

# Summary FYS3110 - Quantum Mechanics

Stressed students

17. januar 2022

## Formalism

A **quantum state** describes a system at a given time. It contains information about the probabilities of obtaining different values when performing any kind of measurement on the system. The measurements will change the state. Mathematically it is represented as a normalised complex vector. A classical state on the other hand, is *defined* by a set of values for its observables, rather than probabilities. Measuring a classical state does not change it.

## The inner product

- $\langle u|v\rangle = \langle v|u\rangle^*$
- $\langle u|(\alpha|v_1\rangle + \beta|v_2\rangle) = \alpha\langle u|v_1\rangle + \beta\langle u|v_2\rangle$
- $\langle v|v\rangle \geq 0$ , only equal to 0 iff  $|v\rangle = 0$

In a function space the ket is the function itself, while the bra gives the instruction to integrate.

A complex vector space with a finite inner product is called a **Hilbert space**.

## Sets of kets

A set  $|i\rangle$  is *linearly independent* if none of the kets in it can be expressed as a linear combination of the others.

$$|j\rangle \neq \sum_{i \neq j} \alpha_i |i\rangle$$

The set *spans* the vector space if

$$|v\rangle = \sum_{i=1}^N v_i |i\rangle$$

A linearly independent spanning set is called a *basis*.

A basis is orthonormal if

$$\langle i|j\rangle = \delta_{ij}$$

We can change from one basis  $|i\rangle$  to another  $|i'\rangle$  by using the matrix  $S$ , which has matrix elements

$$S_{ji} = \langle i'_j|i_i\rangle$$

Letting this matrix act on a state transforms it from the  $|i\rangle$ -basis to the  $|i'\rangle$ -basis. The inverse transformation is given by the inverse of the matrix, which is also equal to its hermitian conjugate. The transformation matrix is therefore unitary. The transformation matrix can also change the basis for an operator  $K$ :

$$\hat{K}' = S\hat{K}S^\dagger$$

## Discrete basis

$$|f\rangle = \sum_{i=1}^{\infty} f_i |i\rangle$$

We define the identity operator as

$$\hat{I} = \sum_{i=1}^{\infty} |i\rangle \langle i|$$

The coefficients  $c_n$  of a linear combination will be given by *Fourier's trick*:

$$c_n = \langle i_n|i\rangle$$

## Continuous basis

$$|f\rangle = \int dx' f(x') |x'\rangle$$

Here we define

$$\langle x|x'\rangle = \delta(x - x')$$

where  $\delta(x - x')$  is the Dirac-delta. In this case, the identity operator is

$$\hat{I} = \int dx' |x'\rangle \langle x'|$$

We can “transform” from our ket-representation into function space by the following operation:

$$f(x) = \langle x|f\rangle$$

## Operators

The hermitian conjugate  $\hat{Q}^\dagger$  of an operator  $\hat{Q}$  is defined as

$$\langle u|\hat{Q}^\dagger|v\rangle = \langle v|\hat{Q}|u\rangle^*$$

for any  $u$  and  $v$ . It is often sufficient to simply use  $u = v$ . This is equivalent (in matrix representation) to saying  $\hat{Q}^\dagger = \hat{Q}^{*T}$ . An important property of the hermitian conjugate is

$$\hat{Q}|v\rangle = \langle v|\hat{Q}^\dagger$$

A **hermitian operator** is equal to its hermitian conjugate. Hermitian operators have several important properties which make them suitable for representing physical observables:

- their eigenvalues are real
- different eigenvalues have orthogonal eigenkets
- the eigenkets form a basis for the Hilbert space

An eigenvalue  $\lambda$  is a measureable result, while the corresponding state  $|\lambda\rangle$  is a state on which a measurement will yield  $\lambda$  with absolute certainty.

The collection of eigenvalues for an operator is called its *spectrum*. The spectrum is *degenerate* if two or more linearly independent eigenkets have the same eigenvalues. An operator with a non-degenerate spectrum has a complete spanning set of eigenkets, while the set has to be constructed for the degenerate case. Only *discrete* spectra have eigenkets in Hilbert space, and constitute physically realisable states.

The **spectral representation** of an operator writes it in terms of its eigenkets- and values.

$$\hat{Q} = \sum_i \lambda_i |\lambda_i\rangle \langle \lambda_i|$$

It is important to note that 0 can be an eigenvalue, while  $|0\rangle$  is *not* an eigenket!

A *projection operator* is defined as

$$\hat{P} = |i\rangle \langle i|$$

and it picks out the components of the original state in the direction of  $|i\rangle$ . When a measurement is performed on a system, then the state collapses into a projection of the eigenstate onto the original state. For example: when an eigenvalue  $\lambda$  is measured from a state  $|\psi\rangle$ , then the state immediately after the measurement is  $|\lambda\rangle \langle \lambda|\psi\rangle$ .

## Our good friend Ehrenfest

*Ehrenfest's theorem* states that

$$\frac{d}{dt}\langle Q \rangle = \frac{i}{\hbar} \langle [\hat{H}, \hat{Q}] \rangle + \left\langle \frac{\partial \hat{Q}}{\partial t} \right\rangle \quad (1)$$

Generally this means that the expectation values follow classical laws. For example one can find that

$$\langle p \rangle = m \frac{d}{dt} \langle x \rangle \quad \text{and} \quad \langle E \rangle = \langle K \rangle + \langle V \rangle$$

This theorem is also useful when determining if an expectation value will evolve in time, as one only has to check whether its corresponding operator commutes with the Hamiltonian.

## Compatible operators

The commutator of two operators is given by

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$$

If the commutator equals 0, the operators *commute*. The observables of two commuting operators may be measured simultaneously. One will also be able to find a complete set of eigenstates for both operators.

## Uncertainty relations

We have a general uncertainty relation given by

$$\sigma_A \sigma_B \geq \left| \frac{1}{2i} \langle [\hat{A}, \hat{B}] \rangle \right|$$

where  $\langle [\hat{A}, \hat{B}] \rangle$  is the expectation value of the commutator.

We can use this to calculate Heisenberg's uncertainty relation:

$$[\hat{x}, \hat{p}] = \hat{x}\hat{p} - \hat{p}\hat{x} = x \left( -i\hbar \frac{\partial}{\partial x} \right) + i\hbar \frac{dx}{dx} = -xi\hbar \frac{\partial}{\partial x} + i\hbar = i\hbar$$

We then get

$$\sigma_x \sigma_p \geq \left| \frac{1}{2i} \langle [\hat{x}, \hat{p}] \rangle \right| = \frac{1}{2i} i\hbar = \frac{\hbar}{2}$$

## Postulates

### Minimal approach (everybody agrees)

Quantum mechanics makes statements about

- Observable quantities: Outcome of measures
- Probabilities: relative number of occurrences in repeated experiments
- OK FAPP: OK For All Practical Purposes

### The two main schools of disagreements

- Instrumentalists (Copenhagen interpretation):
  - Inappropriate to consider an individual system to have values for all its physical properties.
  - Measurement is fundamental, and quantum mechanics is only concerned about the outcome, with predicting outcomes.
- Realists:
  - An individual system has values for all its physical properties.
  - Measurements play no fundamental role.
  - Probabilities reflect our lack of knowledge (objective and not subjective).
  - Quantum mechanics is incomplete, and should be fixed, hidden variables.
  - Hidden Variable Theory (with spatially separated degrees of freedom)  $\Rightarrow$  Bell inequalities must hold. These inequalities are violated when measurements are conducted.

## Translations in time

### The propagation operator

We define the propagation operator  $U$  as

$$U(t) |\Psi(x, 0)\rangle = |\Psi(x, t)\rangle$$

where

$$U(t) = e^{-iHt/\hbar}$$

Another explicit form of  $U$  is

$$U(t_0 + dt, t_0) = I - i\Omega(t_0)dt$$

where  $\Omega(t) \equiv H(t)/\hbar$ . The Hamiltonian is therefore the *generator of translations in time*.  $U$  is unitary. Writing out the first definition of  $U$  using the Taylor expansion for  $e^x$ , we obtain

$$|\Psi(x, t)\rangle = \sum_n c_n U(t) |n\rangle = \sum_n c_n e^{-iE_n t/\hbar} |n\rangle \quad (2)$$

### The Heisenberg Picture

Instead of applying the time translation to the wave functions, we now apply it to the operators. The modified operators are called *Heisenberg Picture operators*, and are defined as

$$Q_H(t) = U^\dagger(t) Q U(t) \quad (3)$$

As such, the time dependence is carried by the operators, and not the wave functions:

$$\langle Q \rangle = \langle \Psi_H | Q_H(t) | \Psi_H \rangle$$

### Time-Translation Invariance

For an infinitesimal time interval  $\delta$ , we have that

$$U(t_0 + \delta, t_0) \approx 1 - \frac{i}{\hbar} H(t_0) \delta \quad (4)$$

Time-translation invariance means that the time evolution is time independent of which time interval we are considering:

$$U(t_1 + \delta, t_1) = U(t_2 + \delta, t_2) \quad (5)$$

This ensures that if the system starts in state  $|\alpha\rangle$  and evolves for a time  $\delta$ , it will end up in the same state  $|\beta\rangle$  as if the system started in the same state at another time and evolved for the same time  $\delta$ .

