Introduction

Quantum mechanics is a very important theory with a wide range of applications. Invention of computers, lasers and nuclear magnetic tomography followed from deep understanding of quantum mechanics.

Quantum mechanics is a precise, mathematical theory, but its meaning, i.e. interpretation is an open to discussions. Therefore applications of quantum theory to the real world involve some art. Your aim is to master both: the mathematical formalism and the art of using it in practice.

Quantum mechanics is probably the most difficult subject you have encountered during your undergraduate studies. Some prominent physicists joked that it could not be understood at all (see slide) but I am not so pessimistic. The way to understand quantum mechanics is through mathematics and this is what I expect you to achieve.

Let us revise the key concepts you have learnt in Professor Dauncey’s course last term...
How to master this course?

Richard Feynman: “Nobody understands quantum mechanics.”

Revision of Prof Dauncey’s lectures

<table>
<thead>
<tr>
<th>1D</th>
<th>3D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Position</td>
<td>( \hat{x} )</td>
</tr>
<tr>
<td>Momentum</td>
<td>( \hat{p} = -i\hbar \frac{\partial}{\partial x} )</td>
</tr>
<tr>
<td>Kinetic energy</td>
<td>( \hat{T} = \frac{\hat{p}^2}{2m} )</td>
</tr>
<tr>
<td>Potential</td>
<td>( \hat{V}(x) )</td>
</tr>
<tr>
<td>Hamiltonian</td>
<td>( \hat{H} = \hat{T} + \hat{V}(x) )</td>
</tr>
<tr>
<td>Wavefunction</td>
<td>( \psi(x,t) )</td>
</tr>
</tbody>
</table>
| Normalisation | \( \int |\psi(x,t)|^2 \, dx = 1 \) | \( \int |\psi(r,t)|^2 \, d^3r = \int |\psi(r,t)|^2 \, d^3r = 1 \)

Quantum Theory revision

- Wavefunction \( \Psi(\hat{r}, t) \)
  (everything we can know about the object)

  e.g. the probability of finding an electron
  in volume \( d^3r \)
  at time \( t \)

  \[
  P(\hat{r}, t) \, d^3r = |\Psi(\hat{r}, t)|^2 \, d^3r = \psi^* \psi \, d^3r
  \]

- Schrödinger equation (one particle)

  \[
  \hat{E} \Psi = \hat{H} \Psi \quad \hat{H} = \hat{T} + \hat{V}
  \]

  \[
  \hat{E} = i \hbar \frac{\partial}{\partial t} \quad \hat{T} = \frac{\hat{p}_{x}^2}{2m} \quad \hat{V} = \hat{V}(\hat{r}, t)
  \]

  \[
  \hat{p} = -i \hbar \hat{\nabla} \\
  \hat{p} = \hat{p}
  \]

  position representation

TDSE

N particles: \( \Psi = \Psi(\hat{r}_1, \hat{r}_2, \ldots, \hat{r}_N, t) \)
1 Introduction

We have seen that a measurement of a variable will give back one of the eigenvalues of the Hermitian operator associated with the variable. The actual eigenvalue is randomly chosen from the possible ones included in the wavefunction expansion in terms of the operator eigenstates.

We now want to think about the time dependence of the wavefunction in general, which requires us to consider the case with no measurements and the case with. We will also need to start thinking a bit about conserved quantities as these are important in mechanics.

2 Time dependence without measurements

The final postulate is one which we have effectively been assuming all along.

Postulate 5: Between measurements, the development of the wavefunction with time is governed by the time-independent Schrödinger equation.

\[
\frac{\hbar}{2}\frac{\partial}{\partial t} \psi(r,t) = \frac{i}{\hbar} \hat{H} u(r) e^{-iEt/\hbar} = \hat{H} u(r) e^{-iEt/\hbar}
\]

- superposition of energy eigenstates

\[\sum_n \alpha_n \psi_n(r,t) \]

true for any \(\alpha_n = \text{Re} \alpha_n + i\text{Im} \alpha_n\)

provided that

\[\int |\psi(r,t)|^2 dr = 1\]

\[\psi_n(r,t) = u_n(r) e^{-iEt/\hbar}\]

\[\hat{H} u_n(r) = E_n u_n(r)\]

Practical way of finding time evolution of \(\psi\)

1. Solve TISE
2. Multiply by phase factors
3. Choose a suitable superposition
4. Normalise if necessary

\[E_n/\hbar = \text{Bohr (angular) frequency}\]
Vibrations of a diatomic molecule

approximation by a harmonic oscillator

Energy

Intennuclear Separation (r)

True

Dissociation Energy

v = 0

v = 1

v = 2

v = 3

v = 4

v = 5

v = 6

n

Applications of Quantum Mechanics, Leszek Frasinski, Jan-Feb 2012, slide 8

What we have learnt in Lecture 1

How to progress through this course:

• Quantum mechanics (QM) is not an intuitive subject.
• The first step is to master QM formalism.
• The real-world applications of the formalism can be learnt by problem solving.
• The meaning of QM becomes clearer later.

Conclusions from the revision:

• Quantum mechanics does not tell us precisely how a particle moves; we
  know only the probability density of finding the particle given by the
  modulus squared of the wavefunction.
• To find the time evolution of the wavefunction, in principle we should
  solve the TDSE, but in practice it is often sufficient to solve TISE and
  construct a superposition of energy eigenstates multiplied by the time-
  dependent phase factors.
• Computer simulations provide a valuable aid for understanding the
  formalism.
Course overview

- Lecture 1 – QM revision
- Lecture 2 – Atomic units
- Lecture 3 – Spherical harmonics
- Lecture 4 – Hydrogen atom
- Lecture 5 – Dirac notation
- Lecture 6 – Einstein coefficients
- Lecture 7 – Resonant field
- Lecture 8 – Selection rules
- Lecture 9 – Helium atom
- Lecture 10 – Indistinguishability
- Lecture 11 – Periodic table
- Lecture 12 – Pilot wave

Plan for today

- The proper use of units in general
  - typography
  - tables and graphs
  - radian and steradian

- Atomic units
  - base and derived atomic units
  - examples of unit conversion
  - correct and incorrect ways of writing atomic units
  - writing equations “in atomic units”, i.e. in reduced physical quantities
Typography

- Physical quantities should be printed in italic (sloping) font; units should be printed in roman (upright) font, e.g. $x = 5 \text{ nm}$ (not $x = 5 \text{ nm}$, or $x = 5 \text{ nm}$).
- Subscripts and superscripts that are symbols for physical quantities or numbers should be printed in italic font; other subscripts and superscripts should be printed in roman font, e.g. $u_{nlm}$ for hydrogen-atom wavefunctions, $m_e$ for electron rest mass, $e$ for elementary charge, $k_B$ for Boltzmann constant.
- Vectors should be printed in italic bold font, e.g. $E(r)$ for electric field at point $r$, $E(r)$ for electric field with spherical symmetry.

The correct use of units – see an article on Blackboard

The language of science

I. M. Mills

Abstract: Some aspects of the use and misuse of scientific language are discussed, particularly in relation to quantum calculations, the names and symbols for quantities and units, and the choice of units – including the possible use of non-SI units. The discussion is intended to be constructive, and to suggest ways in which common usage can be improved.

1. Introduction

In English-speaking countries, there is some debate about the decline in standards of scientific language in our society and the lack of rigor and discipline in teaching grammar and syntax in our schools. There is a similar problem concerning the language of science, just as the use of good English is known all that they need to know on this subject. In this paper, I adopt a different approach, in the hope that it may stimulate the reader’s awareness of some of the problems. I discuss briefly three aspects of the language of science which test the popular usage and understanding could be improved. With benefit to us all, the first concerns the use of quantum symbols, the second concerns the importance of using carefully...
Atomic unit of length

The hydrogen-like radial functions are often expressed in terms of the Bohr radius

\[ a_0 = \frac{4\pi\varepsilon_0\hbar^2}{m_e^2} = 5.3 \times 10^{-11} \text{m} \]

---

Atomic units

<table>
<thead>
<tr>
<th>Physical quantity</th>
<th>Name of unit</th>
<th>Symbol for unit</th>
<th>Value of unit in SI</th>
</tr>
</thead>
<tbody>
<tr>
<td>mass</td>
<td>electron rest mass</td>
<td>( m_e )</td>
<td>9.109 3897 (54) \times 10^{-31} \text{kg}</td>
</tr>
<tr>
<td>charge</td>
<td>elementary charge</td>
<td>( e )</td>
<td>1.602 177 33(48) \times 10^{-19} \text{C}</td>
</tr>
<tr>
<td>action</td>
<td>Planck constant/2(\pi)^1</td>
<td>( \hbar )</td>
<td>1.054 572 66(63) \times 10^{-34} \text{J} \cdot \text{S}</td>
</tr>
<tr>
<td>length</td>
<td>bohr(^1)</td>
<td>( a_0 )</td>
<td>5.291 772 49 (24) \times 10^{-11} \text{m}</td>
</tr>
<tr>
<td>energy</td>
<td>hartree(^1)</td>
<td>( E_h )</td>
<td>4.359 748 26 (26) \times 10^{-19} \text{J}</td>
</tr>
<tr>
<td>time</td>
<td>( h/E_h )</td>
<td></td>
<td>2.418 884 334 (29) \times 10^{-17} \text{s}</td>
</tr>
<tr>
<td>velocity(^2)</td>
<td>( a_0E_h/a_0 )</td>
<td></td>
<td>2.187 691 42 (10) \times 10^9 \text{m} \cdot \text{s}^{-1}</td>
</tr>
<tr>
<td>force</td>
<td>( E_h/a_0 )</td>
<td></td>
<td>8.238 729 5 (25) \times 10^{-4} \text{N}</td>
</tr>
<tr>
<td>momentum, linear</td>
<td>( h/a_0 )</td>
<td></td>
<td>1.992 534 3 (12) \times 10^{-24} \text{N} \cdot \text{s}</td>
</tr>
<tr>
<td>electric current</td>
<td>( eE_h/h )</td>
<td></td>
<td>6.626 621 1 (20) \times 10^{-19} \text{A}</td>
</tr>
<tr>
<td>electric field</td>
<td>( E_0/e_0a_0 )</td>
<td></td>
<td>5.142 208 2 (15) \times 10^{11} \text{V} \cdot \text{m}^{-1}</td>
</tr>
<tr>
<td>electric dipole moment</td>
<td>( e_0a_0 )</td>
<td></td>
<td>8.876 757 9 (26) \times 10^{-28} \text{C} \cdot \text{m}</td>
</tr>
<tr>
<td>magnetic flux density</td>
<td>( h/e_0a_0 )</td>
<td></td>
<td>3.351 880 8 (71) \times 10^{10} \text{T}</td>
</tr>
<tr>
<td>magnetic dipole moment(^2)</td>
<td>( e_0h/m_e )</td>
<td></td>
<td>1.854 803 08 (62) \times 10^{-23} \text{J} \cdot \text{T}^{-1}</td>
</tr>
</tbody>
</table>

(1) \( \hbar = h/(2\pi) \); \( a_0 = 4\pi\varepsilon_0\hbar^2/m_e^2 \); \( E_h = h^2/m_ea_0^2 \).
(2) The numerical value of the speed of light, when expressed in atomic units, is equal to the reciprocal of the fine structure constant \( \alpha \) (ratio of velocity) \( c\hbar/2\pi = \alpha^{-1} = 137.035 9886(14) \).
(3) The atomic unit of magnetic dipole moment is twice the nuclear magneton, \( \mu_n \).
What we have learnt in Lecture 2

Typography
- There are strict rules when to use roman, italic and bold fonts for mathematical and physical symbols in printed documents.

Units
- When working out a formula for unit conversion remember that units obey the same algebraic rules as variables and numbers.
- Numbers in tables and on graph axes should be labelled as ratios of a physical quantity and its unit.

Atomic units
- Atomic units are constructed from a few fundamental constants.
- Do not write “a.u.”, always look up or derive the correct name for the atomic unit.
- Writing equations “in atomic units” really means using reduced quantities, i.e. dividing all physical quantities by the corresponding atomic unit; reduced quantities are dimensionless (unitless).
- There is a simple shortcut to convert an SI equation to “atomic units”, but there is no simple prescription to do the reverse.

