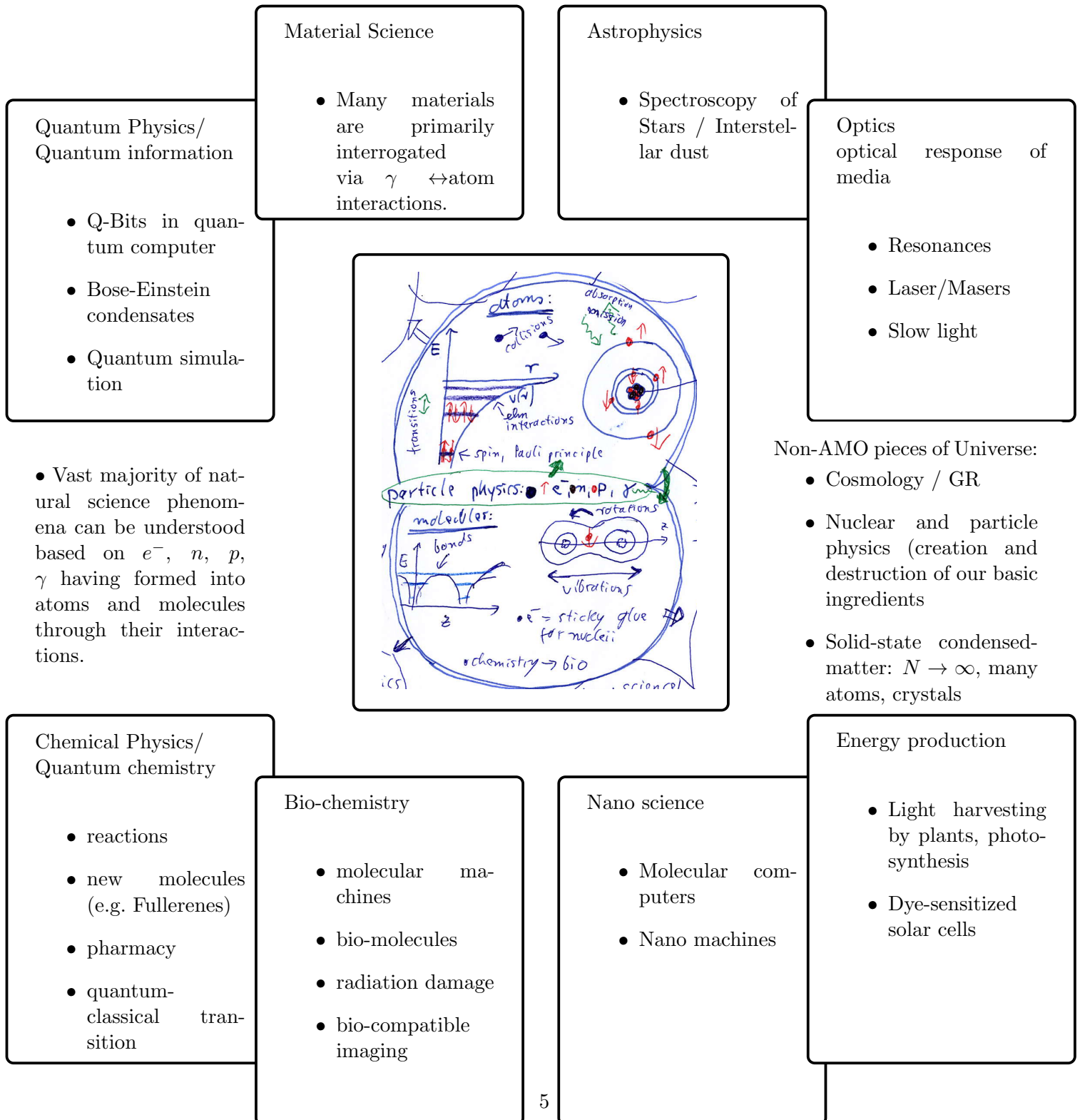
<b>0 Administrative affairs</b>	<b>1</b>
<b>1 Motivation and Review</b>	<b>5</b>
1.1 Toolkit for building a universe with life	5
1.2 Review and Notation	7
1.2.1 Basic concepts of quantum-mechanics	7
1.2.2 Orbital angular momentum and Spin	9
1.2.3 The Hydrogen(ic) atom	10
1.2.4 Quantum dynamics/ time-dependence	13
1.2.5 Approximation methods	14
1.2.6 Many particles	16
<b>2 Atoms</b>	<b>18</b>
2.1 Single (active) electron Atoms	18
2.1.1 Relativistic corrections, effect of spins, fine structure	19
2.1.2 Lamb-Shift	22
2.1.3 Hyperfine-structure	23
2.1.4 Hierarchy of level splittings	25
2.1.5 Alkali Rydberg atoms	25
2.2 Interaction of one electron atoms with static electric and magnetic fields	28
2.2.1 The Stark effect: (Electric fields)	28
2.2.2 The Zeeman effect (Magnetic fields)	31
2.3 Two Electron Atoms	36
2.3.1 The Schrödinger Equation for two-electron atoms	36
2.3.2 Spin Wave functions and Pauli Exclusion Principle	38