If we plug Equation (4) into Equation (5), we get that

$$\frac{\partial H}{\partial t} = 0$$

The general Ehrenfest theorem (Equation(1)) says that

$$\frac{d}{dt} \langle H \rangle = \frac{i}{\hbar} \langle [H, H] \rangle + \left\langle \frac{\partial H}{\partial t} \right\rangle = 0 \quad (6)$$

Therefore, **energy conservation is a consequence of time-translation invariance.**

The Heisenberg picture and the Schrödinger picture (where the wave functions are time-dependent) are of course equivalent.

## The harmonic oscillator

The quantum problem is now to solve the SE with the potential

$$V(x) = \frac{1}{2}m\omega^2 x^2$$

This is sufficient to solve the time-independent SE:

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + \frac{1}{2}m\omega^2 x^2 \psi = E\psi \quad (7)$$

### The algebraic method:

We write Equation (7) in a more neat way

$$\frac{1}{2m} \left[ \hat{p}^2 + (m\omega x)^2 \right] |\psi\rangle = E |\psi\rangle \quad (8)$$

with  $\hat{p} \equiv -i\hbar d/dx$ . We introduce

$$\hat{a} \equiv \frac{1}{\sqrt{2\hbar m\omega}} (i\hat{p} + m\omega x) \quad (9)$$

$$\hat{a}^\dagger \equiv \frac{1}{\sqrt{2\hbar m\omega}} (-i\hat{p} + m\omega x) \quad (10)$$

these are the annihilation and creation operators (or simply the lowering and raising operators. This gives us

$$x = \sqrt{\frac{\hbar}{2m\omega}} (a^\dagger + a) \quad \text{and} \quad p_x = i\sqrt{\frac{\hbar m\omega}{2}} (a^\dagger - a)$$

We multiply them with each other and get

$$\hat{a}\hat{a}^\dagger = \frac{1}{\hbar\omega}\hat{H} + \frac{1}{2} \Rightarrow \hat{H} = \hbar\omega \left( \hat{a}\hat{a}^\dagger - \frac{1}{2} \right)$$

We can also do this backwards

$$\hat{a}^\dagger\hat{a} = \frac{a}{\hbar\omega}\hat{H} - \frac{1}{2} \Rightarrow \hat{H} = \hbar\omega \left( \hat{a}^\dagger\hat{a} + \frac{1}{2} \right)$$

We will now skip a whole lot of maths and proofs and say that

$$\hat{H}(\hat{a}^\dagger|\psi\rangle) = (E + \hbar\omega)(\hat{a}^\dagger|\psi\rangle)$$

$$\hat{H}(\hat{a}|\psi\rangle) = (E - \hbar\omega)(\hat{a}|\psi\rangle)$$

This is the origin of the raising and lowering operators; they raise or lower the energy level of the wave function in the potential of the harmonic oscillator.

If one uses the lowering operator enough times, one will eventually reach the bottom  $E_0$ . If the lowering operator is used again, one gets

$$\hat{a}|0\rangle = 0$$

We can use this to find the ground state  $|0\rangle$  by solving this equation

$$\begin{aligned} \frac{1}{\sqrt{2\hbar m\omega}} \left( \hbar \frac{d}{dx} + m\omega x \right) |0\rangle &= 0 \Rightarrow \frac{d}{dx} |0\rangle = -\frac{m\omega}{\hbar} x |0\rangle \\ \Rightarrow \psi_0(x) &= \langle x|0\rangle = \left( \frac{m\omega}{\pi\hbar} \right)^{1/4} e^{-\frac{m\omega}{2\hbar} x^2} \end{aligned}$$

From this we find that

$$|n\rangle = \frac{1}{\sqrt{n!}} (\hat{a}^\dagger)^n |0\rangle \quad \text{with} \quad E_n = \left( n + \frac{1}{2} \right) \hbar\omega$$

in particular, we have that

$$[a, a^\dagger] = 1$$

In addition, we have that

$$a|n\rangle = \sqrt{n}|n-1\rangle \quad \text{and} \quad a^\dagger|n\rangle = \sqrt{n+1}|n+1\rangle \quad (11)$$

## The analytic method

We now have the following solution to the SE with the same Hamiltonian as in the algebraic method:

$$\psi_n(x) = \langle x|n\rangle = \left( \frac{m\omega}{\pi\hbar} \right) \frac{1}{\sqrt{2^n n!}} H_n(\xi) e^{-\xi^2/2} \quad (12)$$



where we have substituted  $\xi = \sqrt{\frac{m\omega}{\hbar}}x$ .  $H_n(\xi)$  are the Hermite polynomials, which are a bitch to calculate, and should only be searched for on Google in the most desperate of times.

For a harmonic oscillator in two (or more) dimensions, we only have to construct  $a$ -operators that work in different spaces (i.e. either the  $x$ -dimension,  $a_x$ , or the  $y$ -dimension,  $a_y$ ).

## Angular momentum

The angular momentum operators are given by

$$L_x = yp_z - zp_y \quad L_y = zp_x - xp_z \quad L_z = xp_y - yp_x \quad (13)$$

we remember that the definition of  $\vec{p}$  is

$$\vec{p} = (\hat{p}_x, \hat{p}_y, \hat{p}_z) = -i\hbar \left( \frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z} \right)$$

## Eigenvalues

the components  $\hat{L}_x$ ,  $\hat{L}_y$ , and  $\hat{L}_z$  do not commute:

$$[\hat{L}_x, \hat{L}_y] = i\hbar\hat{L}_z \quad [\hat{L}_y, \hat{L}_z] = i\hbar\hat{L}_x \quad [\hat{L}_z, \hat{L}_x] = i\hbar\hat{L}_y$$

In other words: they are incompatible observables. Here too we have an uncertainty relation:

$$\sigma_{L_x}\sigma_{L_y} \geq \frac{\hbar}{2}|\langle L_z \rangle|$$

Each of the  $L_i$ -components commute with the  $L^2$ , such that you can find the magnitude of the angular momentum in addition to its magnitude in one of the Cartesian coordinates. If we have an angular momentum function  $|l, m\rangle$  and act on it with the operators  $L^2$  and  $L_z$ , we get the eigenvalues

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

where  $l = 0, 1, \dots$  and  $m = -l, -l+1, \dots, l-1, l$ . In analogy with the harmonic oscillator, we can construct ladder operators

$$L_{\pm} \equiv L_x \pm iL_y$$

with the following eigenvalues:

$$\hat{L}_{\pm} |l, m\rangle = \hbar \sqrt{l(l+1) - m(m \pm 1)} |l, m \pm 1\rangle$$

## Eigenstates

If we now change our coordinate system to spherical coordinates and do some funky maths, we get

$$\hat{L}^2 = -\hbar^2 \left[ \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left( \sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right] \quad (14)$$

and

$$\hat{L}_x = -i\hbar \left( -\sin\phi \frac{\partial}{\partial\theta} - \cos\phi \cot\theta \frac{\partial}{\partial\phi} \right) \quad (15)$$

$$\hat{L}_y = -i\hbar \left( +\cos\phi \frac{\partial}{\partial\theta} - \sin\phi \cot\theta \frac{\partial}{\partial\phi} \right) \quad (16)$$

$$\hat{L}_z = -i\hbar \frac{\partial}{\partial\phi} \quad (17)$$

It has become a convention to use the  $L_z$ -component, as this is by far the easiest to do maths with. The ladder operators now become

$$\hat{L}_{\pm} = \pm\hbar e^{\pm i\phi} \left( \frac{\partial}{\partial\theta} \pm i \cot\theta \frac{\partial}{\partial\phi} \right) \quad (18)$$

The eigenfunctions of this equation are the spherical harmonics  $Y_l^m(\theta, \phi)$ . They can also be written as

$$Y_l^m(\theta, \phi) = \Theta_l^m(\theta) e^{im\phi}$$

We must require that

$$Y_l^m(\theta, \phi + 2\pi) = Y_l^m(\theta, \phi)$$

which means that  $e^{im \cdot 2\pi}$  must be equal to 1. This is why  $m$  only has integer values, which also requires  $l$  to have integer values. When only deriving the values from  $l$  they appeared able to have half-integer values as well, but due to the single-valuedness of the spherical harmonics they are only able to be integers.

## The angular equation

Continuing on with some more dreadful math will yield

$$\Theta(\theta) = A_l^m P_l^m(\cos(\theta))$$

where  $A_l^m$  is a normalisation constant, and  $P_l^m$  is an associated Legendre function. The complete spherical harmonics are therefore

$$Y_l^m(\theta, \phi) = \sqrt{\frac{(2l+1)(l-m)!}{4\pi(l+m)!}} e^{im\phi} P_l^m(\cos\theta)$$

Thankfully, several of these can be found in table 4.3 in Griffiths. It is important to note that these functions are orthonormal. We can transform from  $|lm\rangle$  representation to spherical harmonic representation by using

$$\psi(\theta, \phi) = \langle \theta, \phi | \psi \rangle$$

## Particle in a central-symmetric potential

We have the following Hamiltonian:

$$\hat{H} = -\frac{\hbar^2}{2M} \left( \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2} \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right) \right] \right) + V(r)$$

This absolute beast of an equation simply comes from using  $\nabla^2$  in spherical coordinates.