Equations “in atomic units”

\[
\left(-\frac{\hbar^2}{2m_e} \nabla^2 + V(\mathbf{r})\right) u(\mathbf{r}) = E u(\mathbf{r})
\]

define reduced quantities:
\[
\begin{align*}
\mathbf{r}' &= \mathbf{r}/a_0 \\
E' &= E/E_n \\
m' &= m/m_e
\end{align*}
\]

pure numbers (dimensionless)
\[
\begin{align*}
\hbar &= \hbar/a_0 \\
\mathbf{p}' &= a_0 \mathbf{p} \\
\mathbf{V}' &= \mathbf{V}/E_n \\
\mathbf{E}' &= \mathbf{E}/E_n \\
\mathbf{E}' u(\mathbf{r}') &= E_n E u(\mathbf{r})
\end{align*}
\]

\[
\left(-\frac{\hbar^2}{2m_e} \mathbf{p}'^2 - \frac{1}{r'} \right) u(\mathbf{r}') = E_n E u(\mathbf{r})
\]

\[
\left(-\frac{\hbar^2}{2m_e} \mathbf{p}'^2 - \frac{1}{r} \right) u(\mathbf{r}) = E' u(\mathbf{r}')
\]

- Shortcut: SI → reduced quantities (“in atomic units”)

\[
\begin{align*}
\hbar, e, m_e, 4\pi\varepsilon_0 &\quad \rightarrow 1 \\
m &\quad \rightarrow m/m_e \\
c &\quad \rightarrow \frac{1}{\hbar} \approx 137.036 \\
\text{fine structure constant $\alpha$ (dimensionless)}
\end{align*}
\]

see handout on atomic units
Applications of Quantum Mechanics – Lecture 3

Course overview
- Lecture 1 – QM revision
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- Lecture 12 – Pilot wave

Plan for today
- Central potential
  - reduced mass
  - spherical coordinates
  - radial wavefunctions and spherical harmonics

Parity operator
- even and odd functions
- functions that are neither odd nor even

Visualisation of spherical harmonics
- chemist’s view
- physicist’s view

A wave function is an eigenfunction of $\hat{P}$ when it is either odd or even.
Spherical coordinates

Laplacian

\[ \nabla^2 \right|_{\mathbb{R}^3} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \]

Spherical harmonics

<table>
<thead>
<tr>
<th>( n )</th>
<th>( \ell )</th>
<th>( Y_{\ell m} (\theta, \phi) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>( \sqrt{\frac{1}{4\pi}} )</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>( \sqrt{\frac{3}{4\pi}} \cos \theta )</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>( \pm \sqrt{\frac{3}{8\pi}} \sin \theta e^{\pm i\phi} )</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>( \sqrt{\frac{5}{16\pi}} (3 \cos^2 \theta - 1) )</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>( \pm \sqrt{\frac{15}{8\pi}} \sin \theta \cos \theta e^{\pm i\phi} )</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>( \sqrt{\frac{15}{32\pi}} \sin^2 \theta e^{\pm 2i\phi} )</td>
</tr>
</tbody>
</table>

Parity:

\[ Y_{\ell m} (\pi - \theta, \phi + \pi) = (-1)^\ell Y_{\ell m} (\theta, \phi) \]

Superposition:

\[ \sum \text{odd} = \text{odd} \]
\[ \sum \text{even} = \text{even} \]
\[ \sum (\text{even} + \text{odd}) = \text{no parity!} \]

\[ \text{Parity of } u_{\ell m} \]

\[ \hat{\rho} u_{\ell m} (\vec{r}) = u_{\ell m} (\vec{r}) = \frac{R_{\ell m} (r)}{r} Y_{\ell m} (\theta, \phi + \pi) \]

Even parity

\[ Y_{\ell m} (\theta, \phi + \pi) = (-1)^\ell Y_{\ell m} (\theta, \phi) \]

Odd parity

\[ Y_{\ell m} (\theta, \phi + \pi) = -(-1)^\ell Y_{\ell m} (\theta, \phi) \]

\[ \text{Parity of } Y_{\ell m} (\theta, \phi) \]

\[ \frac{\partial}{\partial \phi} (-1)^\ell Y_{\ell m} (\vec{r}) \]

(1) eigenfunction of \( \hat{\rho} \)

(2) \( \ell \) even/odd \( \rightarrow \) \( u_{\ell m} \) even/odd

\[ u_{\ell m} (\vec{r}) \] visualisation

Chemist's view:

Length = value of \( |Y_{10} (\theta, \phi)|^2 \)

see Prof. D. Cann's Lecture 25
What we have learnt in Lecture 3

Central potential
- Using the centre of mass allows us to simplify the problem of two particles (electron and nucleus) to a one-particle of reduced mass.
- In the spherical coordinates the wavefunction separates into radial and spherical parts.

Parity operator
- Eigenfunctions of the parity operator can be only even or odd.
- A superposition of functions with different parities gives undefined parity.
- Spherical harmonics have parity determined by the orbital angular momentum quantum number $l$.

Visualisation of spherical harmonics, $Y_{lm}$
- Plotting surfaces given by $|Y_{lm}|^2$ is useful in chemistry.
- Plotting the $Y_{lm}$ magnitude as intensity and phase as colour gives a better insight into physics.

Physicist’s view

$Y_{lm}(\theta,\phi)$ as a sphere (of complex values)

Visualisation of spherical harmonics, $Y_{lm}$

Settings: v Stopped
Phasor count: 3 rows
View: v Position
v Phase as color
$Y_{00}$ $Y_{11}$ $Y_{10}$ $Y_{11}$
$Y_{22}$ $Y_{21}$ $Y_{10}$ $Y_{20}$ $Y_{21}$ $Y_{22}$

Compare with formulae on a slide
Course overview
- Lecture 1 – QM revision
- Lecture 2 – Atomic units
- Lecture 3 – Spherical harmonics
- **Lecture 4 – Hydrogen atom**
- Lecture 5 – Dirac notation
- Lecture 6 – Einstein coefficients
- Lecture 7 – Resonant field
- Lecture 8 – Selection rules
- Lecture 9 – Helium atom
- Lecture 10 – Indistinguishability
- Lecture 11 – Periodic table
- Lecture 12 – Pilot wave

Plan for today

The radial equation
- effective potential (effect of the centrifugal force)
- outline of the solution

Hydrogenic eigenfunctions
- classification and terminology of the quantum numbers
- energy levels for Coulombic and non-Coulombic potentials

Visualisation of hydrogen atom
- applet `qmatom`
- stationary and non-stationary states
The radial equation

Prof Dauncey’s Lecture 26

We will look for solutions of the form

\[ u(r) = R(r)Y_{lm}(\theta, \phi) \]

where \( Y_{lm}(\theta, \phi) \) are the eigenstates of \( L^2 \) and \( L_z \). This means we have

\[ L^2 Y_{lm} = (l(l+1)) R^2 Y_{lm} \]

hence, we have

\[ -\frac{n^2}{2m^2} V_{lm} \frac{d}{dr} \left( r^2 \frac{d}{dr} \right) + \frac{1}{2m^2} 2l(l+1)Y_{lm} + V(r)Y_{lm} = EY_{lm} \]

Dividing throughout by \( Y_{lm} \) then gives

\[ -\frac{n^2}{2m^2} \frac{d}{dr} \left( r^2 \frac{d}{dr} \right) + \frac{l(l+1)}{2m^2} R + V(r)R = ER \]

which is an equation for the radial dependence of the energy eigenstate with all the angular dependence taken out. We can make this look very similar to the 1D TISE. Defining \( \chi(r) = -R(r) \), then this can be written as

\[ -\frac{n^2}{2m^2} \frac{d^2}{dr^2} + \left[ V(r) + \frac{l(l+1)}{2m^2} \right] \chi = E\chi \]

See handout how to solve it
Radial wavefunctions for $n = 2$

$$R_{20} = \frac{\chi_{20}}{r}$$

Energy levels of a hydrogenic atom

Second Year Quantum Mechanics - Lecture 26
Central potentials
Paul Dauncey, 10 Dec 2009

4 Hydrogen atom

The energy eigenvalues themselves are

$$E_n = -\frac{m e^4}{2(4\pi \varepsilon_0)^2 h^2 n^2} = -\frac{e^2}{4\pi \varepsilon_0 \alpha_0^2} \frac{1}{n^2} = -13.6 \frac{eV}{n^2}$$

$$E_n = -\frac{e^2}{4\pi \varepsilon_0 \alpha_0^2} \frac{Z^2}{2n^2} = -\frac{E_h}{2} \frac{Z^2}{n^2} \Rightarrow E_h = 27.2 eV$$
Eigenvalues of angular momentum

- The eigenvalues of $L^2$ and $L_z$ were
  - $L^2$ eigenvalues = $(l+1)\hbar^2$, for integer $l$, where $l \geq 0$
  - $L_z$ eigenvalues = $m_\ell \hbar$, for integer $m_\ell$, where $|m_\ell| \leq l$
- $L^2$ eigenstates have a $2l+1$ degeneracy
  - Corresponding to the $2l+1$ possible values of $m_\ell$
- Classical picture: simply rotation of the vector
  - Degeneracy arises as there are many possible $L_z$ values for a fixed $L^2$ value

Energy levels of hydrogen atom

Eigenfunctions of a hydrogenic atom

$H, He^+, Li^{2+}, ...$

$U_{nlm}(r) = R_{nl}(r) \ Y_{lm}(\theta, \phi)$

<table>
<thead>
<tr>
<th>Quantum number</th>
<th>Quanta</th>
</tr>
</thead>
<tbody>
<tr>
<td>Principal: $n = 1, 2, 3, ...$</td>
<td>$E_n$</td>
</tr>
<tr>
<td>Orbital: $l = 0, 1, \ldots (n-1)$</td>
<td>$\hbar^2 l(l+1)$</td>
</tr>
<tr>
<td>Magnetic: $m = -l, -l+1, \ldots l$</td>
<td>$m_\ell \hbar$</td>
</tr>
</tbody>
</table>

see Prof. Dannecy's Lectures 24, 25

<table>
<thead>
<tr>
<th>$n$</th>
<th>$l$</th>
<th>$L$</th>
<th>$m$</th>
<th>degeneracy $= 2l+1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>0, 1</td>
<td>1</td>
<td>0, ±1</td>
<td>3</td>
</tr>
<tr>
<td>3</td>
<td>0, 1, 2</td>
<td>2</td>
<td>0, ±1, ±2</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>±1, ±2</td>
<td>7</td>
</tr>
</tbody>
</table>

Ground state $U_{100} = 1s$

Coulombic potential: same energy

$U_{200} = 2s$

non-Coulombic: different energies

$U_{210} = 2p$

n, l, $\ell$ subshells

triply degenerate

see Grotrian diagram of $H$
Hydrogenic wavefunctions

\[ \psi_{nlm}(r, \theta, \phi) = u_{nlm}(r) e^{-i\frac{E_n}{\hbar} t} \]

\[ u_{nlm}(r) = R_{nl}(r) Y_{lm}(\theta, \phi) \]

\[ E_n = -\frac{\hbar^2}{2m} \frac{Z^2}{r^2}, \quad E_n = \frac{\hbar^2}{2m} a_0^2 = 27.2 \text{ eV} \]

\[ R_{10}(r) = 2 \left( \frac{Z}{a_0} \right)^{3/2} e^{-Z/r} \]

\[ R_{20}(r) = 2 \left( \frac{Z}{2a_0} \right)^{3/2} \left( 1 - \frac{Z}{2a_0} \right) e^{-Zr/2a_0} \]

\[ R_{21}(r) = \frac{1}{\sqrt{3}} \left( \frac{Z}{2a_0} \right)^{1/2} \left( 1 - \frac{Z}{a_0} - \frac{Z^2}{2a_0^2} \right)e^{-Zr/2a_0} \]

\[ R_{30}(r) = 2 \left( \frac{Z}{2a_0} \right)^{3/2} \left( 1 - \frac{Z}{3a_0} + \frac{Z^2}{2a_0^2} \right) e^{-Zr/3a_0} \]

\[ R_{31}(r) = \frac{4\sqrt{3}}{9} \left( \frac{Z}{3a_0} \right)^{1/2} \left( 1 - \frac{Z}{2a_0} - \frac{Z^2}{3a_0^2} \right)e^{-Zr/3a_0} \]

What we have learnt in Lecture 4

The radial equation

- This is a 1D problem of finding functions \( R_{nl}(r) \).
- It is simplified by introducing function \( \chi = r R_{nl}(r) \).
- Boundary conditions at \( r \to 0 \) and \( r \to \infty \) give a discrete set of \( \chi \), which is labelled by quantum numbers – this is the origin of quanta in general.

Hydrogenic eigenfunctions

- Quantum numbers \( n l m \) have names derived from the quanta of the physical quantities they label.
- The ranges of \( n l m \) values are interrelated.
- There are symbols to denote the first few \( n l m \) states: 1s, 2s, 2p, etc.

