Lecture 21 - Let's wrap it up

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Abstract

In this lecture we will simply summarize the most important messages from the previous lectures.

1 Lecture 1

We started the semester with the most important cooking recipes of quantum mechanics (Jendrzejewski et al., a).

1.1 Schrödinger picture

1. We have to identify a relevant Hilbert space.

2. Identify the observables that all us to fully describe the quantum state.

Then we solve the Schrödinger equation:

$$i\hbar\partial_t \left|\psi(t)\right\rangle = \hat{H}(t) \left|\psi(t)\right\rangle. \tag{1}$$

For a time-independent Hamilton operator $\hat{H}$, we find eigenstates $\left|\phi_n\right\rangle$ with corresponding eigenenergies E_n :

$$\hat{H} \left|\phi_n\right\rangle = E_n \left|\phi_n\right\rangle. \tag{2}$$

If we know the initial state of a system

$$\left|\psi(0)\right\rangle = \sum_n \alpha_n \left|\phi_n\right\rangle, \tag{3}$$

where $\alpha_n = \left\langle\phi_n|\psi(0)\right\rangle$, we know the full dimension time evolution

$$\left|\psi(t)\right\rangle = \sum_n \alpha_n \left|\phi_n\right\rangle \exp{-iE_n t/\hbar}. \tag{4}$$

1.2 Entanglement

Consider a quantum system S formed by two subsystems S_1 and S_2. For each of them we write:

$$|\psi_1\rangle = \sum_m^M a_m |\alpha_m\rangle, \tag{5}$$

$$|\psi_2\rangle = \sum_n^N b_n |\beta_n\rangle. \tag{6}$$

The full wavefunction $|\psi\rangle$ has the general form:

$$|\psi\rangle = \sum_m^M \sum_n^N c_{mn} |\alpha_m\rangle \otimes |\beta_n\rangle. \tag{7}$$

The system is entangled if we *cannot* write

$$|\psi\rangle = \sum_m^M \sum_n^N a_m b_n |\alpha_m\rangle \otimes |\beta_n\rangle \tag{8}$$

2 Lecture 2

We continued with the cooking recipes in the second lecture (Jendrzejewski et al., b).

2.1 Heisenberg picture

We can also look at the evolution of the system in terms of evolving operators:

$$\frac{d}{dt}\hat{A}_H = \frac{i}{\hbar}\left[\hat{H}, \hat{A}_H\right] + \partial_t \hat{A}_H \tag{9}$$

2.2 Statistical Mixtures and Density Operator

If only the subsystem of a pure quantum state is accessible to measurements, or the state of the system is not known at the microscopic level (statistical ensemble!), the state of the system has to be described by a Hermitian density operator

$$\hat{\rho} = \sum_{n=1}^N p_n |\phi_n\rangle \langle \phi_n|. \tag{10}$$

Here, $\langle \phi_n|$ are the eigenstates of $\hat{\rho}$, and p_n are the probabilities to find the system in the respective states $|\phi_n\rangle$. With this knowledge we can now determine the result of a measurement of an observable A belonging to an operator $\hat{A}$.

$$\langle \hat{A}\rangle = \mathrm{tr}(\hat{\rho} \cdot \hat{A}) = \sum_n p_n \langle \phi_n| \hat{A} |\phi_n\rangle. \tag{11}$$

The time evolution of the density operator can be expressed with the von Neumann equation:

$$i\hbar\partial_t\hat{\rho}(t) = [\hat{H}(t), \hat{\rho}(t)]. \tag{12}$$

2.3 Uncertainty Relation

The product of the variances of two noncommuting operators has a lower limit:

$$\Delta \hat{A} \cdot \Delta \hat{B} \geq \frac{1}{2} \left| \left\langle \left[\hat{A}, \hat{B} \right] \right\rangle \right|, \tag{13}$$

where the variance is defined as $\Delta \hat{A} = \sqrt{\left\langle \hat{A}^2 \right\rangle - \left\langle \hat{A} \right\rangle^2}$.

2.4 Ehrenfest Theorem

With the Ehrenfest theorem, one can determine the time evolution of the expectation value of an operator $\hat{A}$:

$$\frac{d}{dt} \left\langle \hat{A} \right\rangle = \frac{1}{i\hbar} \left\langle \left[\hat{A}, \hat{H} \right] \right\rangle + \left\langle \partial_t \hat{A} t \right\rangle. \tag{14}$$

3 Lecture 3

We now went on to a discussion of the two-level atom (Jendrzejewski et al., c), which has two eigenstates $|0\rangle$.

3.1 Eigenstates

The eigenstates can be expressed in matrix notation:

$$|0\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \qquad |1\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}, \tag{15}$$

We can then write the Hamiltonian in its most general form as:

$$\hat{H} = \frac{\hbar}{2} \begin{pmatrix} \Delta & \Omega_x - i\Omega_y \\ \Omega_x + i\Omega_y & -\Delta \end{pmatrix} \tag{16}$$

Another useful way of thinking about the two-level system is as a spin in a magnetic field. Let us remind us of the definitions of the of the spin-1/2 matrices:

$$s_x = \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad s_y = \frac{\hbar}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad s_z = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{17}$$

We then obtain:

$$\hat{H} = \mathbf{B} \cdot \hat{\mathbf{s}} \text{ with } \mathbf{B} = (\Omega_x, \Omega_y, \Delta) \tag{18}$$

By diagonalizing Eq. (16) we obtain the energies:

$$E_\pm = \pm \frac{\hbar}{2} \sqrt{\Delta^2 + |\Omega|^2} \tag{19}$$

The Eigenstates then read:

$$|\psi_+\rangle = \cos\left(\frac{\theta}{2}\right) e^{-i\varphi/2} |0\rangle + \sin\left(\frac{\theta}{2}\right) e^{i\varphi/2} |1\rangle, \tag{20}$$

$$|\psi_-\rangle = -\sin\left(\frac{\theta}{2}\right) e^{-i\varphi/2} |0\rangle + \cos\left(\frac{\theta}{2}\right) e^{i\varphi/2} |1\rangle, \tag{21}$$

where

$$\tan(\theta) = \frac{|\Omega|}{\Delta} \tag{22}$$

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3.2 Rabi oscillations

The most common question is then what happens to the system if we start out in the bare state $|0\rangle$ and then let it evolve under coupling with a laser ? So what is the probability to find it in the other state $|1\rangle$:

$$P_1(t) = |\langle 1|\psi(t)\rangle|^2. \tag{23}$$

$P_1(t)$ can be expressed with Δ and Ω alone. The obtained relation is called Rabi's formula:

$$P_1(t) = \frac{1}{1 + \left(\frac{\Delta}{|\Omega|}\right)^2} \sin^2\left(\sqrt{|\Omega|^2 + \Delta^2} \frac{t}{2\hbar}\right) \tag{24}$$

3.3 Bloch sphere

We can visualize the two level system as a spin-1/2, evolving on the Bloch sphere. So let us go back to the formulation of the Hamiltonian in terms of spins as in Eq. (18). Applying a field in x-direction leads to a rotation of the spin around the x axis with velocity Ω. We can now use this general picture to understand the dynamics as rotations around an axis, which is defined by the different components of the magnetic field.