The term in the square bracket is equal to  $-L^2/\hbar^2$ , which simplifies things to

$$\hat{H} = -\frac{\hbar^2}{2M} \left( \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) \right) + V(r) + \frac{L^2}{2Mr^2}$$

The mass is here denoted with an uppercase  $M$ , so as to not confuse it with the quantum number  $m$ . The above operator commutes with both  $L^2$  and  $L_z$ , which means that they all share a common complete set of eigenstates. These states are on the form

$$\psi_E(r, \theta, \phi) = R(r)Y_l^m(\theta, \phi)$$

Setting  $u(r) = rR(r)$  and doing loads of math yields the *radial equation*

$$\left[ -\frac{\hbar^2}{2M} \frac{\partial^2}{\partial r^2} + V(r) + \frac{\hbar^2}{2M} \frac{l(l+1)}{r^2} \right] u = Eu$$

The third term is called the *centrifugal barrier*.

## The Hydrogen atom

We imagine the Hydrogen atom as a proton at the origin surrounded by an electron.

They are bound together by the Coulomb potential:

$$V(r) = -\frac{e^2}{4\pi\epsilon_0} \frac{1}{r}$$

We will be working with the reduced mass, which is equal to

$$m = \frac{m_e m_p}{m_e + m_p} \approx \frac{m_e m_p}{m_p} = m_e$$

This gives the following radial equation:

$$\left[ -\frac{\partial^2}{\partial r^2} - \frac{e^2 m}{4\pi\epsilon_0 \hbar^2} \frac{2}{r} + \frac{l(l+1)}{r^2} \right] u(r) = \frac{2mE}{\hbar^2} u(r)$$

Setting  $\rho = r/a_0$  gives

$$\left[ -\frac{\partial^2}{\partial \rho^2} - \frac{2}{\rho} + \frac{l(l+1)}{\rho^2} \right] u = \frac{2ma_0^2}{\hbar^2} E u \Rightarrow h_l u = -\frac{1}{\lambda^2} u$$

where  $E/E_1 = 1/\lambda^2$  with  $E_1 = -13.6\text{eV}$ . Now Olav did some very strange math involving the following operators:

$$\hat{A}_l = -\frac{\partial}{\partial \rho} - \frac{l+1}{\rho} + \frac{1}{l+1} \quad \hat{A}_l^\dagger = \frac{\partial}{\partial \rho} - \frac{l+1}{\rho} + \frac{1}{l+1}$$

These operators have never been heard from again in problem sets or exams (to my knowledge), so the important thing here is the conclusions found from the subsequent calculations. One can find that

$$\lambda = l_{\text{max}} + 1 \equiv n$$

which gives

$$E_n = \frac{E_1}{n^2}$$

An important note here is that a general central-symmetric potential has eigenvalues (energies) dependent on both  $n$  and  $l$ . Hydrogen is a special case where the energies only depend on  $n$ .

More painful math gives the normalised wave function for Hydrogen:

$$\psi_{nlm} = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-l-1)!}{2n(n+l)!}} e^{-r/na_0} \left(\frac{2r}{na_0}\right)^l \left[ L_{n-l-1}^{2l+1} \left(\frac{2r}{na_0}\right) \right] Y_l^m(\theta, \phi)$$

$L_{n-l-1}^{2l+1}$  is an associated Laguerre polynomial. The ground state is

$$\psi_{100}(r, \theta, \phi) = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}$$

## Spin

Particles also have an intrinsic angular momentum, called **spin**. It is an internal degree of freedom, with many algebraic properties similar to the extrinsic angular momentum  $L$ .

$$S^2 |sm\rangle = \hbar^2 s(s+1) |sm\rangle \quad \text{and} \quad S^z |sm\rangle = \hbar m |sm\rangle$$

$s$  can have half integer values, while  $m_s = -s, -s + 1, \dots, s$ . We also have similar commutation relations:

$$[S^x, S^y] = i\hbar S^z, \quad [S^y, S^z] = i\hbar S^x, \quad [S^z, S^x] = i\hbar S^y$$

It is important to note that spin is in its own vector space, meaning that the spin-operators will commute with any non-spin operator. Finally, we of course have ladder operators.

$$S^\pm = S^x \pm iS^y$$

Similarly to  $L$ , their eigenvalues are

$$S^\pm |s, m_s\rangle = \hbar \sqrt{s(s+1) - m(m \pm 1)} |s, m_s \pm 1\rangle$$

We will for the most part be working with  $s = 1/2$ , where the eigenstates are

$$|1/2, 1/2\rangle = |\uparrow\rangle \quad \text{and} \quad |1/2, -1/2\rangle = |\downarrow\rangle$$

This is the spin in the  $z$ -direction, meaning that the  $x$ - or  $y$ -directions have to be written as linear combinations of these two states. We then have

$$|\uparrow_x\rangle = \frac{1}{\sqrt{2}}(|\uparrow\rangle + |\downarrow\rangle)$$

We can also use these arrows and spectral decomposition to write out the different spin operators.

$$\begin{aligned} S^z &= \frac{\hbar}{2}(|\uparrow\rangle\langle\uparrow| - |\downarrow\rangle\langle\downarrow|) \\ S^+ &= \hbar |\uparrow\rangle\langle\downarrow| \\ S^- &= \hbar |\downarrow\rangle\langle\uparrow| \\ S^x &= \frac{1}{2}(S^+ + S^-) = \frac{\hbar}{2}(|\uparrow\rangle\langle\downarrow| + |\downarrow\rangle\langle\uparrow|) \\ S^y &= \frac{1}{2i}(S^+ - S^-) = \frac{\hbar}{2i}(|\uparrow\rangle\langle\downarrow| - |\downarrow\rangle\langle\uparrow|) \end{aligned}$$

In matrix representation, the operator for each Cartesian direction  $i$  is given by  $S^i = \frac{\hbar}{2}\sigma^i$ , where  $\sigma^i$  are the *Pauli spin matrices*.

$$\sigma^x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \sigma^y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad \sigma^z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

## Electron spin in a magnetic field

A rotating charge generates a current

$$I = \frac{qv}{2\pi r}$$

which in turn gives the magnetic moment

$$|\mu| = I\pi r^2 = \frac{q \cdot mvr}{2m} \Rightarrow \vec{\mu} = \frac{q}{2m} \vec{L}$$

For an electron, the magnetic moment is

$$\vec{\mu} = \gamma \cdot \vec{S}$$

The Hamiltonian is therefore

$$\hat{H} = -\vec{\mu} \cdot \vec{B} = -\gamma \vec{B} \cdot \vec{S}$$

If the magnetic field points in the  $z$ -direction, then the expression simplifies to

$$\hat{H} = -\gamma B \frac{\hbar}{2} (|\uparrow\rangle \langle\uparrow| - |\downarrow\rangle \langle\downarrow|)$$

## Composite systems

We can represent a system with several degrees of freedom with tensor products. For example a spatial state with a spin state:

$$|nlm_l sm_s\rangle = |nlm_l\rangle \otimes |sm_s\rangle$$

or two spin particles:

$$|\uparrow, \downarrow\rangle = |\uparrow\rangle \otimes |\downarrow\rangle$$

or two different Cartesian directions:

$$|n_x, n_y\rangle = |n_x\rangle \otimes |n_y\rangle$$

The very important part here is that for the spatial part of the total state will *only* interact with other spatial terms. This is because the different sub-terms “live” in different Hilbert spaces. Any two operators belonging to different degrees of freedom will therefore commute.

This also makes the inner product of a composite system very simple to calculate. For ex

$$(\langle a| \otimes \langle b| \otimes \langle c|)(|d\rangle \otimes |e\rangle \otimes |f\rangle) = \langle a|d\rangle \langle b|e\rangle \langle c|f\rangle$$

Performing a measurement on a composite system has a slightly more complicated calculation, as the projection operator will now be something similar to

$$\hat{P} = |\lambda\rangle \langle \lambda| \otimes \hat{I} \otimes \hat{I} \otimes \cdots \otimes \hat{I}$$

depending on which degree of freedom is being measured. This means that the probability of a measurement  $\lambda$  on a state  $|\psi\rangle$  is now

$$P_\lambda = \langle \psi | \hat{P} | \psi \rangle = \langle \psi | (|\lambda\rangle \langle \lambda| \otimes \hat{I} \otimes \hat{I} \otimes \cdots \otimes \hat{I}) | \psi \rangle$$

## Combining angular momenta

When combining two kinds of angular momentum  $\vec{X}$  and  $\vec{Y}$  (two spins, one spin and one orbital, etc) the total angular momentum  $\vec{T}$  is equal to

$$\vec{T} = \vec{X} \otimes \hat{I} + \hat{I} \otimes \vec{Y}$$

(The sum can be written without the tensor product, so it is important to remember that there will be two different vector spaces at play even though it is not explicitly stated mathematically like the term above.) Eigenstates of this system will be on the form  $|t, m_t\rangle$ , which in turn can be written as a linear combination of  $|x, m_x\rangle \otimes |y, m_y\rangle$ -states using a Clebsch-Gordan table. These tables normally use a notation on the form  $|J, M_J\rangle$  for the total angular momentum, but it is important to not confuse this with  $\vec{J} = \vec{L} + \vec{S}$ . Any two kinds of angular momentum can be combined. The total angular momentum operators will have the following eigenvalues for the total state:

$$\hat{T}^2 |t, m_t\rangle = \hbar^2 t(t+1) |t, m_t\rangle \quad \text{and} \quad \hat{T}_z |t, m_t\rangle = \hbar m_t |t, m_t\rangle$$

The total value  $t$  is given by

$$t \in \{|x - y|, |x - y| + 1, \dots, (x + y)\}$$

with

$$m_t \in \{-t, -t + 1, \dots, t\}$$

It is often very useful to use the  $\vec{T}$ -operators when faced with a coupled operator on the form  $\vec{X} \cdot \vec{Y}$ , because it can be rewritten by utilising

$$\vec{T}^2 = (\vec{X} + \vec{Y})(\vec{X} + \vec{Y}) = X^2 + 2\vec{X} \cdot \vec{Y} + Y^2$$

This is useful if the total angular momentum value is given, otherwise the dot product should be rewritten in terms of its Cartesian components or ladder operators:

$$\vec{X} \cdot \vec{Y} = X_x Y_x + X_y Y_y + X_z Y_z = \frac{1}{2}(X_+ Y_- + X_- Y_+) + X_z Y_z$$

This makes it possible to find eigenvalues of states dependent on the individual  $i, m_i$ -values instead of total  $t, m_t$ -values.