Visualisation of hydrogen atom

- Hydrogenic wavefunctions are difficult to imagine because they have complex values in the 3D space.
- Computer simulations are helpful here.
Course overview

• Lecture 1 – QM revision
• Lecture 2 – Atomic units
• Lecture 3 – Spherical harmonics
• Lecture 4 – Hydrogen atom
• **Lecture 5 – Dirac notation**
• Lecture 6 – Einstein coefficients
• Lecture 7 – Resonant field
• Lecture 8 – Selection rules
• Lecture 9 – Helium atom
• Lecture 10 – Indistinguishability
• Lecture 11 – Periodic table
• Lecture 12 – Pilot wave

Plan for today

Introduction to Dirac notation

• Dirac notation as a shorthand
• Dirac notation reveals a new concept

Previous formulae in Dirac notation

• completeness
• operators
• hydrogen atom
Dirac notation is widely used in research papers

Contemporary Physics, 2001, volume 42, number 1, pages 23-50

The physics of forgetting: Landauer’s erasure principle and information theory

M. B. Plenio and V. Vitelli

Hence, when the unitary transformation $\hat{U}$ is applied to the joint state of the three particles $|\psi_{321}\rangle$, the state of the particle on Bob’s side is unaffected whereas the state of the two on Alice’s side is changed according to equation (93):

$$\hat{U}|\psi_{321}\rangle = |000\rangle|\phi_1\rangle + (a^2 - b^2)\frac{1}{\sqrt{2}}|100\rangle|\phi_2\rangle + b|010\rangle|\phi_3\rangle$$

(94)

We can split Alice’s vector states in equation (94) and isolate the state of the entangled pair from the state of the particle added on Alice’s side by writing the latter first in the equation below:

$$\hat{U}|\psi_{321}\rangle = \frac{1}{\sqrt{2}}(a|001\rangle|\phi_1\rangle + a|010\rangle|\phi_2\rangle + b|100\rangle|\phi_3\rangle)$$

(95)

where $|\phi_i\rangle$ is an orthogonal basis. In our previous example, the orthogonal basis was given by the vertically and horizontally polarized states. When the apparatus is brought into contact with the system the joint state of $S$ and $A$ is given by

$$|\psi\rangle = \frac{1}{\sqrt{2}}(a|001\rangle|\phi_1\rangle + a|010\rangle|\phi_2\rangle + b|100\rangle|\phi_3\rangle)$$

(96)

The result of the act of measurement is to create correlations (i.e. entanglement) between the apparatus and the system. The equation above is a generalization of equation (76).

Hilbert space

David Hilbert (1862-1943)

"Physics is much too hard for physicists"
Quantum state evolution and measurement

Second Year Quantum Mechanics - Lecture 8
The postulates of quantum mechanics

Paul Dauncey, 29 Oct 2009

Postulate 5: Between measurements, the development of the wavefunction with time is governed by the time-dependent Schrödinger equation.

Postulate 2: Every dynamical variable may be represented by an Hermitian operator whose eigenvalues represent the possible results of carrying out a measurement of the value of the dynamical variable. Immediately after such a measurement, the wavefunction of the system will be identical to the eigenstate corresponding to the eigenvalue obtained as a result of the measurement.

Postulate 4: When a measurement of a dynamical variable represented by a Hermitian operator is carried out on a system whose wavefunction is \( \psi \), then the probability of the result being equal to a particular eigenvalue \( q_j \), will be \( |\alpha_j|^2 \), where \( \psi = \sum \alpha_i \phi_i \), and the \( \phi_i \) are the eigenstates of the operator corresponding to the \( q_i \).

- **Completeness**

\[
\sum_i |i\rangle \langle i| = \hat{1}
\]

\( \hat{1} \) is an identity operator.

**Proof:**

\[
|\psi\rangle = \hat{1} |\psi\rangle = \sum_i |i\rangle \langle i| |\psi\rangle = \sum_i \alpha_i |i\rangle = |\psi\rangle
\]

\( \alpha_i \in \mathbb{C} \)

Meaning: we decompose \( |\psi\rangle \) into \( |i\rangle \) and compose it back

\[
\left[ \int d^3r \, |\varphi\rangle \langle \varphi| = \hat{1} \right]
\]

e.g.

\[
\langle i | i \rangle = \langle i | \int d^3r \, |\varphi\rangle \langle \varphi| i \rangle = \\
= \int d^3r \, \langle i | \varphi \rangle \langle \varphi| i \rangle = \delta_{ij}
\]

\[
u_i (\varphi) = \langle \varphi| i \rangle
\]

\[
u_i^* (\varphi) = \langle i | \varphi \rangle
\]

for two vectors \( \varphi, \varphi' \) we have

\[
\langle \varphi | \varphi' \rangle = \delta(\varphi - \varphi')
\]

(orthogonality)
Previous formulae

Lecture 3:
\[
\hat{P} u_{nml}(r) = (-1)^l u_{nml}(r)
\]
\[
\hat{L}^2 Y_{lm} (\theta, \varphi) = l(l+1)\hbar^2 Y_{lm} (\theta, \varphi)
\]
\[
\int u^*_{nml}(r) u_{n'lm'}(r) d^3r = \delta_{nn'} \delta_{ll'} \delta_{mm'}
\]

What we have learnt in Lecture 5

The concept of Dirac notation
- Dirac notation can be used just as a shorthand for “normal” formulae.
- Eigenvectors |i⟩ form a base in Hilbert space.
- Physical state is described by a unit vector |ψ⟩, which evolves according to the time-dependent Schrödinger equation.
- When a measurement is performed |ψ⟩ is aligned with this |i⟩ which corresponds to the eigenvalue q_i revealed by the measurement.

Some formulae in Dirac notation
- ⟨i|j⟩ = δ_{ij}  orthonormality
- \sum_i |i⟩⟨i| = 1 completeness
- ⟨φ|Q|ψ⟩ = ⟨ψ|Q^+|φ⟩ complex conjugate of a matrix element
- operators
  \[
  \hat{Q} |i⟩ = q_i |i⟩
  \]
  \[
  \langle Q | |ψ⟩ = \int d^3r \quad ψ^∗(r) \hat{Q} ψ(r) 
  \]
  \[
  \langle ψ | Q | ψ⟩ = \int d^3r \quad ψ^∗(r) \hat{Q} ψ(r) 
  \]
  \[
  \langle ψ | Q | ψ⟩^* = \langle ψ | Q^+ | φ⟩
  \]
  Q acts to the right
  Q^+ acts to the left

- \text{H-atom} see slide for previous versions
  \[
  u_{nlm}(r) = \langle r^2 | nlm \rangle
  \]
  \[
  Y_{lm}(\theta, \varphi) = \langle \theta, \varphi | lm \rangle
  \]
  \[
  ⟨nlm | n'l'm'⟩ = δ_{nn'} δ_{ll'} δ_{mm'}
  \]
  parity \[
  \hat{P} |nlm⟩ = (-1)^l |nlm⟩
  \]
  \[
  \hat{L}^2 |lm⟩ = l(l+1)\hbar^2 |lm⟩
  \]

- flexible notation
  |ψ⟩, |i⟩, |i⟩_Q, |+-⟩, |↑⟩, |↓⟩
  |cat⟩ = \frac{1}{\sqrt{2}} (|\text{dead}⟩ + |\text{alive}⟩)
  etc.
Applications of Quantum Mechanics – Lecture 6

Course overview
- Lecture 1 – QM revision
- Lecture 2 – Atomic units
- Lecture 3 – Spherical harmonics
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- Lecture 11 – Periodic table
- Lecture 12 – Pilot wave

Plan for today

Intensity of light
- electromagnetic wave
- spectrum of incoherent light
- energy density of light

Einstein coefficients
- absorption
- stimulated emission
- spontaneous emission

Theory behind Einstein coefficients
- time-dependent interactions
- adiabatic approximation (“variation of constants”)
- 2-level system
**Intensity of electromagnetic wave (plane-polarized)**

**Poynting vector** \( \mathbf{P} = \mathbf{F} \times \mathbf{H} \)

**Flux (power density)** \( S = |\mathbf{P}| \)

\[ F = F_0 \cos(\omega t) \]

\[ H = H_0 \cos(\omega t) \]

\[ \sqrt{\varepsilon_0} F_0 = \sqrt{\mu_0} H_0 \]

\[ c^2 \varepsilon_0 H_0 = 1 \]

\[ H_0 = c \varepsilon_0 F_0 \]

\[ S = c \varepsilon_0 F_0^2 \cos^2(\omega t) \]

**Intensity (irradiance)** \( I = S_{\text{average}} = \frac{1}{T} \int_0^T S \, dt = c \varepsilon_0 F_0^2 \frac{1}{2} \)

---

**The path to laser invention**

- **Technology**
- **Theory**
- **Implementation**

---

**Einstein coefficients**

- **transition (probability) rate**, \( \mathcal{W} \)
  \( \frac{1}{s} \)

- **absorption**
  \[ W_{21} = B_{21} \mathcal{G}(\omega) \]

- **stimulated emission**
  \[ W_{21} = B_{21} \mathcal{G}(\omega) \]

- **spontaneous emission**
  \[ W'_{21} = A_{21} \]

Next, derive \( A_{21}, B_{21}, B_{12} \) from \( \mathcal{R}M \)
Previous formulae

Lecture 1:

\[ \hat{H}_0 u_n(r) = E_n u_n(r) \]
\[ \psi_n(r, t) = u_n(r) e^{-i E_n t / \hbar} \]
\[ \psi(r, t) = \sum_n a_n \psi_n(r, t) \]
\[ i \hbar \frac{\partial}{\partial t} \psi(r, t) = \hat{H}_0 \psi(r, t) \]  

**TDSE**

\[ a_n = a_n(t) \]

**adiabatic approximation:**

\[ \frac{d}{dt} a_n(t) \ll \frac{E_n}{\hbar} \approx \frac{E_h}{\hbar} = \frac{1}{24 \text{ as}} \]  

(True for all chemistry)

allows us to separate slow and fast time variation

\[ |\psi(t)\rangle = \sum_n a_n(t) e^{-i \frac{E_n}{\hbar} t} |n\rangle \]

**Time-dependent interactions**

\[ \hat{H}_0 |n\rangle = E_n |n\rangle, \quad \langle m| \hat{R} |n\rangle = i \hbar \delta_{mn} \]

\[ |\psi_n(t)\rangle = e^{-i \frac{E_n}{\hbar} t} |n\rangle \]

\[ |\psi(t)\rangle = \sum_n a_n |\psi_n(t)\rangle \]

but when \[ \hat{H} = \hat{H}_0 + \hat{V}(t) \]

we need **TDSE**

\[ i \hbar \frac{\partial}{\partial t} |\psi(t)\rangle = \hat{H} |\psi(t)\rangle \]

\[ a_n = a_n(t) \]
### Adiabatic approximation of 2-level system

1. \( |\psi(t)\rangle = a_1 e^{-i\omega_1 t} |1\rangle + a_2 e^{-i\omega_2 t} |2\rangle \) into TDSE.
2. \( i\hbar \left( a_1 e^{-i\omega_1 t} |1\rangle + a_2 e^{-i\omega_2 t} |2\rangle \right) = \left( \hat{H}_0 + \hat{V} \right) a_1 e^{-i\omega_1 t} + i\hbar \omega_1 a_1 e^{-i\omega_1 t} + \left( \hat{H}_0 + \hat{V} \right) a_2 e^{-i\omega_2 t} + i\hbar \omega_2 a_2 e^{-i\omega_2 t} \)

\[ \text{Eq. (6.1)} \]

### Special case: 2-level system

1. \( |\psi(t)\rangle = a_1 e^{-i\omega_1 t} |1\rangle + a_2 e^{-i\omega_2 t} |2\rangle \)
2. \( E_2 |1\rangle \quad \omega_2 = E_2 / \hbar \)
3. \( E_1 |1\rangle \quad \omega_1 = E_1 / \hbar \)

\[ \text{Eq. (6.1)} \]

### What we have learnt in Lecture 6

**Intensity of light:**
- is proportional to the square of the electric field amplitude.
- is the spectral intensity integrated over all angular frequencies.
- is the energy density in a light beam propagating with the speed of light.

**Einstein coefficients:**
- describe 3 elementary processes involving interaction of light with atoms.
- provided the key concepts for the invention of lasers.