2.3.3	Approximate methods for 2 electron groundstate wavefunction	38
2.3.4	Excited States of Two electron atoms	42
2.4	Many-electron atoms	44
2.4.1	Central field approximation	45
2.4.2	Spin and Pauli-exclusion principle	46
2.4.3	Ground state energetic ordering and periodic table	48
2.4.4	Approximation methods for many-electron systems	49
2.4.5	Corrections to the central field. L-S/J-J coupling	53
<b>3</b>	<b>Interaction of Atoms with Electromagnetic Radiation</b>	<b>56</b>
3.1	Atomic Transitions	56
3.1.1	Electromagnetic fields and charged particles	56
3.1.2	Transition Rates	58
3.2	Selection Rules	61
3.2.1	More on Spontaneous Emission	65
3.3	Rabi-Oscillations	66
3.4	Spectral Lines	70
3.4.1	Thermal gas of atoms	70
3.4.2	Line shapes	71
3.4.3	Oscillator strength and sum rules	73
3.5	The photo-electric effect, photo ionization	74
3.6	Scattering of radiation by atoms	76
3.6.1	Rayleigh Scattering	77
3.7	Interaction of many-electron atoms with radiation	79
<b>4</b>	<b>Molecules</b>	<b>80</b>
4.1	General Molecular Structure	80

4.2	Born-Oppenheimer separation	81
4.3	Electronic Structure of Molecules	84
4.3.1	Hund-Mulliken Molecular Orbital (MO) Method	87
4.4	Symmetries in homo-nuclear di-atomic molecules	89
4.5	More General overview of chemical bonds	91
4.6	Molecular ro-vibronic states	93
4.7	Molecular spectra	96
4.7.1	Rotational transitions	98
4.7.2	Ro-vibrational transitions	99
4.7.3	Molecular electronic transitions	102
4.7.4	Raman Scattering / Raman spectra	104
4.7.5	Coupling between rotations and vibrations	107
4.7.6	Fluorescence and Phosphorescence	107
<b>5</b>	<b>Frontiers of Modern AMO physics</b>	<b>109</b>
5.1	Ultrafast	109
5.1.1	Frequency combs/ Femtosecond lasers	110
5.1.2	Strong fields, tunnel ionization	111
5.2	Ultra Cold	113
5.2.1	Bose-Einstein Condensation	113
5.2.2	Laser cooling and trapping	115
5.2.3	Condensate mean-field	116
5.3	Atomic clocks	117
5.4	Quantum-simulation	118
5.4.1	Bose-Hubbard model	118
5.4.2	Strongly interacting Rydberg systems	119

# 1 Motivation and Review

## 1.1 Toolkit for building a universe with life



- You will mostly not have to advance fundamental atomic- or molecular physics itself, we are approaching a complete understanding. Exceptions are very exotic or extreme circumstances, such as  $U^{89+}$ .
- However you are likely to need a solid AMO background in many other physics disciplines, and if only to understand standard experimental interrogation techniques for materials or other objects.
- Atoms and basic molecules are fully governed by quantum mechanics: This course will thus fully use your knowledge of QM-I/II to understand how atoms and molecules are built and interact with their surroundings.

## Course outline

- 1) Motivation and Review:  $\sim 1$  week
  - Why is AMO compulsory course?, brief review of QM-I/QM-II
- 2) Atoms:  $\sim 4-5$  weeks
  - single  $e^-$ , Rydberg atoms, fine-/ hyperfine structure, Stark/Zeeaman effect, two and more  $e^-$ , periodic table, brief overview of advanced methods (HT, TF, DFT...).
- 3) Interactions of atoms with electromagnetic radiation:  $\sim 3-4$  weeks
  - electronic transitions, line shapes and intensities, selection rules, scattering of light, absorption-spontaneous and stimulated emission of photons, Rabi oscillations.
- 4) Molecules:  $\sim 4-5$  weeks
  - Born-Oppenheimer approximation, diatomic molecules, rotations and vibrations, polyatomic molecules, chemical bonds, spectroscopy
- 5) Frontiers of modern AMO physics<sup>1</sup>:  $\sim 2$  weeks
  - ultra-fast processes, HHG, femtosecond lasers, strong fields, Bose-Einstein condensates, laser cooling and trapping, atomic clocks, quantum simulation

---

<sup>1</sup>time permitting

## 1.2 Review and Notation

- See QM text-books for much more complete review.
- Please ask *whenever anything* is unclear here, because these concepts are essential for the rest of the course.