## Total angular momentum $\mathbf{J}$

The sum of the angular momentum and spin of a system is given by

$$\vec{J} = \vec{L} \otimes \hat{I} + \hat{I} \otimes \vec{S}$$

with

$$j \in \{|l - s|, |l - s| + 1, \dots, l + s\} \quad \text{and} \quad m_j \in \{-j, -j + 1, \dots, j\}$$

This operator has analogous commutation relations, eigenstates and lowering- and raising operators to  $\vec{L}$  and  $\vec{S}$ .

## Identical particles

### Two-particle systems

The Hamiltonian is

$$H = \frac{\hbar^2}{2m_1} \nabla_1^2 + \frac{\hbar^2}{2m_2} \nabla_2^2 + V(\vec{r}_1, \vec{r}_2, t) \quad (19)$$

### Bosons and fermions

If we have two non-interacting particles, and particle 1 is in state  $|a(\vec{r})\rangle$ , and particle 2 is in state  $|b(\vec{r})\rangle$ , then we have that

$$|\vec{r}_1, \vec{r}_2\rangle = |a(\vec{r}_1)\rangle \otimes |b(\vec{r}_2)\rangle$$



In quantum mechanics, one cannot distinguish between two identical particles. We therefore construct states for which this does not matter. There are two ways of doing this:

$$|\pm\rangle = A(|a\rangle \otimes |b\rangle \pm |b\rangle \otimes |a\rangle) \quad (20)$$

This allows for two types of identical particles: bosons (integer spin, symmetric states) and fermions (half-integer spin, anti-symmetric states). Two fermions cannot exist in the same spatial and spin-states at the same time. This is known as *Pauli's Exclusion Principle*

### Exchange forces

If we have a particle in state  $|a\rangle$  and another in state  $|b\rangle$ , and these are orthonormal, we have that

$$|\psi(a, b)\rangle = |a\rangle \otimes |b\rangle \quad (21)$$

for distinguishable particles. If they are identical bosons or fermions, their wave functions will be in accordance to Equation (20), with the normalisation constant  $A = \frac{1}{\sqrt{2}}$ .

If we were to calculate the mean distance between the particles, we get, for the two different particles:

- Distinguishable particles:  $\langle (x_1 - x_2)^2 \rangle = \langle x^2 \rangle_a + \langle x^2 \rangle_b - 2\langle x \rangle_a \langle x \rangle_b$
- Indistinguishable particles:  $\langle (x_1 - x_2)^2 \rangle_{\pm} = \langle x^2 \rangle_a + \langle x^2 \rangle_b - 2\langle x \rangle_a \langle x \rangle_b \mp 2|\langle x \rangle_{ab}|^2$

For bosons, we see that they tend to be closer together than fermions. The system behaves as if there were a force of attraction between identical bosons and a force of repulsion between two identical fermions. We call these forces exchange forces (even though they are not forces at all; it is a geometric consequence of their symmetries).

### Spin

When adding two-particle systems with spin, we get

$$\psi(\vec{r}_1, \vec{r}_2)\chi(1, 2) = -\psi(\vec{r}_2, \vec{r}_1)\chi(2, 1) \quad (22)$$

Given that the spacial part and the spin part of the wave function have opposite symmetries.

## The symmetrisation principle

We now construct an exchange operator such that

$$\hat{P} |1, 2\rangle = |2, 1\rangle$$

with eigenvalues  $\pm 1$ . It commutes with the Hamiltonian and does not have any time-dependency. If a state starts as a symmetric one, it will stay this way, and vice versa for anti symmetric states. There is a symmetry axiom stating that:

$$|1, 2\rangle = \pm |2, 1\rangle$$

The plus is for bosons, while the negative sign is for fermions. For many-particle systems we have that

$$|1, \dots, j, \dots, i, \dots, n\rangle = \pm |1, \dots, i, \dots, j, \dots, n\rangle$$

## Atoms and atomic structure

For a neutral atom with atomic number  $Z$  and charge  $Ze$ , the Hamiltonian is given by

$$\hat{H} = \sum_{j=1}^Z \left[ -\frac{\hbar^2}{2m} \nabla_j^2 - \left( \frac{1}{4\pi\epsilon_0} \right) \frac{Ze^2}{r_j} \right] + \frac{1}{2} \left( \frac{1}{4\pi\epsilon_0} \right) \sum_{j \neq k}^Z \frac{e^2}{|\vec{r}_j - \vec{r}_k|}$$

This Hamiltonian does not work in spin-space, so all spin states are degenerate. For the separable Coulomb problem, we have that

$$\Psi(r_1, r_2, \dots, r_N) = \psi_{n_1, l_1, m_1}(r_1) \cdots \psi_{n_N, l_N, m_N}(r_N) \chi(m_{s_1}, \dots, m_{s_N})$$

Since electrons are indistinguishable fermions, the wave function must be anti-symmetric under the interchange of particles.  $\psi_{n,l,m}$  has the energy

$$E = \frac{E_{1,Z}}{n^2} = -\frac{m}{2\hbar^2} \left( \frac{Ze^2}{4\pi\epsilon_0} \right)^2 = -Z^2 \cdot 13.6 \text{ eV}.$$

The typical radius is

$$a_{0,Z} = \frac{4\pi\epsilon_0\hbar^2}{Zme^2} = \frac{a_0}{Z} \approx \frac{0.5\text{\AA}}{Z}$$

The lowest energy is obtained by filling the states with as low  $n$  as possible. However, there can be at most two electrons in a single  $n, l, m$ -state (Pauli's exclusion principle), with different spin. One can have at most  $2n^2$  electrons in each energy shell.

Nevertheless, this is without  $e$ - $e$ -repulsion, and not at all realistic. If we do take this repulsion into regard, the inner electrons will “screen” the outer ones, effectively changing the Coulomb potential:

$$\text{Near nucleus: } V = -\frac{Ze^2}{4\pi\epsilon_0 r}$$

$$\text{Far out: } V = -\frac{\#e^2}{4\pi\epsilon_0 r}$$

$$\text{Outside last electron: } V = 0$$

where  $\# < Z$  is  $Z$  minus the number of electrons between the electron in question and the nucleus. A set  $(n, l)$  is a subshell, and takes  $2(2l + 1)$  electrons a subshell is denoted

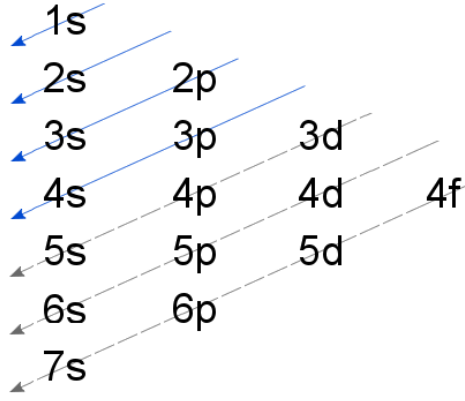
$(n, l)$	$(1, 0)$	$(2, 0)$	$(2, 1)$	$(3, 0)$	$(3, 1)$	$(3, 2)$
Name	$1s$	$2s$	$2p$	$3s$	$3p$	$3d$
$l$ -value	0	1	2	3	4	5
Letter	s	p	d	f	g	h

An electron configuration is denoted  $(1s)^2 (2s)^2 (2p)^5$  etc. This is not necessarily an eigenstate of an atom, and one might need to superpose different electron-configurations to get a proper eigenstate, however, they are good approximations in most cases.

- Higher  $l \Rightarrow$  higher energy. They are further out, and see a weaker the potential (screening).
- Closed (filled) subshells are more stable because the next energy level is “far” off.
- Inert elements (noble gasses in our universe) has their  $p$ -shells completely filled, and nothing outside.

## Madelung’s rule

Madelung’s rule can be summarised as in Figure (1). This is the order in which electrons will fill up the energy levels in an atom.



Figur 1: Madelung's rule summarised. Only accurate up to  $Z = 20$  (calcium). After this, the interactions between electrons and the nucleus become too complicated.

## Helium

Ignoring the repulsive forces between the electrons, we can solve the SE. We are left with a separable solution akin to

$$|\psi(\vec{r}_1, \vec{r}_2)\rangle = |nlm\rangle \otimes |n'l'm'\rangle$$

with half the Bohr radius, and four times the Bohr energies. The ground state is given by

$$|\psi_0(\vec{r}_1, \vec{r}_2)\rangle = |100\rangle |100\rangle \simeq \frac{8}{\pi a_0^3} e^{-2(r_1+r_2)/a_0}$$

The ground state energy then becomes  $-109$  eV, quite far off the actual measured energy of  $-78.975$  eV. The ground states of heavier atoms may be found in a similar way (by solving  $H|nlm\rangle = E|nlm\rangle$ ).