4 Lecture 4

We now moved on to understand how some multi-level system, i.e. an atom, evolves under the influence of an oscillating field (Jendrzejewski et al., d). We wrote down the Hamiltonian:

$$\hat{H} = \hat{H}_0 + \hat{V}(t). \tag{25}$$

Here, $\hat{H}_0$ belongs to the atom and $V(t)$ describes the time-dependent field and its interaction with the atom. We assume that $|n\rangle$ is an eigenstate of $\hat{H}_0$ and write:

$$\hat{H}_0 |n\rangle = E_n |n\rangle. \tag{26}$$

The system $|\psi(t)\rangle$ can be expressed as follows:

$$|\psi(t)\rangle = \sum_n \gamma_n(t) e^{-iE_n t/\hbar} |n\rangle, \tag{27}$$

we obtained a set of coupled differential equations

$$i\hbar \dot{\gamma}_k e^{-iE_k t/\hbar} = \sum_n \gamma_n e^{-E_n t/\hbar} \langle k| \hat{V} |n\rangle, \tag{28}$$

$$i\hbar \dot{\gamma}_k = \sum_n \gamma_n e^{-i(E_n - E_k)t/\hbar} \langle k| \hat{V} |n\rangle \tag{29}$$

They determine the full time evolution.

4.1 Rotating wave approximation

We will now assume that the coupling term in indeed an oscillating field with frequency ω_L, so it reads:

$$\hat{V} = \hat{V}_0 \cos(\omega_L t) = \frac{\hat{V}_0}{2}\left(e^{i\omega_l t} + e^{-i\omega_l t}\right) \tag{30}$$

The relevant quantity is then the detuning $\delta = \omega_L - \omega_0$. If it is much smaller than any other energy difference $E_n - E_i$, we directly reduce the system to the following closed system:

$$i\hbar\dot{\gamma}_i = \Omega\tilde{\gamma}_f \tag{31}$$

$$i\hbar\dot{\tilde{\gamma}}_f = \delta\tilde{\gamma}_f + \Omega^*\gamma_i \tag{32}$$

with $\gamma_f = \tilde{\gamma}_f e^{i\delta t/\hbar}$.

4.2 Adiabatic elimination

For far detuning, where $\delta \gg \Omega$ the final state $|f\rangle$ gets barely populated and the time evolution can be approximated to to be zero. This approximation is known as *adiabatic elimination*:

$$i\hbar\dot{\gamma}_i = \frac{|\Omega|^2}{\delta}\tilde{\gamma}_i \tag{33}$$

The last equation described the evolution of the initial state with an energy $E_i = \frac{|\Omega|^2}{\delta}$.

4.3 Perturbation theory

We assume that we can write:

$$\hat{V}(t) = \lambda\hat{H}_1(t) \tag{34}$$

, where λ is a small parameter. Having identified the small parameter λ, we make the *perturbative ansatz*

$$\gamma_n(t) = \gamma_n^{(0)} + \lambda\gamma_n^{(1)} + \lambda^2\gamma_n^{(2)} + \cdots \tag{35}$$

and plug this ansatz in the evolution equations and sort them by terms of equal power in λ.

The 0th order reads

$$i\hbar\dot{\gamma}_k^{(0)} = 0. \tag{36}$$

For the 1st with the initial conditions $\psi(t = 0) = |i\rangle$ we get:

$$i\hbar\dot{\gamma}^{(1)} = e^{i(E_f - E_i)t/\hbar}\langle f|\hat{H}_1|i\rangle \tag{37}$$

Integration with $\gamma_f^{(1)}(t = 0) = 0$ yields

$$\gamma_f^{(1)} = \frac{1}{i\hbar}\int_0^t e^{i(E_f - E_i)t'/\hbar}\langle f|\hat{H}_1(t')|i\rangle\,\mathrm{d}t', \tag{38}$$

so that we obtain the probability for ending up in the final state:

$$P_{i\to f}(t) = \lambda^2\left|\gamma_f^{(1)}(t)\right|^2. \tag{39}$$

Ffor a constant perturbation this results in **Fermi's golden rule**:

$$P_{i\to f} = T\frac{2\pi}{\hbar^2}\left|\langle f|\hat{V}|i\rangle\right|^2\delta(\omega_0) \tag{40}$$

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5 Lecture 5

We now moved on to the most fascinating topic of AMO, the hydrogen atom (Jendrzejewski et al., e). It's Hamiltonian then reads:

$$\hat{H} \simeq \frac{\hat{p}_r^2}{2m_p} - \frac{Ze^2}{4\pi\epsilon_0 r} \tag{41}$$

This Hamiltonian commutes with the angular momentum operator $\vec{L}$, whose components have the commutation relationship:

$$[L_i, L_j] = i\hbar\epsilon_{ijk}L_k \tag{42}$$

So we can decompose the solution over the eigenvalues of

$$\hat{\vec{L}}^2 \left|l, m_l\right\rangle = \hbar^2 l(l+1)\left|l, m_l\right\rangle \tag{43}$$

$$\hat{L}_z \left|l, m_l\right\rangle = \hbar m_l \left|l, m_l\right\rangle \tag{44}$$

- l is a non-negative integer and it is called the **orbital angular momentum quantum number**.
- m_l takes values $-l, -l+1, ..., l-1, l$ and it is sometimes called the **projection of the angular momentum**.

The corresponding wave functions are

$$\langle\theta, \phi|l, m_l\rangle = Y_{lm}(\theta, \phi). \tag{45}$$

Where $Y_{lm}(\theta, \phi)$ are the **spherical harmonics**. We then make the ansatz:

$$\psi(r, \theta, \phi) = R(r)Y_{lm}(\theta, \phi) \tag{46}$$

Substituting $R(r) = u(r)/r$ leads to

$$-\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2}u(r) + \underbrace{\left(-\frac{Ze^2}{4\pi\epsilon_0 r} + \frac{\hbar^2}{2\mu}\frac{l(l+1)}{r^2}\right)}_{V_{\text{eff}}}u(r) = E\,u(r), \tag{47}$$

which is known as the "radial wave equation". It is a very general result for *any* central potential. The energies read:

$$E_n = -\frac{R_{y,\text{m}}}{n^2} \qquad \text{with} \qquad n = 1, 2, 3, \cdots \tag{48}$$

$$R_{y,\text{m}} = \frac{\mu Z^2 e^4}{32\pi^2\epsilon_0^2\hbar^2} \tag{49}$$

The typical energy scale for distances is the Bohr radius for infinite nuclear mass

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} \tag{50}$$

$$= \frac{\hbar}{m_e c\alpha} = 0.5 \text{ angstrom} = 0.05 \text{ nm}. \tag{51}$$

For the energy we get

$$R_{y,\infty} = \frac{m_e e^4}{32\pi^2 \epsilon_0^2 \hbar^2} \tag{52}$$

$$= \frac{1}{2} \underbrace{m_e c^2}_{511 \text{ keV}} \alpha^2 \approx 13.6 \text{ eV}. \tag{53}$$

The constant

$$\alpha = \frac{e^2}{4\pi\epsilon_0 \hbar c} = \frac{1}{137.035999139(31)} \tag{54}$$

is the fine structure constant.