### 1.2.1 Basic concepts of quantum-mechanics

**Quantum states:** Position space representation of free particle state (matter-wave)

$$\phi_{\mathbf{k}}(\mathbf{r}) = A \exp [i(\mathbf{k} \cdot \mathbf{r} - \omega t)], \quad \mathbf{r} \in \mathbb{R}^3, \quad \phi \in \mathbb{C}. \quad (1.1)$$

*comments:*

- Bold face symbols denote vectors,  $\cdot$  scalar product.
- Momentum  $\mathbf{p} = \hbar \mathbf{k}$
- de-Broglie wavelength

$$\lambda_{\text{dB}} = \frac{\hbar}{|\mathbf{p}|} \quad (1.2)$$

- Frequency and energy

$$\omega_{\mathbf{k}} = \frac{\hbar \mathbf{k}^2}{2m}, \quad E_{\mathbf{k}} = \hbar \omega. \quad (1.3)$$

for a free particle of mass  $m$ .

- $A$ : Normalisation factor, such that

$$\int_{\mathcal{V}} d^3\mathbf{r} |\phi_{\mathbf{k}}(\mathbf{r})|^2 = 1, \quad (1.4)$$

where the integral runs over some finite quantisation volume  $\mathcal{V}$ .

**Operators and Observables:** Quantum mechanical *observables* are represented by *Hermitian operators* ( $\hat{O} = \hat{O}^\dagger$ ), e.g.

**Hamiltonian operator:**

$$\hat{H} = \frac{\hat{p}^2}{2m} = -\frac{\hbar^2}{2m} \nabla_{\mathbf{r}}^2, \quad (1.5)$$

**Momentum operator:**

$$\hat{p} = -i\hbar \nabla_{\mathbf{r}}, \quad (1.6)$$

### Reminder on Operators:

- linear mapping  $\hat{O} : f \rightarrow g$ , for  $f, g$  functions  $\in \mathcal{H}$ ,  $\mathcal{H}$  Hilbert-space, space of normalizable functions with inner product/ norm.  
Example:  $(-i\hbar\nabla_{\mathbf{r}})[\exp(-x^2)] \rightarrow i\hbar 2x \exp(-x^2)$
- analogous to matrices, which are linear maps on your common vector spaces, e.g.  $\mathbb{R}^3$ ,  
 $M : \mathbf{v} \rightarrow \mathbf{w}$ ,  $M\mathbf{v} = \mathbf{w}$
- in this analogy a function can be thought of as an  $\infty$ -dimensional vector

**Energy spectra** Energy eigenstates  $\phi_k(\mathbf{r})$  satisfy the *time-independent Schrödinger equation* (TISE)

$$\hat{H}\phi_k(\mathbf{r}) = E_k\phi_k(\mathbf{r}). \quad (1.7)$$

*comments:*

- e.g.  $\phi_k(\mathbf{r})$  from Eq. (1.1) and  $\hat{H}$  from Eq. (1.5).
- A general quantum state  $\Psi(\mathbf{r})$  can be written as *superposition* of eigenstates of the Hamiltonian (or any other Hermitian Operator)

$$\Psi(\mathbf{r}) = \sum_k c_k \phi_k(\mathbf{r}). \quad (1.8)$$

- Probability  $p_k$  to find/measure energy  $E_k$  is

$$p_k = \left| \int d^3\mathbf{r} \phi_k^*(\mathbf{r}) \Psi(\mathbf{r}) \right|^2 = |c_k|^2. \quad (1.9)$$

- Expectation value / mean value of  $E$  in the state  $\Psi(\mathbf{r})$ :

$$\bar{E} = \langle \hat{H} \rangle = \int d^3\mathbf{r} \Psi^*(\mathbf{r}) \hat{H} \Psi(\mathbf{r}) = \sum_k |c_k|^2 E_k. \quad (1.10)$$



**More on states and operators:** We can also use *abstract* quantum states (bra/ket) to write

$$\hat{H}|\phi_k\rangle = E_k|\phi_k\rangle \quad (1.11)$$

instead of Eq. (1.7). This leaves out the specification of a basis (or representation) for the quantum state. We can recover the usual **position space representation**

$$\phi_k(\mathbf{r}) = \langle \mathbf{r} | \phi_k \rangle \quad (1.12)$$

and **momentum space representation**

$$\tilde{\phi}_k(\mathbf{p}) = \langle \mathbf{p} | \phi_k \rangle. \quad (1.13)$$

through equally abstract position and momentum space bases  $|r\rangle$  and  $|p\rangle$ .

Importantly, many operators do not commute, for example

$$[\hat{r}, \hat{p}] = \hat{r}\hat{p} - \hat{p}\hat{r} = i\hbar \neq 0. \quad (1.14)$$

In those cases the corresponding observables (here momentum and position) cannot be known (measured) simultaneously.