## The periodic table

In order to determine the configurations of atoms, we write the hieroglyph

$$^{2S+1}L_J$$

where  $S$  is spin and  $J = S + L$ . We use Hund's rules to find these configurations.

- **Hund's first rule:** The state with the highest total spin, will have the lowest energy.
- **Hund's second rule:** The state with highest total orbital angular momentum  $L$ , consistent with overall antisymmetrisation, will have the lowest energy.

- **Hund's third rule:** if a subshell is no more than half filled, the lowest energy level has  $J = |L - S|$ ; if it is more than half filled, then  $J = L + S$  has the lowest energy.

Filled orbitals have  $L = 0$  and  $S = 0$ , so we are only interested in the shells which are not filled.

## Solids

### Zeroth approximation: box with $N$ particles (fermions)

$$H = \sum_{i=1}^N \frac{p_i^2}{2m} + V(r_i) \qquad V = \begin{cases} 0, & \text{inside} \\ \infty, & \text{outside} \end{cases}$$

We then get

$$\psi(x, y, z) = \frac{8}{\sqrt{L_x L_y L_z}} \sin(k_x x) \sin(k_y y) \sin(k_z z)$$

where  $k_i = n_i \pi / L_i$  and  $n_i$  is a positive integer. The energies are

$$E_k = \frac{\hbar^2}{2m} k^2$$

We now imagine the  $k$ -values as coordinates in a  $k$ -space (the positive octant). The further we are from the origin, the higher the energy. A single state takes up the volume  $\pi^3 / L_x L_y L_z = \pi^3 / V$ . The number of electrons in such a box is then

$$N = \frac{V}{3\pi^2} k_F^3$$

where  $k_F$  is the Fermi wave vector, and marks the boundary between filled and empty single-particle states.

## Bloch's theorem

**Theorem 1** *In a periodic potential of period  $a$ , the eigenfunctions satisfy*

$$\psi(x + a) = e^{i\bar{k}a} \psi(x), \text{ where } \bar{k} \text{ is real and independent of } x.$$

This is useful when modelling an atom as a string (or a big ring). The possible values for  $\bar{k}$  are  $\bar{k} = \frac{2\pi n}{Na}$ , where  $n \in \{0, 1, \dots, N + 1\}$ , and  $N$  is the number of atoms on the string / ring.

## Kronig-Penney model

Here we have a potential (for the electron on our circular molecule with space  $a$  between the atoms)

$$V(x) = \alpha \sum_{j=0}^{N-1} \delta(x - ja)$$

This is, of course, completely unrealistic. We now have the wave function

$$\psi(x) = A \sin(bx) + B \cos(bx), \quad E = \frac{\hbar^2}{2m} k^2$$

We have that

$$A = \frac{B(x^{i\bar{k}a} - \cos(ka))}{\sin(ka)}$$

and that the following have to hold:

$$\cos(\bar{k}a) = \cos(ka) + \frac{m\alpha a}{\hbar^2} \frac{\sin(ka)}{ka}$$

This gives rise to band structure of a periodic potential.

## Symmetry and degeneracy

We define a unitary operator  $T$  ( $T^{-1} = T^\dagger$ ) such that  $T |\psi(0)\rangle = |\psi'(0)\rangle$ .  $T$  is a symmetry of the Hamiltonian if  $T^{-1} |\psi'(t)\rangle = |\psi(0)\rangle$  for all  $t$  and  $\psi(0)$ . The operator  $T$  will also commute with  $H$ .

**Consequences:**

- The expectation value of  $T$ ,  $\langle T \rangle = \langle \psi(0) | T | \psi(0) \rangle$  is conserved (not time-dependent).
- Eigenstates of  $T$  will remain eigenstates as  $t$  changes.
- Can construct a common complete set of eigenstates for  $H$  and  $T$ .
- Often a degenerate energy spectrum.

In general we say that symmetries give rise to conservation laws.

## Translation in space

$$T_a \psi(x) = \psi(x + a) = e^{a \frac{d}{dx}} \psi(x)$$

The last part of this equation was found by Taylor expanding  $\psi(x + a)$ . As  $\frac{d}{dx} = \frac{i}{\hbar} \hat{p}$ , we get that

$$T_a = e^{ia\hat{p}/\hbar}$$

We can therefore say that *momentum generates translation*. This operator, like the momentum operator, commutes with the Hamiltonian. Thus momentum is conserved.

## Translation in time

We have already found that translations in time are generated by the Hamiltonian:

$$U(t) = e^{-iHt/\hbar}$$

This means that energy is conserved.

## Rotation

Similar to translation, we can find a rotational operator

$$R_z(\phi) = e^{i\phi L_z/\hbar}$$

This operator rotates a state an angle  $\phi$  around the  $z$ -axis. It tells us that angular momentum generates rotation, and that angular momentum is conserved. For a central symmetric potential  $V(r)$ , we have  $[H, R_z] = 0$ . So eigenfunctions of  $L_z$  are also energy-eigenfunctions  $|E, m\rangle$ .  $R_x |E, m\rangle$  is also an eigenstate with energy  $E$ , but  $R_x |E, m\rangle \neq |E, m\rangle \Rightarrow \text{degeneracy}$ .

## Parity (space-inversion)

We define the unitary parity operator such that

$$\Pi |\vec{r}\rangle = |-\vec{r}\rangle$$

for all  $|\vec{r}\rangle$  and their superpositions. Its eigenvalues are  $\pm 1$ , for even parity and odd parity, respectively. In addition, we have that

$$\Pi^\dagger \vec{r} \Pi = -\vec{r} \qquad \Pi^\dagger \vec{p} \Pi = -\vec{p}$$

(Here,  $\vec{r}$  and  $\vec{p}$  are the position and momentum operators). With these relations, we see that a Hamiltonian is parity-symmetric if  $[H, \Pi] = 0$ . For the free particle Hamiltonian is parity-symmetric.

## The variational principle

The variational principle is a way of finding the upper bound of a ground state  $E_{gs}$ . Say that the ground state could not be found, then we apply a large range of different trial functions, where the different functions can get different results who should all be larger than the actual ground state.

### The variational principle equation

$$E_{gs} \leq \frac{\langle f | H | f \rangle}{\langle f | f \rangle} = \langle H \rangle = E_{tr}$$

$$E_{gs} \leq E_{tr}$$

where  $f$  is some trial function and  $H$  is the Hamiltonian. This equation more or less states that for any trial equation we will get an expectation value larger than the ground state. Curiously if we say just happen upon a trial function  $|0\rangle$  which also happens to be the ground eigenstate of that particular Hamiltonian we get

$$E_{gs} \leq \langle 0 | H | 0 \rangle = E_{gs} \langle 0 | 0 \rangle \Rightarrow E_{gs} = E_{gs}$$

however this rarely happens. Examples of how the variational principle is used can be found in section 8.1 page 328.

There is a certain algorithmic way when using the variational principle called the variational method:

### The variational method

1. Pick/guess a class of trial wave function parametrised by some number.
2. Compute the trial energy  $E_{tr}$  for the trial wave function.
3. Minimise  $E_{tr}$  w.r.t the variational parameter. The minimisation can often be done by derivation.



4. The lowest  $E_{tr}$  gives an upper bound of  $E_{gs}$ .

As known the expectation values follow classical laws, so an easy way of calculating the expected energy is with

$$\langle H \rangle = \langle K \rangle + \langle V \rangle$$

One possible class of trial functions are Gaussians

$$f(x) = A \exp\{-bx^2\}$$

where  $b$  is the variational parameter. Moreover you could also split a trial function into a piece wise function and integrate over the parts (as in example 8.3).

Other important things about the variational method is that while it is extremely powerful and easy to use, it only gives you an upper bound on the ground state. It ONLY gives this upper bound, and you do not know the distance to the true ground energy either.

## Variational method - Helium

Further we will show how the variational method can be used on the Helium atom. It consist of 2 electrons in orbit around the nucleus of 2 protons (and 2 neutrons which we will neglect). The simplest Hamiltonian for this system is

$$H = -\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2) - \frac{e^2}{4\pi\epsilon_0} \left( \frac{2}{r_1} + \frac{2}{r_2} - \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right)$$

Where the difficult term to calculate is the last one. We use a trial wavefunction of two components, which is the ground state of the hydrogen. We assume non-interacting probabilities.

$$\psi(r_1, r_2) = \psi_{100}(\mathbf{r}_1)\psi_{100}(\mathbf{r}_2) = \left( \frac{Z^3}{\pi a_0^3} \right)^{1/2} \exp\{-Zr_1/a_0\} \left( \frac{Z^3}{\pi a_0^3} \right)^{1/2} \exp\{-Zr_2/a_0\}$$

Where  $Z$  is the variational parameter. Here the wavefunctions are also normalised.

$$E_{tr} = \int d^3r_1 d^3r_2 \psi^*(\mathbf{r}_1, \mathbf{r}_2) H \psi(\mathbf{r}_1, \mathbf{r}_2)$$

After calculating this we find that the variational principle gives an estimate of

$$\langle H \rangle = -77.5 \text{eV}$$

and with the experimental value being  $-79\text{eV}$  we can see that this is not so bad. The calculations for this can be found in Griffiths page 333-336.