6 Lecture 6

We had a short intermezzo on the harmonic oscillator and then talked about the electric dipole operator (Jendrzejewski et al., f):

6.1 The harmonic oscillator

Its hamiltonian reads:

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{m\omega^2}{2}\hat{x}^2 \tag{55}$$

We will define $p = P\sqrt{m\omega}$ and $x = \frac{X}{\sqrt{m\omega}}$. The next step is then to define the ladder operators:

$$\hat{a} = \frac{1}{\sqrt{2\hbar}}(X + iP) \tag{56}$$

$$\hat{a}^\dagger = \frac{1}{\sqrt{2\hbar}}(X - iP) \tag{57}$$

$$\tag{58}$$

So the Hamiltonian can now be written as:

$$\hat{H} = \hbar\omega\left(\hat{N} + \frac{1}{2}\right) \text{ with } \hat{N} = a^\dagger a \tag{59}$$

The Fock basis is defined by:

$$\hat{N}|n\rangle = n|n\rangle \tag{60}$$

The ladder operators act as:

$$\hat{a}|n\rangle = \sqrt{n}|n-1\rangle \tag{61}$$

$$\hat{a}^\dagger|n\rangle = \sqrt{n+1}|n+1\rangle \tag{62}$$

So we can construct the full basis by just defining the action of the lowering operator on the zero element $a|0\rangle = 0$ and the other operators are then constructed as:

$$|n\rangle = \frac{(a^\dagger)^n}{\sqrt{n!}}|0\rangle \tag{63}$$

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6.2 Electric dipole operator

We now saw the the action of an oscillating electric field on the atom can be described by

$$\hat{H}_1(t) = -e\hat{\vec{r}} \cdot \vec{E}(t) = -\hat{\vec{D}} \cdot \vec{E}(t) \tag{64}$$

Now we choose

$$\vec{E} = E_0 \vec{\epsilon} \cos\left(\omega t - \vec{k} \cdot \vec{r}\right) \tag{65}$$

and do time-dependent perturbation theory (see (Jendrzejewski et al., a)):

$$|\psi(t)\rangle = \gamma_1(t)e^{-iE_1 t/\hbar} |1\rangle + \gamma_2(t)e^{-iE_2 t/\hbar} |2\rangle \tag{66}$$

$$+ \sum_{n=3}^{\infty} \gamma_n e^{-iE_n t/\hbar} |n\rangle \tag{67}$$

As initial condition we choose

$$\gamma_i(0) = \begin{cases} 1 & \text{for} \quad i = 1 \\ 0 & \text{for} \quad i > 1 \end{cases} \tag{68}$$

We write $\omega_0 = (E_2 - E_1)/\hbar$ and get for the second order:

$$\gamma_2(t) = \overbrace{\frac{E_0}{2\hbar} \left\langle 2|\hat{\vec{D}} \cdot \vec{\epsilon}|1\right\rangle}^{\text{Rabi frequency } \Omega} \underbrace{\left(\frac{e^{i(\omega_0+\omega)t} - 1}{\omega_0 + \omega} + \frac{e^{i(\omega_0-\omega)t} - 1}{\omega_0 - \omega} \right)}_{\text{time evolution of the system}} \tag{69}$$

The term before the round brackets is called dipole matrix element:

$$\left\langle 2|\hat{\vec{D}} \cdot \vec{\epsilon}|1\right\rangle = e \int \psi_2(\vec{r}) \cdot \vec{r} \cdot \vec{\epsilon} \cdot \psi_1(\vec{r}) \, d\vec{r}. \tag{70}$$

From the form of (70), we found that the orbital angular momentum has to change for dipole transitions $\Delta l = \pm 1$. The selection rules for different polarizations of light are then visualized in Fig. 1
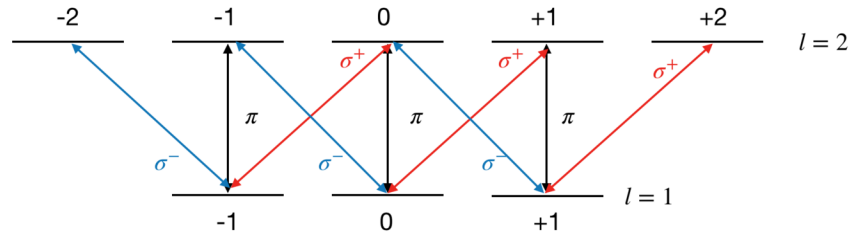

Figure 1: Dipole selection rules for different polarizations of light.

7   Lecture 7

We moved on to the discussion of stationnary perturbation theory examplified at the hydrogen atom (Jendrzejewski et al., g).

7.1 Pertubation theory

We set up the problem as:

$$\left(\hat{H}_0 + \lambda \hat{W}\right) |\psi\rangle = E |\psi\rangle \tag{71}$$

λ is a very small parameter and $\hat{H}_0$ is describing the hydrogen atom system. We will note the eigenvalues and eigenstates of this system as:

$$\hat{H}_0 |\psi_n\rangle = \epsilon_n \psi_n \tag{72}$$

While, we do not know the exact solution of $|\psi\rangle$ and the energy E, we decide to decompose them in the following expansion of the small parameter λ:

$$|\psi\rangle = |0\rangle + \lambda |1\rangle + \lambda^2 |2\rangle + O(\lambda^3) \tag{73}$$

$$E = E_0 + \lambda E_1 + \lambda^2 E_2 + O(\lambda^3) \tag{74}$$

To zeroth order in λ we obtain:

$$\hat{H}_0 |0\rangle = E_0 |0\rangle \tag{75}$$

For the first order we obtain:

$$E_1 = \langle \psi_n | \hat{W} |\psi_n\rangle \tag{76}$$

$$|1\rangle = \sum_{i \neq n} \frac{\langle \psi_i | \hat{W} |\psi_n\rangle}{(\epsilon_n - \epsilon_i)} |\psi_i\rangle \tag{77}$$

Second order pertubation results in:

$$E_2 = \sum_{i \neq n} \frac{|\langle \psi_i | \hat{W} |\psi_n\rangle|^2}{(\epsilon_n - \epsilon_i)} \tag{78}$$

7.2 Static external magnetic fields

The potential energy of a bound electron in a magnetic field $\vec{B} = B_0 \vec{e}_z$ is then:

$$V_B = -\vec{M}_L \cdot \vec{B} \tag{79}$$

$$= \frac{\mu_B}{\hbar} L_z B_0 \tag{80}$$

Its contribution is directly evaluated from Eq. (76) to be:

$$E_{Zeeman} = \mu_B m B_0 \tag{81}$$

This is the Zeeman splitting of the different magnetic substates.

7.3 Relativistic corrections

We can write for the energy:

$$E_n = \frac{1}{2} \underbrace{m_e c^2}_{\text{rest mass energy}} Z^2 \alpha^2 \frac{1}{n^2} \tag{82}$$

We conclude:

- Relativistic effects are most pronounced for deeply bound states of small quantum number n.

- Relativistic effects effects will become important once $(Z\alpha) \approx 1$, so they will play a major role in heavy nuclei.