## 1.2.2 Orbital angular momentum and Spin

**Orbital angular momentum** The operator  $\hat{L}$  for orbital angular momentum is defined analogous to classical physics

$$\hat{\mathbf{L}} = \hat{\mathbf{r}} \times \hat{\mathbf{p}}, \quad (1.15)$$

$$[\hat{L}_i, \hat{L}_j] = i\hbar\epsilon_{ijk}\hat{L}_k \quad (1.16)$$

Eigenstates  $|l, m\rangle$  are defined by the angular momentum quantum number  $l$  and the one for the z-component  $m$ .

$$\hat{\mathbf{L}}^2|l, m\rangle = \hbar^2l(l+1)|l, m\rangle, \quad (1.17)$$

$$\hat{L}_z|l, m\rangle = \hbar m|l, m\rangle. \quad (1.18)$$

**Spin** Spin  $\hat{S}$  is an "abstract" angular momentum. That means it fulfills the angular momentum commutation relations

$$[\hat{S}_i, \hat{S}_j] = i\hbar\epsilon_{ijk}\hat{S}_k, \quad (1.19)$$

just like Eq. (1.16), but there is no underlying relation Eq. (1.15).

Spin-states  $|s, m_s\rangle$  are defined analogously to orbital angular momentum.

$$\hat{\mathbf{S}}^2|s, m_s\rangle = \hbar^2s(s+1)|s, m_s\rangle, \quad (1.20)$$

$$\hat{S}_z|s, m_s\rangle = \hbar m_s|s, m_s\rangle. \quad (1.21)$$

comments:

- The concept of spin arises naturally when doing *relativistic* quantum mechanics for charged particles.
- Most frequently we will encounter spin  $s = \frac{1}{2}$  (e.g. electron spin), for which we use the short-hand symbols  $|\uparrow\rangle = |s = \frac{1}{2}, m_s = \frac{1}{2}\rangle$  and  $|\downarrow\rangle = |s = \frac{1}{2}, m_s = -\frac{1}{2}\rangle$ .
- It is frequently helpful to *add* different quantum mechanical angular momenta  $\hat{\mathbf{L}}_1$  and  $\hat{\mathbf{L}}_2$ , such as orbital angular momentum and spin of the same electron, or two different spins, or orbital angular-momenta of two different particles.
- This is called **angular momentum coupling**. We define a total (or coupled) angular momentum operator

$$\hat{\mathbf{J}} = \hat{\mathbf{L}}_1 + \hat{\mathbf{L}}_2 \quad (1.22)$$

(where one of the  $\hat{L}$  may in fact be a spin).

- This two-body problem could be described in a **separate / uncoupled basis**:

$$\hat{\mathbf{L}}_n^2 |l_1, m_1; l_2, m_2\rangle = \hbar^2 l_n(l_n + 1) |l_1, m_1; l_2, m_2\rangle, \quad (1.23)$$

$$\hat{L}_{z,n} |l_1, m_1; l_2, m_2\rangle = \hbar m_n |l_1, m_1; l_2, m_2\rangle, \quad n \in \{1, 2\}. \quad (1.24)$$

- Sometime is is advantageous to use a **combined / coupled angular momentum basis**:

$$\hat{\mathbf{J}}^2 |j, l_1, l_2, m_j\rangle = \hbar^2 j(j + 1) |j, l_1, l_2, m_j\rangle, \quad (1.25)$$

$$\hat{J}_z |j, l_1, l_2, m_j\rangle = \hbar m_j |j, l_1, l_2, m_j\rangle, \quad (1.26)$$

where  $j$  is the total *angular momentum quantum number*, and  $m_j$  the one for its z-component.

- One also finds relations how we can express one basis through the other one:

$$|j, l_1, l_2, m_j\rangle = \sum_{m_1, m_2} C_{l_1, l_2; m_1, m_2}^{j, m_j} |l_1, m_1, l_2, m_2\rangle. \quad (1.27)$$

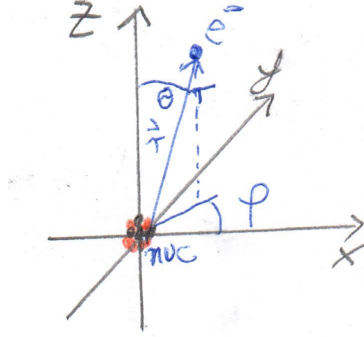
The coefficients  $C_{l_1, l_2; m_1, m_2}^{j, m_j}$  are called *Clebsch-Gordan coefficients*. You can find out how to calculate them in your QM textbook or various online apps, e.g. <https://www.volya.net/index.php?id=vc>

- By using the definition Eq. (1.22) and angular momentum algebra, one can find the constraints on quantum numbers  $l_1 + l_2 \geq j \geq |l_1 - l_2|$  and  $m_j = m_1 + m_2$ . This means all Clebsch-Gordan coefficients where these relations are not fulfilled will be equal to zero.