**Theory behind Einstein coefficients**
- Adiabatic approximation allows us to use the method of "variation of constants".
- 2-level system is often sufficient to model interaction of light with atoms.
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Plan for today
Atoms in electromagnetic fields
- dipole approximation
- transition dipole moment
Link to Einstein coefficients
- symmetry of the equations describing time evolution
- thermodynamic equilibrium
- relation to the transition dipole moment
Resonant laser field
- Rabi (angular) frequency
- application to quantum computers
- population oscillation

Recap: adiabatic approximation of 2-level system
\[ \langle 1 | = a_1 e^{-i\omega_1 t} | 1 \rangle + a_2 e^{-i\omega_2 t} | 2 \rangle \]
\[ \langle 2 | = a_1 e^{-i\omega_1 t} | 1 \rangle + a_2 e^{-i\omega_2 t} | 2 \rangle \]
\[ \text{take scalar product of } \langle 1 | \text{ with both sides:} \]
\[ i \hbar \frac{d}{dt} \langle 1 | e^{i\omega_2 t} a_1 + i \hbar \langle 1 | e^{i\omega_1 t} a_2 \rangle = \left( \langle 1 | \right) e^{i\omega_2 t} a_1 + \left( \langle 1 | \right) e^{i\omega_1 t} a_2 \]
\[ \text{Equation (6.2) } \]

Scalar product of \( \langle 2 | \) with (6.1)
Atom in electromagnetic wave

atom sees electric field \( F(t) = \varepsilon F_0 \cos(\omega t - \mathbf{k} \cdot \mathbf{r}) \)

\[ k = \frac{2\pi}{\lambda} \]

Potential energy matrix element

\[ \hat{V}(t) = \varepsilon \mathbf{E} \cdot \hat{r} F_0 \cos(\omega t - \mathbf{k} \cdot \mathbf{r}) \]

\[ \langle i | \hat{V}(t) | j \rangle = \varepsilon \mathbf{E} \cdot \int \mathbf{r} \langle i | \mathbf{r} \rangle \langle \mathbf{r} | j \rangle \]

\[ = \varepsilon \int d^3 \mathbf{r} \sum_{i,j} \langle i | \mathbf{r} \rangle \langle \mathbf{r} | j \rangle = \varepsilon \int d^3 \mathbf{r} \sum_{i,j} \mathbf{r} \cdot \mathbf{u}_i(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}_j) \]

\[ = \varepsilon \int d^3 \mathbf{r} \mathbf{r} \cdot \sum_{i,j} \mathbf{u}_i(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}_j) \]
Recall: Einstein coefficients

\[ \alpha_2(t) \quad V_2(t) \quad \alpha_1(t) \quad V_1(t) \]

\[ \text{transition (probability) rate, } \frac{W_1}{1/s} \]

* absorption

\[ W_{12} = B_{12} \frac{g_1}{g_2} \]

* stimulated emission

\[ W_{21} = B_{21} g_2 \]

* spontaneous emission

\[ W_{21}' = A_{21} \]

Relations between Einstein coefficients

\[ N_1 + N_2 \text{ atoms in thermal equilibrium} \]

\[ W_{12} \quad \downarrow \quad W_{21} \quad \downarrow \quad W_{21}' \]

\[ N_1, W_{12} = N_2 (W_{21} + W_{21}') \]

\[ N_1 B_{12} g_2 = N_2 (B_{21} g_2 + A_{21}) \]

Boltzmann distribution

\[ \frac{N_2}{N_1} = e^{-\frac{\hbar \omega}{kT}} \]

Planck distribution

\[ g_2(\omega) = \frac{\hbar^2 \omega^3}{\pi^2 c^3} \frac{1}{e^{\hbar \omega/kT} - 1} \]

Note: For degenerate levels \( N_2/N_1 = (g_2/g_1) \exp(-\hbar \omega/kT) \), which leads to \( B_{12} = B_{12} g_2/g_1 \) but in this course we assume equal degeneracy (also called multiplicity), \( g_1 = g_2 \).

\[ V_{ij} \text{ into (6.2):} \]

\[ i \frac{d}{dt} \alpha_i = 0 - \alpha_2 \mu F_e \cos(\omega t) e^{i(\omega_2 - \omega)t} = -\omega_0 \text{ by def.} \]

\[ = \alpha_2 \left( -\frac{\mu F_e}{2} \right) (e^{i(\omega_2 - \omega)t} + e^{-i(\omega_2 + \omega)t}) \]

\[ \text{v. fast, averages to 0} \]

\[ \Omega = -\frac{\mu F_e}{2 \hbar} \]

\[ \frac{i \frac{d}{dt} a_1(t)}{a_2(t)} = \frac{\Omega}{2} e^{i(\omega_2 - \omega)t} a_2(t) \]

\[ \frac{i \frac{d}{dt} a_2(t)}{a_2(t)} = \frac{\Omega}{2} e^{-i(\omega - \omega_2)t} a_1(t) \]

Relating Einstein coefficients

\[ B_{21} = B_{12} \]

from (7.1), k\to2 symmetry

\[ A_{21} = \frac{\kappa c^2}{\pi^2 \epsilon_0} B_{21} \]

from thermal equilibrium

\[ B_{12} = \frac{\kappa c^2}{\epsilon_0 \hbar} \]

see Bransden Joachain "QM", chapter 11
Atoms in electromagnetic fields

- The dipole approximation is very good at optical frequencies.
- The transition dipole moment is the product of electron charge and the matrix element of the position vector projection on the polarization axis.

Link to Einstein coefficients

- The Einstein coefficients for absorption and stimulated emission are equal.
- The relation between the Einstein coefficients for spontaneous and stimulated emission is revealed in thermodynamic equilibrium.
- The Einstein coefficient for absorption is proportional to the square of the transition dipole moment.

Resonant laser field

- The Rabi frequency is proportional to the product of the transition dipole moment and the electric field amplitude.
- In a resonant field the population of the two levels oscillates with the Rabi frequency.

Special case: Resonant field

\[
\omega = \omega_0 \quad \text{from (7.1):}
\]

\[
\begin{align*}
\frac{d}{dt} a_1(t) &= i \Omega a_2(t) \\
\frac{d}{dt} a_2(t) &= i \Omega a_1(t)
\end{align*}
\]

solutions:

\[
\begin{align*}
a_1(t) &= \cos(\Omega t) \\
a_2(t) &= -i \sin(\Omega t)
\end{align*}
\]

(\text{check them!})

\[
t = 0 \quad a_1 = 1, \quad a_2 = 0
\]

One atom, probability

\[
P_2 = |a_2(t)|^2 = a_2^*(t)a_2(t) = \sin^2(\Omega t)
\]

Rabi frequency \( \Omega \)

Application: \( \pi/4 \) & \( \pi/2 \) pulses in a quantum computer

\[
\begin{cases}
\pi/4 & \Rightarrow \text{superposition } |1\rangle \& |2\rangle \\
\pi/2 & \Rightarrow \text{full transfer } |1\rangle \Rightarrow |2\rangle
\end{cases}
\]

\( N \) atoms, coherent process

\[
\Rightarrow \text{population oscillation}
\]

\[
N(t) = N \sin^2(\Omega t)
\]

(population \( \equiv \) occupation number)
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  - Lecture 9 – Helium atom
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  - Lecture 12 – Pilot wave

Plan for today

1D simulations of infinite well interacting with radiation

- Rabi oscillations
- relevance to Assessed Problem Sheet
- strong field: breakdown of adiabatic approximation, multiphoton transitions

Theory of selection rules

- angular parts of energy eigenfunctions
- symmetries of transition dipole moment
- selection rules for \( l m \) quantum numbers

3D simulations of hydrogen atom interacting with radiation

- selection rules for \( l m \) quantum numbers
- plane and circular polarizations

Simulation: 1D well + radiation

\[ u_n(x) = A e^{i lx} \]

- Colour

Stop, clear
- increase phasor area
- reduce Simulation Speed to min
- View: Magnitude + Phase
- Initialise the ground state
- set E-field in resonance with the 1st excited state

- Run slow simulation and note:
  - phase changes
  - wavefunction distortions
  - field changes

- Accelerate simulation, stop and note:
  - superposition of states  
  - equal phasor amplitudes

- Run until all in upper state, stop and note:
  - the shape of wavefunction is \( |\sin(x)| \times \text{sign}(\sin(x)) \)

- Run fast and note:
  - Rabi oscillations
  - intertwined absorption and stimulated emission related to the oscillating charge

set Radiation Intensity = max
- Initialise the ground state and Efield
- observe a distortion of the well

- the electric field is no longer weak; breakdown of the adiabatic approximation; many states are excited: multiphoton excitation
Recap 1: Atom in electromagnetic field

\[ \alpha_2(t) \quad |2\rangle \]
\[ \alpha_1(t) \quad |1\rangle \]

Electric field:

\[ \vec{F}(t) = e \vec{e} F_0 \cos(\omega t - \vec{k} \cdot \vec{r}) \]

\[ |\vec{p} \rangle = |1\rangle \]

Electric dipole moment operator

\[ \vec{p} = q \vec{v} = -e \vec{F} \]

Potential energy:

\[ V(t) = -\vec{F} \cdot \vec{r} = -e \vec{F} \cdot \vec{r} = e \vec{e} F_0 \cos(\omega t) \]

\[ V_{ij} = \langle i | \hat{V}(t) | j \rangle = e \langle i | \vec{e} \cdot \vec{F} \rangle F_0 \cos(\omega t) \]

\[ \langle i | v(t) | j \rangle = e \langle i | \vec{e} \cdot \vec{F} \rangle F_0 \cos(\omega t) \]

\[ \langle i | v(t) | j \rangle = e \langle i | \vec{e} \cdot \vec{F} \rangle F_0 \cos(\omega t) \]

Transition dipole moment:

\[ \mu = -e \langle 2 | \vec{e} \cdot \vec{F} | 1 \rangle \]

\[ B_{12} = -\frac{\mu M^2}{\varepsilon_0 \hbar} \]

Recap 2: Rabi oscillations

Oscillating electric field:

\[ \vec{F} = e \vec{e} F_0 \cos(\omega t) \]

Transition dipole moment:

\[ \mu = -e \langle 2 | \vec{e} \cdot \vec{r} | 1 \rangle \]

Rabi angular frequency:

\[ \Omega = -\frac{\mu F_0}{2 \hbar} \]

Resonant field:

\[ \left\{ \begin{array}{l} i \frac{d}{dt} a_1(t) = \Omega a_2(t) \\ i \frac{d}{dt} a_2(t) = \Omega a_1(t) \end{array} \right. \]

Probability oscillations:

\[ P_2 = |a_2(t)|^2 = \sin^2(\Omega t) \]

Selection rules:

\[ u_i(R) = \text{unlm}(R) \]

\[ \mu = -e \int d^3r \text{Unlm}(R) \vec{e} \cdot \vec{r} \text{Unlm}(R) \neq 0 \quad \text{only if opposite parity} \]

\[ \Rightarrow \text{selection rule: odd} \leftrightarrow \text{even} \]

More rules from \( \text{Unlm}(R) = R_{nl}(r) Y_{lm}(\theta, \phi) \)

\[ \mathbb{E} \parallel \mathbb{z} \]

\[ \mathbb{E} \times \mathbb{r} = r \cos \Theta \]

\[ d^3r = r^2 \sin \Theta dr d\Theta d\Phi \]

\[ \mu = -e \int R_{nl}^*(r) \frac{R_{nl}(r)}{r^2} d^3r \int \left( \mathbb{Y}_{lm}^*(\theta, \phi) \cos \Theta \mathbb{Y}_{lm}(\theta, \phi) \sin \Theta d\Theta d\Phi \right) \]

\[ r = |\vec{r}| = |\vec{r}| \]

\[ \text{always} \neq 0 \quad \text{if} \quad \{ \Delta l = l' - l = \pm 1 \} \quad \text{and} \quad \Delta m = m' - m = 0 \]

E.g. \( u_{100} \rightarrow u_{211} \)

\[ \mu = -e \langle 211 | \cos \Theta | 100 \rangle \]

\[ \int d\Theta f(\theta, \phi) \int d\phi Y_{lm}^*(\theta, \phi) Y_{lm}(\theta, \phi) \]

\[ \omega \alpha e^{i\gamma} \alpha | \]

\[ = 0 \]

\[ \mathbb{E} \parallel \mathbb{z} \]

\[ \mathbb{E} \parallel \mathbb{y} \]

\[ \Rightarrow \mu \neq 0 \text{ if } \Delta m = \pm 1 \]
Recap 3: Symmetry of the transition dipole moment

\[
V_{ij}^* = \langle i | \hat{V} | j \rangle = e \langle i | \hat{\mu} \cdot \vec{r} | j \rangle F_0 \cos(\omega t)
\]

\[
= \frac{e}{\hbar} \int r \ u_i^*(r) \hat{\mu} \cdot \vec{r} \ u_j(r)
\]

\[
= 0 \quad \text{if} \quad i = j
\]

\[
= -\mu \quad \text{if} \quad i \neq j
\]

transition dipole moment \( \mu = -e \langle 2 | \hat{\mu} \cdot \vec{r} | 1 \rangle \)

\( \mu = \mu^* = -e \langle 1 | \hat{\mu} \cdot \vec{r} | 2 \rangle \)

\( l \leftrightarrow 2 \) symmetry

Spherical harmonics

\[ Y_{00} = \sqrt{\frac{1}{4\pi}} \]

\[ Y_{10} = \sqrt{\frac{3}{4\pi}} \cos \theta \]

\[ Y_{11} = \mp \sqrt{\frac{3}{8\pi}} \sin \theta e^{\pm i\phi} \]

\[ Y_{20} = \sqrt{\frac{5}{16\pi}} (3 \cos^2 \theta - 1) \]

\[ Y_{21} = \mp \sqrt{\frac{15}{8\pi}} \sin \theta \cos \theta e^{\pm i\phi} \]

\[ Y_{22} = \sqrt{\frac{15}{32\pi}} \sin^2 \theta e^{\pm 2i\phi} \]

Parity:

\[ Y_{lm}(\pi - \theta, \phi + \pi) = (-1)^l Y_{lm}(\theta, \phi) \]

Electric dipole transitions allowed if

- odd \( \rightarrow \) even
  \( \Delta L = \pm 1 \)
  \( \Delta m = 0 \)
  \( \vec{E} \parallel z \)
  \( \Delta m = \pm 1 \) \( \vec{E} \perp z \)

Polarization vs spin of photons

- Propagation \( \parallel z \)
  \( \Delta L = 0 \)
  \( \Delta m = \pm 1 \) \( \vec{E} \parallel z \)

- Propagation \( \parallel y \), \( \pm \perp z \), \( \Delta L = 0 \), \( \Delta m = 0 \)
  \( \parallel x \)

- Spin 1 allows \( \Delta L = 0 \) but
  odd \( \rightarrow \) even forbids it

If allowed, the typical \( |m| \approx e \alpha \). See Grotrian diagram of H.
Transitions allowed by the selection rule $\Delta l = \pm 1$ are shown. The wavelengths are in ångströms (0.1 nm).