It leads to spin-orbit coupling:

$$\hat{H}_{LS} = \frac{g_e}{4\pi\epsilon_0} \frac{e^2}{2m_e^2 c^2 r^3} \hat{\vec{L}} \cdot \hat{\vec{S}} \tag{83}$$

, where $\vec{S}$ is the spin$1/2$ of the electron. It breaks the conservation of orbital angular momentum. However, the sum of spin and orbital angular momentum:

$$\vec{J} = \vec{L} + \vec{S} \tag{84}$$

will commute. We can now rewrite eq. (83) in terms of the conserved quantities through the following following little trick:

$$\hat{\vec{L}} \cdot \hat{\vec{S}} = \frac{1}{2} \left(\hat{\vec{J}}^2 - \hat{\vec{L}}^2 - \hat{\vec{S}}^2 \right) \tag{85}$$

This directly implies that $\hat{J}^2$, $\hat{L}^2$ and $\hat{S}^2$ are new conserved quantities of the system. We use:

$$\left\{ \hat{H}_0, \hat{\vec{L}}^2 \hat{\vec{S}}, \hat{\vec{J}}, \hat{J}_z \right\}. \tag{86}$$

The corresponding basis states $|n, l, j, m_j\rangle$ are given by:

$$|n, l, j, m_j\rangle = \sum_{m_l, m_s} |n, l, m_l, m_s\rangle \underbrace{\langle n, l, m_l, m_s | n, l, j, m_j\rangle}_{\text{Clebsch-Gordan coefficients}} \tag{87}$$

8   Lecture 8

We moved on to the helium atom (Jendrzejewski et al., s):

$$H = -\frac{\hbar^2}{2m_e}\nabla_{r_1}^2 - \frac{\hbar^2}{2m_e}\nabla_{r_2}^2 + \frac{e^2}{4\pi\epsilon_0}\left(-\frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}} \right) \tag{88}$$

In natural units we found:

$$\tilde{H} = -\frac{1}{2}\nabla_{\tilde{r}_1}^2 - \frac{1}{2}\nabla_{\tilde{r}_2}^2 + \left(-\frac{Z}{\tilde{r}_1} - \frac{Z}{\tilde{r}_2} + \frac{1}{\tilde{r}_{12}} \right) \tag{89}$$

Within these units we have for the hydrogen atom $E_n = \frac{Z^2}{2}\frac{1}{n^2}$

8.1   Symmetries

The **exchange** operator is defined as:

$$P_{12}\psi(r_1, r_2) = \psi(r_2, r_1) \tag{90}$$

So we can see that there are two sets of eigenvalues with $\lambda = \pm 1$.

$$P_{12}\psi_{\pm} = \pm\psi_{\pm} \tag{91}$$

We will call:

- ψ_+ are para-states

- ψ_- are ortho-states

It is a first symmetry of the helium atom.

8.2 Spin and Pauli principle

So we can decompose the total wave function as:

$$\overline{\psi} = \psi(\mathbf{r}_1, \mathbf{r}_2) \cdot \chi(1,2) \tag{92}$$

To construct the full wave function we need to take into account the *Pauli* principle, which telles us for Fermions that the *full* wavefunction should anti-sysmmetrc under exchange of particles:

$$\overline{\psi}(q_1, q_2, \cdots, q_i, \cdots, q_j, \cdots) = -\overline{\psi}(q_1, q_2, \cdots, q_j, \cdots, q_i, \cdots) \tag{93}$$

This tells us that each quantum state can be only occupied by a single electron at maximum. Sorting out the solutions we have

$$\chi_- = \frac{1}{\sqrt{2}} \left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle \right) \tag{94}$$

$$\chi_{+,1} = |\uparrow\uparrow\rangle \tag{95}$$

$$\chi_{+,1} = \frac{1}{\sqrt{2}} \left(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle \right) \tag{96}$$

$$\chi_{+,-1} = |\downarrow\downarrow\rangle \tag{97}$$

$$\tag{98}$$

So χ_+ is associated with spin 1 and χ_- is associated with spin 0.

8.3 Level scheme

We can now continue through the level scheme of Hydrogen and try to understand our observations. No radiative transitions between $S = 0$ and $S = 1$, which means that we will basically have two independent schemes. They are characterized by:

- electronic excitations, which are the main quantum numbers N.
- orbital angular momentum, with quantum number L.
- total spin with quantum number S
- total angular momentum J, but the spin-orbit coupling in Helium is actually extremly small.

We will then use the term notation:

$$N^{2S+1}L_J \tag{99}$$

the superscript is giving the multiplicity or the number of different J levels.

8.4 Independent particle model

We will now go back to the influence of the interaction on the eigenenergies of the system. Going back to Eq. (89), we will treat the single particle Hamiltonians as unperturbed system and H_{12} as the perturbation:

$$H_0 = -\frac{1}{2}\nabla_{r_1}^2 - \frac{Z}{r_1} - \frac{1}{2}\nabla_{r_2}^2 - \frac{Z}{r_2} \tag{100}$$

$$H_1 = -\frac{1}{r_{12}} \tag{101}$$

At this stage we can try to calculate the groundstate energy. The electron interaction leads within first order perturbation theory to an energy shift of:

$$E_0^{(1)} = \langle \psi_0 | \frac{1}{r_{12}} | \psi_0 \rangle = \frac{5}{8}Z \tag{102}$$

In the variational approach, we will try to find the minimal energy of the ground state. Namely we will minimize:

$$E_{var} = \frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle} \tag{103}$$

To apply the variational approach, we introduce a *screened charge* Z_{eff} in the the groundstate of the hydrogen atom, which reads:

$$\psi_{var}(r_1, r_2) = e^{-Z_{eff}(r_1 + r_2)} \tag{104}$$

It becomes minimal at

$$Z_{eff} = Z - \frac{5}{16} \tag{105}$$

9   Lecture 9

We moved on to the properties of the excited states (Jendrzejewski et al., h).

9.1   Exchange Interaction

To attack this problem we approach it pertubatively in the free independent particle model. And we found for the singlet, triplet states:

$$\Delta E_S = J_{nl} + K_{nl} \tag{106}$$
$$\Delta E_T = J_{nl} - K_{nl} \tag{107}$$

The first term is called *direct* (Coulomb) term and the second term is known as *exchange* term.

9.2   Dipole selection rules

Due to the LS coupling scheme, we get:

$$|\psi(\vec{r_1}, \vec{r_2})\rangle \otimes |\chi(1,2)\rangle. \tag{108}$$

There is no entanglement between the degrees of freedom and no mixed symmetry between spin and spatial degree of freedom! If we plug this into the dipole coupling we get,:

$$\left\langle i | \hat{\vec{r}} | f \right\rangle = \langle \chi(1,2) | \chi'(1,2) \rangle \cdot \left\langle \psi(\vec{r_1}, \vec{r_2}) | \hat{\vec{r}} | \psi'(\vec{r_1}, \vec{r_2}) \right\rangle \tag{109}$$

1. The first factor has to be zero if the total spin is not the same. Then the relative alignment is not the same. Thus, there are no dipole transitions between singlet and triplet atoms!

2. From the second factor we infer that transitions can only occur between states of opposite parity, e.g., $\Delta l = \pm 1$, together with angular momentum conservation.

10   Lecture 10

In lecture 10 we studied the propagation of light through dielectric media (Jendrzejewski et al., i). We assume a mono-chromatic plane wave to come in, such that we can write down the electric field as:

$$\vec{E}_{in} = E_0 \vec{\epsilon} e^{ikz - i\omega_L t} \tag{110}$$

This incoming field will polarizes the gas of dipoles. For the propagation we will do the following assumptions:

- The atoms are independent.

- We can describe them as small dipoles.

- We can describe the light in the semi-classical approximation.

We can then write the dipole operator as:

$$\langle \vec{D} \rangle = E_0 \vec{\alpha} \tag{111}$$

We call α the **polarizability**. For a large gas with a constant density of dipoles n, we obtain a macroscopic polarization of:

$$\vec{P} = n \langle \vec{D} \rangle \tag{112}$$

$$= \epsilon_0 \chi \vec{E} \tag{113}$$

$$\chi = \frac{n\alpha}{\epsilon_0} \tag{114}$$

χ is the susceptibility of the gas.