### 1.2.3 The Hydrogen(ic) atom

- Hydrogen-"ic": Like Hydrogen, but might have larger nuclear charge  $q = Z|e|$ . For example  $\text{He}^+$ , with  $Z = 2$ .
- Covered in your QM courses, now also logical starting point for AMO course.

- Simplest atom and *only* analytically solvable one.
- Center of mass-frame: 3D problem,  $\mathbf{r} \approx$  electron co-ordinate and  $m \approx$  electron mass in the following. (reduced mass  $m_{\text{red}} = m_e M / (m_e + M) \approx m_e$ ).



- Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla_{\mathbf{r}}^2 + V(\mathbf{r}), \quad V(\mathbf{r}) = -\frac{Ze^2}{4\pi\epsilon_0} \frac{1}{|\mathbf{r}|} \quad (1.28)$$

- Laplacian in 3D spherical co-ordinates  $r, \theta, \varphi$  (using  $r = |\mathbf{r}|$ )

$$\nabla_{\mathbf{r}}^2 = \Delta = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \underbrace{\frac{1}{r^2 \sin(\theta)} \frac{\partial}{\partial \theta} \left( \sin(\theta) \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2(\theta)} \frac{\partial^2}{\partial \varphi^2}}_{= -\hat{\mathbf{L}}^2 / (\hbar^2 r^2)} \quad (1.29)$$

- Solve TISE (1.7) in 3D, using *separation of variables*, find

$$\hat{H} \phi_{nlm}(\mathbf{r}) = E_{nl} \phi_{nlm}(\mathbf{r}) \quad (1.30)$$

with Ansatz

$$\phi_{nlm}(\mathbf{r}) = \phi_{nlm}(r, \theta, \varphi) = R_{nl}(r) \underbrace{Y_{lm}(\theta, \varphi)}_{\text{spherical harmonics}} \quad (1.31)$$

- Spherical harmonics fulfill

$$\hat{\mathbf{L}}^2 Y_{lm}(\theta, \varphi) = \hbar^2 l(l+1) Y_{lm}(\theta, \varphi), \quad (1.32)$$

$$\hat{L}_z Y_{lm}(\theta, \varphi) = -i\hbar \frac{\partial}{\partial \varphi} Y_{lm}(\theta, \varphi) = \hbar m Y_{lm}(\theta, \varphi). \quad (1.33)$$

Thus they are the position space representation of angular momentum states, see Eq. (1.25).

**Radial Schrödinger equation:** Obtained by inserting Eq. (1.31) into Eq. (1.30)

$$\left\{ -\frac{\hbar^2}{2m} \left[ \frac{1}{r} \frac{d}{dr} \left( r^2 \frac{d}{dr} \right) \right] + \underbrace{\frac{\hbar^2 l(l+1)}{2mr^2}}_{\equiv V_{\text{eff}}(r)} + V(r) \right\} R_{nl}(r) = E_{nl} R_{nl}(r). \quad (1.34)$$

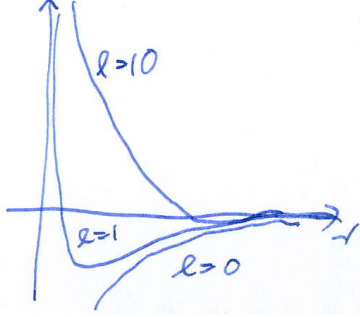


Figure 1.

left:  $V_{\text{eff}}(r)$  contains the effect of a centrifugal force pushing the electron outwards, if  $l > 0$ .

### Energy eigenstates of Hydrogen atom

$$\phi_{nlm}(\mathbf{r}) = \phi_{nlm}(r, \theta, \varphi) = R_{nl}(r)Y_{lm} \quad \text{3D wavefunction} \quad (1.35)$$

$$R_{nl}(r) = \mathcal{N}_{nl} e^{-\rho/2} \rho^l L_{n-l-1}^{2l+1}(\rho) \quad \text{radial wavefunction.} \quad (1.36)$$

$$Y_{lm}(\theta, \varphi) = (-1)^m \sqrt{\frac{2l+1}{4\pi} \frac{(l-m)!}{(l+m)!}} P_l^m(\cos[\theta]) e^{im\varphi} \quad \text{angular wavefunction} \quad (1.37)$$

$$\rho = \frac{2Zr}{na_0} \quad \text{scaled radius} \quad (1.38)$$

$$\mathcal{N}_{nl} = \sqrt{\left(\frac{2Z}{na_0}\right)^3 \frac{(n-l-1)!}{2n(n+l)!}} \quad \text{normalisation factor} \quad (1.39)$$

$$L_a^b(\rho) \quad \text{generalised/associate Laguerre polynomials} \quad (1.40)$$

$$P_l^m(\cos[\theta]) \quad \text{generalised Legendre polynomial} \quad (1.41)$$