## The hydrogen molecule ion

In this section we will see if a single electron can bind 2 protons. The Hamiltonian for the ion is

$$H = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{r} + \frac{1}{r'}\right)$$

where  $r$  and  $r'$  is the distance from the electron to the respective protons. The main way to check if this state is stable is to see if for a given trial function this state has less energy than the energy of a normal hydrogen atom and a free proton. We neglect the kinetic energy of the proton so the energy we wish to be below is  $E_1$  for hydrogen.

The trial function considered is

$$\psi = A [\psi_0(r) + \psi_0(r')]$$

where

$$\psi_0(r) = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}.$$

This method is called **LCAO** or the molecular wave function as a **L**inear **C**ombination of **A**tomical **O**rbitals. The normalisation factor  $A$  becomes

$$|A|^2 = \frac{1}{2(1 + I)}$$

where  $I$  is

$$I = e^{-R/a} \left[ 1 + \left(\frac{R}{a_0}\right) + \frac{1}{3} \left(\frac{R}{a_0}\right)^2 \right]$$

and  $R$  is the distance between the protons. The results are

$$\langle H \rangle = \left[ 1 + 2 \frac{(D + X)}{(1 + I)} \right] E_1$$

where  $D$  and  $X$  are

$$D = \frac{a_0}{R} - \left(1 + \frac{a_0}{R}\right) e^{-2R/a_0}$$

$$X = \left(1 + \frac{R}{a_0}\right) e^{-R/a_0}$$

(in Olav's notes) And according to the variational principle the ground state is less than  $\langle H \rangle$ . This is only the electron's energy if we add the proton proton repulsion

$$V_{pp} = -\frac{2a_0}{R} E_1.$$

The plot of the energy as a function of  $x = R/a_0$  can be found on page 340. Evidently this state of 2 protons and 1 electron is stable and bonding does occur as there exists a region where the energy is below  $E_1$ . The bond is covalent. The trial energy amounts to 1.8 eV and the experimental value amounts to 2.8 eV so as usual the variational principle overshoots the actual value by a fair margin. For better trial functions however the value for the binding energy of the system will only get larger, but since we have already proven that it is bound such is not necessary.

## Time-independent perturbation theory

### Non-degenerate perturbation theory

Perturbation theory is an approximation method where you take exactly solvable systems and add a small/tiny perturbation (change). The Hamiltonian can often be expressed as

$$H = H^0 + H'$$

where  $H^0$  is the “unperturbed” state, for example a harmonic oscillator, and  $H'$  is the small perturbation. By the virtue of power series we can expand the perturbation with different powers of corrections, usually only the first and second order corrections are calculated.

#### First order energy correction

The first order perturbation for the  $n$ 'th energy state can be calculated by

$$E_n^1 = \langle \psi_n^0 | H' | \psi_n^0 \rangle$$

where the superscript 1 in the energy characterises it as the first order perturbation correction,  $\psi_n^0$  is the eigenstate of the unperturbed Hamiltonian and  $H'$  is the perturbation to the system.

#### First order state correction

We can also calculate the first order perturbation correction to the state  $\psi_n$  by the following

$$|\psi_n^1\rangle = \sum_{m \neq n} \frac{\langle \psi_m^0 | H' | \psi_n^0 \rangle}{(E_n^0 - E_m^0)} |\psi_m^0\rangle$$

where the sum means that you sum over all the eigenstates of the unperturbed Hamiltonian EXCEPT the eigenstate you are looking at. As long as the system is non-degenerate the denominator is safe and will always be non-zero.

## Second order energy correction

With this you can calculate the second order perturbation correction to the energy

$$E_n^2 = \langle \psi_n^0 | H' | \psi_n^1 \rangle = \sum_{m \neq n} \frac{|\langle \psi_m^0 | H' | \psi_n^0 \rangle|^2}{(E_n^0 - E_m^0)}$$

where the superscript 0 again indicates that these are the energies(eigenvalues) and eigenstates of the unperturbed Hamiltonian. One could go further to the 3. order correction, but usually it is of little interest with this method, as the perturbation corrections only get smaller and smaller as the power of correction gets larger.

Moreover when you have calculated the corrections it is important to remember that they are only corrections and that they need to be summed up with the unperturbed energy to actually give an estimate up to n'th order.

$$E_n = E_n^0 + E_n^1 + E_n^2 + \dots$$

$$|\psi_n\rangle = |\psi_n^0\rangle + |\psi_n^1\rangle + |\psi_n^2\rangle + \dots$$

However with only first and second order perturbation the energy becomes

$$E_n = E_n^0 + \langle \psi_n^0 | H' | \psi_n^0 \rangle + \sum_{m \neq n} \frac{|\langle \psi_m^0 | H' | \psi_n^0 \rangle|^2}{(E_n^0 - E_m^0)}$$

## Degenerate perturbation theory

If the unperturbed states are degenerate, then normal non-degenerate perturbation fails. The main reason for this is that the second order energy and first order state correction blow up because of the denominator becoming zero. However, there exist states where both the numerator and the denominator becomes zero. Further, almost all applications of perturbation theory involves degeneracy, so this is not a minor problem.

### With non-good states

The way we calculate the perturbation energy is by calculating the matrix  $W$ . An example would be if you have an unperturbed Hamiltonian  $H^0$  with

$$H^0\psi_a^0 = E^0\psi_a^0 \quad H^0\psi_b^0 = E^0\psi_b^0$$

with both states being normalised. Any combination of those states

$$\psi^0 = \alpha\psi_a^0 + \beta\psi_b^0$$

is still an eigenstate of the unperturbed Hamiltonian with eigenvalue  $E_0$ . Moreover the perturbation will often lift the degeneracy and the state will split into 2 or more values. The good states are on the same form as  $\psi^0$ , however they are usually not known. The way we calculate the corrections (if we do not know what the good states are), is by calculating the matrix  $W$  with matrix elements

$$W_{ij} = \langle \psi_i^0 | H' | \psi_j^0 \rangle$$

$$\begin{bmatrix} W_{aa} & W_{ab} \\ W_{ba} & W_{bb} \end{bmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = E_1 \begin{pmatrix} \alpha \\ \beta \end{pmatrix}$$

The matrix elements should *only* be calculated with the degenerate states! The eigenvalues of the matrix  $W$  gives the first order corrections, and the corresponding eigenvectors tell us the coefficients  $\alpha$  and  $\beta$  that determine the good states. The first order perturbation energy will then be

$$E_{\pm}^1 = \frac{1}{2} \left[ W_{aa} + W_{bb} \pm \sqrt{(W_{aa} - W_{bb})^2 + 4|W_{ab}|^2} \right]$$

Where the two roots correspond to the two perturbed energies. Some trivia is that  $W_{ba} = W_{ab}^*$ . Another thing is that the good states have to be orthogonal to each other.

### With good states

**Theorem 2** *Let  $A$  be a hermitian operator that commutes with  $H^0$  and  $H'$ . If  $\psi_a^0$  and  $\psi_b^0$  (the degenerate eigenfunctions of  $H^0$ ) are also eigenfunctions of  $A$ , with distinct eigenvalues*

$$A\psi_a^0 = \mu\psi_a^0 \quad , \quad A\psi_b^0 = \nu\psi_b^0, \quad \mu \neq \nu$$

*then  $\psi_a^0$  and  $\psi_b^0$  are the “good” states to use in perturbation theory.*

Once the “good” states are found, either by solving the matrix or by using the theorem of “good” states, we can use the said states as our unperturbed states and apply ordinary non-degenerate perturbation theory. In most cases the operator  $A$  will be suggested by symmetries that commute with  $H$ .

Moreover if you are faced with degenerate states, look for an hermitian operator  $A$  that commutes with  $H^0$  and  $H'$ . Pick as your unperturbed states the states that are eigenfunctions of both  $H^0$  and  $A$  (naturally with distinct eigenvalues as to avoid any further degeneracy.) Then you use ordinary non-degenerate perturbation theory.

### Higher-order degeneracy

In the previous section we looked at a two-fold degeneracy, but the method can easily be generalised to  $n$ -fold degeneracy with  $W$  then being an  $n \times n$  matrix.

$$W_{ij} = \langle \psi_i^0 | H' | \psi_j^0 \rangle$$

Moreover when calculating  $W$  for the “good” states it will automatically be diagonal, as the different eigenstates of both  $H^0$  and  $A$  have to be orthogonal to each other.

## Fine structure of Hydrogen

### The Feynman-Hellmann theorem

**Theorem 3** *If one has a Hamiltonian with corresponding energies depending on a parameter  $\beta$ , then*

$$\frac{\partial E}{\partial \beta} = \langle \psi^0 | \frac{\partial H}{\partial \beta} | \psi^0 \rangle$$

Until now we have only considered the simplified Bohr Hamiltonian of the hydrogen

$$H_{Bohr} = -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0} \frac{1}{r}$$

which consists of the electron kinetic energy and the coulomb potential. However this can be made more accurate by taking into account the **fine structure**, which is the addition of the **relativistic correction** and the **spin-orbit coupling**. Compared to the Bohr energies the fine structuring is a very tiny perturbation, smaller than a factor of  $\alpha^2$  where

$$\alpha = \frac{e^2}{4\pi\epsilon_0 \hbar c} \approx \frac{1}{137.036}$$

## Relativistic correction

The classic kinetic aspect of the Hamiltonian is

$$K = \frac{p^2}{2m}$$

while the relativistic formula is  $K = \sqrt{p^2 c^2 + m^2 c^4} - mc^2$  and from this the lowest order relativistic correction becomes

$$H'_r = -\frac{p^4}{8m^3 c^2}$$

and which means that the first order relativistic correction to the energy becomes

$$E'_r = -\frac{(E_n)^2}{2mc^2} \left[ \frac{4n}{l+1/2} - 3 \right]$$

While the hydrogen atom's energies are very degenerate, it is actually completely fine to use non-degenerate perturbation theory given the fact that the states  $|nlm\rangle$  are the “good” states! Which is quite remarkable. Moreover we can see that the energy degeneracy has been lifted from the quantum number  $l$ .