10.1 Propagation of light

At this stage we would like to understand the propagation of an electric field through such a polarized medium. The general Maxwell equation actually reduces to:

$$\frac{\partial}{\partial z}\mathcal{E} + \frac{1}{c}\frac{\partial}{\partial t}\mathcal{E} = \frac{ik}{2\epsilon_0}\mathcal{P} \tag{115}$$

This equation becomes especially transparent, if we investigate it for very long times, such that we can perform a Fourier transformation and obtain:

$$\frac{\partial}{\partial z}\mathcal{E} = i\frac{\omega}{c}\mathcal{E} + \frac{ik}{2\epsilon_0}\mathcal{P} \tag{116}$$

$$= i\left(\frac{\omega}{c} + \frac{k}{2}\chi(\omega)\right)\mathcal{E} \tag{117}$$

$$\mathcal{E}(\omega, z) = E_0 e^{i\left(\frac{\omega}{c} + \frac{k}{2}\chi(\omega)\right)z} \tag{118}$$

We can then see that:

- The imaginary part of the susceptibility leads to absorption on a scale $l^{-1} = \frac{k}{2}\text{Im}(\chi(0))$

- The real part describes a phase shift. The evolution of the electric field can be seen as propagating with a wavevector $k \to k + \frac{k}{2}\text{Re}(\chi(0))$, so the dielectric medium has a refractive index $n = 1 + \frac{\text{Re}(\chi(0))}{2}$

If the electric field has a certain frequency distribution, we obtain:

$$\mathcal{E}(t, z) = e^{izk\chi(0)/2}\mathcal{E}(t - z/v_g, 0) \tag{119}$$

$$v_g = \frac{c}{1 + \frac{\omega_L}{2}\frac{d\chi}{d\omega}} \tag{120}$$

So the group velocity is controlled by the derivative of the susceptibility !

10.2   The two-level system

In this basis, the dipole element reads:

$$\langle D \rangle = \langle e | D | g \rangle \, \gamma_e^* \gamma_g \tag{121}$$

$$= d\sigma_{eg} \tag{122}$$

In the second line we introduced the notations:

- $d = \langle e | D | g \rangle$

- The product $\gamma_e^* \gamma_g$ can identified with the off-diagonal component of the density operator $\sigma = | \psi \rangle \langle \psi |$. We will often call it **coherence**.

This density operator approach allows us to introduce spontaneous decay in a very straight-forward fashion. So the full equations read now:

$$\dot{N}_g = i\Omega(\sigma_{eg} - \sigma_{ge}) + \Gamma N_e \tag{123}$$

$$\dot{\sigma}_{ge} = -i\delta\sigma_{ge} + i(N_g - N_e)\Omega - \Gamma_2\sigma_{ge} \tag{124}$$

At this stage we can find the steady-state solutions by setting $\dot{N}_g = \dot{\sigma}_{ge} = 0$. This leads too:

$$N_e = \frac{1}{2} \frac{\Omega^2 \frac{\Gamma_2}{\Gamma}}{(\omega_0 - \omega_L)^2 + \Gamma_2^2 + \Omega^2 \frac{\Gamma_2}{\Gamma}} \tag{125}$$

$$\sigma_{ge} = i\frac{\Omega}{2} \frac{\Gamma_2 - i(\omega_L - \omega_0)}{\Gamma_2^2 + (\omega_0 - \omega_L)^2 + \Omega^2\Gamma_2/\Gamma} \tag{126}$$

For very small coupling strength we can neglect the Ω dependence in the coherence and hence the susceptibility reads:

$$\alpha = \frac{d^2}{2} \frac{(\omega_L - \omega_0) + i\Gamma_2}{\Gamma_2^2 + (\omega_0 - \omega_L)^2} \tag{127}$$

We obtain now rather directly that:

- Absorption is maximal on resonance.

- There is no dephasing on resonance.

- For large detunings the absorption can be increasingly neglected and the media becomes refractive as it only keeps an optical index.

The population and coherence in the two-level system will saturate as a substantial amount of atoms is excited and the excited fraction is limited to $1/2$ of the atoms. This kind of observations motivates for practical purposes to introduce the saturation intensity $I_{sat} \propto \frac{\Gamma^2}{2}$, which allows us to rewrite the previous to equations as:

$$N_e = \frac{1}{2} \frac{I/I_{sat}}{1 + I/I_{sat}} \tag{128}$$

11 Lecture 11

We now went on to the laser (Jendrzejewski et al., j). For the propagation of light we found in general:

$$\frac{dI}{dz} = (N_e - N_g)\sigma I \tag{129}$$

So if we have most atoms in the excited state and neglect the atoms in the ground state we can actually have light amplification. Amplification will happen if the intensity after a round trip is higher than the initial one:

$$G^{(0)} > \frac{1}{(1-T)(1-A)} \tag{130}$$

11.1 Steady-state operation

Assuming that the lasing condition is fullfilled, we have to have an electric field, which remains exactly constant after each round trip.This implies to conditions:

- The gain has to cancel the losses:

$$G = \frac{1}{(1-T)(1-A)} \tag{131}$$

- The phase after the round trip has to be a multiple of 2π

For a cavity of length L, the wavelength λ_p has to be an integer fraction:

$$L_{cav} = p\lambda_p \text{ with } p \in \mathbb{N} \tag{132}$$

$$\omega_p/2\pi = p\frac{c}{L} \tag{133}$$

12 Lecture 12

Having set up the very basics for atom-light interaction we dived into the study of entanglement (Jendrzejewski et al., k).

We learned about parametric down-conversion on a non-linear crystal, which is heavily pumped. Importantly, we saw that it allows for th creation of entangled photons.

The two emitted photons are analyzed by rotatable polarizers $\hat{A}(\theta)$, which has two detection paths ± 1. We can express it then in our basis states of vertical polarization $|V\rangle$ and horizontal polarization $|H\rangle$. The polarizer aligned with H has eigenvalues:

$$\hat{A}|H\rangle = +|H\rangle \tag{134}$$

$$\hat{A}|V\rangle = -|V\rangle \tag{135}$$

The possible outcome of our experiments are the four states $\{HH, HV, VH, VV\}$ and hence we could decompose our full wavefunction as:

$$|\psi\rangle = c_0|HH\rangle + c_1|HV\rangle + c_2|VH\rangle + c_3|VV\rangle \tag{136}$$

We then found that the created state we entangled. We could quantify it through the density operator:

$$\hat{\rho} = \sum_i \eta_i|i\rangle\langle i| \tag{137}$$

- The reduced density operator, which shows mixed states if there is entanglement:

$$\hat{\rho}_1 = \text{tr}_2(\hat{\rho}) \tag{138}$$

In this case, $\hat{\rho}$ is the density operator of a pure state and tr_2 is the trace over the Hilbert space of particle 2.

- The von Neumann entropy, which measures the remaining uncertainty within a quantum state:

$$S = -\text{tr}(\hat{\rho}\ln\hat{\rho}) \tag{139}$$

$$= -\sum_i \eta_i \ln \eta_i = \sum_i \eta_i \ln \frac{1}{\eta_i} \tag{140}$$

The experimental observation were then compared to Bell's inequalities for local observables:

$$S = E(\theta_1, \theta_2) - E(\theta_1, \theta_2') + E(\theta_1', \theta_2) + E(\theta_1', \theta_2') \tag{141}$$

$$-2 \leq S \leq 2 \tag{142}$$

The E are the expectation values for the rotated beam splitters. This is known as the Bell–Clauser–Horn–Shimony–Holt (CHSH) inequalities.

13 Lecture 13

We then moved on to the study of multi-electron systems (Jendrzejewski et al., l).

In natural units, the Hamiltonian can be written as:

$$\hat{H} = \sum_i^N \left(-\frac{1}{2}\vec{\nabla}_{r_i}^2 - \frac{Z}{r_i} \right) + \sum_{i<j} \frac{1}{r_{ij}}. \tag{143}$$

13.1 The central field approximation

This problem is hard to solve, but we could massively simplify it through the central field approximation:

$$\hat{H} = \hat{H}_s + \hat{H}_1 \tag{144}$$

$$\hat{H}_s = \sum_i^N \left(-\frac{1}{2}\vec{\nabla}_{r_i}^2 + V_{\text{cf}}(r_i) \right) \tag{145}$$

$$V_{\text{cf}}(r_i) = -\frac{Z}{r_i} + S(r_i), \tag{146}$$

The perturbation is then difference between the spherically symmetric part of the interaction and the true electron-electron interaction:

$$\hat{H}_1 = \sum_{i<j} \frac{1}{r_{ij}} - \sum_i S(r_i) \tag{147}$$

$S(r_i)$ describes now the screening of the nucleus due to the other electrons. We now focused on the study of the part with spherical symmetry $\hat{H}_s$, which further made all the particles independent. The ψ_i can be split up into a radial and an angular part. For the radial part we get $u(r) = r \cdot R(r)$:

$$\left(-\frac{1}{2}\frac{d^2}{dr^2} + V_{\text{cf}}(r) + \frac{l(l+1)}{2r^2} \right) u_{nl} = E_{nl}u_{nl}(r). \tag{148}$$

The major difference to the H atom is that the degeneracy of the l levels is lifted because of V_{cf}. The effective potential has then to be calculated numerically.

13.2   The periodic table

We then have the following quantum numbers:

- n, which is electron shell.

- l, which is the orbital angular momentum with $l < n$.

- s, which is the spin of the electron and it can be $\pm 1/2$

As the electrons are fermions we can fill up each of the nl states with two of them. We then write down the configuration of the electron by writing down the numbers of electrons per nl configuration. So we get the periodic table shown. We typically use the following notation:

- A *configuration* is the distribution of the electrons over the different orbits.

- Electrons with the same n are part of the same *shell*.

- Electrons with the same n and l are part of the same *sub-shell*.

- The inner shells are typically filled and form the *core*.

- The outermost shell is typically named the *valence* shell.

13.3   The quantum defect

For alakils we could describe the screening effect empirically through the *quantum defect*. We simply write down the energy levels as:

$$E_{nl} \cong -R_{y,\infty} \cdot \left(\frac{1}{n - \delta_l} \right)^2 , \tag{149}$$

14   Lecture 14

We now also added the residual coupling and the spin to the problem (Jendrzejewski et al., p).

14.1   On the residual coupling

This conservation of single angular momenta will be broken by $\hat{H}_1$. However, these forces are internal, which implies that the total angular momentum $\vec{L} = \sum_i \vec{l}_i$ is conserved. So we should label the states in the complex Hamiltonian by $\vec{L}$. The total angular momentum will then set the symmetry of the spatial wavefunction. This has wide-reaching consquence on the spin degree of freedom through exchange interaction.

14.2   The Pauli principle and spin

- According to the Pauli principle, each single-particle state can be occupied only by one electron. After distributing all electrons over different single-particle eigenstates ("orbitals"), the resulting state needs to be fully antisymmetrized (Slater determinant).

- There is a simplification for atoms with many electrons: The angular momenta and spins of a complete subshell with n, l, $\{m_{-l}, \cdots, m_l\}$ add to zero and can be ignored in the further considerations ("shell structure").

- Alkali atoms are the simplest atoms with shell structure: All but one *valence* electron add to $L = 0, S = 0$. The ground state thus has $L = 0, S = 1/2$.

- For more complex atoms, the valence electrons couple to a total orbital angular momentum L with a given symmetry according to particle exchange.

14.3 Fine splitting

To take into account the spin, we can decompose the Hamiltonian as follows:

$$\hat{H} = \underbrace{\sum_i^N \left(\frac{1}{2} \vec{\nabla}_{\vec{r}_i}^2 + V_{\text{cf}}(r_i) \right)}_{\hat{H}_0} + \underbrace{\sum_{j>i}^N \left(\frac{1}{r_{ij}} - S(r_i) \right)}_{\hat{H}_1} + \underbrace{\sum_i^N c_i(\vec{r}_i) \hat{\vec{L}}_i \cdot \hat{\vec{S}}_i}_{\hat{H}_2} \tag{150}$$

The term $\hat{H}_0$ is from the central field and the independent particle model. The Hamiltonian $\hat{H}_1$ results from the residual electrostatic interaction and the Hamiltonian $\hat{H}_2$ comes from the spin-orbit coupling of individual electrons.

The question is now which term dominates. Since $\hat{H}_2 \propto (Z\alpha)^2$, we can ignore it if Z is small. This is the case for light atoms. So far, we have been concerned with the "Russell-Saunders" coupling, also known as LS coupling. However, for atoms with large Z, the term $\hat{H}_2$ in the Hamiltonian (150) might become large, since it is proportional to $(Z\alpha)^2$. We can ignore $\hat{H}_1$ instead.

According to $\hat{H}_2$ the individual electron orbital angular momentum l pairs with the spin s of the same electron to form the total electron angular momentum j. This will lead us to the concept of jj coupling.

14.4 Hyperfine splitting

The nucleus has a spin angular momentum $\vec{I}$, which leads to a magnetic moment:

$$\vec{\mu}_I = g_I \mu_N \vec{I} \tag{151}$$

We have introduced the new constants:

- g_I, which is always in the order of one, but it changes due to the changing structure of the different nuclei.

- The *nuclear magneton* $\mu_N = \frac{e\hbar}{2m_p} = \frac{m_e}{m_p} \mu_B$.

As with the spin-orbit coupling this nuclear spin will experience the magnetic field produced by the motion of the electrons $\vec{B}_{el}$ and we have:

$$H_{hfs} = -\vec{\mu}_I \cdot \vec{B}_{el} \tag{152}$$

$$= A_{hfs} \vec{I} \vec{J} \tag{153}$$

This couples $\vec{I}$ and $\vec{J}$ and the full structure is given by total angular momentum:

$$\vec{F} = \vec{J} + \vec{I} \tag{154}$$

We saw then that it can have big practical importance in hydrogen, Cs clocks and cold atoms.

15 Lecture 15

We moved on to simple diatomic molecules (Jendrzejewski et al., q). We started out with the molecular hydrogen ion. The full Hamiltonian of the system at study would read:

$$\hat{H} = -\frac{1}{2}\nabla_{\mathbf{r}}^2 - \frac{1}{2M}\left(\nabla_{\mathbf{R}_A}^2 + \nabla_{\mathbf{R}_B}^2\right) + V(\mathbf{r}, \mathbf{R}_A, \mathbf{R}_B) \tag{155}$$

15.1 The Born-Oppenheimer approximation

The idea of the **Born-Oppenheimer approximation** is to separate the fast electronic motion from the slow motion of the heavy nuclueus ($M = 1836$). So the ansatz is:

$$\Psi(\mathbf{R}_A, \mathbf{R}_B, \mathbf{r}) = \psi_e(\mathbf{R}_A, \mathbf{R}_B, \mathbf{r}) \cdot \psi_n(\mathbf{R}_A, \mathbf{R}_B) \tag{156}$$

After some approximations we obtain:

$$\psi_e \hat{T}_n \psi_n + \left(\hat{T}_e \psi_e + V \psi_e\right) \psi_n = E \psi_e \psi_n \tag{157}$$

So we will first solve the *electronic motion*:

$$\left(\hat{T}_e + \hat{V}\right) \psi_e = E_e(\mathbf{R}_A, \mathbf{R}_B) \psi_e \tag{158}$$

To be explicit we obtain for the ionic hydrogen:

$$H_e = -\frac{1}{2}\nabla_{\mathbf{r}}^2 - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R} \tag{159}$$

At this stage we can just focus on the electronic part to understand the structure of simple diatomic molecules, while assuming that R is an independent parameter. Most importantly, we will focus at usual on symmetries, which will tell us more about the allowed states in the system.

In the second step we solve the nuclear motion:

$$\hat{T}_n \psi_n + E_e \psi_n = E \psi_n \tag{160}$$

15.2 Symmetries of the electronic wavefunction

This discussion follows along similiar lines as for the hydrogen atom and the helium atom. We basically can categorize the different states by their properties. This will help us later enormously to understand allowed transition etc.

For any (diatomic) molecule we break the spherical symmetry that we relied on for the atomic systems. This means that angular momentum is not a conserved quantity anymore.

However, the Hamiltonian (159) is invariant under the rotation around the axis of the diatomic molecule, so L_z is conserved. Here the quantum number can have the integer values $\Lambda = 0, 1, 2, \cdots$. We also note them $\Sigma, \Pi, \Delta, \Phi$ or $\sigma, \pi, \delta, \phi$ for single electrons.

We can further perform an reflection containing the axis of the molecule $\mathbf{R}$. So for each Λ we have positive and negative values. We can use them to categorize states by $\Lambda^{\pm}$.

We further have symmetry under parity operation for *homo-nuclear, diatomic* molecules A_2, see (159).

If the system does not have explicit spin-orbit coupling, the total spin S of the system will be conserved. So the full notation for electronic states is typically:

$$^{2S+1}\Lambda_{g,u}^{\pm} \tag{161}$$

Most of the time the ground state of the system is $^1\Sigma_g^+$.

15.3   Linear combination of atomic orbitals

We then moved on to study the stability of the states through decomposition of the molecule wavefunction over the atomic orbitals of its components. We could make the simple Ansatz:

$$\psi_e(\mathbf{r}) = c_1 \psi_{1s}(\mathbf{R}_A) + c_2 \psi_{1s}(\mathbf{R}_B) \tag{162}$$

Going through the symmetry requirements, we find that we can write the full wavefunction as:

$$\psi_{g,u}(\mathbf{r}) = \frac{1}{\sqrt{2 \pm 2S}} \left(\psi_{1s}(\mathbf{R}_A) \pm \psi_{1s}(\mathbf{R}_B) \right) \tag{163}$$

The contribution S describes the overlap of the two atomic orbitals

$$S = \int d\mathbf{r} \psi_{1s}^*(\mathbf{R}_A) \psi_{1s}(\mathbf{R}_B) \tag{164}$$

We can then evaluate the energy of the two states through the variational principle:

$$E_{g,u} = \langle \psi_{g,u} | \hat{H}_e | \psi_{g,u} \rangle \tag{165}$$

$$= \frac{1}{2 \pm 2S} \left(\langle \psi_A | \pm \langle \psi_B | \right) \hat{H}_e \left(|\psi_A\rangle \pm |\psi_B\rangle \right) \tag{166}$$

$$= \frac{E_{AA} \pm E_{AB}}{1 \pm S} \tag{167}$$

$$\tag{168}$$

In the most simplistic interpretation the gerade state does not have a node in the middle and it is therefore of smaller kinetic energy.

15.4   Neutral hydrogen molecule

In the following we will only consider the electronic part, which adds up too:

$$\hat{H} = H_{0,1} + H_{0,2} + \frac{1}{r_{12}} + \frac{1}{R} \tag{169}$$

$$H_{0,i} = -\frac{1}{2}\nabla_{\mathbf{r}_i}^2 - \frac{1}{r_{A,i}} - \frac{1}{r_{B,i}} \tag{170}$$

So we can make the Ansatz:

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \psi_g(\mathbf{r}_1) \cdot \psi_g(\mathbf{r}_2) \tag{171}$$

$$= \frac{1}{2+2S} \left(\psi_{1s}(\mathbf{r}_{A1})\psi_{1s}(\mathbf{r}_{B2}) + \psi_{1s}(\mathbf{r}_{B1})\psi_{1s}(\mathbf{r}_{A2}) + \psi_{1s}(\mathbf{r}_{A1})\psi_{1s}(\mathbf{r}_{A2}) + \psi_{1s}(\mathbf{r}_{B1})\psi_{1s}(\mathbf{r}_{B2}) \right) \tag{172}$$

The first two terms describe **kovalent binding**. They describe situations where each electron is associated with one core. The last two terms describe **ionic binding** as one associated both electrons with a single atom and then looks one the attraction of another ionic core. This is quite similiar to the interaction in the H_2^+ molecule.

Within this approach, one actually finds a binding energy of $E_b = -2.64\,\text{eV}$ at an equilibrium distance of $R_e = 1.4a_0$. A substantial approximation was here that we neglected the interaction between the electrons, which should repel.

As the two electrons should repel each other, we can assume that the ionic binding is strongly suppressed. So the wavefunction is now assumed to be:

$$\psi_{HL} = \frac{1}{\sqrt{2+2S^2}} \left(\psi_{1s}(\mathbf{r}_{A1})\psi_{1s}(\mathbf{r}_{B2}) + \psi_{1s}(\mathbf{r}_{B1})\psi_{1s}(\mathbf{r}_{A2}) \right) \tag{173}$$

Again, the wavefunction cannot be factorized and the two electrons are entangled because of the interactions. Recognize the common theme with the Helium atom. Calculation of the binding energy within this approximation leads to $E_b = -3.14\,\text{eV}$ and $R_e = 1.6a_0$.

16 Lecture 16

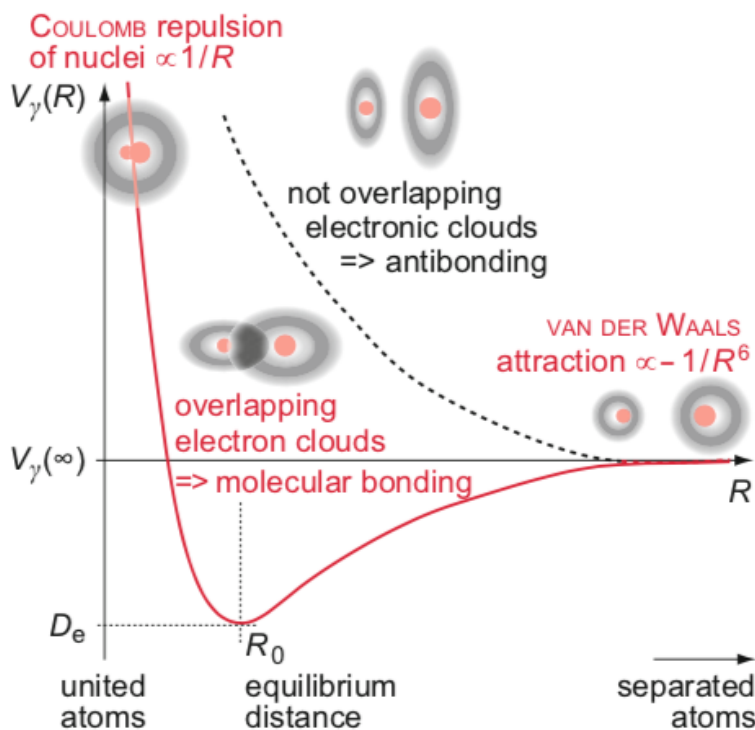We then went into the different binding mechanism (Jendrzejewski et al., r) as visualized in Fig. 2

Figure 2: Binding in diatomic molecules

We saw that we can have a general expression for the **van-der-Waals interaction**:

$$E_2 = -\frac{C_6}{R^6} \tag{174}$$

16.1 Molecular orbit theory

We would like to put together more complex molecules step-by-step. The idea was to build up from the orbits of the hydrogen ion. We then saw that certain orbits will repel each other.

In a first step, there has to be sufficient wave function overlap, such that there can be constructive and destructive interference. This implies that the orbit has to be large enough to 'see' the other atom, but not to diffuse. This typically implies that only the valence shell has to be considered.

Only orbits of the same symmetry group can form a bond. The main symmetry property here is the total L_z with respect to the axis of the molecule. We have:

- s, p_z and d_{z^2} have $L_z = 0$ (Σ).
- p_x, p_y as well as d_{yz}, d_{zx} have $|L_z| = 1 (\Pi)$

Having a sufficient overlap is obviously not enough, the two orbits also have to have the same a similiar energy, which is easily fulfilled in a homonuclear molecule.

17   Lecture 17

We finally discussed the transitions in molecules (Jendrzejewski et al., m). In the center of mass frame we get the nuclear motion:

$$\left(-\frac{1}{2M}\Delta_{\vec{R}} + E_e(\vec{R})\right)\psi_{\mathrm{n}}(\vec{R}) = E\psi_{\mathrm{n}}(\vec{R}), \tag{175}$$

We can separate the angular motion and radial motion They describe the rotational and vibrational levels of the nucleus. For the "rigid" molecule where the distance between the atoms is fixed, the rotational energy is simply given by:

$$E_{\mathrm{rot}}(R) = \frac{J \cdot (J+1)}{2MR^2} \text{ (a.u.)} \tag{176}$$

where M is the reduced mass of the nuclei in atomic units and J is the angular momentum quantum number. The molecule H_2 has then a rotational frequency $\omega/2\pi = 3 \cdot 10^{12} \cdot J(J+1)$.

The vibrational leves can be found from a harmonic approximation of the Bron-Oppenheimer potential. The harmonic expansion around the minimum reads:

$$E_e \approx E_0 + \frac{1}{2}M\omega_0^2(R - R_0)^2 \tag{177}$$

For the example of H_2, we get $\omega/2\pi \sim 10^{14}$ Hz. A better approximation of the vibrational level structure is the **Morse potential**. In this case we approximate the molecular potential curves by:

$$E_e(R) \approx V_{\mathrm{morse}}(R) \tag{178}$$

$$V_{\mathrm{morse}}(R) = hcD_e(1 - e^{-ax})^2 \text{ with } a = \sqrt{\frac{k}{2hcD_e}} \tag{179}$$

$$x = R - R_0 \tag{180}$$

17.1   Molecular transitions

We are now ready to discuss the different transitions that might appear in the spectrum. We will start out with the transitions of the lowest frequency, the rotational transitions.Pure rotational transitions exist in polar molecules. The transition rules are di-atomic molecules: $\Delta J = \pm 1$ and $\Delta M_J = 0, \pm 1$. For more complex molecules these transition rules can vary quite substantially as the rotational degree of freedom might have to be described by an additional quantum number.

Vibrational transistions will only happen in molecules for which the permanent electric dipole changes as a function of distance. Once again they are non-existant in homo-nuclear molecules.

A transition of the ground state molecular branch to a higher electronic shell will happen at constant internuclear radius as they are much faster than the nuclei motion. This implies that an electronic transition will typically excite the molecule into a high vibrational branch. The factor $S(\nu, \nu') = |\langle \nu | | \nu' \rangle|^2$ is then called the Franck-Condon factor and it describes the strength of the transitions.

18   Lecture 18

We now moved on to the quantization of electromagnetic field (Jendrzejewski et al., n). We took a lagrangian in quantized in the Coulomb gauge. We expressed the Lagrangien in terms of the vector potential and found

that the electric field is the conjugate variable to the vectore potential. This resulted in the classical Hamiltonian:

$$H = \int d\vec{k} \mathcal{H}(\vec{k}) \tag{181}$$

$$\mathcal{H}(\vec{k}) = \sum_i \left(\frac{1}{\epsilon_0} \Pi_i^*(\vec{k}, t) \Pi_i(\vec{k}, t) + \epsilon_0 c^2 k^2 A_i^*(\vec{k}, t) A_i(\vec{k}, t) \right) \tag{182}$$

Using raising and lowering operators it took the quanitized form:

$$H = \int d\vec{k} \mathcal{H}(\vec{k}) \tag{183}$$

$$\hat{\mathcal{H}}(\vec{k}) = \sum_i \frac{\hbar\omega_k}{2} \left(\hat{a}_i(\vec{k}) \hat{a}_i^\dagger(\vec{k}) + \hat{a}_i^\dagger(\vec{k}) \hat{a}_i(\vec{k}) \right) \tag{184}$$

$$= \sum_i \hbar\omega_k \left(\hat{a}_i^\dagger(\vec{k}) \hat{a}_i(\vec{k}) + \frac{1}{2} \right) \tag{185}$$

We can also express the actual field operators in terms of the normal modes:

$$\hat{E}(\vec{r}) = i \int \frac{d\vec{k}}{(2\pi)^{3/2}} \sum_i \left(\frac{\hbar\omega}{2\epsilon_0} \right) \vec{e}_i \left(\hat{a}_i(\vec{k}) e^{i\vec{k}\vec{r}} - \hat{a}_i^\dagger(\vec{k}) e^{-i\vec{k}\vec{r}} \right) \tag{186}$$

$$\hat{B}(\vec{r}) = \frac{i}{c} \int \frac{d\vec{k}}{(2\pi)^{3/2}} \sum_i \left(\frac{\hbar\omega}{2\epsilon_0} \right) (\vec{k} \times \vec{e}_i) \left(\hat{a}_i(\vec{k}) e^{i\vec{k}\vec{r}} - \hat{a}_i^\dagger(\vec{k}) e^{-i\vec{k}\vec{r}} \right) \tag{187}$$

$$\hat{A}(\vec{r}) = \int \frac{d\vec{k}}{(2\pi)^{3/2}} \sum_i \left(\frac{\hbar}{2\epsilon_0\omega} \right) \vec{e}_i \left(\hat{a}_i(\vec{k}) e^{i\vec{k}\vec{r}} + \hat{a}_i^\dagger(\vec{k}) e^{-i\vec{k}\vec{r}} \right) \tag{188}$$

19 Lecture 19

Next we the interaction of atoms and light in cavity environments (Jendrzejewski et al., o). They allowed us to write the Jaynes-Cummings model:

$$H_{JC} = \hbar\omega_0 |e\rangle \langle e| + \hbar\omega_L \hat{a}^\dagger \hat{a} + \frac{\hbar\Omega_0}{2} \left(|g\rangle \langle e| + |e\rangle \langle g| \right) \left(\hat{a} + \hat{a}^\dagger \right) \tag{189}$$

Here, we found that we should only think about the dressed atoms as they are strongly coupled to the photon.

20 Lecture 20

We then discussed how we can engineer quantum computers from systems like trapped ions (ion).

21 Lecture 21

A few words about quantum simulation with cold atoms.

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