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e} = \frac{\hbar}{m_e c \alpha} \quad \text{Bohr radius } (\alpha \sim 1/137 \text{ fine-structure constant}). \quad (1.42)$$

### Corresponding energy eigenvalues

$$E_{nl} = E_n = -\frac{m_e e^4 Z^2}{8\epsilon_0^2 \hbar^2 n^2} = -Z^2 \frac{\mathcal{R}}{n^2}, \quad (1.43)$$

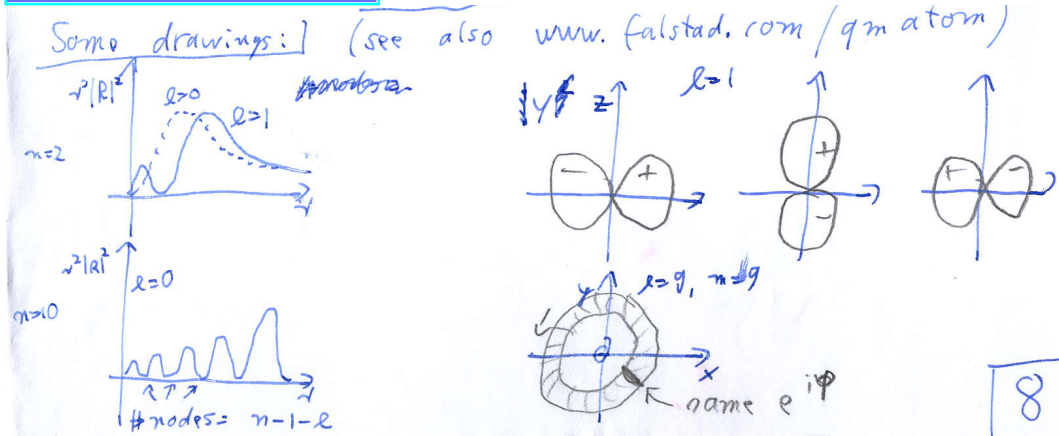
$$\mathcal{R} = \frac{m_e e^4}{8\epsilon_0^2 \hbar^2}, \quad \text{Rydberg constant} \quad (1.44)$$

Integer quantum numbers

- **principal** quantum number  $n = 0, 1, 2, \dots \infty$
- **angular momentum** quantum number  $l = 0, \dots, n-1$
- **azimuthal** quantum number  $m = -l, \dots, l$
- (**electron spin** orientation  $m_s = -\frac{1}{2}, \frac{1}{2}$ )
- Note, we had earlier allowed quantum numbers  $nl$  for the energy, which would be used for

a general central potential  $V(r)$ . In the case of the Coulomb potential (or any precise  $1/r$  form), there is an *accidental degeneracy* due to which energy does not in fact depend on  $l$ , see Eq. (1.43).

To leading (non-relativistic) order listed above, Hydrogen energies and spatial wave functions do not depend on spin. In chapter 2 we will see some small corrections due to spin. See also <http://falstad.com/qmatom/>



#### 1.2.4 Quantum dynamics/ time-dependence

##### Time-dependent Schrödinger equation TDSE

$$i\hbar \frac{\partial}{\partial t} |\Psi(t)\rangle = \hat{H}(t) |\Psi(t)\rangle. \quad (1.45)$$

- We can always write

$$|\Psi(t)\rangle = \sum_n c_n(t) |\phi_n\rangle, \quad (1.46)$$

where  $|\phi_n\rangle$  is any orthonormal basis of our choice, and reduce (1.45) to a set of coupled ODEs for  $i\hbar \frac{\partial c_n(t)}{\partial t} = \dots$ .

- If the Hamiltonian is actually *time-independent*  $\hat{H}(t) = \hat{H} = \text{const}$ , we then have

$$|\Psi(t)\rangle = \sum_n c_n(0) \exp\left[-i \frac{E_n}{\hbar} t\right] |\phi_n\rangle, \quad (1.47)$$

where  $|\phi_n\rangle$  are the eigenstates from Eq. (1.7) and  $c_n(0) = \langle \phi_n | \Psi(0) \rangle$  are fixed by the initial conditions. *Self-test: show this in a few lines from Eq. (1.45) and Eq. (1.7).*

- If the Hamiltonian is fully time-dependent, the solution of Eq. (1.45) is generally difficult. We can use numerical calculations, e.g. based on (1.46), or perturbation theory.

### 1.2.5 Approximation methods

#### Time-independent perturbation theory (non-degenerate)

Let

$$\hat{H} = \hat{H}_0 + \lambda \hat{H}', \quad (1.48)$$

where  $\lambda$  is a small parameter and the spectrum (eigenstates and eigenvectors) of  $\hat{H}_0$  is known  $\hat{H}_0 |\phi_k^{(0)}\rangle = E_k^{(0)} |\phi_k^{(0)}\rangle$  and *non-degenerate*.