What we have learnt in Lecture 8

Selection rules:
- reflect symmetries of energy eigenfunctions;
- for the magnetic quantum number depend on the polarization vector;
- can be illustrated on an example by integrating the product of spherical harmonics and the position vector projection on the polarization axis;
- are a consequence of angular momentum conservation;
- are shown on Grotrian diagrams.

Computer simulations can show:
- the evolution of the wavefunction being transferred from one state to another under the influence of an electromagnetic wave;
- the processes of absorption and stimulated emission;
- Rabi oscillations;
- breakdown of the adiabatic approximation;
- the dependence of the selection rules on the choice of polarization.
Course overview

- Lecture 1 – QM revision
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- Lecture 8 – Selection rules
- **Lecture 9 – Helium atom**
- Lecture 10 – Indistinguishability
- Lecture 11 – Periodic table
- Lecture 12 – Pilot wave

Plan for today

Helium atom with electron spins ignored
- Independent Particle Approximation
- the ground state
- energy correction in the 1st order perturbation

Spins included
- electron spin recap
- full wavefunction for hydrogen atom
- full wavefunction for helium atom
Time independent perturbation

Second Year Quantum Mechanics - Lecture 20
Time independent perturbation theory
Paul Dauncey, 24 Nov 2009

we write the total Hamiltonian as
\[ \hat{H} = \hat{H}_0 + \hat{H}_1 \]
where the eigenstates and eigenvalues of \( \hat{H}_0 \) are known

We can write the full solutions as
\[ E_n = E_n + \delta E_n \]
\[ u_n(x) = u_n(x) + \delta u_n(x) \]
\[ \delta E_n = \int u_n^* \hat{H}_1 u_n \, dx - \langle \hat{H}_1 \rangle_n \]

\[ \hat{H}_1 = V \]

Hydrogenic energies and wavefunctions:

\[ E_n = -\frac{E_h}{2} \frac{Z^2}{n^2} \]
\[ E_h = \frac{\hbar^2}{m_e a_0} = 27.2 \text{ eV} \]
\[ \psi_{nlm}(r, \theta) = u_{nlm}(r) e^{-iE_{nl}/\hbar} \]
\[ u_{nlm}(r) = R_{nl}(r) Y_{lm}(\theta, \varphi) \]
Electron-electron repulsion

Coulomb integral:

\[ J = \frac{e^2}{4 \pi \varepsilon_0} \int \psi_{n_1, m_1}(\mathbf{r}_1) \psi_{n_2, m_2}(\mathbf{r}_2) \left( \frac{1}{r_{12}} \right) d\tau_1 d\tau_2. \]

Spin

Second Year Quantum Mechanics - Lecture 28

Spin

Paul Dauncey, 15 Dec 2009

We can define three dimensionless matrices

\[ \sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \]

which are the “Pauli spin matrices” and then write:

\[ \hat{\sigma}_x = -i \alpha_x, \quad \hat{\sigma}_y = -i \beta_y, \quad \hat{\sigma}_z = \frac{\hbar}{2} \alpha_z \]

Hence, the eigenvectors of \( \hat{S}_z \) are:

\[ \alpha_+ = \chi_+ = \uparrow = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad \text{spin up} \]
\[ \beta_- = \chi_- = \downarrow = \begin{pmatrix} 0 \\ 1 \end{pmatrix}, \quad \text{spin down} \]

IPA:

\[ \psi_0 = U_{100}(\mathbf{r}_1) U_{100}(\mathbf{r}_2) \] (spin ignored)

\[ |\psi_0\rangle = |100\rangle |100\rangle \]

1st order perturbation:

\[ E' = E_0 + \langle \psi_0 | \hat{V} | \psi_0 \rangle \]

\[ J = \text{Coulomb integral} \]

\[ J = \langle 100 | \langle 100 | \hat{V} | 100 \rangle | 100 \rangle = \frac{e^2}{4 \pi \varepsilon_0} \int d^3r_1 d^3r_2 \ U_{100}(\mathbf{r}_1)^* U_{100}(\mathbf{r}_2) \frac{1}{r_{12}} U_{100}(\mathbf{r}_1) U_{100}(\mathbf{r}_2) = \]

\[ \frac{|U_{100}(\mathbf{r}_1)|^2}{|U_{100}(\mathbf{r}_2)|^2} \]

charge densities

\[ \cdots = \frac{5}{4} E_h = 34.0 \text{ eV} \]

see Hundout 5 for an example

Generally, for He-like ions: \( J = \frac{5}{8} Z E_h \)

\[ 54.4 \text{ eV} \]

\[ \text{He}^+ \]

\[ 24.6 \text{ eV} \]

\[ \text{He} \]

\[ J = 34 \text{ eV} \]

rather poor correction

reason: \( \hat{V} \) is not small
Angular momentum:

\[
\hat{L}^2 Y_{lm}(\theta, \varphi) = l(l+1)\hbar^2 Y_{lm}(\theta, \varphi)
\]

\[
\hat{L}_z Y_{lm}(\theta, \varphi) = m\hbar Y_{lm}(\theta, \varphi)
\]

What we have learnt in Lecture 9

Helium atom with electron spins ignored

- There is no analytical solution – perturbation theory has to be used.
- Independent Particle Approximation is the starting point (0th order).
- The 1st order energy correction gives poor accuracy but good insight into physics.

Spins included

- Electron with spin can be described by a product of position and spin wavefunctions; this description is exact if there is no spin-orbit interaction and often remains a good approximation even if there is such interaction.
- The spin function for helium atom depends on the total spin of both electrons; the relevant quantum numbers are:
  - total spin \( S \)
  - total spin projection \( M_S \).
- The values of these quantum numbers are:
  - \( S = 0, M_S = 0 \) for a singlet state,
  - \( S = 1, M_S = -1, 0, +1 \) for a triplet state.
Applications of Quantum Mechanics – Lecture 10

Course overview
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- Lecture 7 – Resonant field
- Lecture 8 – Selection rules
- Lecture 9 – Helium atom
- Lecture 10 – Indistinguishability
- Lecture 11 – Periodic table
- Lecture 12 – Pilot wave

Plan for today

Indistinguishability of electrons in the ground state
- symmetry of the total wavefunction (with respect to electron interchange)
- symmetry of singlet and triplet states
- fermions and bosons

Indistinguishability of electrons in excited states
- the need to symmetrise the total wavefunction
- perturbation from the electron-electron Coulomb interaction
- the Coulomb and exchange integrals
The consequence of indistinguishability

Statistical Physics, Spring 2010

Lecture Notes

2.3 Bosons and Fermions

Besides indistinguishability of particles, quantum mechanics leads to a further complication, which has equally profound implications for macroscopic physics. Consider the quantum wave function \( \psi(x_1, x_2) \) of two identical particles. As usual, the probability to find particles at positions \( x_1 \) and \( x_2 \) is given by \( |\psi(x_1, x_2)|^2 \). Since swapping the positions of the two particles does not change the state, we must have

\[
|\psi(x_1, x_2)|^2 = |\psi(x_2, x_1)|^2. \tag{2.3}
\]

This requires

\[
\psi(x_2, x_1) = e^{i\theta} \psi(x_1, x_2), \tag{2.4}
\]

where \( \theta \) is some real number. If we repeat this, we find

\[
\psi(x_1, x_2) = (e^{i\theta})^n \psi(x_1, x_2), \tag{2.5}
\]

and therefore \( e^{i\theta} = \pm 1 \). This means that

\[
\psi(x_2, x_1) = \pm \psi(x_1, x_2). \tag{2.6}
\]

Fermions correspond to the \( - \) sign. They obey the Pauli exclusion principle, which means that two particles cannot be in the same state.

A cut through Fermi hole and Fermi heap

\[
\psi_A(r_1, r_2) = -\psi_A(r_2, r_1) \quad \psi_S(r_1, r_2) = +\psi_S(r_2, r_1)
\]

Fermi heap and hole animation

Indistinguishability

\[
H(r_1^2) \Psi(r_1^2, r_2^2) = E \Psi(r_1^2, r_2^2)
\]

no change \quad must change sign

- **Fermions**: \( \Psi_A \): \( \Psi_A(1, 2) = -\Psi_A(2, 1) \)

  Pauli exclusion principle: No two electrons in an atom can have the same set of quantum numbers.

- **Bosons**: \( \Psi_S \): \( \Psi_S(1, 2) = \Psi_S(2, 1) \)

  Many bosons can be in the same state.

Example: photons in a laser beam.

Carbon 1s2py Fermi heap (left) and Fermi hole (right). The post marks the position of one electron in the xy plane. The height of the surface is the probability density of the other electron. The Fermi heap shows the clumping of the two electrons, while the Fermi hole shows that the two electrons are never found in the same place.

http://www.bu.edu/quantum/notes/GeneralChemistry/FermiHoleAndHeaps.html
Time independent perturbation

Second Year Quantum Mechanics - Lecture 20
Time independent perturbation theory
Paul Dau, 24 Nov 2009

we write the total Hamiltonian as
\[ \hat{H}' = \hat{H}_0 + \hat{H}_1 \]
where the eigenstates and eigenvalues of \( \hat{H}_0 \) are known

We can write the full solutions as
\[ E_n' = E_n + \delta E_n, \quad u_n'(x) = u_n(x) + \delta u_n(x) \]
\[ \delta E_n = - \int u_n^* \hat{H}_1 u_n \, dx = - \langle \hat{H}_1 \rangle_n \]

Coulomb and exchange integrals

Coulomb integral (direct):
\[ J_{nl} = \frac{\epsilon^2}{4\pi\epsilon_0} \int d^3r_1 d^3r_2 u_{ls}(r_1) u_{nl}^*(r_2) \frac{1}{r_{12}} u_{ls}(r_1) u_{nl}(r_2) \]

Exchange integral (\( n \geq 2 \)):
\[ K_{nl} = \frac{\epsilon^2}{4\pi\epsilon_0} \int d^3r_1 d^3r_2 u_{ls}(r_1) u_{nl}^*(r_2) \frac{1}{r_{12}} u_{ls}(r_2) u_{nl}(r_1) \]
Indistinguishability of electrons in helium

- When the positions of the two electrons are interchanged:
  - the TISE must not change;
  - the Hamiltonian does not change;
  - the total wavefunction must change sign.
- With respect to electron interchange the spin part of the total wavefunction is:
  - antisymmetric for the singlet;
  - symmetric for the triplet.
- The antisymmetry of the total electronic wavefunction makes:
  - the spin part of the singlet wavefunction antisymmetric;
  - the spin part of the triplet wavefunction symmetric.
- Triplet is not allowed in the ground state.

Excited states of helium

- Symmetric and antisymmetric wavefunctions have to be constructed from superpositions of hydrogenic wavefunctions.
- Fermi heap and Fermi hole are purely quantum effects reflecting the symmetry of two-electron wavefunctions.
- The Coulomb integral shifts the energy up; the exchange integral removes singlet-triplet degeneracy.
Applications of Quantum Mechanics – Lecture 11

Course overview
- Lecture 1 – QM revision
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- Lecture 12 – Pilot wave

Plan for today

Energy of singlet and triplet states
- Fermi hole/heap and the exchange integral

Spectroscopic notation for multielectron atoms
- components of angular momentum
- the selection rule for spin

Shell model of atoms
- shells and subshells

Periodic table of elements
- subshell filling order
- periodicity of chemical properties

Recap 1: Helium ground state

Recap 2: Helium excited states

Why triplets have lower energy than singlets?
Symmetry of helium excited states

He excited states

\[ \Psi^0 = u_{100}(r_1) u_{nlm}(r_2) \chi_{\text{sym}}^{1}(1,2) \]

no symmetry, no good!