## Spin-Orbit Coupling

The spin orbit coupling arises from the magnetic field which the electron feels. From the electron's point of view the proton is spinning around it, and this sets up a magnetic field. The spin-orbit correction Hamiltonian becomes

$$H'_{so} = \left( \frac{e^2}{8\pi\epsilon_0} \right) \frac{1}{m^2 c^2 r^3} \mathbf{S} \cdot \mathbf{L}$$

The energy correction of the first order becomes

$$E_{so}^1 = \frac{(E_n)^2}{mc^2} \left[ \frac{n(j(j+1) - l(l+1) - 3/4))}{l(l+1/2)(l+1)} \right]$$

Adding the relativistic correction and the spin-orbit coupling we find the first order fine structure perturbation

$$E_{fs}^1 = \frac{(E_n)^2}{2mc^2} \left( 3 - \frac{4n}{j+1/2} \right)$$

combining this with the energies from the Bohr formula we arrive at the energy levels of Hydrogen including the fine structure.

$$E_{nj} = -\frac{13.6eV}{n^2} \left[ 1 + \frac{\alpha^2}{n^2} \left( \frac{n}{j+1/2} - \frac{3}{4} \right) \right]$$

Fine structure breaks the degeneracy in  $l$ , but still preserves degeneracy in  $j$ . The quantum numbers  $m_l$  and  $m_s$  are no longer “good”, the new “good” quantum numbers are  $n, l, s, j$  and  $m_j$ .

## The Zeeman effect

When an atom is placed in a uniform external magnetic field  $\mathbf{B}_{\text{ext}}$ , the energy levels are shifted. This phenomenon is known as the Zeeman effect. For a single electron the perturbation is

$$H'_Z = -(\mu_l + \mu_s) \cdot \mathbf{B}_{\text{ext}}$$

where  $\mu_s = -\frac{e}{m}\mathbf{S}$  and  $\mu_l = -\frac{e}{2m}\mathbf{L}$  so

$$H'_Z = \frac{e}{2m}(\mathbf{L} + 2\mathbf{S}) \cdot \mathbf{B}_{\text{ext}}$$

The nature of the Zeeman splitting depends heavily on the strength of the external magnetic field compared with the internal field from the spin-orbit coupling. If  $B_{\text{ext}} \ll B_{\text{int}}$ , then the fine structure dominates and  $H'_Z$  can be counted as the small perturbation. If  $B_{\text{ext}} \gg B_{\text{int}}$  then the fine structure becomes the perturbation because the Zeeman effect dominates.

### Weak-field Zeeman effect

For  $B_{\text{ext}} \ll B_{\text{int}}$ , fine structure dominates and the unperturbed Hamiltonian is

$$H_{\text{Bohr}} + H'_{fs}$$

which is the fine structure corrected Bohr Hamiltonian. The energy correction is then

$$E_z^1 = \mu_B g_j B_{\text{ext}} m_j$$

where  $\mu_B = \frac{e\hbar}{2m} = 5.788 \times 10^{-5} \text{eV/T}$  is called the Bohr magneton,  $m_j$  is the eigenvalue of the total angular momentum in the z direction and  $g_j$  is called the Landé g-factor

$$g_j = \left[ 1 + \frac{j(j+1) - l(l+1) + s(s+1)}{2j(j+1)} \right]$$

So the energy would then be

$$E = E_{nj} + E_z^1.$$

A trick that was used in these calculations is  $\mathbf{S} \cdot \mathbf{J} = \frac{1}{2}(J^2 - S^2 - L^2)$ , which lifts the degeneracy in  $m$  since  $H'_Z$  picks out a specific direction in space.



## Strong-Field Zeeman splitting

If  $B_{\text{ext}} \ll B_{\text{int}}$ , the Zeeman effect dominates and we take the unperturbed Hamiltonian to be

$$H_{\text{Bohr}} + H'_Z$$

and the perturbation to be  $H'_{fs}$ . The Zeeman Hamiltonian is

$$H'_Z = \frac{e}{2m} B_{\text{ext}} (L_Z + 2S_Z)$$

where the unperturbed energies are

$$E_{nm_l m_s} = -\frac{13.6\text{eV}}{n^2} + \mu_B B_{\text{ext}} (m_l + 2m_s)$$

The first order energy correction (fine structure) comes as

$E'_{fs} = \langle nlm_l m_s | (H'_r + H'_{so}) | nlm_l m_s \rangle$  which then becomes

$$E_{fs}^1 = \frac{13.6\text{eV}}{n^3} \alpha^2 \left[ \frac{3}{4n} - \left( \frac{l(l+1) - m_l m_s}{l(l+1/2)(l+1)} \right) \right]$$

For  $l = 0$  we see that the last term is undefined, however we just set it to 1 because Olav the merciful, destroyer of grade averages has said so. So the new energy then becomes

$$E = E_{nm_l m_s} + E_{fs}^1$$

## Hyperfine splitting in hydrogen

The proton also contains a magnetic dipole, however it is much smaller than the electron's:

$$\boldsymbol{\mu}_p = \frac{g_p e}{2m_p} \mathbf{S}_p, \quad \boldsymbol{\mu}_e = -\frac{e}{m_e} \mathbf{S}_e$$

The proton is a composite structure, so its gyromagnetic ratio is not as simple as the electrons, hence it has the explicit g-factor  $g_p$  whose value has been measured to be 5.59 as opposed to the electrons 2.00. The Hamiltonian and the derivations can be found on page 311-312. The energy correction is then

$$E_{hf}^1 = \frac{\mu_0 g_p e^2}{3\pi m_p m_e a_0^3} \langle \mathbf{S}_p \cdot \mathbf{S}_e \rangle$$

This is called the **spin-spin coupling**, because it involves the dot product of two spins. In the presence of the spin-spin coupling the individual spin angular momentum is no longer conserved, however the total spin is, so the “good” states are the eigenstates of

the total spin. The trick is using  $\mathbf{S}_p \cdot \mathbf{S}_e = \frac{1}{2}(S^2 - S_e^2 - S_p^2)$  and with both the proton and electron having spin 1/2, in the triplet state, both the spins are parallel and we have that the total spin is 1. In the singlet state they are opposed so the total spin would be 0. We then get

$$E_{hf}^1 = \frac{4g_p\hbar^4}{3m_pm_e^2c^2a_0^4} \begin{cases} +1/4, & (\text{triplet}) \\ -3/4, & (\text{singlet}) \end{cases}$$

## Quantum dynamics

All the physics we have learned so far can be called *quantum statistics*, where the time dependant Schrodinger equation

$$i\hbar \frac{\partial \Psi}{\partial t} = H\Psi$$

is solved by separating the variables

$$\Psi(\mathbf{r}, t) = \psi(\mathbf{r}) \exp\{-iEt/\hbar\}$$

If we want to allow transitions (also called quantum jumps) between energy levels we must introduce time dependant potentials. There are few exactly solvable problems in quantum dynamics, however if the time-dependant Hamiltonian is small it can be treated as a perturbation.

## Time dependant perturbation theory

Set  $H' = V(\mathbf{r}, t)$ , which is a weak time-varying potential, this gives the Hamiltonian  $H = H^0 + H'$  with  $H^0 |k\rangle = E_k |k\rangle$ . The time dependence of the unperturbed kets is  $|k, t\rangle = \exp\{-iE_k t/\hbar\} |k\rangle$ , which means that for the full system it is

$$|\Psi(t)\rangle = \sum_k a_k(t) |k, t\rangle.$$

We can find the coefficient for an energy state  $|k\rangle$  as a function of time with

$$a_n(t) = a_n(0) + \frac{1}{i\hbar} \sum_k \int_0^t dt' V_{nk}(t') \exp\{i(E_n - E_k)t'/\hbar\} a_k(t')$$

Where  $V_{nk}(t') = \langle n | V | k \rangle = \int d^3r \psi_n^*(\mathbf{r}) V(\mathbf{r}, t) \psi_k(\mathbf{r})$  and  $f_k$  is the state

For small  $V$  the last term is a small correction to the first. So the lowest nontrivial order  $\mathcal{O}(V^0)$  is  $a_n(0)$ .

For  $\mathcal{O}(V^1)$  we have

$$a_n(t) = a_n(0) + \frac{1}{i\hbar} \sum_k \int_0^t dt' V_{nk}(t') \exp\{i(E_n - E_k)t'/\hbar\} a_k(t')$$

Typically we know the initial state, which we take to be an energy eigenstate

$|i\rangle \Rightarrow a_k(0) = \delta_{k,i}$ . The probability then for finding the system in energy eigenstate  $|f\rangle$  at time  $t$  is (with first order correction)  $c_f(t) = |a_f(t)|^2$ , where

$$a_f(t) = \frac{1}{i\hbar} \int_0^t dt' V_{fi}(t') \exp\{i(E_f - E_i)t'/\hbar\}$$

and  $V_{fi}(t) = \langle f | V(t) | i \rangle$ .