We write the full eigen-energies and eigen-states of (1.48) as

$$\begin{aligned} E_k &= E_k^{(0)} + \lambda E_k^{(1)} + \lambda^2 E_k^{(2)} + \lambda^3 E_k^{(3)} + \dots \\ |\phi_k\rangle &= |\phi_k^{(0)}\rangle + \lambda |\phi_k^{(1)}\rangle + \lambda^2 |\phi_k^{(2)}\rangle + \lambda^3 |\phi_k^{(3)}\rangle + \dots, \end{aligned} \quad (1.49)$$

insert these expansions into the TISE (1.7) and solve order by order in  $\lambda$

#### First order energy correction (non-degenerate PT)

$$E_k^{(1)} = \langle \phi_k^{(0)} | \hat{H}' | \phi_k^{(0)} \rangle. \quad (1.50)$$

- Beware, hidden danger!!: using this if  $E_k^{(0)}$  is in fact degenerate gives *wrong results*. (See why in derivation in your QM course).

#### Time-independent perturbation theory (degenerate)

Let us assume  $E_k^{(0)}$  is  $\alpha$ -fold degenerate and label the unperturbed degenerate eigenfunctions  $|\phi_{kr}^{(0)}\rangle$ , for  $r = 1, \dots, \alpha$ . The perturbation  $\hat{H}'$  will in general *break the degeneracy*, yielding new eigenfunctions

$$|\chi_{kr}^{(1)}\rangle = \sum_s c_{ks} |\phi_{ks}^{(0)}\rangle. \quad (1.51)$$

New eigenfunctions and energy shifts are found from

#### Diagonalisation in degenerate subspace (degenerate PT)

$$\underline{\underline{H'}} \cdot \mathbf{c} = E_{kr}^{(1)} \mathbf{c}, \quad \text{the matrix } \underline{\underline{H'}} \text{ has elements } H'_{us} = \langle \phi_{ku}^{(0)} | \hat{H}' | \phi_{ks}^{(0)} \rangle \quad (1.52)$$

- The vector  $\mathbf{c} = [c_{k0}, c_{k1}, \dots, c_{k\alpha}]^T$  ( $T$  means "transposed" of the vector) contains the coefficients that give the new eigenvector in Eq. (1.51).
- $\underline{\underline{H'}}$  is the perturbing Hamiltonian in the degenerate subspace.

## Time-dependent perturbation theory

Now instead of (1.48) we start from

$$\hat{H}(t) = \hat{H}_0 + \lambda \hat{H}'(t), \quad (1.53)$$

thus assuming the unperturbed Hamiltonian  $\hat{H}_0$  is still time-independent. We modify (1.47) to now include time-dependent weights of each part

$$|\Psi(t)\rangle = \sum_n c_n(t) \exp\left[-i \frac{E_n^{(0)}}{\hbar} t\right] |\phi_n\rangle, \quad (1.54)$$

again with a perturbation expansion

$$c_n(t) = c_n^{(0)} + \lambda c_n^{(1)}(t) + \lambda^2 c_n^{(2)}(t) + \lambda^3 c_n^{(3)}(t) + \dots \quad (1.55)$$

If we assume our system starts in state  $a$ , that means  $c_n^{(0)} = \delta_{na}$ , where  $\delta$  is the Kronecker delta, then

### First order time-dependent perturbation theory coefficients

$$\dot{c}_b^{(0)} = \frac{\partial}{\partial t} c_b^{(0)} = 0, \quad (1.56)$$

$$\dot{c}_b^{(1)} = \frac{\partial}{\partial t} c_b^{(1)} = (i\hbar)^{-1} \int_0^t dt' H'_{ba}(t') \exp[i\omega_{ba}t']. \quad (1.57)$$

- $\omega_{ba} = (E_b^{(0)} - E_a^{(0)})/\hbar$
- $H'_{ba}(t') = \langle \phi_b^{(0)} | \hat{H}'(t') | \phi_a^{(0)} \rangle$

## Periodic perturbation

Lets look at a special case of (1.53) that will be important later:

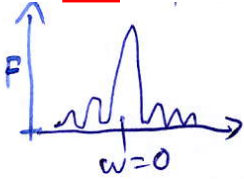
$$\lambda \hat{H}'(t) = \hat{A} \exp[i\omega t] + \hat{A}^\dagger \exp[-i\omega t]. \quad (1.58)$$