Need \( \Psi_A \):

- either \( \Psi_A = \Psi_S(1,2) \chi_{\text{sym}}^{1}(1,2) \)
- or \( \Psi_A = \Psi_A(1,2) \chi_{\text{sym}}^{2}(1,2) \)

\[ \Psi_S = \frac{1}{\sqrt{2}} \left( u_{1s}(r_1) u_{nl}(r_2) + u_{nl}(r_1) u_{1s}(r_2) \right) \]

\[ \Psi_A = \frac{1}{\sqrt{2}} \left( u_{1s}(r_1) u_{nl}(r_2) - u_{nl}(r_1) u_{1s}(r_2) \right) \]

Fermi heap and Fermi hole

\[ \psi_S(r_1, r_2) = +\psi_S(r_2, r_1) \]

\[ \psi_A(r_1, r_2) = -\psi_A(r_2, r_1) \]

High multiplicity \( \Rightarrow \) low energy

Hund's rule

<table>
<thead>
<tr>
<th>Singlet</th>
<th>Triplet</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Psi_A = \psi_S \chi_{\text{sym}}^{1}(1,2) )</td>
<td>( \Psi_A = \psi_A \chi_{\text{sym}}^{2}(1,2) )</td>
</tr>
<tr>
<td>high energy</td>
<td>low energy</td>
</tr>
</tbody>
</table>

Combined angular momenta (of electrons)

- total spin \( S = S_1 + S_2 \)
- total orbital \( L = L_1 + L_2 \)
- total angular \( J = S + L \)

\( S \) is (almost) conserved

\[ \Delta S = 0 \text{ for radiative transitions} \]

\[ \psi \text{ (selected)} \]

\[ \psi \text{ (selected)} \]
Combining two spins ½

Lecture 9:

- H atom
  \[ \Psi(\vec{r}) = u_{n_1 m}(\vec{r}) \chi_\pm \]

- He atom
  \[ \Psi(r_1, r_2) = \Psi(r_1, r_2) \chi_\pm \]

  Total spin:
  \[ S = S_1 + S_2 \]
  \[ S = 0, 1 \]
  singlet \( M_S = 0 \)
  triplet \( M_S = -1, 0, 1 \)

Grotrian diagram of helium atom

Spectroscopic notation (many electrons)

e.g. He \( 1s^2 3d^1 \) \( 2e^- \) \( S = 1 \) \( L = 2 \) \( J = 1 \)

\( N \) \( 1s^2 2s^2 2p^3 4s^0 \) \( 5e^- \) \( S = 3/2 \) \( L = 0 \) \( J = 3/2 \)

Parity (optional)
\( P = (-1)^{\ell + s} \)

Multiplicity
Letter "o" if odd \( (P = -1) \)

No. of electrons with the same \( nl \) (if \( k > 1 \))

(Chemical symbol) \((n_1 l_1, n_2 l_2) \ldots \)

Configuration (term level)

Shell model

See Subshell filling 1

See Subshell filling 2

\( 4p \) etc.

\( 3d \)

\( 4s \)

\( 3p \)

\( 2s \)

\( 2p \)

\( 1s \)

\( 1s \)

\( 1s \)

\( 1s \)
Subshell filling 1

H 1s
Be 1s²2s²
B 1s²2s²2p
K [Ar]4s
Ca [Ar]4s²
Sc [Ar]3d⁴4s²
He 1s²
e [Ne]3s²3p²

Subshell filling 2

s
full shells
d
f
p

What we have learnt in Lecture 11

Hund’s rule (no. 1):
- For a given configuration the term with the largest multiplicity \((2S+1)\) has the lowest energy; the energy of the other terms increases with decreasing multiplicity.
- This rule is the consequence of the electron repulsion being on average lower in the states with Fermi hole than with Fermi heap.

The spectroscopic notation for a state of an atom tells us:
- the \(nl\) quantum numbers of individual electrons in a given configuration;
- the \(SLJ\) quantum numbers of their combined angular momenta.

The shell model of a multielectron atom
- gives us a description of the energy of an electronic configuration;
- explains the periodic table of elements;
- reveals the chemical properties of elements.
Course overview
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Plan for today

How to understand quantum reality?
The Copenhagen interpretation (used in this course so far):
• the fundamental mystery
• can we observe the wavefunction?
• wavefunction collapse
• who is the observer?

Pilot wave interpretation
• formalism
• key concepts
• simple examples

Explanations:
• Feynman’s mystery
• Schrödinger’s cat
• parallel universes

“The Feynman Lectures on Physics” vol. III

Richard Feynman (1918-1988)

...mysterious behaviour in its most strange form.

“The Feynman Lectures on Physics” vol. III
What are X-ray lasers for?

The free electron laser at Stanford

Imaging Atomic Structure and Dynamics with Ultrashort X-ray Scattering

Molecular tomography

Can we observe the wavefunction?

\[ |\psi\rangle = \sum_i a_i |i\rangle \]

\[ P_i = |a_i|^2 \]

\[ \hat{Q}|i\rangle = q_i |i\rangle \]

Wavefunction: not an observable!

Eigenfunction: not an observable!

Operator: an observable

Eigenvalue: observation result

Wavefunction collapse

\[ |\psi\rangle = \sum_i a_i |i\rangle \]

\[ \hat{Q}|i\rangle = q_i |i\rangle \]

\[ \hat{Q}|\psi\rangle \to |i\rangle \]

**The measurement problem**

$$|\psi\rangle$$

$$|\psi_1\rangle$$

$$|\psi_2\rangle$$

$$\psi = \frac{\partial}{\partial t} |\psi\rangle = \hat{H}|\psi\rangle$$

**Parallel universes (many-world interpretation of QM)**

$$|\psi\rangle = \sum_i a_i |i\rangle$$

$$|\psi\rangle \rightarrow |i\rangle$$

**Einstein on the nature of reality**

*I want to know God's thoughts; the rest are details.*

*God does not play dice with the universe.*

*God is subtle but he is not malicious.*

*Did God have any choice in the creation of the world?*

**Can we grasp quantum reality?**

*What is complementary to the notion of truth? Answer: clarity.*

*The more success the quantum theory has, the sillier it looks.*

*J. S. Bell*  
*Speakable and Unspeakable in Quantum Mechanics*  
*SECOND EDITION*  
*With a new Introduction by Alain Aspect.*
Pilot-wave interpretation

“The impossible has been done”
[John Bell, Foundations of Physics 12 989–99 (1982)]

David Bohm  Louis de Broglie

Pilot-wave key concepts

wavefunction $\psi = R e^{iS/t}$

real $R(r, t), S(r, t)$

quantum potential $Q = -\frac{\hbar^2}{2m} \nabla^2 R$

classical force $F = -\nabla(V + Q)$

velocity $\vec{v} = \frac{\nabla S}{m}$ and wave

Applications of Quantum Mechanics, Leszek Frasiński, Jan-Feb 2012, slide 104

Hydrogen atom in the ground state

$\psi = R e^{iS/t}$

see Blackboard

Radial wavefunction for H 1s

Lecture 4:

Pilot wave:
$Q = \frac{\hbar^2}{2m} \frac{\nabla^2 R}{R}$

$e^-$ is motionless!

$Q$ ensures the stability of matter
Free particle

\[ \psi = R e^{i \omega t / \hbar} \]
\[ \bar{v} = \frac{\bar{V} S}{m} \]
\[ Q = -\frac{\hbar^2 \nabla^2 R}{2mR} \]

\[ S = \hbar (\bar{r}^2 - \omega t) \]
\[ \bar{r}^2 = \frac{\hbar^2}{m} \]
\[ E = \hbar \omega \]
\[ \psi = \frac{\hbar^2}{m \bar{r}} \nabla S \equiv \frac{\hbar^2}{m \bar{r}} \nabla \bar{r} \]
\[ \nabla^2 \bar{r} = 0 \]

Tunnelling through a potential barrier

\[ Q = \frac{\hbar^2 \nabla^2 R}{2mR} \]

\[ V (\psi^2) \]
\[ E = V + Q \]

Tunnelling through a potential barrier

C Dewdney and B J Hiley

Probability current

Second Year Quantum Mechanics - Handout 1

Probability density and current density

Paul Denny, 19 Oct 2010

1 Classical gas flow

Imagine a cloud of gas moving from left to right. The gas density is given by \( \rho(x,t) \) and is denoted by the curve in the figure. Consider an elementary spatial interval \( x \) to \( x + dx \).
Pilot wave as a hydrodynamic interpretation

\[ \frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0 \]

\[ \frac{\partial \mathbf{v}}{\partial t} = -\nabla \phi + \frac{\rho}{m} \mathbf{a} \]

force \( F = \frac{d\mathbf{p}}{dt} = \mathbf{a} \cdot \nabla \rho + \frac{\rho}{m} \frac{d\mathbf{a}}{dt} \)

convective \( \frac{\partial \rho}{\partial t} \)

classical \( \frac{\partial \mathbf{v}}{\partial t} \)

quantum potential

\[ \psi = R e^{i Q / h} \]

\[ Q = -\frac{\hbar^2}{2m} \nabla^2 R \]

An explanation of Feynman's mystery

\[ |\text{cat}\rangle = \frac{1}{\sqrt{2}} (|\text{alive}\rangle + |\text{dead}\rangle) \]

Saving Schrödinger’s cat

There are parallel universes but only our Universe is real

|ψ⟩
What we have learnt in Lecture 12

The Copenhagen interpretation:

- particles do not have properties, such as a positions, before they are measured;
- uses the concept of wavefunction collapse;
- needs an observer who is outside the theoretical framework.

The pilot-wave interpretation:

- is formally equivalent to the Copenhagen interpretation;
- is experimentally indistinguishable from the Copenhagen interpretation;
- reaches the classical limit when the quantum potential approaches zero;
- uses the quantum potential to explain the stability of matter;
- does not require the wavefunction to collapse after a measurement;
- successfully explains quantum paradoxes, for example:
  - which slit the electron passes through when forming an interference pattern;
  - why we do not observe Schrödinger’s cat states;
  - why out of many parallel universes only our Universe is real.
Frequently Asked Questions

I have copied questions that have been emailed to me together with my answers. You may find them useful during revision.

Exam format

1. I am wondering if everything you have put on Blackboard is examinable. And if there is any material you haven't put on Blackboard that is also examinable. For instance, do we have to read the recommended texts and solve the problems within them?

There is no clear-cut answer to this question because to pass the exam you need to understand quantum mechanics. And to gain this understanding different people may need to read and practise different things. Nevertheless, to help you to concentrate on the most important material I have grouped it into the following categories:

A. Directly examinable material (exam questions will be based on it):
   - Lectures 1–11
   - Problem Sheets 1–7, except problem 4 of Problem Sheet 3
   - Assessed Problem Sheets
   - Classworks, including clicker answers (see Slides)
   - the use of Useful Formulae (they will be provided at the exam)

B. Indirectly examinable material (understanding it helps to answer exam questions):
   - Quantum Mechanics course from the previous term
   - Lecture 12
   - Handouts 1–7
   - Java Animations
   - Journal Articles
   - FAQ

C. Recommended textbooks (listed Handout 1) should be used as a reference – look there if the materials listed above do not provide you with a sufficient understanding.

2. Will we need to know “Useful Formulae” by heart for the exam?

You do not need to remember any of the Useful Formulae – all of them will be given at the exam. You will need, however, to locate the relevant formula and understand what it means.
3. If in the exam we have to calculate a physical quantity in atomic units, is it acceptable to calculate the quantity in SI units and then convert the units to atomic units?

You can do it this way – it is often longer but perfectly acceptable.

4. Will I need to have an extensive knowledge of Dirac notation? My worry is in fact that although I think I’ve mastered its use, I am not very comfortable with it and would prefer to use the standard integral form instead.

At the exam it is not necessary to write the solution using the Dirac notation. However, it may be used in the question, so you need to understand it sufficiently to be able to convert it to the normal notation of integrals and wavefunctions.

5. Is the last lecture on the pilot wave an examinable topic?

Only indirectly. At the exam there will be problems to solve and you need to understand quantum mechanics to be able to arrive at the solutions. If the last lecture helps you with this understanding, revising it can be useful. If you find it confusing, you can ignore it.

6. When I am checking my answers to your AQM problem sheets I always find that my answers are a few decimal places out from yours. I generally don’t round my working out and store calculated numbers in the calculator. How will the numerical answers be marked in the exam, will there be a margin of error for the answers due to rounding?

Typically an accuracy of 3 significant figures is required. Your mark will not be reduced if your final result differs only by 1 in the last required (typically the 3rd) significant figure.

Past exam papers

7. Which past exam papers do you recommend doing?

As explained in Handout 1 on course organisation, the 2008 and earlier courses were given by other lecturers and are significantly different to the current one. Therefore only the 2009 and later papers are worth practising. Questions from exams earlier than 2009 that are relevant to the current course you can find in Problem Sheets.

8. In the 2006 past paper, the solution of question 1(iii) states that the radius \( r = a_0 \). However, I think there as a mistake because I have obtained \( r = 2a_0 \) using the expressions given in the exam.

Yes, there is a mistake in the \( R_{10} \) function in this exam paper: the exponent should read “(–Zr/a_0)”.

9. In 2009 paper, answer 5(i), I don't understand the second step: \( E/E_h = (e/C) / (E_h/J) \times (E/eV) \). Could you go through this in more detail?

I multiply LHS by 1 = \( (e \times C \times V) / (e \times C \times V) = (e \times J) / (C \times eV) \).

10. In 2009 paper, comparing answer 5(ii) with the \( u_0 \) wavefunction given in Useful Formulae, it seems that \( m/h = 1 \). Why is it so?
As working in atomic units is simpler, I convert the equation for \( u_0 \) from SI to atomic units by replacing \( m_e \rightarrow 1 \) and \( \hbar \rightarrow 1 \) (see Lecture 2, Page 4). You should get the same answer, if you do the calculation in SI units and convert to the atomic ones at the very end – but this is a longer way and more prone to mistakes.

11. In 2009 exam paper, question 5(ii), I don't understand why the \( \varepsilon r \) part of the transition dipole moment becomes just \( x \). Could you explain this to me please?

This is because the problem is one-dimensional. I choose \( \varepsilon \) parallel to \( x \) and there is no \( y \) or \( z \).

**Problem Sheets and Classworks**

12. In Problem Sheet 3, problem 1, I still do not understand why answers to part (a) and part (b) differ. Why are we getting two different answers to apparently the same question?

The questions are different: part (a) asks for the most likely location while part (b) asks for the most likely distance.

It can be helpful to consider a similar problem with a rush hour in England, when we ask:

(a) At which location is an Englishman most likely to be?
   **Answer:** In London (because of the highest population density).

(b) At what distance from London is an Englishman most likely to be?
   **Answer:** About 100 miles from London (because not everyone is here).

13. Regarding Problem Sheet 3, problem 4 and Handout 3: For the exam, do we have to be able to reproduce the method of finding eigenfunctions to the hydrogenic atom satisfying specific boundary conditions?

No, you need to understand only a general principle how it is done. If you do these calculations just once as homework, you will have sufficient understanding.

14. In Problem Sheet 5, problem 2, we are asked to calculate the matrix element \( \langle i \mid x \mid j \rangle \). Initially I was under the impression that this was the equivalent of finding the expectation value but that does not seem correct. Would you mind expanding on what the matrix element corresponds to physically?

This matrix element is equivalent to finding the expectation value of the position, \( x \), but in a state \( \mid \psi \rangle \) that is a superposition of energy eigenstates \( \mid i \rangle \) and \( \mid j \rangle \). If we take, for example,

\[
\mid \psi \rangle = (\mid i \rangle + \mid j \rangle)/\sqrt{2}
\]

then we calculate:

\[
\langle \psi \mid x \mid \psi \rangle = \langle (i) + (j) \rangle/\sqrt{2} \cdot x \cdot (i) + (j) \rangle/\sqrt{2} = \\
= (\langle i \mid x \mid i \rangle + \langle j \mid x \mid i \rangle + \langle i \mid x \mid j \rangle + \langle j \mid x \mid j \rangle)/2 = \\
= (0 + \langle j \mid x \mid i \rangle + \langle i \mid x \mid j \rangle + 0)/2 = (2 \langle i \mid x \mid j \rangle )/2 = \langle i \mid x \mid j \rangle,
\]

where the zeros are from integrations of odd functions.
The above calculation tells us that only a superposition of energy eigenstates absorbs or emits radiation. So, one may ask, if an atom is initially in the ground state (which is an energy eigenstate) how can it absorb radiation ever? The answer is that at the beginning the radiation perturbs the ground state admixing to it a little of the excited state, so the absorption can start, then the admixture increases, so the absorption increases, etc. until the atom is fully transferred to the excited state. You can observe this process by running applets qm1drad and qmatomrad described in Lecture 8.

15. In Problem Sheet 6, problem 1, I still do not understand answers (b) and (c).

Because the two electrons are on very distant shells, the overlap of their wavefunctions is negligible and the energy of the system can be considered as a sum of two one-electron energies:

(1) the energy of the 1s electron, where the screening by the 5d electron is very small and can be simply ignored;

(2) the energy of the 5d electron, where the 1s electron screens the nucleus almost perfectly, the charge of the nucleus is effectively reduced by one elementary charge.

It is helpful to show this sum graphically:

The reasoning in answer (c) is similar – only 5d is replaced by 4p.

16. In Problem Sheet 6, problems 1 and 2, I am confused because in answer 1 (b) the energies of \( n = 1 \) and \( n = 5 \) are added together but in answer 2 (c) the energy of \( n = 1 \) is not added to the \( nl \) energy. Why are these two cases different?

The choice of zero for the potential energy is arbitrary. Usually it is chosen when all particles are far apart from each other. This is the case in problem 1. However, we can choose the energy to be zero for a different state, for example when only one electron is far away and the second electron is in the 1s state. This is the case in problem 2 and the energy values in the table are listed according to this convention. To be consistent with this choice, \( E(\text{He}^+ 1s) = 0 \) and nothing is added to the energy of the electron in the \( nl \) state. The final results (the proton energy in problem 1 or the \( J \) and \( K \) integrals in problem 2) are independent of the zero-energy choice.

17. There seems to be inconsistency in the answer to Problem Sheet 6, problem 2(c). On the solutions the argument appears to be that \( J \) and \( K \) are decreasing we are approaching the independent particle approximation (IPA) for the energy of the outer electron. It is suggested that the fact that \( J \) and \( K \) are both decreasing for large \( n \) makes sense because the outer electron separation from the nucleus will be large and hence its interaction with the...
compact 1s state small. It is then suggested that the fact that $K$ is decreasing for large $l$ makes sense for the same reason. However, the fact that $J$ increases for large $l$ is not addressed. This contradicts the theory: at large $l$ one expects the outer electron to interact less with the inner electron and hence for the energies to tend towards IPA values with $J$ and $K$ going to zero. Furthermore, the $J$ term is consistently larger than $K$ so if we are to compare our perturbation results with IPA results then we should surely be more concerned with the behaviour of the $J$ term than the $K$ one. Could you explain this issue?

Regarding the $J$ and $K$ variation with quantum numbers, I agree that the explanation I provide in the answer is somewhat simplistic. It correctly explains what is asked for in the question, but it fails to explain the finer variation you consider. To do it properly we would have to look at higher orders of the perturbation calculation calculus, which is beyond this course. Faced with quite a complex problem, I decided that a partial explanation is better than none at all.

18. In Problem Sheet 6, I am confused about the solution to problem 4(b), because the $\alpha\beta$ and $\alpha\beta^*$ combinations are surely symmetric and thus not allowed, because Pauli Exclusion Principle requires them to be anti-symmetric.

The alphas and betas describe only the spin part of the wavefunction. There is also the spatial part, which could be also symmetric or antisymmetric. Only the product of the two must be always antisymmetric.

19. In Problem Sheet 7, problem 6 (f), I still do not understand the answer. Part (d) gives an answer of a constant $5/4\pi$. How does this show that $P_2$ is either spherically symmetrical or that the 3d sub-shell is fully occupied?

There is no angular dependence in $P_2$, therefore this sub-shell is spherically symmetrical. The reason why there is no spherical dependence is that all $P_{2m}$ components are present in $P_2$; if any component was missing, $P_2$ would depend on $\theta$ and there would be no spherical symmetry.

20. In classwork 4, question 4, you ask us to sketch the diagrams for the $H^-$ atom, the IPA atom and the perturbed atom. On the answer sheet, I understand the first three diagrams, namely the "IPA $H^-$", the "Perturbed atom" and the "H atom". However I do not understand the final "Real $H^-$" diagram, or how to calculate the values of 14.4 and 0.8 eV.

The 14.4 eV, which is the real energy of the $H^-$ ion, comes from experiments. It can be also calculated very accurately using higher orders of the perturbation theory but this is beyond the scope of the lecture course. If this was an exam question, the value 14.4 eV would be given.

The 0.8 eV is simply the difference between the energies of $H^-$ and H, which means that 0.8 eV is needed to detach an electron from $H^-$ turning it into H. If we do not supply this energy, the electron detachment cannot occur spontaneously, i.e. the $H^-$ ion is stable. This is in contrast to the 1st order perturbation result shown in the previous diagram.
Lecture Notes

21. In Lecture 3, page 2, in the first line there is a small triangle under the last equality sign. What does it mean?

The triangle marks this particular equality sign. I need it because I interrupt the derivation with a slide to assess the parity of spherical harmonics. I carry on 3 lines below referring to this equality again.

22. I have a question related to Dirac Notation. If you had a wavefunction which is the product of angular and radial wavefunctions i.e. \( \psi(r) = R(r)A(\theta, \phi) \) then is the following correct: \( \langle R|\hat{A}\rangle \)? If so then how do you interpret \( \langle R\rangle \) as it is a function or \( r \) only? Do you integrate with respect to \( dr \) or \( r^2 dr \) as you would do for a triple integral and why?

Yes, you can write \( \langle R|\hat{A}\rangle \).

\( \langle R|R \rangle \) is not a function of \( r \); \( \langle R|R \rangle = 1 \). The dependence on \( r \) comes from the position part, \( |r\rangle = |\theta \rangle |\phi \rangle \): 

\[ \psi(r) = R(r)A(\theta, \phi) = \langle r|R \rangle \langle \theta \phi |A \rangle = \langle r|\psi \rangle. \]

When integrating, the \( r^2 \) factor comes from the volume element \( d^3r = r^2 dr \sin \theta d\theta d\phi \).

You can convert \( \langle R|R \rangle \) to integration by expanding the unity operator:

\[ \hat{1} = \int d^3r|\langle r|\rangle = \int r^2 dr \int \sin \theta d\theta \int d\phi |\langle r|\theta \phi \rangle \langle \theta \phi |r \rangle| = \int r^2 dr |\langle r|\rangle = \hat{1} = \int r^2 dr |\langle r|\rangle = \]

and inserting it in the middle of \( \langle R|R \rangle \):

\[ \langle R|R \rangle = \langle R|\hat{1}|R \rangle = \int r^2 dr \langle R|r\rangle \langle r|R \rangle = \int r^2 dr |R(r)|^2. \]

23. I have a problem involving Dirac notation. If \( |\psi\rangle = |R \rangle |Y \rangle \), where \( |Y \rangle \) is a spherical harmonic, is it correct to evaluate \( \langle \psi|\hat{r}^2|\psi\rangle = \langle Y|\langle r^2|\hat{R}|Y \rangle \) in the following manner: we evaluate \( \langle R|x^2|\hat{R} \rangle \) first to get some number, \( N \), and then we evaluate \( \langle Y|\hat{f}(x, \theta, \phi) |Y \rangle = N \langle Y|Y \rangle = N \)? If the above is correct, however, then wouldn't this always imply that \( \langle R|\hat{f}(x, \theta, \phi) |R \rangle \) = \( \langle R|\hat{f}(r, \theta, \phi) |R \rangle \)?

The above is correct provided that \( r = (r, \theta, \phi) \) is a variable, not an operator. Moreover, in this case the result is even simpler:

\[ \langle Y|\langle f(r, \theta, \phi) |Y \rangle = \langle Y|\langle f(r, \theta, \phi) |R \rangle |R \rangle |Y \rangle = f(r, \theta, \phi) \langle R|R \rangle \langle Y|Y \rangle = f(r, \theta, \phi). \]

(Which means your “number” \( N = r^2 \).)

However, if the intention is to evaluate the expectation value of \( f \), then the variables should be replaced by operators; \( \hat{r} = \hat{r}(\hat{r}) \), where \( \hat{r} \) now acts on vectors \( |R \rangle \) and \( |Y \rangle \). We cannot evaluate the result of this action directly, but we know the eigenvectors of the position operator: \( \hat{r}|r \rangle = r|r \rangle \). Therefore we insert a unity operator made of these eigenvectors in the formula for the expectation value:
24. Lecture 6, “special case of 2-level systems” states that the matrix element of the unperturbed Hamiltonian, $\langle 1 | H_0 | 2 \rangle = 0$. Why is it so? Isn’t it the expectation value of the energies of levels 1 and 2? So wouldn’t it be non-zero?

The matrix element is equal to zero because states $|1\rangle$ and $|2\rangle$ are orthogonal:

$$\langle 1 | H_0 | 2 \rangle = \langle 1 | E_2 | 2 \rangle = E_2 \langle 1 | 2 \rangle = E_2 0 = 0,$$

where is $E_2$ the energy of $|2\rangle$. Note that operators act to the right and adjoint operators act to the left. However, here it can be either way because $H_0$ is self-adjoint, i.e. hermitian:

$$H_0 |2\rangle = E_2 |2\rangle,$$

$$\langle 1 | H_0 = \langle 1 | E_1$$

(Of course, the result of the action is simply proportional to the state vector only if it is an eigenvector of the operator.)

25. In Lecture 6 I do not understand what is meant by the expression suggesting that we use an adiabatic approximation: the rate of change of $a_n(t)$ is significantly less than $E_n / \hbar$. Where does this relation come from? Hence, what is the "variation of constant" method mentioned in the last slide?

The adiabatic approximation asks for the $a_n(t)$ coefficients to vary slowly when compared with the phase factors. It simplifies the method of solving the TDSE, specifically, in Lecture 7, Page 3, we can use Rotating Wave Approximation to neglect the fast-varying terms in the differential equations for $a_n(t)$.

26. In Lecture 6, in the derivation of $V_{21}$ and $V_{12}$ we take the scalar product of equation 6.1, first with the first excited state and then with the second excited state. Is there any reason for this other than to obtain a simplified pair of simultaneous equations 6.2?

You correctly state that we want to simplify equation 6.1. As this is an equation for kets in an abstract Hilbert space, we need to convert it to an equation for wavefunctions in our normal, position space. The way to do this conversion is always by taking scalar products with appropriate bra vectors.

27. In Lecture 6, is the expression for the Rabi frequency in terms of $\mu$ and $F_0$, the definition of the Rabi frequency?
You can use the framed equation for $\Omega$ on Page 3 as the definition of Rabi frequency. However, a more intuitive definition is to use the equation for $P_2$ or $N_2$ on Page 4.

28. In Lecture 7, where does the dipole approximation come from? In particular, why is $\lambda$ related to $a_0$?

The dipole approximation simplifies the solution. If we do not make it, the electromagnetic field has spatial variation across the atom and the matrix element for the transition moment is much more complicated. If the wavelength of the EM wave is much longer than the size of the atom, we can ignore this spatial variation. The dipole approximation works very well in the IR, visible and UV regions of the spectrum. Only for X-rays it starts to fail significantly.

29. I was going through the notes for lecture 7 and I came across something I didn't quite understand. In the notes, there is the proof for the matrix element $\langle i | \varepsilon \cdot r | j \rangle = 0$ for $\varepsilon$, $r$ as vectors, $i$ and $j$ base states, $i = j$. The justification for this was that the element $\langle i | r | j \rangle$ was always odd for $i = j$.

However, the matrix element $\langle i | \varepsilon \cdot r | j \rangle$ contains $\varepsilon \cdot r$, not $r$, and $\varepsilon \cdot r$ is a scalar which should have even parity. This would imply that $\langle i | \varepsilon \cdot r | j \rangle \neq 0$ for $i = j$, wouldn't it?

It is true that $H \cdot r$ is a scalar but it has the odd parity. You can see that it changes the sign if you substitute $-r$ for $r$. Or, in more detail, you can write $\varepsilon \cdot r = r \cos \alpha$ and notice that indeed $r$ is even but $\cos \alpha$ changes the sign if you change $\alpha$ by $180^\circ$.

30. Why are Einstein coefficients $B_{21}$ and $B_{12}$ equal?

$B_{21} = B_{12}$ follows from the symmetry of equation (7.1): the rates of change of the probability amplitudes $a(t)$ are symmetrical, therefore the transition probability rates and the corresponding Einstein coefficients are equal.

31. The formula given in Lecture 7 (and in Useful Formulae) for the Einstein coefficient for absorption:

$$B_{12} = \frac{\pi \mu^2}{\varepsilon_0 \hbar^2}$$

differs from formula 11.67 in "Quantum Mechanics" by Bransden & Joachain (B&J):

$$B_{ba} = \frac{\pi}{3 \hbar^2 \varepsilon_0} |D_{ba}|^2.$$ 

Why are they different?

Apart from a trivial difference in the symbols used for subscripts, there is a factor $1/3$ in the B&J formula. This is because they assume unpolarised, isotropic radiation and averaging the scalar product $\varepsilon r$ over all directions gives the factor $1/3$ (see the transition from formula 11.56 to 11.57 in B&J). Note that $\mu$ and $D_{ba}$ are not the same physical quantity: the former is a scalar, the latter is a vector. The relation between the two and the factor $1/3$ can be derived as follows:
32. Let us have a particle in a steady state: an electron in a 1D finite square well, in the ground state. Let us say now that we measure its position and we find it in some position inside the well. The particle has been disturbed, its spacial wavefunction has now collapsed to something similar to a Gaussian which is a superposition of energy eigenstates and the system will evolve according to the TDSE. My question is, since it is oscillating like this, will it eventually emit a photon and collapse to a steady state? What is the typical timescale of the event and on which parameters does this time depend?

If the potential well approximates a real system, e.g. an atom, then indeed, the system will decay to the ground state, usually emitting a photon. The lifetime of atomic excited states are typically on the nanosecond timescale, but can be much longer if selection rules forbid electric dipole transition. The lifetime of each of the excited state is given by the inverse of the sum of the Einstein coefficients for the spontaneous emission to all states that are below the excited one, and the coefficients, as you know, depend on the transition dipole moments.

33. In Lecture 10 we defined the symmetric spatial wavefunction as
\[
\psi = \left( u_{1s}(\mathbf{r}_1) u_{nl}(\mathbf{r}_2) + u_{nl}(\mathbf{r}_1) u_{1s}(\mathbf{r}_2) \right) / \sqrt{2}.
\]
What happens when the electrons are both at the ground state? Then we have \( \psi = \sqrt{2} u_{1s}(\mathbf{r}_1) u_{1s}(\mathbf{r}_2) \), but this wavefunction is not normalised as \( |\psi|^2 d\mathbf{r} = 2 \) ?

You are right, \( \psi \) would be incorrectly normalised if you took the same \( nl \) for both electrons. The reason is that the superposition formula assumes that both components are orthogonal, which is obviously not true when they are the same.

You can pinpoint the problem by taking a superposition of two arbitrary states:
\[
|\psi\rangle = A(|a\rangle + |b\rangle)
\]
and calculating the normalisation constant \( A \):
\[
\langle \psi | \psi \rangle = A^2 (\langle a | a \rangle + \langle b | b \rangle + \langle a | b \rangle + \langle b | a \rangle) = A^2 (2 + \langle a | b \rangle + \langle a | b \rangle^*) = 1,
\]
so \( A = 1/\sqrt{2} \) only if \( \langle a | b \rangle = 0 \).

Nevertheless, Lecture 10 is correct because is discusses only excited states, where the two electrons have different quantum numbers. The ground state is discussed in Lecture 9, with a different normalisation constant.
34. Why is there only the Coulomb integral in the ground state of helium? Why do we ignore the exchange integral? Shouldn’t we add $K_{nl}$ to $J_{nl}$ to get a more accurate energy of the ground state?

The best way to see why we do not need the exchange integral in the ground state of helium is to look at the solution 3(c) of Problem sheet 6. In the ground state both electrons are in the 1s state, thus $a = b$, the lower minus sign is impossible (because the wavefunction would disappear) and $K$ is the same as $J$. It may appear that the energy correction should be $2J$ but in fact it is only $J$. The reason is that for the ground state the normalisation constant has to be smaller than for the excited states by factor $1/\sqrt{2}$ (see above) and it reduces $2J$ to $J$.

The bottom line is that mathematically we need only the $J$ integral, but physically the exchange term is already included in the direct one for the ground state of helium.

35. In the lecture on the helium atom, you stated that the quantum number $M_S$ could have three values $+1, 0, -1$ when the spin vectors are parallel. I am unsure why you can have a value of 0; doesn’t this imply the vectors are in the opposite directions?

According to the angular momentum quantization rule the quantum numbers change in steps of 1. You can interpret $M_S = 0$ as spin 1 being perpendicular to the quantization axis. This is described in terms of the vector model in section 6.7 of Handout 6.

36. I have a little problem with the helium atom. During your lectures, you did a first-order perturbation for excited states. You did this using time-independent perturbation and so calculated it by taking the expectation value of the perturbing energy (i.e. the coulombic repulsion between electrons). You write this down as the sum of a Coulomb integral and an exchange integral. From the notes, the Coulomb integral just looks like the expectation value of the repulsion energy in the excited state. I do not understand the exchange integral however. Why is it needed, and why does it act positively on singlet states and negatively on triplet states?

The exchange integral comes from the indistinguishability of electrons. I recommend you go through Problem 6.3 to see its formal origin. Unfortunately, unlike the Coulomb integral, the exchange integral has no classical interpretation.

The reason why the triplet state has lower energy than the singlet one comes from Hund's rule, which was explained at the beginning of Lecture 11.

37. What is the reason for the singlet state having greater electron-electron repulsion than the triplet? If we take $r_1 = r_2$ we find the singlet has a heap; doesn’t this somehow imply the repulsion must be less?

The reason for the Fermi heap in the singlet is purely due to indistinguishability of electrons. No real force that can be associated with potential energy is considered at this stage. Only when we notice that the electrons are on average closer to each other in the heap than in the hole, we deduce that the Coulomb repulsion and energy must be higher in the singlet than in the triplet. The calculation of the exchange integral confirms that this is indeed the case.
38. The energy diagram of the shell model drawn in Lecture 11 is unclear to me. How does it relate to the Grotarian diagram for helium? Why, for example, is the 2p level not split into a singlet and triplet in the shell model? Is the singlet-triplet splitting ignored here?

The shell model shows only the ground state of a range of elements. It should not be confused with Grotarian diagrams, which show mostly excited states of a particular element.

Let us look, for example, at carbon, which has six electrons. The four electrons on the 1s and 2s sub-shells do not contribute to the total spin because these sub-shells are full. We need to consider only the two electrons on the 2p sub-shell. They can form a singlet or a triplet but the latter is of lower energy (from Hund’s rule) and this is the ground state. Indeed, if you look at the periodic table (the high-resolution one) the ground state of carbon is a triplet, \(^3\text{P}_0\). The same electron configuration, \(1s^22s^22p^2\), also gives a singlet, \(^1\text{P}_0\), but this is an excited state and is not shown on the shell diagram.

39. When we look at the Grotian diagram we see lines connecting the different states. However we do not see lines connecting the singlet states to the triplet states. Does this imply that such transitions (for e.g. 1s singlet to 2p triplet) are not allowed? If so, why is it not possible? I could imagine the spin of an electron interacting with a magnetic field causing it to change.

Transitions between singlets and triplets are forbidden by the \(\Delta S = 0\) selection rule (see Lecture 11, bottom of Page 2). This selection rule is not strict but works very well in light elements, such as helium, where the magnetic field from the orbital motion of the electron is quite weak and has low probability changing its spin state.

40. Can we tell from the electron configuration whether an electron is in a triplet state or a singlet state? Or does this only apply to 2-electron system?

Two-electron systems can form only singlets and triplets. Systems with other number of electrons may form states of other multiplicities – see the periodic table for some examples. The possible multiplicities for three- and more-electron systems can be worked out from the electron configuration but the method of doing so falls outside the syllabus of the course.

41. If you were given a term, e.g. \(^4\text{F}\), how do you determine its parity with just this information without the configuration? Would it be just \((-1)^L\)?

What you suggest does not work. Taking the nitrogen atom as an example, the \(^4\text{F}\) term can be produced by configuration \(1s^22s^22p^3\), which is odd because \((-1)^{(1+1+1)} = -1\), or it can be produced by configuration \(1s^22s^22p^23d\), which is even because \((-1)^{(1+1+2)} = 1\).

In general, it is not possible to determine the parity without knowing the configuration. This is why the superscript “o” is used to indicate the parity of a term without quoting the configuration.

42. In Lecture 11, I have a question about the spectroscopic notation slide. For the nitrogen example, the total spin quantum number \(S\) is \(3/2\) which could be calculated from the multiplicity factor \((2S+1)\). But in terms of the configuration, does that mean the 3
electrons in the 2p state all have spin up instead of filling the sub-shell in the order of up, down, up?

The example denotes the ground state of nitrogen. As you have correctly read from the notation, the three 2p electrons have the total (combined) spin $S = 3/2$. The other possibility is $S = 1/2$ but this state has higher energy, which follows from Hund’s rule. The rule tells us that in the periodic table the sub-shells initially fill with electron spins parallel to each other (to maximise the multiplicity), and only when the sub-shell is half full, the following electrons have spins antiparallel to the former ones.

43. In the spectroscopic notation, I appreciate that the electronic configurations of the notation is used extensively, however is the last part of the notation, the term or level, used much? This is not used in any of the problem sheets, classworks or APS’s. Is it important?

Occasionally it is important. You are expected to know how to read the $S$, $L$ and $J$ quantum numbers from the level symbol, (for example, to tell which denotes singlet and which triplet) but you do not need to know how to work out such symbol from the electron configuration – this will come in future courses.