### Sinusoidal perturbations

Set  $V(\mathbf{r}, t) = V_0(\mathbf{r}) \cos \omega t$ , which gives  $V_{fi}(\mathbf{r}, t) = \langle f | V_0(\mathbf{r}) | i \rangle \cos \omega t$ .

We wish to get the probability as a function of time

$$P_f(t) = |a_f(t)|^2$$

We do the first order correction and get that the probability for us to begin in state  $i$  and get to state  $f$  is

$$P_{i \rightarrow f} = \left| \frac{V_{fi}}{\hbar} \right|^2 \frac{\pi t}{2} (\delta(\omega_{fi} - \omega) + \delta(\omega_{fi} + \omega))$$

With  $\omega_{fi} = \frac{E_f - E_i}{\hbar}$  We can see here when  $t$  becomes large that the probability goes over 1! Thankfully, this is only an approximation, so some inaccuracy has to be expected.

The more physical thing to look at is the transition rate  $R_{i \rightarrow f} = \frac{P_{i \rightarrow f}}{t}$ . With the relation  $\delta(ax) = \frac{1}{|a|} \delta(x)$  we get that

$$R_{i \rightarrow f} = \left| \frac{V_{fi}}{\hbar} \right|^2 \frac{2\pi}{\hbar} (\delta(\hbar\omega_{fi} - \hbar\omega) + \delta(\hbar\omega_{fi} + \hbar\omega))$$

Further it can be shown that the transition rate from  $f \rightarrow i$  is the same as the transition rate from  $i \rightarrow f$ . This can be shown by

$$|V_{if}|^2 = \langle f | V_0 | i \rangle \langle i | V_0 | f \rangle = \langle i | V_0 | f \rangle \langle f | V_0 | i \rangle = |V_{fi}|^2$$

So  $R_{f \rightarrow i} = R_{i \rightarrow f}$  with

$$R_{f \rightarrow i} = \left| \frac{V_{if}}{\hbar} \right|^2 \frac{2\pi}{\hbar} (\delta(\hbar\omega_{if} - \hbar\omega) + \delta(\hbar\omega_{if} + \hbar\omega))$$

Hence we know the equations when transitioning from one state to another, but what about one state to a continuum of states? Several states with the same or approximate equal energy can be expressed as  $\rho(E_f)dE_f$  where  $\rho(E_f)$  is the density of energy-states for energy  $E_f$ . The transition from  $i$  to the continuum is then

$$R_{i \rightarrow cont} = \int_{E_f}^{E_f + \Delta} dE_f \rho(E_f) R_{i \rightarrow f}$$

Applying the formula for  $R_{i \rightarrow f}$  and using the delta functions to remove the integral we arrive at **Fermi's golden rule**

$$R_{i \rightarrow E_f} \approx \left| \frac{V_{fi}}{2} \right|^2 \frac{2\pi}{\hbar} \rho(E_f)$$

It states that the transition rate is the square of the matrix element (which encapsulates all the relevant information about the dynamics of the process) times the density of states (how many final states are accessible, the more energy supplied by the perturbation the more roads are open and the faster the traffic will flow) times a constant. An example of this rule can be found on page 424.

## Emission and absorption of radiation

An electromagnetic wave consists of transverse oscillating electric and magnetic fields. An atom in the presence of light responds mostly to the electric aspect which can be described as

$$\mathbf{E} = \vec{E}_0 \cos(\omega t)$$

the perturbed Hamiltonian is

$$H' = -qE_0 \cos(\omega t)$$

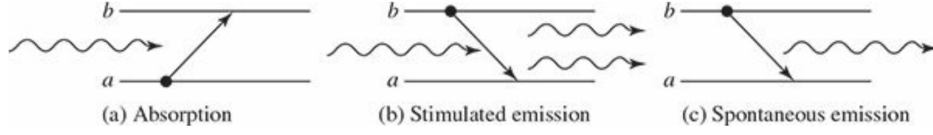
with  $q$  being the charge of the electron. We then coin

$$V_{fi} = -\vec{E}_0 \cdot q \langle f | \vec{r} | i \rangle, \quad \text{where} \quad \vec{\varphi}_{fi} = q \langle f | \vec{r} | i \rangle$$

the translation becomes

$$R_{a \rightarrow b} = |\vec{\varphi}_{ba} \cdot \vec{E}_0|^2 \frac{\pi}{2\hbar} \delta(\hbar\omega_0 - \hbar\omega)$$

with  $a$  and  $b$  being energy states and  $\hbar\omega_0$  being the difference in energy between them. Similar to before the emission is simply  $R_{b \rightarrow a} = R_{a \rightarrow b}$ . How the electrons and photons interact can be shown in fig 2.



Figur 2: Caption

This can create a chain reaction: Populate many atoms in the excited state, then shine light with frequency  $\omega_0$ . Stimulated emission occurs and amplifies the light many times. This is Light Amplification by Stimulated Emission of Radiation, also called LASER.

### Incoherent Perturbation

Let the field be  $\vec{E} = E_0 \hat{n} \cos(\omega t)$  where  $\hat{n}$  is the polarisation of the light. With incoherent light we take the average over the polarisation with the energy density being  $u = \frac{\epsilon_0}{2} E_0^2$ . We then find that the transition rate for stimulated emission from state  $b$  to state  $a$  under the influence of incoherent, unpolarised light from all directions is

$$R_{b \rightarrow a} = \frac{\pi}{3\epsilon_0 \hbar^2} |\wp_{ba}|^2 \rho(\omega_0)$$

where  $\wp_{ba}$  is the matrix element of the electric dipole moment between the two states  $\wp_{ba} = q \langle b | \vec{r} | a \rangle$  and  $\omega_0 = (E_b - E_a)/\hbar$

### Spontaneous emission

#### Einstein A & B coefficients (with thermal equilibrium)

Imagine a container of atoms, with the lower state  $a$  and higher state  $b$ , and number per state being  $N_a$  and  $N_b$ . Let  $A$  be the spontaneous emission rate, which means that the number of particles leaving the upper state by this process per unit time is  $AN_b$ . The number of particles leaving state  $b$  by stimulated emission is proportional to the electromagnetic field  $B_{ba}\rho(\omega_0)$ , so the number of particles leaving state  $b$  by stimulated emission is  $N_b B_{ba}\rho(\omega_0)$ . This gives

$$\frac{dN_b}{dt} = -N_b A - N_b B_{ba}\rho(\omega_0) + N_a B_{ab}\rho(\omega_0)$$

We know that  $B_{ab} = B_{ba}$  and that

$$B_{ba} = \frac{\pi}{3\epsilon_0 \hbar^2} |\wp|^2$$

Assuming thermal equilibrium we get that the spontaneous emission rate  $A$  is

$$A = \frac{\omega_0^3 \hbar}{\pi^2 c^3} B_{ba}$$

$$\Rightarrow A = \frac{\omega_0^3 |\rho|^2}{3\pi \epsilon_0 \hbar c^3}$$

Typically we have several decay channels, so we would have a sum of many different  $A$ -values. Moreover lifetimes of higher excited states are shorter.

### The lifetime of an excited state

The spontaneous emission rate  $A$  is an important result as it allows us to evaluate the lifetime of an excited state. Assume that the number of electrons in an excited state changes as a function of the negative of  $A$ ,  $N_b$  times the change in time. Further we assume that the system does not interact with anything that can “bump” the electrons up again.

$$dN_b = -AN_b dt,$$

The solution to this is

$$N_b(t) = N_b(0) \exp\{-At\}$$

We often write it with a time constant

$$\tau = \frac{1}{A}$$

and we call this the lifetime. If there are more decay modes,  $A$  becomes a sum of all the different decay rates  $A_1, A_2, A_3, \dots$ .

### Selection rules for electric dipole transitions

As we have seen calculating the spontaneous emission has been reduced to the matter of calculating the matrix elements

$$\langle b | \mathbf{r} | a \rangle$$

Where  $a$  and  $b$  are energy eigenstates of some sort. Say that we have the Hamiltonian for Hydrogen. Then the states are defined by  $n, l$  and  $m$ .

$$\langle n'l'm' | \mathbf{r} | nlm \rangle$$

From this we get that **emission between states can only happen when**

$$\Delta l = l' - l = \pm 1, \quad \Delta m = 0, \text{ or } \pm 1.$$

When evaluating  $\mathbf{r} = x + y + z$  in the matrix we can often find that some of the components become 0. More generally if

$$m' = m, \quad \text{then} \quad \langle n'l'm' | x | nlm \rangle = \langle n'l'm' | y | nlm \rangle = 0$$

and if

$$m' = m \pm 1, \quad \text{then} \quad \langle n'l'm' | x | nlm \rangle = \pm i \langle n'l'm' | y | nlm \rangle$$

$$\text{and} \quad \langle n'l'm' | z | nlm \rangle = 0$$

This gives us the remarkable fact that we almost never have to calculate the matrix elements of both  $x$  and  $y$ ! We can get them from each other. Not all transitions to lower-energy states can proceed by electric dipole radiation, most are forbidden by the selection rules. This tells us that the state  $|200\rangle$  can not go any lower, since the change in the angular momentum is 0. This is called a meta-stable state. However it can actually decay, but by other means.