We are starting in  $a$  (since  $c_n^{(0)} = \delta_{na}$  as before), then the transition probability  $a \rightarrow b$  to first order PT will be given by

$$\begin{aligned} P_{ba}^{(1)}(t) &= |\lambda c_b^{(1)}(t)|^2 \\ &= \left| A_{ba} \left( \frac{1 - \exp[i(E_b^{(0)} - E_a^{(0)} + \hbar\omega)t/\hbar]}{E_b^{(0)} - E_a^{(0)} + \hbar\omega} \right) \right. \\ &\quad \left. + A_{ba}^\dagger \left( \frac{1 - \exp[i(E_b^{(0)} - E_a^{(0)} - \hbar\omega)t/\hbar]}{E_b^{(0)} - E_a^{(0)} - \hbar\omega} \right) \right|^2 \end{aligned} \quad (1.59)$$

Here  $A_{ba} = \langle \phi_b^{(0)} | \hat{A} | \phi_a^{(0)} \rangle$ . Now let us define the **detuning**  $\hbar\Delta = |E_b^{(0)} - E_a^{(0)}| - \hbar\omega$ , then

- for large detuning  $P_{ba}^{(1)}(t) \ll 1$ , since  $A_{ba}$  small and  $P_{ba} \sim \left| \frac{A_{ba}}{\Delta} \right|^2$
- On resonance ( $\Delta \approx 0$ ),  
 $P_{ba}^{(1)}(t) = \frac{2}{\hbar^2} |A_{ba}|^2 F(t, \omega_{ba} \mp \omega)$ , where the upper sign is in the absorbing case (second term, Eq. (1.59)), and the lower in the emitting case (first term).  $F(t, \omega) = 2 \frac{\sin^2[\omega t/2]}{\omega^2}$ .



### 1.2.6 Many particles

For each particle we have to add one set of co-ordinates and quantum numbers to the wave-function. Lets denote with

$$q = \{\mathbf{r}, m_s, \dots\} \quad (1.60)$$

the collection of all such variables. For  $N = 2$  particles, we then have to write e.g. energy eigenstates  $\phi_k(q_1, q_2)$ , where the subscripts on  $q_j$  now number the particle  $j$ .

An exemplary Hamiltonian for two equal mass particles that interact (with interaction potential  $U$ ) would be written as

$$\hat{H} = -\frac{\hbar^2}{2m}(\nabla_{\mathbf{r}_1}^2 + \nabla_{\mathbf{r}_2}^2) + V(\mathbf{r}_1) + V(\mathbf{r}_2) + U(\mathbf{r}_1, \mathbf{r}_2). \quad (1.61)$$

- Quantum mechanically we *cannot distinguish* identical particles, while classically we might for example via their history, see box 1.
- Thus wave-function must be "equivalent" under exchange of two particles  $\bullet 1 \leftrightarrow \bullet 2$  ( $q_1 \leftrightarrow q_2$ )
- This requirement leads to ...

**Symmetry requirements for wave-functions of two indistinguishable particles**

$$\Psi(q_1, q_2) = \pm \Psi(q_2, q_1) \quad (1.62)$$

- + for **Bosons** (=integer spin)
- for **Fermions** (=half-integer spin)

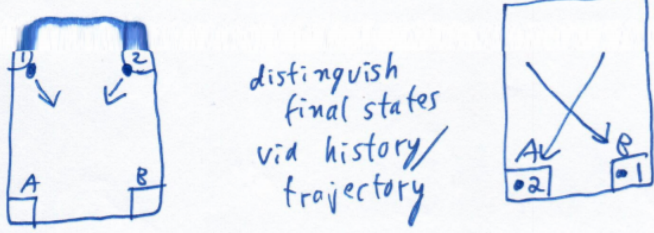
- Allocation to the spins is done in relativistic quantum mechanics (spin-statistics theorem).
- These symmetry properties only matter when particles try to share the *same space* (i.e.  $0 < r_1, r_2 < L$ , not  $0 < r_1 < L$  and  $3L < r_2 < 4L$ ).



- Leads to
  - Pauli exclusion principle:** Two Fermions cannot be in the same quantum state. (i.e. position  $\Psi(\mathbf{r}, \mathbf{r}) = 0$ .)
  - Bose enhancement:** Bosons "like to be" in the same quantum state (see chapter 5).

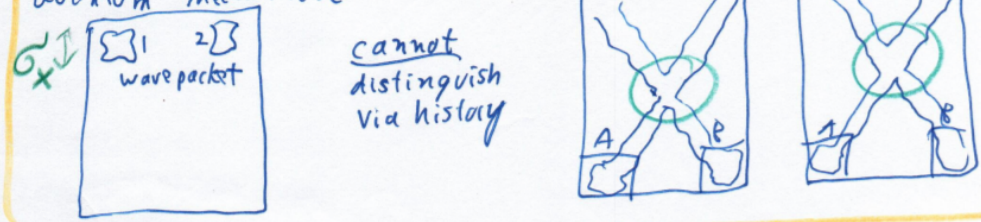
Trajectories of indistinguishable particles (see Shankar p. 260)

Classical identical billiard balls



distinguish final states via history/trajectory

Quantum Mechanical



cannot distinguish via history

Box 1: