Quantum Mechanics of Atoms and Molecules

Lectures, The University of Manchester 2005

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CONTENTS

I. SHORT HISTORICAL INTRODUCTION

I.1 Atoms and Molecules as a Concept

'Is matter infinitely divisible?' *Atomism*: matter is made of stable objects which 'can not be cut into smaller pieces'.

Problem: concept of 'cutting' !

I.1.1 Greek Philosophy

Democritus (400 BC): matter consists of different arrangements of *atoms* and *void*. Different packings and scattering of the atoms lead to different properties of matter, such as hot/cold etc. Introduces a mechanical picture of the universe (no gods). Difference between atoms and molecules not made.

Plato: four-element theory with atoms of corresponding shape: Fire-Tetrahedron, Air-Octahedron, Earth-Cube, Water-Icosahedron. Motivates **Heisenberg** in 20th century to think about group theory, symmetry and atoms.

Have a look at http://en.wikipedia.org/wiki/Atomism.

I.1.2 Chemistry

Lavoisier: *element* as a substance that can not be analyzed into something simpler.

John Dalton (1766-1844): chemical analysis and synthesis is governed by separation and combination of particles in fixed proportions 'law of combination in multiple proportions'. Different atom species have different weights, 'a different atom for each element'. Have a look at http://web.lemoyne.edu/ giunta/dalton.html.

I.1.3 Thermodynamics, Statistical Mechanics

Boltzmann. Einstein: Brownian Motion.

I.1.4 Opponents to Atoms and Molecules

Mach.

I.2 Discovery of Atoms

I.2.1 'Splitting of the Atom'

Rutherford.

Fig. I.1: Democritus Laughing, Hendrick ter Brugghen, 1628; in Rijksmuseum, Amsterdam
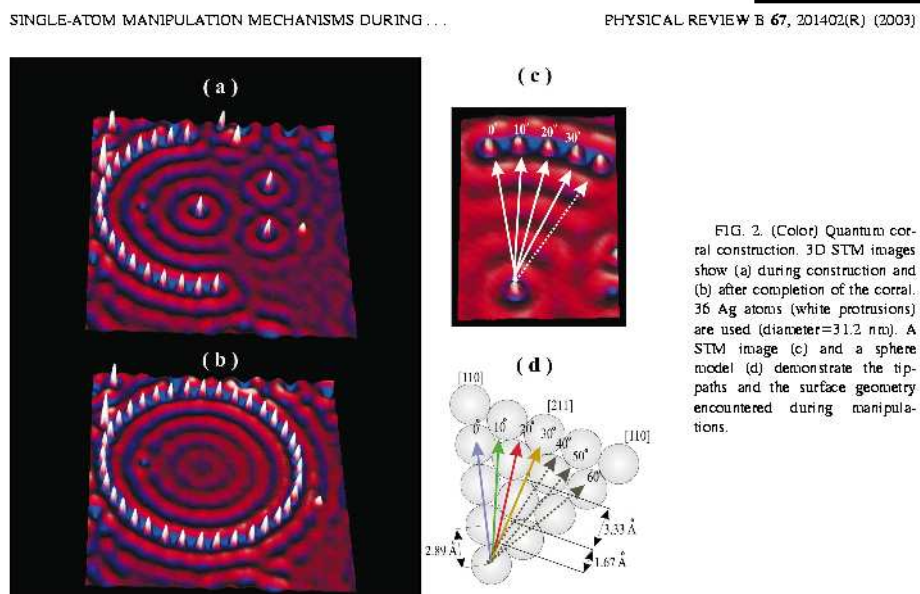

Fig. I.2: Example: 'Positioning of single atoms with sub-atomic level precision on a surface', S.-W. Hla, K.-F. Braun and K.-H. Rieder, PHYSICAL REVIEW B 67, 201402 (2003).

I.3   Theory of Atoms: Quantum Mechanics

I.3.1   'Old Quantum Mechanics'

Niels Bohr. Arnold Sommerfeld. 'Bohr-Sommerfeld-quantization'.

I.3.2   Modern Quantum Mechanics

II. SOME REVISION, FINE-STRUCTURE OF ATOMIC SPECTRA

II.1 Hydrogen Atom (non-relativistic)

This is the simplest model for a three-dimensional atom: a single electron and a single proton interacting via the Coulomb potential.

II.1.1 Non-relativistic Single Particle Quantum Mechanics

The Hamiltonian for two particles of mass m_1 and m_2 interacting via a potential $V(r)$, $r = |\mathbf{r}_1 - \mathbf{r}_2|$, is given by

$$\hat{H}_2 = -\frac{\hbar^2}{2m_1}\Delta_1 - \frac{\hbar^2}{2m_2}\Delta_2 + V(r), \tag{II.1.1}$$

where r is the distance between the two particles with positions $\mathbf{r}_1$ and $\mathbf{r}_2$, and Δ_i is the Laplace operator with respect to coordinate $\mathbf{r}_i$, cf. the textbook Landau-Lifshitz III [1]. This is reduced to a *single particle problem* by introducing center-of-mass and relative coordinates,

$$\mathbf{r} \equiv \mathbf{r}_1 - \mathbf{r}_2, \quad \mathbf{R} \equiv \frac{m_1\mathbf{r}_1 + m_2\mathbf{r}_2}{m_1 + m_2}, \tag{II.1.2}$$

which as in Classical Mechanics leads to a separation

$$\hat{H}_2 = -\frac{\hbar^2}{2(m_1 + m_2)}\Delta_{\mathbf{R}} - \frac{\hbar^2}{2m}\Delta + V(r) \equiv \hat{H}_{\mathbf{R}} + \hat{H}, \tag{II.1.3}$$

where

$$m \equiv \frac{m_1 m_2}{m_1 + m_2} \tag{II.1.4}$$

is called **reduced mass** and $\Delta_{\mathbf{R}}$ and Δ are the Laplacians with respect to $\mathbf{R}$ and $\mathbf{r}$. If we write $\mathbf{r} = (x, y, z)$ we have

$$\Delta = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}. \tag{II.1.5}$$

The Hamiltonian $\hat{H}_2$ is now a sum of two independent Hamiltonians.

Exercise: Check Eq. (II.1.3).

Exercise: Prove that the stationary solutions of $\hat{H}_2$ can be written in product form $\Psi(\mathbf{r}_1, \mathbf{r}_2) = \phi(\mathbf{R})\Psi(\mathbf{r})$.

II.1.2   Coulomb Potential

The hydrogen atom therefore leads to a special case $Z = 1$ of the solution of a stationary Schrödinger equation in the *central potential*

$$V(r) = -\frac{Ze^2}{4\pi\varepsilon_0 r}. \tag{II.1.6}$$

Here, Ze is introduced in order to be able to later generalise from proton charge $+e$ to arbitrary charge Ze. We use *Dirac kets* and write the stationary Schrödinger equation for $\hat{H}$

$$\hat{H}|\Psi\rangle = E|\Psi\rangle \leftrightarrow \left[-\frac{\hbar^2}{2m}\Delta + V(r)\right]\Psi(\mathbf{r}) = E\Psi(\mathbf{r}) \tag{II.1.7}$$

with the Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2m}\Delta - \frac{Ze^2}{4\pi\varepsilon_0 r}. \tag{II.1.8}$$

II.1.3   Orbital Angular Momentum

The central potential has rotational symmetry and therefore a conserved quantity, the angular momentum (*Nöther's theorem* [1]). Here, we introduce polar coordinates and realise that the Laplacian can be written as

$$\Delta = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} - \frac{\mathbf{L}^2}{\hbar^2 r^2}, \tag{II.1.9}$$

where the angular momentum is

$$
\begin{aligned}
\hat{L}_x &= -i\hbar\left(-\sin\varphi\frac{\partial}{\partial\theta} - \cos\varphi\cot\theta\frac{\partial}{\partial\varphi}\right) \\
\hat{L}_y &= -i\hbar\left(\cos\varphi\frac{\partial}{\partial\theta} - \sin\varphi\cot\theta\frac{\partial}{\partial\varphi}\right) \\
\hat{L}_z &= -i\hbar\frac{\partial}{\partial\varphi}.
\end{aligned}
\tag{II.1.10}
$$

and its square is given by

$$\hat{\mathbf{L}}^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]. \tag{II.1.11}$$

The eigenvalue equations for $\hat{\mathbf{L}}^2$ and $\hat{L}_z$ are

$$
\begin{aligned}
\hat{\mathbf{L}}^2 Y_{lm}(\theta,\varphi) &= \hbar^2 l(l+1) Y_{lm}(\theta,\varphi), \quad l = 0,1,2,3,... \tag{II.1.12} \\
\hat{L}_z Y_{lm}(\theta,\varphi) &= \hbar m Y_{lm}(\theta,\varphi), \tag{II.1.13}
\end{aligned}
$$

where the **spherical harmonics** have *quantum numbers l* and *m* and the explicit form

$$
\begin{aligned}
Y_{lm}(\theta,\varphi) &= (-1)^{(m+|m|)/2} i^l \left[\frac{2l+1}{4\pi}\frac{(l-|m|)!}{(l+|m|)!}\right]^{1/2} P_l^{|m|}(\cos\theta)e^{im\varphi} \\
P_l^{|m|}(x) &:= \frac{1}{2^l l!}(1-x^2)^{|m|/2}\frac{d^{l+|m|}}{dx^{l+|m|}}(x^2-1)^l \\
l &= 0,1,2,3,...; \quad m = -l, -l+1, -l+2, ..., l-1, l. \tag{II.1.14}
\end{aligned}
$$

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[1] Emmy Nöther (1882 - 1935)
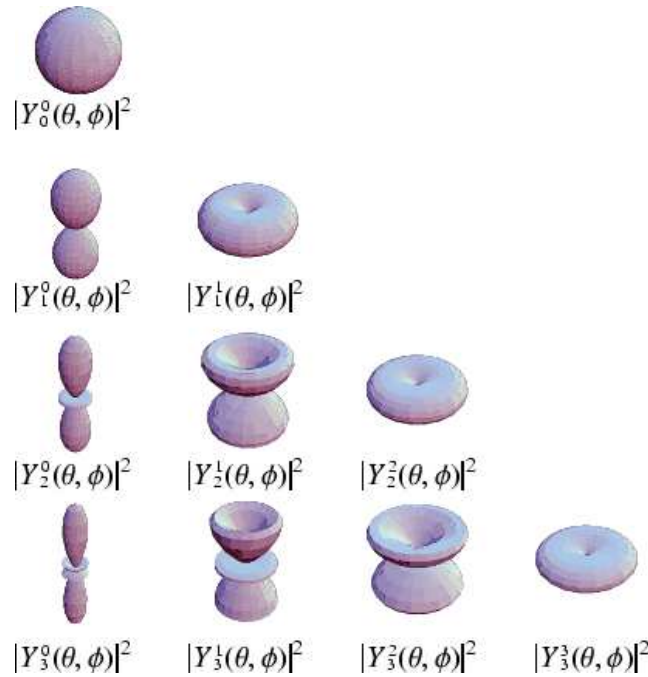
Fig. II.1: Absolute squares of various spherical harmonics. From http://mathworld.wolfram.com/SphericalHarmonic.html

The $P_l^{|m|}$ are called **associated Legendre polynomials**. The spherical harmonics are an orthonormal function system on the surface of the unit sphere $|\mathbf{x}| = 1$. We write the orthonormality relation both in our abstract bra –ket and in explicit form:

$$|lm\rangle \longleftrightarrow Y_{lm}(\theta, \varphi) \tag{II.1.15}$$

$$\langle l'm'|lm\rangle = \delta_{ll'}\delta_{mm'} \longleftrightarrow \int_0^{2\pi}\int_0^\pi Y_{l'm'}^*(\theta,\varphi)Y_{lm}(\theta,\varphi)\sin\theta d\theta d\varphi = \delta_{ll'}\delta_{mm'}.$$

The spherical harmonics with $l = 0, 1, 2, 3, 4, ...$ are denoted as s-, p-, d-, f-, g–,... functions which you might know already from chemistry ('orbitals'). The explicit forms for some of the first sphericals are

$$Y_{00} = \frac{1}{\sqrt{4\pi}}, \quad Y_{10} = i\sqrt{\frac{3}{4\pi}}\cos\theta, \quad Y_{1\pm1} = \mp i\sqrt{\frac{3}{8\pi}}\sin\theta \cdot e^{\pm i\varphi}. \tag{II.1.16}$$

Further information on spherical harmonics in various books and under
http://mathworld.wolfram.com/SphericalHarmonic.html.
The Spherical harmonics are used in many areas of science, ranging from nuclear physics up to computer vision tasks. If you like online physics teaching, have a look at
http://scienceworld.wolfram.com/physics/HydrogenAtom.html .

II.1.4 Radial Solutions

The solutions of Eq. (II.1.7) are now seperated into radial part $R_{nl}(r)$ and spherical part $Y_{lm}(\theta, \varphi)$,

$$\Psi_{nlm}(r,\theta,\varphi) = R_{nl}(r)Y_{lm}(\theta,\varphi), \tag{II.1.17}$$

where radial eigenfunctions for the bound states are characterised by the two integer quantum numbers $n \geq l + 1$ and l,

$$R_{nl}(r) = -\frac{2}{n^2}\sqrt{\frac{(n-l-1)!}{[(n+l)!]^3}}e^{-Zr/na_0}\left(\frac{2Zr}{na_0}\right)^l L_{n+l}^{2l+1}\left(\frac{2Zr}{na_0}\right), \quad l = 0, 1, ..., n-1 \text{ (II.1.18)}$$

$$L_n^m(x) = (-1)^m \frac{n!}{(n-m)!}e^x x^{-m}\frac{d^{n-m}}{dx^{n-m}}e^{-x}x^n \quad \textbf{generalized Laguerre polynomials}.$$

The radial wave functions $R_{nl}(r)$ have $n - l$ nodes. For these states, the possible eigenvalues only depend on n, $E = E_n$ with

$$E_n = -\frac{1}{2}\frac{Z^2 e^2}{4\pi\varepsilon_0 a_0}\frac{1}{n^2}, \quad n = 1, 2, 3, ... \quad \textbf{Lyman Formula}$$

$$a_0 \equiv \frac{4\pi\varepsilon_0\hbar^2}{me^2} \quad \textbf{Bohr Radius}. \tag{II.1.19}$$

In Dirac notation, we write the stationary states as $|nlm\rangle$ with the correspondence

$$|nlm\rangle \leftrightarrow \langle \mathbf{r}|nlm\rangle \equiv \Psi_{nlm}(\mathbf{r}). \tag{II.1.20}$$

The ground state is $|GS\rangle = |100\rangle$ with energy $E_0 = -13.6$ eV. The degree of *degeneracy* of the energy level E_n, i.e. the number of linearly independent stationary states with quantum number n, is

$$\sum_{l=0}^{n-1}(2l+1) = n^2 \tag{II.1.21}$$

Backup literature: lecture notes QM 1

http://brandes.phy.umist.ac.uk/QM/, textbooks Merzbacher [2], Landau-Lifshitz III [1], Gasiorowisz [3].

II.2   A 'Mini-Molecule': Perturbation Theory vs Non-Perturbative Bonding

At this stage, one usually discusses relativistic corrections to the Hydrogen spectrum which are calculated with perturbation theory. The degeneracy of a spectrum of a given Hamiltonian $\hat{H}_0$ can be *lifted* by additional *perturbations* $\hat{H}_1$ such that the spectrum of the *perturbed* Hamiltonian,

$$\hat{H} = \hat{H}_0 + \hat{H}_1, \tag{II.2.1}$$

or at least parts of it, are no longer degenerate. This is all fine, but before doing so we have a critical look at perturbation theory and its limitations, using the simplest quantum mechanical system:

II.2.1   Example: Two-Level System

The two-level system describes a particle in an 'abstract' double well with just two states. We associate a Hamiltonian $\hat{H}_0$ with the two isolated wells: the unperturbated Hamiltonian is a two-by-two matrix,

$$\hat{H}_0 = \begin{pmatrix} \varepsilon_L & 0 \\ 0 & \varepsilon_R \end{pmatrix}, \quad \hat{H}_0|L\rangle = \varepsilon_L|L\rangle, \quad \hat{H}_0|R\rangle = \varepsilon_R|R\rangle, \tag{II.2.2}$$
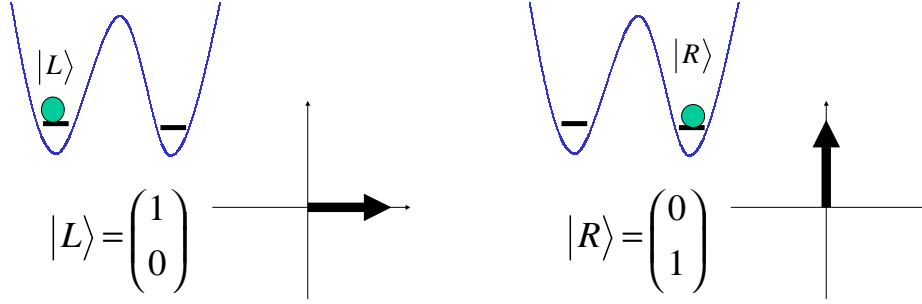
Fig. II.2: Vector representation of left and right lowest states of double well potential.

i.e., $|L\rangle$ is eigenvector of $\hat{H}_0$ with eigenvalue E_L and $|R\rangle$ is eigenvector with eigenvalue E_R. The tunnel effect is considered as a perturbation $\hat{H}_1$ to $\hat{H}_0$,

$$\hat{H}_1 = \begin{pmatrix} 0 & T_c \\ T_c & 0 \end{pmatrix} \rightsquigarrow \mathcal{H}_{\mathrm{TLS}} \equiv \hat{H}_0 + \hat{H}_1 = \begin{pmatrix} \frac{\varepsilon}{2} & T_c \\ T_c & -\frac{\varepsilon}{2} \end{pmatrix}, \tag{II.2.3}$$

with a tunnel coupling T_c (real parameter). We furthermore set $\varepsilon_L \equiv \varepsilon/2$ and $\varepsilon_R = -\varepsilon/2$.

II.2.1.1 Exact solution

We find the exact eigenvectors $|i\rangle$ and eigenvalues ε_i of $\mathcal{H}_{\mathrm{TLS}}$, that is the solutions of

$$\mathcal{H}_{\mathrm{TLS}}|i\rangle = \varepsilon_i|i\rangle, \quad i = \pm, \tag{II.2.4}$$

by diagonalisation of the two-by-two matrix Eq. (II.2.3). The eigenstates $|\pm\rangle$ and eigenvalues $\varepsilon_\pm$ of $\mathcal{H}_{\mathrm{TLS}}$ are

$$|\pm\rangle = \frac{1}{N_\pm}\left[\pm 2T_c|L\rangle + (\Delta \mp \varepsilon)|R\rangle\right], \quad N_\pm \equiv \sqrt{4T_c^2 + (\Delta \mp \varepsilon)^2}$$

$$\varepsilon_\pm = \pm\frac{1}{2}\Delta, \quad \Delta \equiv \sqrt{\varepsilon^2 + 4T_c^2}, \tag{II.2.5}$$

corresponding to *hybridized* wave functions, i.e. *bonding and anti-bonding* superpositions of the two, originally localized states $|L\rangle$ and $|R\rangle$. The corresponding eigenvalues $\varepsilon_\pm = \pm\frac{1}{2}\Delta$ of the double well represent two energy surfaces over the T_c-ε plane, with an *avoided level crossing* of splitting Δ. For $\varepsilon = 0$, one has $|\pm\rangle = (1/\sqrt{2})(\pm\mathrm{sign}(T_c)|L\rangle + |R\rangle)$ such that for the choice $T_c < 0$ the ground state $|-\rangle = (1/\sqrt{2})(|L\rangle + |R\rangle)$ with energy $\varepsilon_- = -\frac{1}{2}\Delta$ is the *symmetric* superposition of $|L\rangle$ and $|R\rangle$.

Exercise: Check these results by doing the diagonalisation! Hint: this leads to a quadratic equation.

II.2.1.2 Second Order Perturbation Theory

If E_i is a (non-degenerate) eigenvalue of $\hat{H}_0$ with (normalised) eigenvector $|i\rangle$, the second order approximation $E_i^{(2)}$ of the corresponding new eigenvalue of $\hat{H}_0 + \hat{H}_1$ is given by

$$E_i^{(2)} = E_i + \langle i|\hat{H}_1|i\rangle + \sum_{i\neq j}\frac{|\langle i|\hat{H}_1|j\rangle|^2}{E_i - E_j} \tag{II.2.6}$$
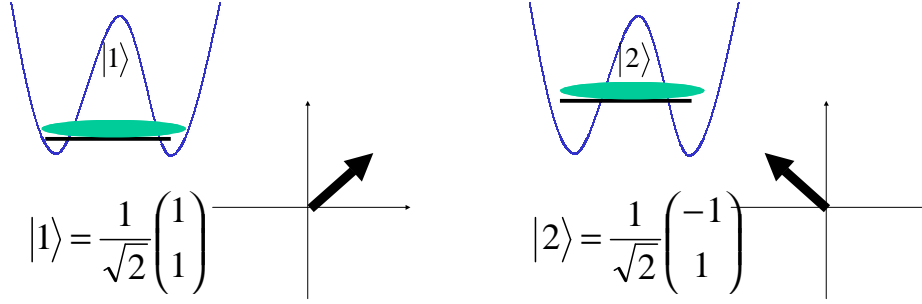
Fig. II.3: New hybridized basis states of the double well potential.

Note that in our case here the unperturbed states are $|i = 1\rangle = |L\rangle$ and $|i = 2\rangle = |R\rangle$, and the energies are $E_1 = \varepsilon/2$ and $E_2 = -\varepsilon/2$. We have $\langle i|\hat{H}_1|i\rangle = 0$ whence the first order correction vanishes. We furthermore have

$$\langle L|\hat{H}_1|R\rangle = \langle R|\hat{H}_1|L\rangle = T_c, \tag{II.2.7}$$

which leads to

$$E_1^{(2)} = \frac{\varepsilon}{2} + \frac{T_c^2}{E_1 - E_2} = \frac{\varepsilon}{2} + \frac{T_c^2}{\varepsilon} \tag{II.2.8}$$

$$E_2^{(2)} = -\frac{\varepsilon}{2} + \frac{T_c^2}{E_2 - E_1} = -\frac{\varepsilon}{2} - \frac{T_c^2}{\varepsilon}. \tag{II.2.9}$$

We compare this to a Taylor expansion of the exact result, Eq. (II.2.4), for the eigenvalues $\varepsilon_\pm$:

$$\varepsilon_\pm = \pm\frac{1}{2}\sqrt{\varepsilon^2 + 4T_c^2} = \pm\frac{1}{2}\varepsilon\sqrt{1 + 4\frac{T_c^2}{\varepsilon^2}} = \pm\frac{1}{2}\varepsilon\left[1 + 2\frac{T_c^2}{\varepsilon^2} + O\left(\frac{T_c}{\varepsilon}\right)^4\right], \tag{II.2.10}$$

which means that

$$\varepsilon_+ = \frac{1}{2}\varepsilon + \frac{T_c^2}{\varepsilon} + O\left(\frac{T_c}{\varepsilon}\right)^4, \quad \varepsilon_- = -\frac{1}{2}\varepsilon - \frac{T_c^2}{\varepsilon} + O\left(\frac{T_c}{\varepsilon}\right)^4, \tag{II.2.11}$$

which co-incides with our perturbation theory, i.e. the expressions Eq. (II.2.8) for $E_1^{(2)}$ and $E_2^{(2)}$! At the same time, we make the following observations:

- the perturbative result is good for a 'small' perturbation: in our case here, this means that the parameter T_c/ε has to be small in order to justify neglecting the $O\left(\frac{T_c}{\varepsilon}\right)^4$ terms.

- If T_c/ε becomes too large, the *perturbation expansion breaks down*: the Taylor series for $\sqrt{1 + x}$ converges only for $|x| < 1$. Here, $x = 4T_c/\varepsilon$ such that $4T_c/\varepsilon < 1$ must be fulfilled.

- Large T_c means strong coupling between the left and right 'mini-atom' and therefore strong bonding between these two atoms into a new, quantum mechanical unit: a molecule. This molecule bonding can therefore, stricly speaking, not be calculated from

perturbation theory in T_c (fortunately, we have the exact solution). In many 'real-world' cases, however, an exact solution is not available and one has to approach the problem from a different angle in order to avoid simple-minded perturbation theory. This is what P. W. Anderson probably meant in a popular science article some years ago, with the (intentionally) slightly provocative title 'Brain-washed by Feynman ?' (Feynman diagrams represent perturbation theory).

Backup literature for this section: textbook Gasiorowisz [3] cp. 11 for time-independent perturbation theory (revise if necessary). Lecture notes QM 1 chapter 3
http://brandes.phy.umist.ac.uk/QM/ for two-level system.

II.3 Hydrogen Atom: Fine Structure

The fine structure is a result of relativistic corrections to the Schrödinger equation, derived from the relativistic *Dirac equation* for an electron of mass m and charge $-e < 0$ in an external electrical field $-\nabla\Phi(\mathbf{r})$. Performing an expansion in v/c, where v is the velocity of the electron and c is the speed of light, the result for the Hamiltonian $\hat{H}$ can be written as $\hat{H} = \hat{H}_0 + \hat{H}_1$, where

$$\hat{H}_0 = -\frac{\hbar^2}{2m}\Delta - \frac{Ze^2}{4\pi\varepsilon_0 r} \tag{II.3.1}$$

is the non-relativistic Hydrogen atom, $(Z = 1)$, cf. Eq. (II.1.7), and $\hat{H}_1$ is treated as a *perturbation* to $\hat{H}_0$, using *perturbation theory*. $\hat{H}_1$ consists of three terms: the kinetic energy correction, the Darwin term, and the Spin-Orbit coupling,

$$\hat{H}_1 = \hat{H}_{\text{KE}} + \hat{H}_{\text{Darwin}} + \hat{H}_{\text{SO}}. \tag{II.3.2}$$

Literature: Gasiorowicz [3] cp. 12 (Kinetic Energy Correction, Spin-Orbit coupling); Weissbluth [4] (Dirac equation, Darwin term); Landau Lifshitz Vol IV chapter. 33,34.

II.3.1 Kinetic Energy and Darwin Term

II.3.1.1 Kinetic Energy Correction

$$\hat{H}_{\text{KE}} = -\frac{1}{2mc^2}\left(\frac{\mathbf{p}^2}{2m}\right)^2. \tag{II.3.3}$$

Exercise: Derive this term.

II.3.1.2 Darwin term

This follows from the Dirac equation and is given by

$$\hat{H}_{\text{Darwin}} = \frac{-e\hbar^2}{8m^2c^2}\Delta\Phi(\mathbf{r}), \tag{II.3.4}$$

where Δ is the Laplacian. For the Coulomb potential $\Phi(\mathbf{r}) = Ze/4\pi\varepsilon_0 r$ one needs

$$\Delta\frac{1}{r} = -4\pi\delta(\mathbf{r}) \tag{II.3.5}$$

with the Dirac Delta function $\delta(\mathbf{r})$ in three dimensions.

II.3.2 Spin-Orbit Coupling

This is the most interesting term as it involves the *electron spin*. Furthermore, this type of interaction has found a wide-ranging interest in other areas of physics, for example in the context of spin-electronics ('spin-transistor') in condensed matter systems.

The general derivation of spin-orbit coupling from the Dirac equation for an electron of mass m and charge $-e < 0$ in an external electrical field $\mathbf{E}(\mathbf{r}) = -\nabla\Phi(\mathbf{r})$ yields

$$\hat{H}_{\mathrm{SO}} = \frac{e\hbar}{4m^2c^2}\sigma[\mathbf{E}(\mathbf{r}) \times \mathbf{p}], \tag{II.3.6}$$

where $\mathbf{p} = m\mathbf{v}$ is the momentum operator and σ is the vector of the *Pauli spin matrices*,

$$\hat{\sigma}_x \equiv \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \hat{\sigma}_y \equiv \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \hat{\sigma}_z \equiv \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{II.3.7}$$

II.3.2.1 Spin-Orbit Coupling in Atoms

In the hydrogen atom, the magnetic moment $\hat{\mu}$ of the electron interacts with the magnetic field $\mathbf{B}$ which the moving electron experiences in the electric field $\mathbf{E}$ of the nucleus,

$$\mathbf{B} = -\frac{\mathbf{v} \times \mathbf{E}}{c^2}. \tag{II.3.8}$$

One has

$$\hat{\mu} = -\frac{e}{2m}g\hat{\mathbf{S}}, \quad g = 2, \tag{II.3.9}$$

where g is the g-factor of the electron and

$$\hat{\mathbf{S}} = \frac{1}{2}\hbar\sigma \tag{II.3.10}$$

is the electron spin operator. Therefore,

$$-\mathbf{v} \times \mathbf{E} = \mathbf{v} \times \nabla\frac{Ze}{4\pi\varepsilon_0 r} = \mathbf{v} \times \frac{\mathbf{r}}{r}\frac{d}{dr}\frac{Ze}{4\pi\varepsilon_0 r} = \frac{1}{m}\hat{\mathbf{L}}\frac{Ze}{4\pi\varepsilon_0 r^3}, \tag{II.3.11}$$

where $\hat{\mathbf{L}}$ is the *orbital angular momentum* operator. This is reduced by an additional factor of 2 (relativistic effects) such that

$$\hat{H}_{\mathrm{SO}} = -\hat{\mu}\mathbf{B} = \frac{Ze^2}{4\pi\varepsilon_0}\frac{1}{2m^2c^2}\frac{\hat{\mathbf{S}}\hat{\mathbf{L}}}{r^3}, \tag{II.3.12}$$

which introduces a *coupling* term between spin and orbital angular momentum. Note that Eq. (II.3.12) can directly been derived by inserting Eq. (II.3.11) as $\mathbf{E} \times \mathbf{v} = -\mathbf{v} \times \mathbf{E}$ into Eq. (II.3.6).

II.3.2.2 Spin-Orbit Coupling in Solids

In *solids*, the spin-orbit coupling effect has shot to prominence recently in the context of *spin-electronics* and the attempts to build a *spin-transistor*. The spin-orbit coupling Eq. (II.3.6),

$$\hat{H}_{\mathrm{SO}} = \frac{e\hbar}{4m^2c^2}\sigma[\mathbf{E}(\mathbf{r}) \times \mathbf{p}], \tag{II.3.13}$$

leads to a *spin-splitting* for electrons moving in solids (e.g., semiconductors) even in absence of any magnetic field. Symmetries of the crystal lattice then play a role (Dresselhaus effect), and in artificial heterostructures or quantum wells, an internal electric field $\mathbf{E}(\mathbf{r})$ can give rise to a coupling to the electron spin. This latter case is called *Rashba effect*.

For a two-dimensional sheet of electrons in the x-y-plane (two-dimensional electron gas, DEG), the simplest case is a Hamiltonian

$$\hat{H}_{\text{SO}} = -\frac{\alpha}{\hbar} \left[\mathbf{p} \times \sigma\right]_z, \tag{II.3.14}$$

where the index $_z$ denotes the z component of the operator in the vector product $\mathbf{p} \times \sigma$ and α is the *Rashba parameter*. In the case of the hydrogen atom, this factor was determined by the Coulomb potential. In semiconductor structures, it is determined by many factors such as the geometry.

The Rashba parameter α can be changed externally by, e.g., applying additional 'back-gate' voltages to the structure. This change in α then induces a change of the spin-orbit coupling which eventually can be used to manipulate electron spins.

II.3.3 Perturbation Theory for Fine Structure

The calculation of the fine structure of the energies for hydrogen now involves two steps: 1. as one has degenerate states of $\hat{H}_0$, one needs *degenerate perturbation theory*. 2. This is however simplified by the fact that the corresponding matrix in the subspace of the degenerate eigenstates can be made diagonal in a suitable basis, using the *total angular moment*

$$\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}}. \tag{II.3.15}$$

II.3.3.1 Degenerate Perturbation Theory

Assume a d-fold degenerate energy level E with d degenerate eigenstates of $\hat{H}_0$

$$|1\rangle, |2\rangle, \ldots, |d\rangle, \quad \hat{H}_0|i\rangle = E|i\rangle. \tag{II.3.16}$$

The perturbation $\hat{H}_1$ leads to new eigenfunctions

$$x_1|1\rangle + x_2|2\rangle + \ldots + x_d|d\rangle \equiv \mathbf{x} \cdot \mathbf{d}^T, \quad \mathbf{d}^T \equiv= (|1\rangle, |2\rangle, \ldots, |d\rangle) \tag{II.3.17}$$

where the notation $\mathbf{x} \cdot \mathbf{d}^T$ is just an abbreviation using the coefficient vector $\mathbf{x}$ and the vector of the degenerate states $\mathbf{d}^T$. The coefficient vectors $\mathbf{x}$ are then determined from the matrix *eigenvalue equation*

$$\underline{\underline{H}}\mathbf{x} = E'\mathbf{x}, \quad \underline{\underline{H}}_{ij} \equiv \langle i|\hat{H}_1|j\rangle \tag{II.3.18}$$

with the Hermitian d times d matrix $\underline{\underline{H}}$ of the matrix elements of the perturbation $\hat{H}_1$ in the sub-space of the degenerate eigenstates $|i\rangle$ of $\hat{H}_0$.

The solutions for E' are determined from $\det\left(\underline{\underline{H}} - E'\underline{\underline{1}}\right) = 0$ or

$$\begin{vmatrix} \langle 1|\hat{H}_1|1\rangle - E' & \langle 1|\hat{H}_1|2\rangle & \ldots & \langle 1|\hat{H}_1|d\rangle \\ \ldots & & & \\ \langle d|\hat{H}_1|1\rangle & \langle d|\hat{H}_1|2\rangle & \ldots & \langle d|\hat{H}_1|d\rangle - E' \end{vmatrix} = 0, \tag{II.3.19}$$

which is an algebraic equation with d real solutions E_i', $i = 1, ..., d$. Correspondingly, one obtains d coefficient vectors $\mathbf{x}_i$ leading to d new linear combinations $\mathbf{x}_i \cdot \mathbf{d}^T$, $i = 1, ..., d$, of states within the d-dimensional subspace spanned by $|1\rangle, |2\rangle, \ldots, |d\rangle$.

Exercise 1: Revise if necessary Gasiorowicz [3] cp. 11.2, plus the corresponding math background: eigenvalues, eigenvalue equations, vector spaces, matrices etc. !

Exercise 2: Revise degenerate perturbation theory by applying it to the 2-level system $\mathcal{H}_{\mathrm{TLS}}$ from section II.2 for the case $\varepsilon = \varepsilon_L - \varepsilon_R = 0$. How good is first order perturbation theory in this case?

II.3.3.2 Degenerate Perturbation Theory for Spin-Orbit Coupling

Including spin, the level E_n of hydrogen belongs to the states

$$|nlsm_lm_s\rangle, \quad s = 1/2, \quad m_s = \pm 1/2, \tag{II.3.20}$$

which are eigenstates of $\hat{L}^2$, $\hat{S}^2$, $\hat{L}_z$, and $\hat{S}_z$ ('uncoupled representation'). With $\hat{\mathbf{L}}$ and $\hat{\mathbf{S}}$ adding up to the total angular momentum $\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}}$, an alternative basis is the 'coupled representation'

$$|nlsjm\rangle, \quad j = l + s, l + s - 1, ..., |l - s|, \quad m = m_l + m_s. \tag{II.3.21}$$

of eigenfunctions of $\hat{J}^2$, $\hat{L}^2$, $\hat{S}^2$, and $\hat{J}_z$. Here, $s = 1/2$ is the total electron spin which of course is fixed and gives the two possibilities $j = l + 1/2$ and $j = l - 1/2$ for $l \geq 1$ and $j = 1/2$ for $l = 0$ (l runs from 0 to $n - 1$).

The perturbation $\hat{H}_{\mathrm{SO}}$, Eq. (II.3.12), can be diagonalised in the $|nlsjm\rangle$ basis, using

$$\hat{\mathbf{S}}\hat{\mathbf{L}} = \frac{1}{2}\left(\hat{\mathbf{J}}^2 - \hat{\mathbf{L}}^2 - \hat{\mathbf{S}}^2\right) \tag{II.3.22}$$

$$\rightsquigarrow \langle nl'sj'm'|\hat{\mathbf{S}}\hat{\mathbf{L}}|nlsjm\rangle = \frac{1}{2}\hbar^2\left(j(j+1) - l(l+1) - s(s+1)\right)\delta_{jj'}\delta_{ll'}\delta_{mm'}.$$

For fixed n, l, and m, ($s = 1/2$ is fixed anyway and therefore a dummy index), the basis of degenerate states from the previous subsection therefore for $l \geq 1$ has two states, $|nlsj = l \pm 1/2m\rangle$, and the two-by-two matrix $\underline{\underline{H}}$ is diagonal,

$$\underline{\underline{H}} \leftrightarrow \langle nlsj'm|\hat{H}_{\mathrm{SO}}|nlsjm\rangle = \frac{Ze^2}{4\pi\varepsilon_0}\frac{1}{2m^2c^2}\left\langle\frac{1}{r^3}\right\rangle_{nl}\frac{1}{2}\hbar^2\begin{pmatrix} l & 0 \\ 0 & -(l+1) \end{pmatrix}, \tag{II.3.23}$$

where $\left\langle\frac{1}{r^3}\right\rangle_{nl}$ indicates that this matrix elements has to be calculated with the radial parts of the wave functions $\langle\mathbf{r}|nlsj = l \pm 1/2m\rangle$, with the result

$$\left\langle\frac{1}{r^3}\right\rangle_{nl} = \frac{Z^3}{a_0^3}\frac{2}{n^3l(l+1)(2l+1)}, \quad l \neq 0. \tag{II.3.24}$$

The resulting energy shifts E_{SO}' corresponding to the two states with $j = l \pm 1/2$ are

$$E_{\mathrm{SO}}' = \frac{Z^4e^2\hbar^2}{2m^2c^2a_0^34\pi\varepsilon_0}\frac{1}{n^3l(l+1)(2l+1)}\begin{cases} l, & j = l + \frac{1}{2} \\ -(l+1), & j = l - \frac{1}{2} \end{cases} \tag{II.3.25}$$
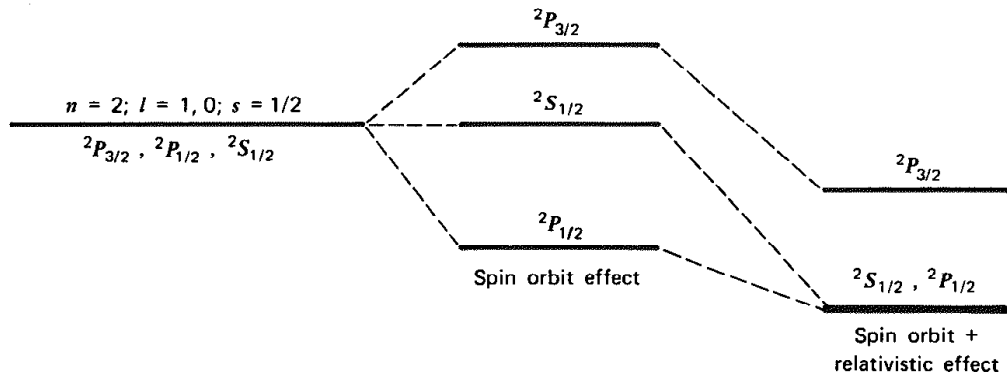
Figure 12-1 Splitting of the $n = 2$ levels by (1) the spin-orbit coupling (which leaves the S state unaffected) and (2) the relativistic effect. The final degeneracy of the $^2S_{1/2}$ and $^2P_{1/2}$ states is actually lifted by quantum electrodynamic effects. The tiny upward shift of the $^2S_{1/2}$ state is called the Lamb shift.

Fig. II.4: Fine-Splitting of the hydrogen level $E_{n=2}$, from Gasiorowicz[3]

II.3.3.3 Putting everything together

Apart from the corrections E'_{SO}, one also has to take into account the relativistic corrections dur to $\hat{H}_{\mathrm{KE}}$ and $\hat{H}_{\mathrm{Darwin}}$ from section II.3.1. It turns out that the final result for the energy eigenvalue in first order perturbation theory with respect to $\hat{H}_1 = \hat{H}_{\mathrm{KE}} + \hat{H}_{\mathrm{Darwin}} + \hat{H}_{\mathrm{SO}}$, Eq. (II.3.1), is given by the very simple expression

$$E_{nlsjm} = E_n^{(0)} + \frac{(E_n^{(0)})^2}{2mc^2}\left[3 - \frac{4n}{j + \frac{1}{2}}\right], \quad j = l \pm \frac{1}{2}. \tag{II.3.26}$$

For a detailed derivation of this final result (though I haven't checked all details), cf. James Branson's page,

  http://hep.ucsd.edu/ branson/

  or Weissbluth [4], cf. 16.4. Gasiorowicz [3] 12-16 seems to be incorrect.

  Final remark: we do not discuss the effects of a magnetic field (anamalous Zeeman effect) or the spin of the nucleus (hyperfine interaction) here. These lead to further splittings in the level scheme.

III. INTRODUCTION INTO MANY-PARTICLE SYSTEMS

III.1 Indistinguishable Particles

In Quantum Mechanics, a system of N particles with internal spin degrees of freedom σ_i is described by a wave function which in the *position representation* reads

$$\Psi(\mathbf{r}_1, \sigma_1; \mathbf{r}_2, \sigma_2; ...; \mathbf{r}_N, \sigma_N). \tag{III.1.1}$$

Here, $|\Psi(...)|^2$ is the probability density for finding particle 1 at $\mathbf{r}_1$ with spin quantum number(s) σ_1, particle 2 at $\mathbf{r}_2$ with spin quantum number(s) σ_2,... etc. Note that for spin 1/2, one would choose for σ_i one of the spin projections, e.g. $\sigma_i = \sigma_i^{(z)} = \pm\frac{1}{2}$.

Remark: Usually, many-particle wave functions and the issue of indistinguishability are discussed in the *position* representation.

III.1.1 Permutations

Two particles are called *indistinguishable* when they have the same 'elementary' parameters such as mass, charge, total spin. As an example, it is believed that all *electrons* are the same in the sense that they all have the same mass, the same charge, and the same spin 1/2. The evidence for this comes from experiments.

If some of the N particles described by the wave function Ψ, Eq. (III.1.1), are indistinguishable, this restricts the form of Ψ. Let us assume that all N particles are pairwise indistinguishable. We define the abbreviations $\xi_i \equiv (\mathbf{r}_i, \sigma_i)$. Since particle j is indistinguishable from particle k, the N-particle wave functions with ξ_j and ξ_k swapped should describe the same physics: they may only differ by a phase factor,

$$\Psi(\xi_1, ..., \xi_j, ..., \xi_k, ..., \xi_N) = e^{i\phi_{jk}}\Psi(\xi_1, ..., \xi_k, ..., \xi_j, ..., \xi_N). \tag{III.1.2}$$

Swapping j and k a second time must yield the original wave function and therefore

$$e^{2i\phi_{jk}} = 1 \rightsquigarrow \phi_{jk} = 0, \pm\pi, \pm2\pi, \pm3\pi, \tag{III.1.3}$$

In fact, the phases $0, \pm2\pi$ etc. are all equivalent: they lead to *symmetrical* wave functions. The phases $\pm\pi, \pm3\pi$ etc. are also all equivalent: they lead to *antisymmentrical* wave functions.

It turns out that this argument (swapping the coordinates) depends on the dimension of the space in which the particles live, and that there is a connection to the spin of the particles. For $d \geq 3$, indistinguishable particles with half-integer spin are called *Fermions* which are described by *antisymmentrical* wave functions. For $d \geq 3$, indistinguishable particles with integer spin are called *Bosons* which are described by *symmentrical* wave functions. For

$d = 3$, this connection between spin and statistics can be proved in relativistic quantum field theory (*Spin-Statistics-Theorem*, W. Pauli 1940).

$$
\begin{aligned}
\Psi(\xi_1, .., \xi_j, ..., \xi_k, .., \xi_N) &= -\Psi(\xi_1, .., \xi_k, ..., \xi_j, .., \xi_N), \quad \text{Fermions} \\
\Psi(\xi_1, .., \xi_j, ..., \xi_k, .., \xi_N) &= \Psi(\xi_1, .., \xi_k, ..., \xi_j, .., \xi_N), \quad \text{Bosons.}
\end{aligned}
\tag{III.1.4}
$$

In two dimensions, things become more complicated. First of all, the connection with spin (integer, half integer in $d = 3$) is different in $d = 2$ because angular momentum in general is no longer quantized: rotations in the x-y plane commuted with each other, i.e. the rotation group $SO(2)$ is abelian and has only one generator which can have arbitrary eigenvalues. Second, topology is different in two dimensions, in particular when discussing wave functions excluding two particles sitting on the same place $\mathbf{x}_k = \mathbf{x}_j$ which leads to effective configuration spaces which are *no longer simply connected*.

In two dimensions, one obtains a plethora of possibilities with exciting new possibilities for 'fractional spin and statistics'. These are important and have been discovered recently in, e.g., the fractional quantum Hall effect. For further literature on this topic, cf. S. Forte, 'Quantum mechanics and field theory with fractional spin and statistics', Rev. Mod. Phys. **64**, 193.

III.1.2 Basis vectors for Fermi and Bose systems

III.1.2.1 Single Particle

We assume to have a Hilbert space with a complete basis of wave vectors $|\nu\rangle$ corresponding to wave functions $\langle \mathbf{r}\sigma | \nu \rangle$ including the spin,

$$
|\nu\rangle \leftrightarrow \psi_\nu(\mathbf{r}\sigma) = \langle \mathbf{r}\sigma | \nu \rangle.
\tag{III.1.5}
$$

Examples:

- harmonic oscillator, $|\nu\rangle = |n\rangle$ with $n = 0, 1, 2, ...$ and the harmonic oscillator wave functions $\psi_n(\mathbf{r})$.

- two-level system with $|\nu\rangle$ and $\nu = +$ and $\nu = -$.

- hydrogen atom with $|\nu\rangle = |nlsjm\rangle$.

The last example shows that ν is a 'multi-index' (index 'vector').

III.1.2.2 N-particle system

We have N particles and N quantum numbers $\nu_1,...,\nu_N$. A basis consists of all product states $|\nu_1, ..., \nu_N\rangle$ corresponding to wave functions $\psi_{\nu_1}(\xi_1)...\psi_{\nu_N}(\xi_N)$, $\xi = \mathbf{r}\sigma$,

$$
|\nu_1, ..., \nu_N\rangle \leftrightarrow \psi_{\nu_1}(\xi_1)...\psi_{\nu_N}(\xi_N) = \langle \xi_1 | \nu_1 \rangle ... \langle \xi_N | \nu_N \rangle.
\tag{III.1.6}
$$

These wave functions still don't have any particular symmetry with respect to permutation of particles. We use them to construct the basis wave functions for Bosons and Fermions.

III.1.2.3 Permutations

There are $N!$ permutations of N particles. We label the permutations by $N!$ indices p and define a permutation operator $\hat{\Pi}_p$, for example

$$\hat{\Pi}_{p=(1,3)}\Psi(\xi_1,\xi_2,\xi_3) = \Psi(\xi_3,\xi_2,\xi_1) \tag{III.1.7}$$

$$\hat{\Pi}_{p=(1,2,3)}\Psi(\xi_1,\xi_2,\xi_3) = \hat{\Pi}_{p=(2,3)}\Psi(\xi_2,\xi_1,\xi_3) = \Psi(\xi_2,\xi_3,\xi_1) \tag{III.1.8}$$

We furthermore define the *symmetrization operator* $\hat{S}$ and the *anti-symmetrization operator* $\hat{A}$,

$$\hat{S} = \frac{1}{\sqrt{N!}}\sum_p \hat{\Pi}_p \tag{III.1.9}$$

$$\hat{A} = \frac{1}{\sqrt{N!}}\sum_p \hat{\Pi}_p \mathrm{sign}(p), \tag{III.1.10}$$

where $\mathrm{sign}(p)$ is the *sign* of the permutation which is either -1 or $+1$, $\mathrm{sign}(p) = (-1)^{n(p)}$ where $n(p)$ is the number of swaps required to achieve the permutation p.

III.1.2.4 N-Boson systems

A basis for symmetric wave functions with N Bosons is constructed in the following way.

1. If we just have one possible state $|\nu_1\rangle$ of the system, the symmetric state and the corresponding wave function is

$$|\underbrace{\nu_1,...,\nu_1}_{N\text{times}}\rangle_S \;\leftrightarrow\; \langle\xi_1,...,\xi_N|\nu_1,...,\nu_1\rangle_S \equiv \psi_{\nu_1}(\xi_1)...\psi_{\nu_1}(\xi_N) \tag{III.1.11}$$

This wave function is obviously symmetric.

2. If we have two particles ($N=2$), the basis is constructed from the states $|\nu_1,\nu_2\rangle$ with corresponding wave functions $\psi_{\nu_1}(\xi_1)\psi_{\nu_2}(\xi_2)$: this product is made symmetric,

$$
\begin{aligned}
|\nu_1,\nu_2\rangle_S \leftrightarrow \langle\xi_1,\xi_2|\nu_1,\nu_2\rangle_S &\equiv \frac{1}{\sqrt{2}}\left[\psi_{\nu_1}(\xi_1)\psi_{\nu_2}(\xi_2) + \psi_{\nu_1}(\xi_2)\psi_{\nu_2}(\xi_1)\right] \\
&= \hat{S}\psi_{\nu_1}(\xi_1)\psi_{\nu_2}(\xi_2). \tag{III.1.12}
\end{aligned}
$$

3. If we just have two possible state $|\nu_1\rangle$ and $|\nu_2\rangle$ for a system with N particles, N_1 particles sit in $|\nu_1\rangle$ and N_2 particles sit in $|\nu_2\rangle$. We now have to symmetrize the states

$$|\underbrace{\nu_1,...,\nu_1}_{N_1\text{times}},\; \underbrace{\nu_2,...,\nu_2}_{N_2\text{times}}\rangle \;\leftrightarrow\; \psi_{\nu_1}(\xi_1)...\psi_{\nu_1}(\xi_{N_1})\psi_{\nu_2}(\xi_{N_1+1})...\psi_{\nu_2}(\xi_{N_2})$$

$$N_1 + N_2 = N. \tag{III.1.13}$$

If we apply the symmetrization operator $\hat{S}$ to this product,

$$\frac{1}{\sqrt{N!}}\sum_p \hat{\Pi}_p \psi_{\nu_1}(\xi_1)...\psi_{\nu_1}(\xi_{N_1})\psi_{\nu_2}(\xi_{N_1+1})...\psi_{\nu_2}(\xi_{N_2}), \tag{III.1.14}$$

we get a sum of $N!$ terms, each consisting of N products of wave functions. For example, for $N_1 = 1$ and $N_2 = 2$ we get

$$\frac{1}{\sqrt{3!}} \sum_p \hat{\Pi}_p \psi_{\nu_1}(\xi_1)\psi_{\nu_2}(\xi_2)\psi_{\nu_2}(\xi_3) = \tag{III.1.15}$$

$$= \frac{1}{\sqrt{N!}}\Big[\psi_{\nu_1}(\xi_1)\psi_{\nu_2}(\xi_2)\psi_{\nu_2}(\xi_3) + \psi_{\nu_1}(\xi_1)\psi_{\nu_2}(\xi_3)\psi_{\nu_2}(\xi_2) \tag{III.1.16}$$

$$+ \psi_{\nu_1}(\xi_2)\psi_{\nu_2}(\xi_1)\psi_{\nu_2}(\xi_3) + \psi_{\nu_1}(\xi_2)\psi_{\nu_2}(\xi_3)\psi_{\nu_2}(\xi_1) \tag{III.1.17}$$

$$+ \psi_{\nu_1}(\xi_3)\psi_{\nu_2}(\xi_1)\psi_{\nu_2}(\xi_2) + \psi_{\nu_1}(\xi_3)\psi_{\nu_2}(\xi_2)\psi_{\nu_2}(\xi_1)\Big], \tag{III.1.18}$$

where in each line in the above equation we have $N_2! = 2!$ identical terms. Had we chosen an example with $N_1 > 1$ and $N_2 > 1$, we would have got $N_1!N_2!$ identical terms in each line of the above equation. The symmetrized wave function therefore looks as follows:

$$\frac{1}{\sqrt{N!}}N_1!N_2! \left[\text{sum of } \frac{N!}{N_1!N_2!} \quad \text{orthogonal wave functions}\right], \tag{III.1.19}$$

which upon squaring and integrating would give

$$\left[\frac{1}{\sqrt{N!}}N_1!N_2!\right]^2 \frac{N!}{N_1!N_2!} = N_1!N_2! \tag{III.1.20}$$

and not one! We therefore need to divide the whole wave function by $1/\sqrt{N_1!N_2!}$ in order to normalise it to one, and therefore the symmetric state with the corresponding normalised, symmetrical wave function is

$$|\nu_1, ..., \nu_1, \nu_2, ..., \nu_2\rangle_S \tag{III.1.21}$$

$$\leftrightarrow \frac{1}{\sqrt{N!}\sqrt{N_1!}\sqrt{N_2!}} \sum_p \hat{\Pi}_p \psi_{\nu_1}(\xi_1)...\psi_{\nu_1}(\xi_{N_1})\psi_{\nu_2}(\xi_{N_1+1})...\psi_{\nu_2}(\xi_{N_2}).$$

This is now easily generalised to the case where we have N_1 particles in state ν_1, N_2 particles in state ν_2,...,N_r particles in state ν_r with

$$\sum_{i=1}^{r} N_r = N. \tag{III.1.22}$$

We then have

$$|\nu_1, ..., \nu_1, \nu_2, ..., \nu_2, ..., \nu_r, ..., \nu_r\rangle_S \tag{III.1.23}$$

$$\leftrightarrow \langle \xi_1, ..., \xi_1, \xi_2, ..., \xi_2, ..., \xi_r, ..., \xi_r | \nu_1, ..., \nu_1, \nu_2, ..., \nu_2, ..., \nu_r, ..., \nu_r\rangle_S \equiv$$

$$\equiv \frac{1}{\sqrt{N!}\sqrt{N_1!}\sqrt{N_2!}...\sqrt{N_r!}} \times$$

$$\sum_p \hat{\Pi}_p \psi_{\nu_1}(\xi_1)...\psi_{\nu_1}(\xi_{N_1})\psi_{\nu_2}(\xi_{N_1+1})...\psi_{\nu_2}(\xi_{N_2})...\psi_{\nu_r}(\xi_{N-N_r+1})...\psi_{\nu_r}(\xi_N).$$

III.1.2.5 N-Fermion systems

In this case, we have to use anti-symmetrized states with anti-symmetric wave functions,

$$|\nu_1, ..., \nu_N\rangle_A = \hat{A}|\nu_1, ..., \nu_N\rangle = \frac{1}{\sqrt{N!}} \sum_p \hat{\Pi}_p \text{sign}(p)|\nu_1, ..., \nu_N\rangle$$

$$\leftrightarrow \quad \langle\xi_1, ..., \xi_N|\nu_1, ..., \nu_1\rangle_A \equiv \frac{1}{\sqrt{N!}} \sum_p \hat{\Pi}_p \text{sign}(p)\psi_{\nu_1}(\xi_1)...\psi_{\nu_N}(\xi_N)$$

$$= \quad \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_{\nu_1}(\xi_1) & \psi_{\nu_1}(\xi_2) & ... & \psi_{\nu_1}(\xi_N) \\ \psi_{\nu_2}(\xi_1) & \psi_{\nu_2}(\xi_2) & ... & \psi_{\nu_2}(\xi_N) \\ ... & & & \\ \psi_{\nu_N}(\xi_1) & \psi_{\nu_N}(\xi_2) & ... & \psi_{\nu_N}(\xi_N) \end{vmatrix}. \tag{III.1.24}$$

These determinants are called **Slater determinants**.

- A permutation of two of the particles here corresponds to a swapping of the corresponding columns in the determinant and therefore gives a minus sign: the wave function is anti-symmetric.

- If two of the quantum numbers $\nu_1, ..., \nu_N$ are the same, the determinant is zero: in a system with identical Fermions, two or more than two particles can not be in the same state (in contrast to Bosons). This important fact is called **Pauli principle**.

Finally, we remark that in Slater determinants we can let the permutations all operate either on the coordinates ξ_i, or all on the indices ν_i:

$$\langle\xi_1, ..., \xi_N|\nu_1, ..., \nu_N\rangle_A \equiv \frac{1}{\sqrt{N!}} \sum_p \text{sign}(p)\psi_{\nu_1}(\xi_{p(1)})...\psi_{\nu_N}(\xi_{p(N)})$$

$$= \quad \frac{1}{\sqrt{N!}} \sum_p \text{sign}(p)\psi_{\nu_{p(1)}}(\xi_1)...\psi_{\nu_{p(N)}}(\xi_N). \tag{III.1.25}$$

Exercise: Explicitly verify this identity for the case of $N = 3$ particles.

This is in particular useful when it comes to calculation of matrix elements. The last form justifies the notation

$$|\nu_1, ..., \nu_1\rangle_A = \frac{1}{\sqrt{N!}} \sum_p \text{sign}(p)|\nu_{p(1)}, ..., \nu_{p(N)}\rangle. \tag{III.1.26}$$

III.2   2-Fermion Systems

In order to get a feeling for how to work with Fermion systems, we start with the simplest case $N = 2$. The basis states are the Slater determinants

$$\langle\xi_1, \xi_2|\nu_1, \nu_2\rangle_A = \frac{1}{\sqrt{2!}} \begin{vmatrix} \psi_{\nu_1}(\xi_1) & \psi_{\nu_1}(\xi_2) \\ \psi_{\nu_2}(\xi_1) & \psi_{\nu_2}(\xi_2) \end{vmatrix}$$

$$= \frac{1}{\sqrt{2}} \left[\psi_{\nu_1}(\xi_1)\psi_{\nu_2}(\xi_2) - \psi_{\nu_1}(\xi_2)\psi_{\nu_2}(\xi_1) \right]. \tag{III.2.1}$$

III.2.1 Two Electrons

Electrons have spin $\frac{1}{2}$ and we now have to work out how the electron spin enters into the Slater determinants. The single particle wave functions for particle 1 are products of orbital wave functions and spin wave functions,

$$\psi(\xi_1) = \psi(\mathbf{r}_1)|\sigma_1\rangle_{(1)}. \tag{III.2.2}$$

For spin-1/2, the spin label σ_1 can take the two values $\sigma_1 = \pm 1/2$ which by convention are denoted as $\uparrow$ and $\downarrow$. The two **spinors** have the following representation in the two-dimensional complex Hilbert space (spin-space),

$$|\uparrow\rangle_{(1)} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}_{(1)}, \quad |\downarrow\rangle_{(1)} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}_{(1)}. \tag{III.2.3}$$

Here, the index $_{(1)}$ means that this spin referes to particle (1).

We now consider the four possibilities for the spin projections σ_1 and σ_2 and the corresponding four sets of basis wave functions,

$$\frac{1}{\sqrt{2}} \left[\psi_{\nu_1}(\mathbf{r}_1)\psi_{\nu_2}(\mathbf{r}_2)|\uparrow\uparrow\rangle_{(12)} - \psi_{\nu_1}(\mathbf{r}_2)\psi_{\nu_2}(\mathbf{r}_1)|\uparrow\uparrow\rangle_{(12)} \right]$$

$$\frac{1}{\sqrt{2}} \left[\psi_{\nu_1}(\mathbf{r}_1)\psi_{\nu_2}(\mathbf{r}_2)|\uparrow\downarrow\rangle_{(12)} - \psi_{\nu_1}(\mathbf{r}_2)\psi_{\nu_2}(\mathbf{r}_1)|\downarrow\uparrow\rangle_{(12)} \right]$$

$$\frac{1}{\sqrt{2}} \left[\psi_{\nu_1}(\mathbf{r}_1)\psi_{\nu_2}(\mathbf{r}_2)|\downarrow\uparrow\rangle_{(12)} - \psi_{\nu_1}(\mathbf{r}_2)\psi_{\nu_2}(\mathbf{r}_1)|\uparrow\downarrow\rangle_{(12)} \right]$$

$$\frac{1}{\sqrt{2}} \left[\psi_{\nu_1}(\mathbf{r}_1)\psi_{\nu_2}(\mathbf{r}_2)|\downarrow\downarrow\rangle_{(12)} - \psi_{\nu_1}(\mathbf{r}_2)\psi_{\nu_2}(\mathbf{r}_1)|\downarrow\downarrow\rangle_{(12)} \right]. \tag{III.2.4}$$

Here,

$$|\uparrow\downarrow\rangle_{(12)} \equiv |\uparrow\rangle_{(1)} \otimes |\downarrow\rangle_{(2)} \tag{III.2.5}$$

is a *product spinor*, i.e. a spin wave function with particle (1) with spin up and particle (2) with spin down, and coresp[ondingly for the other product spinor.

We can now re-write the basis states Eq. (III.2.4) by forming linear combinations of the 'mixed' spinors (exercise: check these !),

$$\psi_S(\xi_1, \xi_2) = \psi_{\nu_1,\nu_2}^{\text{sym}}(\mathbf{r}_1, \mathbf{r}_2)|S\rangle \tag{III.2.6}$$
$$\psi_{T_{-1}}(\xi_1, \xi_2) = \psi_{\nu_1,\nu_2}^{\text{asym}}(\mathbf{r}_1, \mathbf{r}_2)|T_{-1}\rangle \tag{III.2.7}$$
$$\psi_{T_0}(\xi_1, \xi_2) = \psi_{\nu_1,\nu_2}^{\text{asym}}(\mathbf{r}_1, \mathbf{r}_2)|T_0\rangle \tag{III.2.8}$$
$$\psi_{T_{+1}}(\xi_1, \xi_2) = \psi_{\nu_1,\nu_2}^{\text{asym}}(\mathbf{r}_1, \mathbf{r}_2)|T_{+1}\rangle. \tag{III.2.9}$$

Here, the symmetric and antisymmetric orbital wave functions are defined as

$$\psi_{\nu_1,\nu_2}^{\text{sym}}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} \left[\psi_{\nu_1}(\mathbf{r}_1)\psi_{\nu_2}(\mathbf{r}_2) + \psi_{\nu_1}(\mathbf{r}_2)\psi_{\nu_2}(\mathbf{r}_1) \right] \tag{III.2.10}$$

$$\psi_{\nu_1,\nu_2}^{\text{asym}}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} \left[\psi_{\nu_1}(\mathbf{r}_1)\psi_{\nu_2}(\mathbf{r}_2) - \psi_{\nu_1}(\mathbf{r}_2)\psi_{\nu_2}(\mathbf{r}_1) \right]. \tag{III.2.11}$$

Furthermore, the spin wave functions are defined as

$$\begin{aligned} |S\rangle &= \frac{1}{\sqrt{2}} \left[|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle \right] & \text{Singlet state} \\ |T_{-1}\rangle &= |\downarrow\downarrow\rangle & \text{Triplet State} \\ |T_0\rangle &= \frac{1}{\sqrt{2}} \left[|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle \right], & \text{Triplet State} \\ |T_{+1}\rangle &= |\uparrow\uparrow\rangle & \text{Triplet State} \end{aligned} \tag{III.2.12}$$

III.2.2 Properties of Spin-Singlets and Triplets

We have another look at the two-particle spin states Eq. (III.2.12), writing them more explicitly as

$$
\begin{aligned}
|S\rangle &= \tfrac{1}{\sqrt{2}}\left[|\uparrow\rangle_1 \otimes |\downarrow\rangle_2 - |\downarrow\rangle_1 \otimes |\uparrow\rangle_2\right] && \text{Singlet state} \\
|T_{-1}\rangle &= |\downarrow\rangle_1 \otimes |\downarrow\rangle_2 && \text{Triplet State} \\
|T_0\rangle &= \tfrac{1}{\sqrt{2}}\left[|\uparrow\rangle_1 \otimes |\downarrow\rangle_2 + |\downarrow\rangle_1 \otimes |\uparrow\rangle_2\right] && \text{Triplet state} \\
|T_{+1}\rangle &= |\uparrow\rangle_1 \otimes |\uparrow\rangle_2 && \text{Triplet State}
\end{aligned}
\tag{III.2.13}
$$

III.2.2.1 Total Spin

One advantage of working with singlets and triplets is the fact that they are spin states of fixed total spin: rthe singlets has total spin $S = 0$, the three triplets have total spin $S = 1$ and total spin projections $M = -1, 0, 1$:

$$
\begin{aligned}
\hat{S}^2|S\rangle &= \hbar S(S+1)|S\rangle, S = 0, \quad \hat{S}_z|S\rangle = \hbar M|S\rangle, M = 0 \tag{III.2.14}\\
\hat{S}^2|T_{-1}\rangle &= \hbar S(S+1)|T_{-1}\rangle, S = 1, \quad \hat{S}_z|T_{-1}\rangle = \hbar M|T_{-1}\rangle, M = -1 \\
\hat{S}^2|T_0\rangle &= \hbar S(S+1)|T_0\rangle, S = 1, \quad \hat{S}_z|T_0\rangle = \hbar M|T_0\rangle, M = 0 \\
\hat{S}^2|T_{+1}\rangle &= \hbar S(S+1)|T_{+1}\rangle, S = 1, \quad \hat{S}_z|T_{+1}\rangle = \hbar M|T_{+1}\rangle, M = +1.
\end{aligned}
$$

Often the total spin is conserved when we deal with interacting systems. If , for example, the system is in a state that is a linear combination of the three triplets, it has to stay in the sub-space spanned by the triplets and can't get out of it. In that case instead of having a four-dimensional space we just have to deal with a three-dimensional space.

III.2.2.2 Entanglement

There is a fundamental difference between the $M = \pm 1$ states $|T_{\pm 1}\rangle$ on the one side and the $M = 0$ states $|S\rangle$ and $|T_0\rangle$ on the other side:

- $|T_{-1}\rangle = |\downarrow\rangle_1 \otimes |\downarrow\rangle_2$ and $|T_{+1}\rangle = |\uparrow\rangle_1 \otimes |\uparrow\rangle_2$ are product states.

- $|S\rangle = \tfrac{1}{\sqrt{2}}\left[|\uparrow\rangle_1 \otimes |\downarrow\rangle_2 - |\downarrow\rangle_1 \otimes |\uparrow\rangle_2\right]$ and $|T_0\rangle = \tfrac{1}{\sqrt{2}}\left[|\uparrow\rangle_1 \otimes |\downarrow\rangle_2 + |\downarrow\rangle_1 \otimes |\uparrow\rangle_2\right]$ can not be written as product states: they are called **entangled states**.

For product states of two particles 1 and 2 (*pure tensors*),

$$
|\psi\rangle_1 \otimes |\phi\rangle_2, \tag{III.2.15}
$$

one can say that particle 1 is in state $|\psi\rangle$ and particle 2 is in state $|\phi\rangle$. States that can not be written as product states are called entangled states. For example, for the state

$$
|\psi\rangle_1 \otimes |\phi\rangle_2 + |\phi\rangle_1 \otimes |\psi\rangle_2, \tag{III.2.16}
$$

one can not say which particle is in which state: the two particles are entangled. Entanglement is the key concept underlying all modern quantum information theory, such as quantum cryptography, quantum teleportation, or quantum computing.

III.2.3 The Exchange Interaction

III.2.3.1 Spin-independent Hamiltonian

We assume a Hamiltonian for two identical electrons of the form

$$\hat{H} = -\frac{\hbar^2}{2m}\Delta_1 + V(\mathbf{r}_1) - \frac{\hbar^2}{2m}\Delta_2 + V(\mathbf{r}_2) + U\left(|\mathbf{r}_1 - \mathbf{r}_2|\right) \tag{III.2.17}$$

which does not depend on the spin. The Hamiltonian is symmetric with respect to the particle indices 1 and 2. The solutions of the stationary Schrödinger equation $\hat{H}\psi(\mathbf{r}_1, \mathbf{r}_2) = E\psi(\mathbf{r}_1, \mathbf{r}_2)$ for the *orbital* parts of the wave function can be classified into symmetric and anti-symmetric with respect to swapping $\mathbf{r}_1$ and $\mathbf{r}_2$: this is because we have

$$\hat{H}\psi(\mathbf{r}_1, \mathbf{r}_2) = E\psi(\mathbf{r}_1, \mathbf{r}_2) \leftrightarrow \hat{H}\psi(\mathbf{r}_2, \mathbf{r}_1) = E\psi(\mathbf{r}_2, \mathbf{r}_1)$$
$$\leftrightarrow \underline{\hat{H}\hat{\Pi}_{12}\psi(\mathbf{r}_1, \mathbf{r}_2)} = E\hat{\Pi}_{12}\psi(\mathbf{r}_1, \mathbf{r}_2) = \hat{\Pi}_{12}E\psi(\mathbf{r}_1, \mathbf{r}_2) = \underline{\hat{\Pi}_{12}\hat{H}\psi(\mathbf{r}_1, \mathbf{r}_2)}$$
$$\leftrightarrow [\hat{H}, \hat{\Pi}_{12}] = 0, \tag{III.2.18}$$

which means that the permutation operator $\hat{\Pi}_{12}$ commutes with the Hamiltonian. The eigenstates of $\hat{H}$ can therefore be chosen such they are also simultaneous eigenstates of $\hat{\Pi}_{12}$ which are symmetric and antisymmetric wave functions with respect to swapping $\mathbf{r}_1$ and $\mathbf{r}_2$.

Since the total wave function (orbital times spin) must be antisymmetric, this means that for energy levels corresponding to symmetric orbital wave functions lead to spin singlets with total spin $S = 0$. Energy levels corresponding to anti-symmetric orbital wave functions lead to spin triplets with total spin $S = 1$. Even though there is no spin-dependent interaction term in the Hamiltonian, the spin and the possible energy values are not independent of each other!

III.2.3.2 Perturbation Theory

Assume we treat the interaction term $V\left(|\mathbf{r}_1 - \mathbf{r}_2|\right)$ in the Hamiltonian Eq. (III.2.17) as a perturbation,

$$\hat{H} = \hat{H}_0 + \hat{H}_1, \quad \hat{H}_0 = -\frac{\hbar^2}{2m}\Delta_1 + V(\mathbf{r}_1) - \frac{\hbar^2}{2m}\Delta_2 + V(\mathbf{r}_2)$$
$$\hat{H}_1 = U\left(|\mathbf{r}_1 - \mathbf{r}_2|\right). \tag{III.2.19}$$

We seek the first correction to an energy level $E_{\alpha\beta}^{(0)}$ of $\hat{H}_0$,

$$\hat{H}_0\phi_{\alpha\beta}^{\pm}(\mathbf{r}_1, \mathbf{r}_2) = E_{\alpha\beta}^{(0)}\phi_{\alpha\beta}^{\pm}(\mathbf{r}_1, \mathbf{r}_2), \quad E_{\alpha\beta}^{(0)} = E_{\alpha}^{(0)} + E_{\beta}^{(0)}$$
$$\phi_{\alpha\beta}^{\pm}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}}\left[\phi_{\alpha}(\mathbf{r}_1)\phi_{\beta}(\mathbf{r}_2) \pm \phi_{\alpha}(\mathbf{r}_2)\phi_{\beta}(\mathbf{r}_1)\right], \tag{III.2.20}$$

where ϕ_{α} and ϕ_{β} are two eigenstates with eigenenergies $E_{\alpha}^{(0)}$ and $E_{\beta}^{(0)}$ of the (identical) single particle Hamiltonians $-\frac{\hbar^2}{2m}\Delta + V(\mathbf{r})$.

We assume the single particle levels to be non-degenerate. Still, the two-electron level $E_{\alpha\beta}^{(0)}$ is degenerate because it corresponds to the two states $|\phi_{\alpha\beta}^{\pm}\rangle$ ($^+$ for the symmetric and $^-$ for the anti-symmetric state. The corresponding two-by-two matrix of $\hat{H}_1$ we need diagonalise for

the degenerate first order perturbation theory in the sub-space spanned by $|\phi_{\alpha\beta}^{\pm}\rangle$ is however diagonal so that things become easy:

$$\underline{\underline{H}}_1 = \begin{pmatrix} \langle\phi_{\alpha\beta}^+|\hat{H}_1|\phi_{\alpha\beta}^+\rangle & \langle\phi_{\alpha\beta}^+|\hat{H}_1|\phi_{\alpha\beta}^-\rangle \\ \langle\phi_{\alpha\beta}^-|\hat{H}_1|\phi_{\alpha\beta}^+\rangle & \langle\phi_{\alpha\beta}^-|\hat{H}_1|\phi_{\alpha\beta}^-\rangle \end{pmatrix} = \begin{pmatrix} A_{\alpha\beta} + J_{\alpha\beta} & 0 \\ 0 & A_{\alpha\beta} - J_{\alpha\beta} \end{pmatrix}. \quad \text{(III.2.21)}$$

Inserting the definitions, we have $(i, j, = \pm)$

$$\langle\phi_{\alpha\beta}^i|\hat{H}_1|\phi_{\alpha\beta}^j\rangle = \int\int d\mathbf{r}_1 d\mathbf{r}_2 \left[\phi_{\alpha\beta}^i(\mathbf{r}_1, \mathbf{r}_2)\right]^* U\left(|\mathbf{r}_1 - \mathbf{r}_2|\right) \phi_{\alpha\beta}^j(\mathbf{r}_1, \mathbf{r}_2). \quad \text{(III.2.22)}$$

Exercise: Show that $\langle\phi_{\alpha\beta}^+|\hat{H}_1|\phi_{\alpha\beta}^-\rangle = \langle\phi_{\alpha\beta}^-|\hat{H}_1|\phi_{\alpha\beta}^+\rangle = 0$.

The explicit calculation of the remaining diagonal elements $\langle\phi_{\alpha\beta}^+|\hat{H}_1|\phi_{\alpha\beta}^+\rangle$ and $\langle\phi_{\alpha\beta}^-|\hat{H}_1|\phi_{\alpha\beta}^-\rangle$ yields

$$A_{\alpha\beta} = \int\int d\mathbf{r}_1 d\mathbf{r}_2 |\phi_\alpha(\mathbf{r}_1)|^2 U\left(|\mathbf{r}_1 - \mathbf{r}_2|\right) |\phi_\beta(\mathbf{r}_2)|^2$$
(direct term) $\quad \text{(III.2.23)}$

$$J_{\alpha\beta} = \int\int d\mathbf{r}_1 d\mathbf{r}_2 \phi_\alpha^*(\mathbf{r}_2)\phi_\beta^*(\mathbf{r}_1) U\left(|\mathbf{r}_1 - \mathbf{r}_2|\right) \phi_\alpha(\mathbf{r}_1)\phi_\beta(\mathbf{r}_2)$$
(exchange term, exchange integral) $\quad \text{(III.2.24)}$

Exercise: Verify these expressions.

The symmetrical orbital wave function $(+)$ belongs to the $S = 0$ (singlet) spinor, whereas the anti-symmetrical orbital wave function $(-)$ belongs to the $T = 0$ (triplet) spinors. Therefore, the unperturbed energy level $E_{\alpha\beta}^{(0)}$ splits into *two* levels

$$E_{\alpha\beta,S=0}^{(1)} = E_{\alpha\beta}^{(0)} + A_{\alpha\beta} + J_{\alpha\beta}, \quad S = 0 \quad \text{singlet} \quad \text{(III.2.25)}$$

$$E_{\alpha\beta,S=1}^{(1)} = E_{\alpha\beta}^{(0)} + A_{\alpha\beta} - J_{\alpha\beta}, \quad S = 1 \quad \text{triplet.} \quad \text{(III.2.26)}$$

III.2.3.3 Direct and Exchange Term: Discussion

1. For $\alpha = \beta$ the anti-symmetrical orbital state vanishes and one has

$$A_{\alpha\alpha} = J_{\alpha\alpha}. \quad \text{(III.2.27)}$$

In this case there is only one singlet state and there are no triplet states.

2. Extreme examples for the interaction potential:

$$\begin{aligned} a) \quad U\left(|\mathbf{r}_1 - \mathbf{r}_2|\right) &= U = \text{const} \\ &\rightsquigarrow A_{\alpha\beta} = U, \quad J_{\alpha\beta} = U\delta_{\alpha\beta} \quad \text{(III.2.28)} \\ b) \quad U\left(|\mathbf{r}_1 - \mathbf{r}_2|\right) &= U_0\delta(\mathbf{r}_1 - \mathbf{r}_2) \\ &\rightsquigarrow A_{\alpha\beta} = J_{\alpha\beta} = U_0 \int d\mathbf{r}|\phi_\alpha(\mathbf{r})|^2|\phi_\beta(\mathbf{r})|^2. \quad \text{(III.2.29)} \end{aligned}$$

III.3 Two-electron Atoms and Ions

Here, we deal with the Helium atom ($Z = 2$) , Lithium ion Li^+ ($Z = 3$), Beryllium ion Be^{++}($Z = 4$) etc. These are two-electron systems as in section III.2.1 with Hamiltonian Eq. (III.2.17),

$$
\begin{aligned}
\hat{H} &= -\frac{\hbar^2}{2m}\Delta_1 + V(\mathbf{r}_1) - \frac{\hbar^2}{2m}\Delta_2 + V(\mathbf{r}_2) + U\left(|\mathbf{r}_1 - \mathbf{r}_2|\right) \\
V(\mathbf{r}) &= -\frac{Ze^2}{4\pi\varepsilon_0 r}, \quad U\left(|\mathbf{r}_1 - \mathbf{r}_2|\right) = \frac{e^2}{4\pi\varepsilon_0|\mathbf{r}_1 - \mathbf{r}_2|}.
\end{aligned}
\tag{III.3.1}
$$

III.3.1 Perturbation theory in U

A problem with perturbation theory here is the fact that the interaction U between the two electrons is not small.

The unperturbed states $|\alpha\rangle$ and $|\beta\rangle$ for the orbital wave functions (cf. section III.2.3.2) are the eigenstates of the hydrogen problem, Eq. (II.1.20),

$$
|\alpha\rangle = |nlm\rangle, \quad |\beta\rangle = |n'l'm'\rangle.
\tag{III.3.2}
$$

Note that these do not contain a spin index.

III.3.1.1 Ground state

The unperturbed ground state has $|nlm\rangle = |100\rangle$ and $|n'l'm'\rangle = |100\rangle$, i.e. $\alpha = \beta$ with a symmetrical orbital wave function $\phi_{\alpha\alpha}^+(\mathbf{r}_1, \mathbf{r}_2) = \phi_{100}(\mathbf{r}_1)\phi_{100}(\mathbf{r}_2)$ and a singlet spinor $|S\rangle$. The energy to first order in U therefore is

$$
\begin{aligned}
E_{\alpha\alpha}^{(1)} &= E_{\alpha\alpha}^{(0)} + A_{\alpha\alpha}, \alpha = (100) \tag{III.3.3} \\
A_{\alpha\alpha} &= \int \int d\mathbf{r}_1 d\mathbf{r}_2 |\phi_{100}(\mathbf{r}_1)|^2 U\left(|\mathbf{r}_1 - \mathbf{r}_2|\right) |\phi_{100}(\mathbf{r}_2)|^2. \tag{III.3.4}
\end{aligned}
$$

Calculation of A yields

$$
E_{100,100}^{(1)} = E_1^{(0)} + E_1^{(0)} + A_{100,100} = 2\left(-\frac{1}{2}\frac{Z^2 e^2}{4\pi\varepsilon_0 a_0}\right) + \frac{5}{8}\frac{Ze^2}{4\pi\varepsilon_0 a_0}.
\tag{III.3.5}
$$

For $Z = 2$, one has $2E_1^{(0)} = -108.8$eV and $A_{100,100} = 34$eV such that $E_{100,100}^{(1)} = -74.8$eV.

Exercise: Calculate the integral leading to the result Eq. (III.3.5). Solution hints are given in Gasiorowicz [3].

III.3.1.2 Excited states

Now our perturbation theory with $\alpha \neq \beta$ and finite exchange term $J_{\alpha\beta}$ comes into play. Further details: textbooks.

IV. THE HARTREE-FOCK METHOD

IV.1 The Hartree Equations, Atoms, and the Periodic Table

IV.1.1 Effective Average Potential

The basic idea here is to replace the complicated interactions among the electrons by an effective, average potential energy that each electron i at position $\mathbf{r}_i$ experiences.

In the Hartree approach one assumes that particle j is described by a wave function (spin orbital) $\psi_{\nu_j}(\xi_j)$ with orbital part $\psi_{\nu_j}(\mathbf{r}_j)$, and the statistics (anti-symmetrization of all the total N-particle wave function for Fermions, symmetrizatin for Bosons) is neglected. In the following, we discuss electrons.

For electrons interacting via the Coulomb interaction $U(r) = e^2/4\pi\varepsilon_0 r$, the potential seen by an electron i at position $\mathbf{r}_i$ is given by

$$V_{\mathrm{H}}(\mathbf{r}_i) = \frac{-e}{4\pi\varepsilon_0} \sum_{j=1(\neq i)}^{N} \int d\mathbf{r}_j \frac{|\psi_{\nu_j}(\mathbf{r}_j)|^2}{|\mathbf{r}_j - \mathbf{r}_i|}. \tag{IV.1.1}$$

This is the sum over the potentials generated by all other electrons $j \neq i$ which have a charge density $-e|\psi_j(\mathbf{r}_j)|^2$. The corresponding potential energy for electron i is $-eV_{\mathrm{H}}(\mathbf{r}_i)$, and therefore one describes electron i by an *effective single particle Hamiltonian*,

$$
\begin{aligned}
H_{\mathrm{Hartree}}^{(i)} &= H_0^{(i)} + V_{\mathrm{Hartree}}(\mathbf{r}_i) \\
&= -\frac{\hbar^2}{2m}\Delta_i + V(\mathbf{r}_i) + \frac{e^2}{4\pi\varepsilon_0} \sum_{j=1(\neq i)}^{N} \int d\mathbf{r}_j \frac{|\psi_{\nu_j}(\mathbf{r}_j)|^2}{|\mathbf{r}_j - \mathbf{r}_i|},
\end{aligned}
\tag{IV.1.2}
$$

where $V(\mathbf{r}_i)$ is the usual potential energy due to the interaction with the nucleus. The corresponding Schrödinger equations for the orbital wave functions ψ_{ν_i} for electron i are

$$\left[-\frac{\hbar^2}{2m}\Delta_i + V(\mathbf{r}_i) + \frac{e^2}{4\pi\varepsilon_0} \sum_{j=1(\neq i)}^{N} \int d\mathbf{r}_j \frac{|\psi_{\nu_j}(\mathbf{r}_j)|^2}{|\mathbf{r}_j - \mathbf{r}_i|} \right] \psi_{\nu_i}(\mathbf{r}_i) = \varepsilon_i \psi_{\nu_i}(\mathbf{r}_i). \tag{IV.1.3}$$

The total wave function in this Hartree approximation is the simple product

$$\Psi_{\mathrm{Hartree}}(\mathbf{r}_1, \sigma_1; ...; \mathbf{r}_N, \sigma_N) = \psi_{\nu_1}(\mathbf{r}_1, \sigma_1)...\psi_{\nu_N}(\mathbf{r}_N, \sigma_N). \tag{IV.1.4}$$

Remarks:

- The Hartree equation Eq. (IV.1.3) is a set of $i = 1, ..., N$ non-linear coupled integro-differential equations.

- As the solutions ψ_{ν_i} of the equations appear again as terms (the Hartree potential) *in* the equations, these are called **self-consistent** equations. One way to solve them is by iteration: neglect the Hartree term first, find the solutions $\psi_{\nu_i}^{(0)}$, insert them in the Hartree potential, solve the new equations for $\psi_{\nu_i}^{(1)}$, insert these again, and so on until *convergence* is reached.

- The Pauli principle is not properly accounted for in this approach, as we do not have a Slater determinant but only a product wave function. This can be improved by the Hartree-Fock equations which we derive in the next section.

IV.1.2 Angular Average, Shells, and Periodic Table

A further simplification of the Hartree equations, Eq. (IV.1.3), is achieved by replacing the Hartree potential by its angular average,

$$V_{\text{Hartree}}(\mathbf{r}) \to \langle V_{\text{Hartree}} \rangle (r) \equiv \int \frac{d\Omega}{4\pi} V_{\text{Hartree}}(\mathbf{r}). \tag{IV.1.5}$$

This still depends on all the wave functions ψ_{ν_i}, but as the one-particle potential now is spherically symmetric, we can use the decomposition into spherical harmonics, radial wave functions, and spin,

$$\langle \xi | \nu_i \rangle = \psi_{\nu_i}(\xi) = R_{n_i, l_i}(r) Y_{l_i, m_i}(\theta, \phi) | \sigma_i \rangle, \quad \nu_i = (n_i, l_i, m_i, \sigma_i). \tag{IV.1.6}$$

Here, the index $\nu_i = (n_i, l_i, m_i, \sigma_i)$ indicates that we are back to our usual quantum numbers $nlm\sigma$ that we know from the hydrogen atom. In contrast to the latter, the radial functions now depend on n and l because we do not have the simple $1/r$ Coulomb potential as one-particle potential.

An even cruder approximation to $V_{\text{Hartree}}(\mathbf{r})$ would be a *parametrization* of the form

$$V_{\text{Hartree}}(\mathbf{r}) + \frac{e^2}{4\pi\varepsilon_0} \frac{Z}{r} \quad \to \quad V_{\text{eff}}(r) \equiv \frac{e^2}{4\pi\varepsilon_0} \frac{Z(r)}{r} \tag{IV.1.7}$$

$$Z(r \to 0) = Z, \quad Z(r \to \infty) = 1. \tag{IV.1.8}$$

by which one loses the self-consistency and ends up with one single Schrödinger equation for a particle in the potential $V_{\text{eff}}(r)$.

Exercise: Give a physical argument for the condition $Z(r \to 0) = Z, \quad Z(r \to \infty) = 1$ in the above equation.

IV.1.2.1 Periodic Table

The ground states of atoms with $N = Z$ electrons in the period table can now be understood by forming Slater determinants ('*configurations*') with N spin-orbitals $|\nu_i\rangle = |n_i l_i m_i \sigma_i\rangle$. The atoms are thus 'built up' from these solutions. This is denoted as

$$
\begin{array}{lll}
\text{H} & 1s & {}^2S_{1/2} \\
\text{He} & (1s)^2 & {}^1S_0 \\
\text{Li} & (\text{He})(2s) & {}^2S_{1/2} \\
\text{Be} & (\text{He})(2s)^2 & {}^1S_0 \\
\text{B} & (\text{He})(2s)^2(2p) & {}^2P_{1/2} \\
\text{C} & (\text{He})(2s)^2(2p)^2 & {}^3P_0 \\
\dots & \dots &
\end{array}
\tag{IV.1.9}
$$

These are built up by 'filling up the levels' with electrons. For a given (n, l) there are $2(2l+1)$ orbitals (2 spin states for each given m-value).

The *spectroscopic description* is given by the quantum numbers S, L, J (total spin, orbital, angular momentum) in the form

$$^{2S+1}L_J. \tag{IV.1.10}$$

Carbon is the first case where **Hund's Rules** kick in. These 'rules' are rules and no strict theorems, but they seem to work well for the understanding of atoms. Here I cite them after Gasiorowicz (web-supplement)

1. *The state with largest S lies lowest:* spin-symmetric WFs have anti-symmetric orbital WFs and therefore reduced electron-electron interaction.

2. *For a given value of S, the state with maximum L lies lowest:* the higher L, the more lobes (and thereby mutual 'escape routes' for interacting electrons) there are in the Y_{lm}s.

3. *L, S given. (i) not more than half-filled incomplete shell: $J = |L - S|$; (ii) more than half-filled shell: $J = L + S$: due to spin-orbit interaction.*

IV.2   Hamiltonian for N Fermions

This is a preparation for the new method (Hartree-Fock) we learn in the next section where we deal with interactions between a large number of Fermions.

The Hamiltonian for N Fermions is given by the generalization of the $N = 2$ case, Eq. (III.2.17), and reads

$$\hat{H} = \hat{\mathcal{H}}_0 + \hat{U} \equiv \sum_{i=1}^{N} \hat{H}_0^{(i)} + \frac{1}{2}\sum_{i\neq j}^{N} U(\xi_i, \xi_j)$$

$$\hat{H}_0^{(i)} = -\frac{\hbar^2}{2m}\Delta_i + V(\mathbf{r}_i). \tag{IV.2.1}$$

IV.2.1   Expectation value of $\hat{\mathcal{H}}_0$

Let us consider a N-Fermion state (Slater determinant), cf. Eq. (III.1.24),

$$|\Psi\rangle = |\nu_1\nu_2...\nu_N\rangle_A = \frac{1}{\sqrt{N!}}\sum_p \hat{\Pi}_p \text{sign}(p)|\nu_{p(1)}\nu_{p(2)}...\nu_{p(N)}\rangle. \tag{IV.2.2}$$

We wish to calculate the expectation value $\langle\Psi|\hat{\mathcal{H}}_0|\Psi\rangle$ with $\hat{\mathcal{H}}_0$ from Eq. (IV.2.1). Consider for example the free Hamiltonian $\hat{H}_0^{(1)}$ for the first particle,

$$\langle\Psi|\hat{H}_0^{(1)}|\Psi\rangle = \frac{1}{N!}\sum_{pp'} \text{sign}(p)\text{sign}(p')\langle\nu_{p(N)}...\nu_{p(2)}\nu_{p(1)}|\hat{H}_0^{(1)}|\nu_{p'(1)}\nu_{p'(2)}...\nu_{p'(N)}\rangle$$

$$= \frac{1}{N!}\sum_{pp'} \text{sign}(p)\text{sign}(p')\langle\nu_{p(N)}...\nu_{p(2)}|\nu_{p'(2)}...\nu_{p'(N)}\rangle\langle\nu_{p(1)}|\hat{H}_0^{(1)}|\nu_{p'(1)}\rangle.$$

For $N - 1$ numbers we must have $p(2) = p'(2)$,...,$p(N) = p'(N)$ (otherwise the term is zero), but if you have a permutation with $N - 1$ terms fixed, the last term ist automatically fixed and we have $p = p'$, thus (note $\text{sign}(p)^2 = 1$)

$$\langle\Psi|\hat{H}_0^{(1)}|\Psi\rangle = \frac{1}{N!}\sum_p \langle\nu_{p(1)}|\hat{H}_0^{(1)}|\nu_{p(1)}\rangle. \tag{IV.2.3}$$

The sum of the single-particle Hamiltonians yields

$$\langle\Psi|\hat{\mathcal{H}}_0|\Psi\rangle = \tag{IV.2.4}$$
$$= \frac{1}{N!}\sum_p \langle\nu_{p(1)}|\hat{H}_0^{(1)}|\nu_{p(1)}\rangle + \langle\nu_{p(2)}|\hat{H}_0^{(2)}|\nu_{p(2)}\rangle + ... + \langle\nu_{p(N)}|\hat{H}_0^{(N)}|\nu_{p(N)}\rangle,$$

but all the Hamiltonians $\hat{H}_0^{(i)}$ have the same form, the sum $\sum_p$ just gives $N!$ identical terms, and therefore

$$\langle\Psi|\hat{\mathcal{H}}_0|\Psi\rangle = \sum_{i=1}^N \langle\nu_i|\hat{H}_0|\nu_i\rangle, \tag{IV.2.5}$$

where we can omit the index $^{(i)}$ in $\hat{H}_0^{(i)}$ and write $\hat{H}_0$ for the free Hamiltonian of a single particle (note that $\hat{\mathcal{H}}_0$ in Eq. (IV.2.1) is the *total* free Hamiltonian; some books use $\hat{h}_0$ instead of $\hat{H}_0$ to make this distinction clearer, but small letters are not nice as a notation for a Hamiltonian).

IV.2.2 Expectation value of $\hat{U}$

This is only slightly more complicated: consider for example the term $U(\xi_1, \xi_2)$,

$$\langle\Psi|U(\xi_1,\xi_2)|\Psi\rangle = \frac{1}{N!}\sum_{pp'}\text{sign}(p)\text{sign}(p')\langle\nu_{p(N)}...\nu_{p(2)}\nu_{p(1)}|U(\xi_1,\xi_2)|\nu_{p'(1)}\nu_{p'(2)}...\nu_{p'(N)}\rangle$$
$$= \frac{1}{N!}\sum_{pp'}\langle\nu_{p(N)}...\nu_{p(3)}|\nu_{p'(3)}...\nu_{p'(N)}\rangle\langle\nu_{p(2)}\nu_{p(1)}|U(\xi_1,\xi_2)|\nu_{p'(1)}\nu_{p'(2)}\rangle.$$

Again, only those terms survive where $\nu_{p(N)} = \nu_{p'(N)}$,...,$\nu_{p(3)} = \nu_{p'(3)}$. We could have, e.g., $p(1) = 4$ and $p(2) = 7$ in which case neither 4 nor 7 can't be among the $p'(3)$,...,$p'(N)$ (this would yield zero overlap in $\langle\nu_{p(N)}...\nu_{p(3)}|\nu_{p'(3)}...\nu_{p'(N)}\rangle$) and therefore 4 and 7 must be among $p'(1)$ and $p'(2)$.

This means we get *two* possibilities for the permutation pairs p and p' now: one with $\nu_{p(1)} = \nu_{p'(1)}$ and $\nu_{p(2)} = \nu_{p'(2)}$, and the other with $\nu_{p(1)} = \nu_{p'(2)}$ and $\nu_{p(2)} = \nu_{p'(1)}$. In the first case $\nu_{p(1)} = \nu_{p'(1)}$,$\nu_{p(2)} = \nu_{p'(2)}$, $\nu_{p(3)} = \nu_{p'(3)}$,...,$\nu_{p(N)} = \nu_{p'(N)}$ which means the permutaton p' is the same as p. In the second case, p' is the same permutation as p apart from *one* additional swap of $p(1)$ and $p(2)$: this means that $\text{sign}(p') = -\text{sign}(p)$ and therefore

$$\langle\Psi|U(\xi_1,\xi_2)|\Psi\rangle = \frac{1}{N!}\sum_p \langle\nu_{p(2)}\nu_{p(1)}|U(\xi_1,\xi_2)|\nu_{p(1)}\nu_{p(2)}\rangle - \langle\nu_{p(1)}\nu_{p(2)}|U(\xi_1,\xi_2)|\nu_{p(1)}\nu_{p(2)}\rangle.$$

The sum over all pairs i, j now again yields

$$\langle\Psi|\hat{U}|\Psi\rangle = \frac{1}{N!}\sum_p\sum_{i\neq j}\frac{1}{2}\left[\langle\nu_{p(j)}\nu_{p(i)}|U|\nu_{p(i)}\nu_{p(j)}\rangle - \langle\nu_{p(i)}\nu_{p(j)}|U|\nu_{p(i)}\nu_{p(j)}\rangle\right]$$
$$= \frac{1}{2}\sum_{i\neq j}\left[\langle\nu_j\nu_i|U|\nu_i\nu_j\rangle - \langle\nu_i\nu_j|U|\nu_i\nu_j\rangle\right]. \tag{IV.2.6}$$

IV.2.2.1 Spin independent symmetric $\hat{U}$

In this case,

$$U(\xi_i, \xi_j) = U\left(|\mathbf{r}_i - \mathbf{r}_j|\right). \tag{IV.2.7}$$

We write this explicitly with wave functions which are products of orbital wave functions $\psi_\nu(\mathbf{r})$ and spinors $|\sigma\rangle$,

$$\langle \xi | \nu \rangle = \psi_\nu(\mathbf{r})|\sigma\rangle, \tag{IV.2.8}$$

and take advantage of the fact that the interaction U does not depend on spin. Then, Eq. (IV.2.6) becomes

$$
\begin{aligned}
\langle \Psi | \hat{U} | \Psi \rangle &= \frac{1}{2} \sum_{i \neq j} \left[\langle \nu_j \nu_i | U | \nu_i \nu_j \rangle - \langle \nu_i \nu_j | U | \nu_i \nu_j \rangle \right] \\
&= \frac{1}{2} \sum_{i \neq j} \int \int d\mathbf{r} d\mathbf{r}' \Big[\psi^*_{\nu_j}(\mathbf{r}')\psi^*_{\nu_i}(\mathbf{r}) U\left(|\mathbf{r} - \mathbf{r}'|\right) \psi_{\nu_i}(\mathbf{r})\psi_{\nu_j}(\mathbf{r}')\langle \sigma_i | \sigma_i \rangle \langle \sigma_j | \sigma_j \rangle \\
&\quad - \psi^*_{\nu_i}(\mathbf{r}')\psi^*_{\nu_j}(\mathbf{r}) U\left(|\mathbf{r} - \mathbf{r}'|\right) \psi_{\nu_i}(\mathbf{r})\psi_{\nu_j}(\mathbf{r}')\langle \sigma_j | \sigma_i \rangle \langle \sigma_i | \sigma_j \rangle \Big] \\
&= \frac{1}{2} \sum_{i \neq j} \int \int d\mathbf{r} d\mathbf{r}' \Big[|\psi_{\nu_j}(\mathbf{r}')|^2 |\psi_{\nu_i}(\mathbf{r})|^2 U\left(|\mathbf{r} - \mathbf{r}'|\right) \\
&\quad - \psi^*_{\nu_i}(\mathbf{r}')\psi^*_{\nu_j}(\mathbf{r}) U\left(|\mathbf{r} - \mathbf{r}'|\right) \psi_{\nu_i}(\mathbf{r})\psi_{\nu_j}(\mathbf{r}')\delta_{\sigma_i \sigma_j} \Big].
\end{aligned}
\tag{IV.2.9}
$$

Using our direct and exchange term notation, Eq. (III.2.23), we can write this in a very simple form as a sum over direct terms $A_{\nu_i \nu_j}$ and exchange terms $J_{\nu_i \nu_j}$,

$$\langle \Psi | \hat{U} | \Psi \rangle = \frac{1}{2} \sum_{i,j} \left[A_{\nu_i \nu_j} - J_{\nu_i \nu_j} \delta_{\sigma_i \sigma_j} \right]. \tag{IV.2.10}$$

Here, we recognize that we actually don't need the restriction $i \neq j$ in the double sum: this term is zero anyway.

Note that Eq. (IV.2.9) refers to states $|\Psi\rangle$ which are simple Slater determinants. It cannot be used, e.g., for states like the $M = 0$ singlet or triplet which are *linear combinations*

$$|\psi_{1\uparrow}\psi_{2\downarrow}\rangle_A \pm |\psi_{1\downarrow}\psi_{2\uparrow}\rangle_A, \tag{IV.2.11}$$

because these would lead to mixed terms

$$\langle \psi_{2\downarrow}\psi_{1\uparrow} | U | \psi_{1\downarrow}\psi_{2\uparrow} \rangle_A \tag{IV.2.12}$$

in the expectation value!

IV.3 Hartree-Fock Equations

IV.3.1 The Variational Principle

The stationary Schrödinger equation

$$\hat{H}\Psi = \varepsilon\Psi \tag{IV.3.1}$$

can be derived from a *variational principle*. For the ground state of the system, this is formulated as a problem of finding the wave vector Ψ of the system among all possible wave vectors such that the expectation value of the energy (i.e., the Hamiltonian) is minimized,

$$\langle\Psi|\hat{H}|\Psi\rangle = \quad \min, \quad \langle\Psi|\Psi\rangle = 1, \tag{IV.3.2}$$

under the additional condition that Ψ be normalised. We are therefore looking for a minimum of the energy *functional*

$$E[\Psi] \equiv \langle\Psi|\hat{H}|\Psi\rangle \tag{IV.3.3}$$

under the additional condition that Ψ be normalised.

IV.3.1.1 Functional Derivates

1. If the Hilbert space belonging to $\hat{H}$ was finite dimensional (for example in the case of the two-level system), the energy functional would just be a quadratic form and $\Psi = (c_1, c_2)^T$ would just be a two-component vector.

2. For states $|\Psi\rangle$ corresponding to wave functions $\Psi(\mathbf{r})$, the energy functional is a 'function of a (wave) function'. Minimising $E[\Psi]$ means that we have to set its first functional 'derivative' to zero (in very much the same way as we set the first derivative of a function to zero in order to find its minimum).

Definition: The derivative of a function $f(x)$ is defined as

$$\frac{df(x)}{dx} \equiv \lim_{\varepsilon\to0}\frac{f[x+\varepsilon\cdot\delta x] - f[x]}{\varepsilon}. \tag{IV.3.4}$$

(δx is a small deviation around the variable x).

Definition: The functional derivative of a functional $F[\Psi]$ is defined as

$$\frac{\delta F[\Psi]}{\delta\Psi} \equiv \lim_{\varepsilon\to0}\frac{F[\Psi+\varepsilon\cdot\delta\Psi] - F[\Psi]}{\varepsilon}. \tag{IV.3.5}$$

($\delta\Psi$ is a small deviation around the function Ψ).

So we recognise that everything is really quite analogous to ordinary derivative. The functional derivative of $E[\Psi]$ is obtained from calculating

$$E[\Psi+\varepsilon\cdot\delta\Psi] = \int d\mathbf{r}\left\{\Psi(\mathbf{r})+\varepsilon\cdot\delta\Psi(\mathbf{r})\right\}^*\hat{H}\left\{\Psi(\mathbf{r})+\varepsilon\cdot\delta\Psi(\mathbf{r})\right\}$$

$$= \int d\mathbf{r}\Psi^*(\mathbf{r})\hat{H}\Psi(\mathbf{r}) + \varepsilon\int d\mathbf{r}\left[\delta\Psi^*(\mathbf{r})\hat{H}\Psi(\mathbf{r}) + \Psi^*(\mathbf{r})\hat{H}\delta\Psi(\mathbf{r})\right]$$

$$+ \quad \varepsilon^2\int d\mathbf{r}\delta\Psi^*(\mathbf{r})\hat{H}\delta\Psi(\mathbf{r}) \tag{IV.3.6}$$

and therefore

$$\frac{\delta E[\Psi]}{\delta\Psi} = \int d\mathbf{r}\left[\delta\Psi^*(\mathbf{r})\hat{H}\Psi(\mathbf{r}) + \Psi^*(\mathbf{r})\hat{H}\delta\Psi(\mathbf{r})\right]$$

$$\equiv \quad \langle\delta\Psi|\hat{H}|\Psi\rangle + \langle\Psi|\hat{H}|\delta\Psi\rangle. \tag{IV.3.7}$$

IV.3.1.2   Lagrange Multiplier

The additional condition $\langle\Psi|\Psi\rangle = 1$ can be incorporated into the minimisation procedure by adding a term to the energy functional, introducing a *Lagrange multiplier* λ, and thereby defining the functional

$$F[\Psi] \equiv E[\Psi] + \lambda\left[\langle\Psi|\Psi\rangle - 1\right]. \tag{IV.3.8}$$

Its functional derivative is

$$\frac{\delta F[\Psi]}{\delta\Psi} \;=\; \langle\delta\Psi|\hat{H}|\Psi\rangle + \langle\Psi|\hat{H}|\delta\Psi\rangle + \lambda\left[\langle\delta\Psi|\Psi\rangle + \langle\Psi|\delta\Psi\rangle\right]. \tag{IV.3.9}$$

Exercise: Check this equation.

Minimization then means

$$0 = \frac{\delta F[\Psi]}{\delta\Psi} \rightsquigarrow \langle\delta\Psi|\hat{H} + \lambda|\Psi\rangle + \langle\Psi|\hat{H} + \lambda|\delta\Psi\rangle = 0. \tag{IV.3.10}$$

As $\delta\Psi$ is arbitrary and complex, this can only be true if

$$[\hat{H} + \lambda]|\Psi\rangle = 0, \quad \langle\Psi|[\hat{H} + \lambda] = 0 \tag{IV.3.11}$$

which are two equations which are the conjugate complex to each other. Writing $\lambda = -\varepsilon$, this means

$$\hat{H}\Psi = \varepsilon\Psi, \tag{IV.3.12}$$

which is the stationary Schrödinger equation. However, here ε is the lowest eigenvalue with corresponding eigenstate Ψ. We thus recognise:

  Minimization of the functional $F[\Psi] \equiv E[\Psi] - \varepsilon\left[\langle\Psi|\Psi\rangle - 1\right]$ is equivalent to finding the lowest eigenvalue and eigenstate of the stationary Schrödinger equation $\hat{H}\Psi = \varepsilon\Psi$.

IV.3.2   The Variational Principle for Many-Electron Systems

The basic idea of Hartree-Fock now is to determine the lowest eigenenergy with corresponding eigenstate Ψ of an N-electron system not by solving the stationary Schrödinger equation $\hat{H}\Psi = \varepsilon\Psi$, but by minimizing the functional $F[\Psi]$. As these two are equivalent, nothing would have been gained. However, for N-electron systems either of these methods has to be done approximately anyway and the argument is now that the minimization procedure is the better starting point.

  Idea: do not carry out the minimization of the functional over *all* possible states Ψ, but just over a certain sub-class of states, i.e., *those which can be written as a anti-symmetrized products of some single particle states $|\nu_i\rangle$, with the $|\nu_i\rangle$ to be determined*, i.e. Slater determinants $|\nu_1, ..., \nu_N\rangle$. The determination of the $|\nu_i\rangle$ leads to the **Hartree-Fock equations**. Note that here and in the following, $|\nu_i\rangle$ does not refer to any fixed set of basis states but to the states to be determined from the Hartree-Fock equations.

Definition: The single particle states $|\nu_i\rangle$ correspond to single particle wave functions $\psi_{\nu_i}(\mathbf{r}, \sigma)$. The label ν_i includes the spin index. In quantum chemistry, these wave functions are sometimes called **spin-orbitals**, **molecular orbitals**, or **shells**.

IV.3.2.1 Functional Derivative

We use the Hamiltonian Eq. (IV.2.1),

$$
\hat{H} = \hat{\mathcal{H}}_0 + \hat{U} \equiv \sum_{i=1}^{N} \hat{H}_0^{(i)} + \frac{1}{2} \sum_{i \neq j}^{N} U_{ij}
$$

$$
\hat{H}_0^{(i)} = -\frac{\hbar^2}{2m} \Delta_i + V(\mathbf{r}_i), \quad U_{ij} = U(\xi_i, \xi_j). \tag{IV.3.13}
$$

The energy functional now depends on the N wave functions $\psi_{\nu_i}(\mathbf{r}, \sigma)$, $i = 1, ..., N$,

$$
F[\Psi] = F[\psi_{\nu_1}, ..., \psi_{\nu_N}] = F[\{\psi_{\nu_i}\}]. \tag{IV.3.14}
$$

The definition of the functional derivative is not more complicated than in the one-component case,

$$
\frac{\delta F[\Psi]}{\delta \Psi} \equiv \lim_{\varepsilon \to 0} \frac{F[\{\psi_{\nu_i} + \varepsilon \cdot \delta\psi_i\}] - F[\{\psi_{\nu_i}\}]}{\varepsilon}, \tag{IV.3.15}
$$

where we now have $i = 1, ..., N$ independent 'deviations' $\delta\psi_i$ from the functions ψ_i. We furthermore want to ensure that all single particle states $|\nu_i\rangle$ are normalised. Therefore, we introduce our functional $F[\Psi]$ with N Lagrange multipliers λ_i,

$$
F[\Psi] \equiv \langle \nu_N, ..., \nu_1 | \hat{H} | \nu_1, ..., \nu_N \rangle_A + \sum_{i=1}^{N} \lambda_i [\langle \nu_i | \nu_i \rangle - 1]. \tag{IV.3.16}
$$

We have calculated the energy expectation values already in Eq. (IV.2.5) and Eq. (IV.2.9),

$$
\begin{aligned}
F[\{\psi_{\nu_i}\}] = & \sum_{i=1}^{N} \langle \nu_i | \hat{H}_0 | \nu_i \rangle + \frac{1}{2} \sum_{i \neq j} [\langle \nu_j \nu_i | U | \nu_i \nu_j \rangle - \langle \nu_i \nu_j | U_{ij} | \nu_i \nu_j \rangle] \\
& + \sum_{i=1}^{N} \lambda_i [\langle \nu_i | \nu_i \rangle - 1].
\end{aligned} \tag{IV.3.17}
$$

The individual terms are simply calculated:

$$
\begin{aligned}
& \frac{\delta}{\delta \Psi} \sum_{i=1}^{N} \langle \nu_i | \hat{H}_0 | \nu_i \rangle = \\
& = \lim_{\varepsilon \to 0} \frac{1}{\varepsilon} \left[\sum_{i=1}^{N} \langle \nu_i + \varepsilon \delta\nu_i | \hat{H}_0 | \nu_i + \varepsilon \delta\nu_i \rangle - \sum_{i=1}^{N} \langle \nu_i | \hat{H}_0 | \nu_i \rangle \right] \\
& = \sum_{i=1}^{N} \left[\langle \delta\nu_i | \hat{H}_0 | \nu_i \rangle + \langle \nu_i | \hat{H}_0 | \delta\nu_i \rangle \right].
\end{aligned} \tag{IV.3.18}
$$

The term from the interaction U yields

$$
\frac{\delta}{\delta \Psi} \frac{1}{2} \sum_{ij} [\langle \nu_j \nu_i | U | \nu_i \nu_j \rangle - \langle \nu_i \nu_j | U | \nu_i \nu_j \rangle] \tag{IV.3.19}
$$

$$
= \frac{1}{2} \sum_{ij} \left[\langle \delta\nu_j \nu_i | U | \nu_i \nu_j \rangle + \langle \nu_j \delta\nu_i | U | \nu_i \nu_j \rangle + \langle \nu_j \nu_i | U | \delta\nu_i \nu_j \rangle + \langle \nu_j \nu_i | U | \nu_i \delta\nu_j \rangle \right]
$$

$$
- \frac{1}{2} \sum_{ij} \left[\langle \delta\nu_i \nu_j | U | \nu_i \nu_j \rangle + \langle \nu_i \delta\nu_j | U | \nu_i \nu_j \rangle + \langle \nu_i \nu_j | U | \delta\nu_i \nu_j \rangle + \langle \nu_i \nu_j | U | \nu_i \delta\nu_j \rangle \right].
$$

We can use the symmetry property (*Exercise:* proof!)

$$\langle \nu_i \nu_k | U | \nu_l \nu_m \rangle = \langle \nu_k \nu_i | U | \nu_m \nu_l \rangle \tag{IV.3.20}$$

to simplify things by using, e.g., $\langle \nu_j \delta \nu_i | U | \nu_i \nu_j \rangle = \langle \delta \nu_i \nu_j | U | \nu_j \nu_i \rangle$ and changing the summation indices i,j such that

$$\frac{\delta}{\delta \Psi} \frac{1}{2} \sum_{ij} \left[\langle \nu_j \nu_i | U | \nu_i \nu_j \rangle - \langle \nu_i \nu_j | U | \nu_i \nu_j \rangle \right] \tag{IV.3.21}$$

$$= \sum_{ij} \left[\langle \delta \nu_j \nu_i | U | \nu_i \nu_j \rangle + \langle \nu_j \nu_i | U | \nu_i \delta \nu_j \rangle - \langle \delta \nu_i \nu_j | U | \nu_i \nu_j \rangle - \langle \nu_i \nu_j | U | \nu_i \delta \nu_j \rangle \right]$$

$$= \sum_{ij} \left[\langle \delta \nu_j \nu_i | U | \nu_i \nu_j \rangle - \langle \delta \nu_j \nu_i | U | \nu_j \nu_i \rangle + (H.c.) \right],$$

where again in the '$-$' term we have swapped indices, and $H.c$ means that there are two terms which are the hermitian conjugates of the two others.

IV.3.2.2   'Direct' and 'Exchange' Operators

We defining these one-particle operators by their matrix elements (excessive use of Dirac notation, hurrah!)

$$\langle \mu | \hat{J}_i | \nu \rangle \equiv \langle \mu \nu_i | U | \nu_i \nu \rangle \rightsquigarrow \langle \delta \nu_j | \hat{J}_i | \nu_j \rangle = \langle \delta \nu_j \nu_i | U | \nu_i \nu_j \rangle \tag{IV.3.22}$$

$$\langle \mu | \hat{K}_i | \nu \rangle \equiv \langle \mu \nu_i | U | \nu \nu_i \rangle \rightsquigarrow \langle \delta \nu_j | \hat{K}_i | \nu_j \rangle = \langle \delta \nu_j \nu_i | U | \nu_j \nu_i \rangle. \tag{IV.3.23}$$

Note that both these operators depend on the still to be determined single particle states $|\nu_i\rangle$!.

We can now write the functional derivate in a very elegant manner,

$$\frac{\delta}{\delta \Psi} \frac{1}{2} \sum_{ij} \left[\langle \nu_j \nu_i | U | \nu_i \nu_j \rangle - \langle \nu_i \nu_j | U | \nu_i \nu_j \rangle \right] = \sum_{j=1}^{N} \langle \delta \nu_j | \hat{J} - \hat{K} | \nu_j \rangle + (H.c.)$$

$$\hat{J} \equiv \sum_i \hat{J}_i, \quad \hat{K} \equiv \sum_i \hat{K}_i, \tag{IV.3.24}$$

and the total functional derivative becomes

$$\frac{\delta F[\Psi]}{\delta \Psi} = \sum_{j=1}^{N} \langle \delta \nu_j | \hat{H}_0 + \lambda_j + \hat{J} - \hat{K} | \nu_j \rangle + (H.c.). \tag{IV.3.25}$$

As we set the functional derivative to zero

$$\frac{\delta F[\Psi]}{\delta \Psi} = 0 \rightsquigarrow \left(\hat{H}_0 + \lambda_j + \hat{J} - \hat{K} \right) | \nu_j \rangle = 0, \tag{IV.3.26}$$

as all the deviations $\delta \nu_j$ are independent.

IV.3.3   Hartree-Fock Equations

We write out Eq. (IV.3.26) in detail, setting $\lambda_j = -\varepsilon_j$,

$$\left(\hat{H}_0 + \hat{J} - \hat{K} \right) | \nu_j \rangle = \varepsilon_j | \nu_j \rangle \tag{IV.3.27}$$

$$\langle \mu | \hat{J} | \nu \rangle \equiv \sum_i \langle \mu \nu_i | U | \nu_i \nu \rangle, \quad \langle \mu | \hat{K} | \nu \rangle \equiv \sum_i \langle \mu \nu_i | U | \nu \nu_i \rangle,$$

where we again stated the definition of the two operators $\hat{J}$ and $\hat{K}$. How do these equations look in the coordinate representation? Let's write

$$\left(\hat{H}_0 + \hat{J} - \hat{K}\right)|\nu_j\rangle = \varepsilon_j|\nu_j\rangle \rightsquigarrow$$

$$\langle\mathbf{r}|\left(\hat{H}_0 + \hat{J} - \hat{K}\right)|\nu_j\rangle = \varepsilon_j\langle\mathbf{r}|\nu_j\rangle \rightsquigarrow$$

$$\langle\mathbf{r}|\hat{H}_0|\nu_j\rangle + \sum_i \langle\mathbf{r}\nu_i|U|\nu_i\nu_j\rangle - \sum_i \langle\mathbf{r}\nu_i|U|\nu_j\nu_i\rangle = \varepsilon_j\langle\mathbf{r}|\nu_j\rangle \rightsquigarrow$$

$$\hat{H}_0\psi_{\nu_j}(\mathbf{r}) + \sum_i \int d\mathbf{r}'\psi_{\nu_i}^*(\mathbf{r}')U(|r-r'|)\psi_{\nu_i}(\mathbf{r}')\psi_{\nu_j}(\mathbf{r})$$

$$-\sum_i \int d\mathbf{r}'\psi_{\nu_i}^*(\mathbf{r}')U(|r-r'|)\psi_{\nu_j}(\mathbf{r}')\psi_{\nu_i}(\mathbf{r})\delta_{\sigma_i\sigma_j} = \varepsilon_j\psi_{\nu_j}(\mathbf{r}). \qquad \text{(IV.3.28)}$$

These are the Hartree-Fock equations in the position representation; we write them out again,

$$\left[\hat{H}_0 + \sum_i \int d\mathbf{r}'|\psi_{\nu_i}(\mathbf{r}')|^2 U(|r-r'|)\right]\psi_{\nu_j}(\mathbf{r})$$

$$-\sum_i \int d\mathbf{r}'\psi_{\nu_i}^*(\mathbf{r}')U(|r-r'|)\psi_{\nu_j}(\mathbf{r}')\psi_{\nu_i}(\mathbf{r})\delta_{\sigma_i\sigma_j} = \varepsilon_j\psi_{\nu_j}(\mathbf{r}). \qquad \text{(IV.3.29)}$$

This looks like a set of $j = 1, ..., N$ stationary Schrödinger equations, but things are actually more complicated as the equations are non-linear.

IV.3.3.1 Direct Term

The direct term,

$$\text{direct term} \quad \left[\sum_i \int d\mathbf{r}'|\psi_{\nu_i}(\mathbf{r}')|^2 U(|r-r'|)\right]\psi_{\nu_j}(\mathbf{r}) \qquad \text{(IV.3.30)}$$

acts like a *local* one-particle potential on particle j: it depends on all the wave functions $\psi_i(\mathbf{r}')$ that have still to be determined. The direct term has a simple physical interpretation: it is the potential at position $\mathbf{r}$ generated by the total density $\sum_i |\psi_i(\mathbf{r}')|^2$ of all the individual electrons in their states $|\nu_i\rangle$ at position $\mathbf{r}'$. The direct term can be interpreted as a 'direct' re-normalisation of the one-particle Hamiltonian $\hat{H}_0$.

IV.3.3.2 Exchange Term

The exchange term,

$$\text{exchange term} \quad \sum_i \int d\mathbf{r}'\psi_{\nu_i}^*(\mathbf{r}')U(|r-r'|)\psi_{\nu_j}(\mathbf{r}')\psi_{\nu_i}(\mathbf{r})\delta_{\sigma_i\sigma_j} \qquad \text{(IV.3.31)}$$

is more complicated and cannot be written as a simple re-normalisation of the one-particle Hamiltonian $\hat{H}_0$. Its spin-dependence indicates that it originates from the exchange interaction between indistinguishable Fermions.

What we have achieved, though, is a *self-consistent* description of the interacting N-Fermion systems in terms of a single Slater determinant built from the states $\psi_i(\mathbf{r}, \sigma)$. Actually, for spin-independent $\hat{H}_0$ and U only the orbital parts $\psi_i(\mathbf{r}$ enter the Hartree-Fock equations, although the spin-indices do play a role in the exchange term.

IV.3.3.3   Example: $N = 2$, 'closed shell'

In the case $N = 2$, we are back to the Helium atom ($N = 2$ electrons). We assume

$$\psi_{\nu_1}(\mathbf{r}, \sigma) = \psi(\mathbf{r})| \uparrow\rangle, \quad \psi_{\nu_2}(\mathbf{r}, \sigma) = \psi(\mathbf{r})| \downarrow\rangle, \tag{IV.3.32}$$

i.e. we only have two spin orbitals with opposite spin. From the Hartree-Fock equations Eq. (E.4.2), we obtain

$$\left[\hat{H}_0 + \sum_{i=1}^{2} \int d\mathbf{r}' |\psi(\mathbf{r}')|^2 U(|r - r'|)\right] \psi(\mathbf{r})$$

$$-\sum_{i=1}^{2} \int d\mathbf{r}' \psi^*(\mathbf{r}') U(|r - r'|) \psi(\mathbf{r}') \psi(\mathbf{r}) \delta_{\sigma_i \sigma_j} \quad = \quad \varepsilon_j \psi(\mathbf{r}). \tag{IV.3.33}$$

Formally, these are still two equations due to the label j ($= 1, 2$), but the two equations are the same and we may set $\varepsilon_1 = \varepsilon_2 = \varepsilon$. The sum in the exchange part has only one term which is half the direct part, and therefore (we re-insert the explicit expression for $\hat{H}_0$)

$$\left[-\frac{\hbar^2}{2m}\Delta + V(\mathbf{r}) + \int d\mathbf{r}' |\psi(\mathbf{r}')|^2 U(|r - r'|)\right] \psi(\mathbf{r}) = \varepsilon \psi(\mathbf{r}). \tag{IV.3.34}$$

Since we have only one orbital wave function, we only have one equation.

IV.3.3.4   Ground State Energy

The ground state energy in Hartree-Fock can be expressed using our equations Eq. (IV.2.9) and Eq. (IV.2.5),

$$\begin{aligned}
\langle \Psi | \hat{H} | \Psi \rangle &= \langle \Psi | \hat{\mathcal{H}}_0 | \Psi \rangle + \langle \Psi | \hat{U} | \Psi \rangle \tag{IV.3.35} \\
&= \sum_{i=1}^{N} \langle \nu_i | \hat{H}_0 | \nu_i \rangle + \frac{1}{2} \sum_{i \neq j} \langle \nu_j \nu_i | U | \nu_i \nu_j \rangle - \langle \nu_i \nu_j | U | \nu_i \nu_j \rangle \\
&= \sum_{i=1}^{N} \langle \nu_i | \hat{H}_0 + \frac{1}{2}\left(\hat{J} - \hat{K}\right) | \nu_i \rangle, \tag{IV.3.36}
\end{aligned}$$

where again we used the direct and exchange operators $\hat{J}$ and $\hat{K}$, Eq. (IV.3.27). Since the $|\nu_i\rangle$ are the solutions of the HF equations Eq. (IV.3.27),

$$\left(\hat{H}_0 + \hat{J} - \hat{K}\right) |\nu_j\rangle \quad = \quad \varepsilon_j |\nu_j\rangle, \tag{IV.3.37}$$

we obtain

$$\begin{aligned}
E_\Psi \equiv \langle \Psi | \hat{H} | \Psi \rangle &= \sum_{i=1}^{N} \left[\varepsilon_i - \frac{1}{2}\langle \nu_i | \left(\hat{J} - \hat{K}\right) | \nu_i \rangle\right] \tag{IV.3.38} \\
&= \frac{1}{2} \sum_{i=1}^{N} \left[\varepsilon_i + \langle \nu_i | \hat{H}_0 | \nu_i \rangle\right]. \tag{IV.3.39}
\end{aligned}$$

V. MOLECULES

V.1 Introduction

Molecules are system consisting of electrons and nuclei. This definition covers the full range from rather simple molecules like H_2 up to extremely complex situations with billions of nuclei, or in principle even solids or fluids although one usually thinks of something like a microscopic object. The question, of course, is what microscopic really means. In principle, one could have molecules with macroscopic large numbers (like 10^{23}) of electrons and nuclei. Would these behave as quantum or as classical objects?

Even for small molecules, there are in fact some fundamental, conceptual issues in the field of molecular structure, cf. for example the article by B. T. Sutcliffe in ch. 35 of Vol. 1 of the 'Handbook of Molecular Physics and Quantum Chemistry', Wiley (2003). These are related to the question of whether or not molecular structure and properties of molecules can be strictly derived from a microscopic Schrödinger equation of an isolated molecule, including all the Coulomb interaction among the constituents. For example, the total Hamiltonian commutes with the parity operator which means that itsd eigenstates are parity eigenstates and therefore cannot must have zero expectation value of the static dipole moment. This would mean that there exist no molecules with static dipole moments, which apparently is in contradiction to what we learn from chemistry. Another such 'paradoxon' seems to be isomers of polyatomic molecules, and the concept of the chemical bond ('deconstructing the bond') is not an easy one, either. These seem to be open questions.

V.1.1 Model Hamiltonian

We start from a Hamiltonian describing a system composed of two sub-systems, electrons (e) and nuclei (n)

$$\mathcal{H} = \mathcal{H}_{\mathrm{e}} + \mathcal{H}_{\mathrm{n}} + \mathcal{H}_{\mathrm{en}}, \tag{V.1.1}$$

where $\mathcal{H}_{\mathrm{en}}$ is the interaction between the two systems. Note that the splitting of the Hamiltonian $\mathcal{H}$ is not unique: for example, $\mathcal{H}_{\mathrm{n}}$ could just be the kinetic energy of the nuclei with their mutual interaction potential included into $\mathcal{H}_{\mathrm{en}}$ (as in the BO approximation).

The set-up $\mathcal{H} = \mathcal{H}_{\mathrm{e}} + \mathcal{H}_{\mathrm{n}} + \mathcal{H}_{\mathrm{en}}$ is quite general and typical for so-called 'system-bath' theories where one would say the electrons are the 'system' and the nuclei are the 'bath' (or vice versa!). In the theory of molecules, however, things are a little bit more complicated as there is a back-action of from the electrons on the nuclei. This back-action is due to the electronic charge density acting as a potential for the nuclei.

There is no *a priori* reason why the nuclei and the electronic system should not be treated on equal footing. However, the theory has a small parameter

$$\kappa = \left(\frac{m}{M} \right)^{\frac{1}{4}} \tag{V.1.2}$$

given by the ratio of electron mass m and a typical nuclear mass $M \gg m$, and the exponent $1/4$ is introduced for convenience in the perturbation theory used by Born and Oppenheimer in their original paper. The smallness of this parameter makes it possible to use an approximation which is called the **Born-Oppenheimer approximation**.

We assume there is a position representation, where $q \equiv \{\mathbf{x_1}, ..., \mathbf{x_N}\}$ represents the positons of all electrons, $X \equiv \{\mathbf{X_1}, ..., \mathbf{X_N}\}$ the positions of all nuclei, and correspondingly for the momenta p and P,

$$\mathcal{H} = \mathcal{H}(q, p; X, P) = \mathcal{H}_e(q, p) + \mathcal{H}_n(X, P) + \mathcal{H}_{en}(q, X). \tag{V.1.3}$$

Spin is not considered here. Also note that the interaction only depends on (q, X) and not on the momenta.

V.2 The Born-Oppenheimer Approximation

This is the central aproximation used in many calculations.

V.2.1 Derivation

We now try to attack the Schrödinger equation $\mathcal{H}\Psi = \mathcal{E}\Psi$ for the total system (electron plus nuclei).

V.2.1.1 Unsuccessful Attempt

A first guess to solve the stationary Schrödinger equation $\mathcal{H}\Psi = \mathcal{E}\Psi$ for the total system would be a separation *ansatz*

$$\begin{aligned} \mathcal{H}(q, p; X, P)\Psi(q, X) &= \mathcal{E}\Psi(q, X) \\ \Psi(q, X) &= \psi_e(q)\phi_n(X) \quad \text{unsuccessful,} \end{aligned} \tag{V.2.1}$$

which does not work because the interaction $\mathcal{H}_{en}(q, X)$ depends on both q *and* X.

V.2.1.2 More Successful Attempt

As $\mathcal{H}_{en}(q, X)$ depends on the positions of the nuclei X, let us try an *ansatz*

$$\Psi(q, X) = \psi_e(q, X)\phi_n(X) \quad \text{successful} \tag{V.2.2}$$

where now the electronic part depends on the nuclear coordinates X as well. This looks unsymmetric: why shouldn't one have $\Psi(q, X) = \psi_e(q, X)\phi_n(q, X)$? First, there *is* an asymmetry in the problem in the form of $M \gg m$, and $\Psi(q, X) = \psi_e(q, X)\phi_n(q, X)$ is no more better than $\Psi(q, X)$ in the first place.

The idea with writing $\Psi(q, X) = \psi_e(q, X)\phi_n(X)$ is that the electronic part $\psi_e(q, X)$ already solves part of the problem, i.e.

$$\left[\mathcal{H}_e(q, p) + \mathcal{H}_{en}(q, X)\right]\psi_e(q, X) = E(X)\psi_e(q, X), \tag{V.2.3}$$

an equation in which X, of course, appears as an *external classical parameter* that commutes with all other variables. Consequently, the eigenvalue $E(X)$ has to depend on X. We thus obtain

$$\begin{aligned} \mathcal{H}\psi_e\phi_n &\equiv \left[\mathcal{H}_e + \mathcal{H}_n + \mathcal{H}_{en}\right]\psi_e\phi_n \\ &= \left[\mathcal{H}_n + E(X)\right]\psi_e\phi_n \quad (?) = \mathcal{E}\psi_e\phi_n \end{aligned} \tag{V.2.4}$$

where the last questionmark indicated what we would like to have! Since $\mathcal{H}_n$ and $E(X)$ depend on the nuclear coordinates only, one would like to use an equation like

$$[\mathcal{H}_n + E(X)]\,\phi_n(X) = \mathcal{E}\phi_n(X), \tag{V.2.5}$$

because then we would have achieved our goal. However, the operator $\mathcal{H}_n$ contains the nuclear momenta P which operate on the X in $\psi_e(q, X)$, i.e.

$$
\begin{aligned}
\mathcal{H}\psi_e\phi_n &= \psi_e\left[\mathcal{H}_n + E(X)\right]\phi_n + \underline{[\mathcal{H}_n\psi_e\phi_n - \psi_e\mathcal{H}_n\phi_n]} \\
&= \mathcal{E}\psi_e\phi_n + \underline{[\mathcal{H}_n\psi_e\phi_n - \psi_e\mathcal{H}_n\phi_n]}.
\end{aligned} \tag{V.2.6}
$$

This shows that we are almost there if it wasn't for the underlined term. One now tries to find arguments why this term can be neglected. If it can be neglected, then we have achieved the full solution of the Schrödinger equation by the two separate equations

$$
\begin{aligned}
\left[\mathcal{H}_e(q, p) + \mathcal{H}_{en}(q, X)\right]\psi_e(q, X) &= E(X)\psi_e(q, X) \quad \text{electronic part} \\
[\mathcal{H}_n + E(X)]\,\phi_n(X) &= \mathcal{E}\phi_n(X) \quad \text{nuclear part.}
\end{aligned} \tag{V.2.7}
$$

These two equations Eq. (V.2.7) are the central equations of the **Born-Oppenheimer approximation**. Even without solving them, some quite interesting observations can already be made:

- The electronic part is calculated as if the nuclei were at fixed positions X ('clamped nuclei').

- The eigenvalue of the energy of the electronic part serves as a *potential* energy for the nuclei in the nuclear part of the equations.

V.2.2   Discussion of the Born-Oppenheimer Approximation

We now have to justify the neglect of the underlined term in

$$\mathcal{H}\psi_e\phi_n = \mathcal{E}\psi_e\phi_n + \underline{[\mathcal{H}_n\psi_e\phi_n - \psi_e\mathcal{H}_n\phi_n]}. \tag{V.2.8}$$

Up to here, everything was still fairly general. Now we make out choice for $\mathcal{H}_n$ as just the kinetic energy of the nuclei,

$$\mathcal{H}_n = \sum_{i=1}^{N} \frac{P_i^2}{2M_i}. \tag{V.2.9}$$

We simplify the following discussion by writing

$$\mathcal{H}_n = \frac{P^2}{2M} = -\frac{\hbar^2}{2M}\nabla_X^2, \tag{V.2.10}$$

which refers to a) a single relative motion of two nuclei of effective mass M, or alternatively b) represents an 'abstract notation' for $\mathcal{H}_n = \sum_{i=1}^{N} \frac{P_i^2}{2M_i}$ (to which the following transformations can easily be generalised).

We write

$$
\begin{aligned}
\mathcal{H}_n\psi_e\phi_n - \psi_e\mathcal{H}_n\phi_n &= -\frac{\hbar^2}{2M}\left[\nabla_X^2\psi_e(q, X)\phi_n(X) - \psi_e(q, X)\nabla_X^2\phi_n(X)\right] \\
&= -\frac{\hbar^2}{2M}\Big[\nabla_X\left\{\phi_n\nabla_X\psi_e + \phi_e\nabla_X\psi_n\right\} - \psi_e\nabla_X^2\phi_n\Big] \\
&= -\frac{\hbar^2}{2M}\Big[2\nabla_X\phi_n\nabla_X\psi_e + \phi_n\nabla_X^2\psi_e\Big].
\end{aligned} \tag{V.2.11}
$$

This term is therefore determined by the derivative of the electronic part with respect to the nuclear positions X, and it has the factor $1/M$ in front. The 'handwaving' argument now is to say that the derivatives $\nabla_X \psi_e$ and $\nabla_X^2 \psi_e$ are small.

V.2.3   Adiabaticity and Geometric Phases

The electronic part equation

$$[\mathcal{H}_e(q,p) + \mathcal{H}_{en}(q,X)]\,\psi_e(q,X) \;=\; E(X)\psi_e(q,X) \tag{V.2.12}$$

usually should give not only one but a whole set of eigenstates,

$$[\mathcal{H}_e + \mathcal{H}_{en}]\,|\alpha(X)\rangle \;=\; E_\alpha(X)|\alpha(X)\rangle. \tag{V.2.13}$$

Assume that for a fixed X we have orthogonal basis of the electronic Hilbert space with states $|\alpha(X)\rangle$, no degeneracies and a discrete spectrum $E_\alpha(X)$,

$$\langle \alpha(X)|\beta(X)\rangle = \delta_{\alpha\beta}. \tag{V.2.14}$$

Adiabaticity means that when X is changed slowly from $X \to X'$, the corresponding state slowly changes from $|\alpha(X)\rangle \to |\alpha(X')\rangle$ and does not jump to another $\alpha' \neq \alpha$ like $|\alpha(X)\rangle \to |\alpha'(X')\rangle$. In that case, we can use the $|\alpha(X)\rangle$ as a basis for all X and write

$$\Psi(q,X) = \sum_\alpha \phi_\alpha(X)\psi_\alpha(q,X). \tag{V.2.15}$$

Now

$$\mathcal{H}\sum_\alpha |\phi_\alpha\rangle_n \otimes |\psi_\alpha\rangle_e \;=\; \sum_\alpha \left[\mathcal{H}_n + E_\alpha(X)\right]|\phi_\alpha\rangle_n \otimes |\psi_\alpha\rangle_e, \tag{V.2.16}$$

and taking the scalar product with a $\langle \psi_\alpha|$ of the Schrödinger equation $\mathcal{H}\Psi = \mathcal{E}\Psi$ therefore gives

$$[\langle \psi_\alpha|\mathcal{H}_n|\psi_\alpha\rangle_e + E_\alpha(X)]\,|\phi_\alpha\rangle_n = \mathcal{E}|\phi_\alpha\rangle_n \tag{V.2.17}$$

This is the Schrödinger equation for the nuclei within the adiabatic approximation. Now using again

$$\begin{aligned}
\mathcal{H}_n &= -\frac{\hbar^2}{2M}\nabla_X^2 \rightsquigarrow \mathcal{H}_n \psi_\alpha(q,X)\phi_\alpha(X) \\
&= -\frac{\hbar^2}{2M}\Big[\psi_\alpha(q,X)\nabla_X^2 \phi_\alpha(X) + \phi_\alpha(X)\nabla_X^2 \psi_\alpha(q,X) \\
&\quad + 2\nabla_X\phi_\alpha(X)\nabla_X\psi_\alpha(q,X)\Big]
\end{aligned} \tag{V.2.18}$$

and therefore the nuclear Schrödinger equation becomes

$$\begin{aligned}
&[\langle \psi_\alpha|\mathcal{H}_n|\psi_\alpha\rangle_e + E_\alpha(X)]\,|\phi_\alpha\rangle_n = \mathcal{E}|\phi_\alpha\rangle_n \rightsquigarrow \\
&\left[-\frac{\hbar^2}{2M}\nabla_X^2 + E_\alpha(X) - \langle \psi_\alpha|\frac{\hbar^2\nabla_X^2}{2M}|\psi_\alpha\rangle - \langle \psi_\alpha|\frac{\hbar^2\nabla_X}{M}|\psi_\alpha\rangle\nabla_X\right]|\phi_\alpha\rangle_n \\
&= \mathcal{E}|\phi_\alpha\rangle_n
\end{aligned} \tag{V.2.19}$$

which can be re-written as

$$\left[-\frac{\hbar^2}{2M}\nabla_X^2 + E_\alpha(X) - \frac{\hbar^2}{2M}G(X) - \frac{\hbar^2}{M}F(X)\nabla_X \right] |\phi_\alpha\rangle_n = \mathcal{E}|\phi_\alpha\rangle_n$$
$$G(X) \equiv \langle\psi_\alpha|\nabla_X^2\psi_\alpha\rangle, \quad F(X) \equiv \langle\psi_\alpha|\nabla_X\psi_\alpha\rangle \qquad , \qquad (V.2.20)$$

where we followed the notation by Mead and Truhlar in their paper J. Chem. Phys. **70**, 2284 (1979). Eq. (E.5.2) is an important result as it shows that the adiabatic assumption leads to extra terms $F(X)$ and $G(X)$ in the nuclear Schrödinger equation in BO approximation on top of just the potential created by the electrons. In particular, the term $F(X)$ is important as it leads to a non-trivial **geometrical phase** in cases where the curl of $F(X)$ is non-zero. This has consequences for molecular spectra, too. geometric phases such as the abelian **Berry phase** and the non-abelian **Wilczek-Zee holonomies** play an important role in other areas of modern physics, too, one example being 'geometrical quantum computing'. For more info on the geometric phase in molecular systems, cf. the Review by C. A. Mead, Prev. Mod. Phys. **64**, 51 (1992).

V.2.4 Breakdown of the Born-Oppenheimer Approximation

This is a non-trivial, much discussed issue and in actual fact still the topic of present research. From our discussion in the previus section we understand that adiabaticity is lost if transitions between electronic states $|\alpha(X)\rangle \to |\alpha'(X')\rangle$ occur while change X. One example for is the so-called Landau-Zener tunneling between nearby energy levels $E_\alpha(X)$ and $E_{\alpha'}(X)$. Also discussed in this context are the Renner-Teller and the Jahn-Teller effects, cf. the short summary by B. T. Sutcliffe in ch. 36 of Vol. 1 of the 'Handbook of Molecular Physics and Quantum Chemistry', Wiley (2003).

V.3 The Hydrogen Molecule Ion H_2^+

The hydrogen molecule is an example of an diatomic molecule. These contain two nuclei of charge $Z_1 e$ and $Z_2 e$; they are called **homonuclear** for two identical nuclei ($Z_1 = Z_2$) and **heteronuclear** ($Z_1 \neq Z_2$) otherwise. For diatomic molecules the Born-Oppenheimer approximation can be reliably justified (CHECK).

V.3.1 Hamiltonian for H_2^+

(Cf. Weissbluth [4] ch. 26 for this section). The Hamiltonian for the electronic part at fixed positions $\mathbf{x}_a$ and $\mathbf{x}_b$ of the two protons is a Hamiltonian for a single electron at position $\mathbf{x}$,

$$\mathcal{H}_e^{(0)} = \frac{\mathbf{p}^2}{2m} - \frac{e^2}{4\pi\varepsilon_0}\left[\frac{1}{|\mathbf{x}-\mathbf{x}_a|} + \frac{1}{|\mathbf{x}-\mathbf{x}_b|} - \frac{1}{R} \right], \qquad (V.3.1)$$

where $R \equiv |\mathbf{x}_a - \mathbf{x}_b|$ and the (fixed) Coulomb repulsion energy $\propto 1/R$ between the two nuclei has been included for later convenience. The eigenstates of this Hamiltonian can be determined from an exact solution in ellipsoidal coordinates. The corresponding wave functions are called **molecular orbitals (MO)** because these orbitals spread out over the whole molecule.

Instead of discussing the exact solution, it is more instructive to discuss an approximate method that can also be used for more complicated molecules. This method is called **LCAO** (linear combination of atomic orbitals) and has a centrol role in quantum chemistry.

V.3.2   The Rayleigh-Ritz Variational Method

For a given Hamiltonian H we minimise the expectation value of the energy over a sub-set of states $|\Psi\rangle$ that are linear combinations of n given states $|\psi_i\rangle$,

$$E = \min\frac{\langle\Psi|H|\Psi\rangle}{\langle\Psi|\Psi\rangle}, \quad |\Psi\rangle = \sum_{i=1}^{n} x_i|\psi_i\rangle. \tag{V.3.2}$$

The $|\psi_i\rangle$ are assumed to be normalised but not necessarily mutually orthogonal, i.e., one can have $\langle\psi_i|\psi_j\rangle \neq 0$.

The energy $E = E(x_1, ..., x_n)$ is therefore minimized with respect to the n coefficients x_i, $i = 1, ..., n$. It can be written as

$$E = \min_{x_1,...,x_n}\frac{\sum_{i,j=1}^{n} x_i^* H_{ij} x_j}{\sum_{i,j=1}^{n} x_i^* S_{ij} x_j} \equiv \min_{\mathbf{x}}\frac{\mathbf{x}^\dagger \underline{\underline{H}}\mathbf{x}}{\mathbf{x}^\dagger \underline{\underline{S}}\mathbf{x}}, \tag{V.3.3}$$

where one has introduced the matrices $\underline{\underline{H}}$ and $\underline{\underline{S}}$ with matrix elements

$$H_{ij} = \langle\psi_i|H|\psi_j\rangle, \quad S_{ij} = \langle\psi_i|\psi_j\rangle. \tag{V.3.4}$$

We find the minimum of

$$f(\mathbf{x}) \equiv \frac{\mathbf{x}^\dagger \underline{\underline{H}}\mathbf{x}}{\mathbf{x}^\dagger \underline{\underline{S}}\mathbf{x}} \tag{V.3.5}$$

by setting the gradient to zero. We treat x and its complex conjugate x^* as independent variables and calculate

$$\frac{\partial}{\partial x_k^*}\left(\mathbf{x}^\dagger \underline{\underline{H}}\mathbf{x}\right) = \frac{\partial}{\partial x_k^*}\sum_{ij} x_i^* H_{ij} x_j = \sum_j H_{kj} x_j = (\underline{\underline{H}}\mathbf{x})_k$$

$$\rightsquigarrow \nabla^*\left(\mathbf{x}^\dagger \underline{\underline{H}}\mathbf{x}\right) = \underline{\underline{H}}\mathbf{x} \tag{V.3.6}$$

Correspondingly,

$$\nabla^*\left(\mathbf{x}^\dagger \underline{\underline{S}}\mathbf{x}\right) = \underline{\underline{S}}\mathbf{x}. \tag{V.3.7}$$

Thus,

$$\nabla^* f(\mathbf{x}) = \frac{\underline{\underline{H}}\mathbf{x}}{\mathbf{x}^\dagger \underline{\underline{S}}\mathbf{x}} - \frac{\mathbf{x}^\dagger \underline{\underline{H}}\mathbf{x}\underline{\underline{S}}\mathbf{x}}{(\mathbf{x}^\dagger \underline{\underline{S}}\mathbf{x})^2} = \frac{\underline{\underline{H}}\mathbf{x}}{\mathbf{x}^\dagger \underline{\underline{S}}\mathbf{x}} - \frac{f(\mathbf{x})\underline{\underline{S}}\mathbf{x}}{\mathbf{x}^\dagger \underline{\underline{S}}\mathbf{x}} = \frac{(\underline{\underline{H}} - f(\mathbf{x})\underline{\underline{S}})\mathbf{x}}{\mathbf{x}^\dagger \underline{\underline{S}}\mathbf{x}}$$

$$\rightsquigarrow (\underline{\underline{H}} - E\underline{\underline{S}})\mathbf{x} = 0, \tag{V.3.8}$$

since $E = f(\mathbf{x})$ at the minimum! A necessary condition for a minimum therefore is the equation $(\underline{\underline{H}} - E\underline{\underline{S}})\mathbf{x} = 0$, which has a solution for $\mathbf{x}$ only if

$$\det\left|\underline{\underline{H}} - E\underline{\underline{S}}\right| = 0. \tag{V.3.9}$$

Exercise: Check which equations one obtains when taking the derivative ∇ instead of ∇^* !

We summarise:

$$E_{\text{Rayleigh−Ritz}} \equiv \min\frac{\langle\Psi|H|\Psi\rangle}{\langle\Psi|\Psi\rangle}, \quad |\Psi\rangle = \sum_{i=1}^{n} x_i|\psi_i\rangle \tag{V.3.10}$$

$$\rightsquigarrow (\underline{\underline{H}} - E\underline{\underline{S}})\mathbf{x} = 0$$

$$H_{ij} \equiv \langle\psi_i|H|\psi_j\rangle, \quad S_{ij} \equiv \langle\psi_i|\psi_j\rangle, \mathbf{x} \equiv (x_1, ..., x_n)^T.$$

The minimization problem thus led us to an eigenvalue problem.

V.3.3 Bonding and Antibonding

(Cf. Atkins and Friedman [5], ch. 8.3, for this section). We now apply the Rayleigh-Ritz variational method to the Hydrogen Molecule Ion H_2^+, restricting ourselves to just $n = 2$ *real* wave functions (atomic orbitals) ψ_i $(i = 1, 2)$, i.e.

$$\text{MO} = \Psi = \text{LCAO} = x_1\psi_1 + x_2\psi_2 \tag{V.3.11}$$
$$\psi_1(\mathbf{r}) = \psi_{n=1,l=0,m=0}(\mathbf{r} - \mathbf{r}_a), \quad \psi_2(\mathbf{r}) = \psi_{n=1,l=0,m=0}(\mathbf{r} - \mathbf{r}_b)$$

with two hydrogen groundstate s-orbitals for nuclei at $\mathbf{r}_a$ and $\mathbf{r}_b$, respectively.

V.3.3.1 Rayleigh-Ritz Results

We require the matrices $\underline{\underline{H}}$ and $\underline{\underline{S}}$,

$$\underline{\underline{H}} = \begin{pmatrix} \alpha & \beta \\ \beta & \alpha \end{pmatrix}, \quad \underline{\underline{S}} = \begin{pmatrix} 1 & S \\ S & 1 \end{pmatrix} \tag{V.3.12}$$
$$\alpha \equiv \langle\psi_1|H|\psi_1\rangle = \langle\psi_2|H|\psi_2\rangle, \quad \beta = \langle\psi_1|H|\psi_2\rangle, \quad S = \langle\psi_1|\psi_2\rangle.$$

We have to solve

$$\det|\underline{\underline{H}} - E\underline{\underline{S}}| = 0 \rightsquigarrow \det \begin{vmatrix} \alpha - E & \beta - ES \\ \beta - ES & \alpha - E \end{vmatrix} = 0$$
$$\rightsquigarrow (\alpha - E)^2 - (\beta - ES)^2 = 0 \rightsquigarrow \alpha - E = \pm(\beta - ES)$$
$$E_+ = \frac{\alpha + \beta}{1 + S}, \quad E_- = \frac{\alpha - \beta}{1 - S}. \tag{V.3.13}$$

This give the eigenvalues of the energy, $E_\pm$. We find the eigenvectors (x_1, x_2) from

$$(\alpha - E_\pm)x_1 + (\beta - E_\pm S)x_2 = 0 \tag{V.3.14}$$
$$E_+ \; : \; ((1 + S)\alpha - (\alpha + \beta))x_1 + ((1 + S)\beta - (\alpha + \beta)S)x_2 = 0$$
$$(S\alpha - \beta)x_1 + (\beta - S\alpha)x_2 = 0 \rightsquigarrow x_1 = x_2 \equiv x_+.$$
$$E_- \; : \; ((1 - S)\alpha - (\alpha - \beta))x_1 + ((1 - S)\beta - (\alpha - \beta)S)x_2 = 0$$
$$(-S\alpha + \beta)x_1 + (\beta - S\alpha)x_2 = 0 \rightsquigarrow x_1 = -x_2 \equiv x_-. \tag{V.3.15}$$

The normalisation constant is determined from

$$1 = \langle\Psi|\Psi\rangle = x_1^2 + x_2^2 + 2x_1 x_2\langle\psi_1|\psi_2\rangle = x_1^2 + x_2^2 + 2x_1 x_2 S$$
$$\rightsquigarrow 1 = x_+^2 + x_+^2 + 2x_+^2 S \rightsquigarrow x_+ = \frac{1}{\sqrt{2(1 + S)}} \tag{V.3.16}$$
$$\rightsquigarrow 1 = x_-^2 + x_-^2 - 2x_-^2 S \rightsquigarrow x_- = \frac{1}{\sqrt{2(1 - S)}}. \tag{V.3.17}$$

Summarising, we therefore have obtained the two molecular orbitals (MOs) with energies $E_\pm$,

$$E_+ \; : \; \Psi_+ = \frac{1}{\sqrt{2(1 + S)}}(\psi_1 + \psi_2) \quad \text{bonding} \tag{V.3.18}$$

$$E_- \; : \; \Psi_- = \frac{1}{\sqrt{2(1 - S)}}(\psi_1 - \psi_2) \quad \text{antibonding}. \tag{V.3.19}$$

Note that the normalisation factor is different for the two MOs, this is due to the fact that the original AOs (atomic orbitals) are not orthogonal.

V.3.3.2   Explicit Calculation of α, β, S

This is required in order to find the values for the two energies $E_\pm$, and also in order to find out which of the two states $\Psi_\pm$ has lower energy! The calculations are performed by introducing elliptical coordinates $1 \le \mu \le \infty$, $-1 \le \nu \le 1$, $0 \le \phi \le 2\pi$,

$$\mu = \frac{r_a + r_b}{R}, \quad \nu = \frac{r_a - r_b}{R} \tag{V.3.20}$$

and noting that the volume element in these coordinates is

$$dV = \frac{1}{8}R^3(\mu^2 - \nu^2)d\mu d\nu d\phi. \tag{V.3.21}$$

The result for α, β, and S is found as a function of the (fixed) distance R between the two protons. Using this together with Eq. (V.3.13), one finally obtains

$$
\begin{aligned}
E_+ &= E_{1s} + \frac{e^2}{4\pi\varepsilon_0 a_0}\left[\frac{1}{R} - \frac{j+k}{1+S}\right] \\
E_- &= E_{1s} + \frac{e^2}{4\pi\varepsilon_0 a_0}\left[\frac{1}{R} + \frac{j-k}{1-S}\right] \\
R &\equiv |\mathbf{r}_a - \mathbf{r}_b|/a_0, \quad S \equiv \left(1 + R + \frac{1}{3}R^2\right)e^{-R} \\
j &\equiv a_0 \int dV \frac{|\psi_{1s}(\mathbf{r} - \mathbf{r}_a)|^2}{|\mathbf{r} - \mathbf{r}_b|} = \frac{1}{R}\left(1 - (1+R)e^{-2R}\right) \\
k &\equiv a_0 \int dV \frac{\psi_{1s}(\mathbf{r} - \mathbf{r}_a)\psi_{1s}(\mathbf{r} - \mathbf{r}_b)}{|\mathbf{r} - \mathbf{r}_a|} = (1 + R)e^{-R}.
\end{aligned}
\tag{V.3.22}
$$

Be careful because I haven't checked these explicit expressions, which are from Atkins/Friedman [5] ch. 8.3.

REMARKS:

- The energies j and k are here written as dimensionless quantities.

- The energy j is due to the electron charge density around nucleus a in the Coulomb field of nucleus b. The energy k is an interference term.

- One has $j > k$ and therefore the energy E_+ corresponding to the bonding state is the lower of the two: Occupation of the **bonding orbital** Ψ_+ lowers the energy of the molecule and 'draws the two nuclei together', as we will see from the curve $E_+(R)$ below which represents the potential in BO approximation for the two nuclei. The bonding orbital corresponds to a wave function with even parity with respect to with respect to reflections at the plane that lies symmetrically between the two nuclei.

- The **antibonding orbital** Ψ_- has a larger energy. It corresponds to an odd wave function.

- For the Hydrogen ion, sometimes one uses the notation (cf. Weissbluth [4] ch. 26.2)

$$
\begin{aligned}
\Psi_+ &\equiv 1\sigma_g^+ \quad \text{bonding MO} & \text{(V.3.23)} \\
\Psi_- &\equiv 1\sigma_u^+ \quad \text{antibonding MO,} & \text{(V.3.24)}
\end{aligned}
$$

  where the indices mean even for g (German 'gerade') and odd for u (German 'ungerade') and σ^+ referring to a symmetry (see below).

The charge distribution in Ψ_+ and Ψ_- is shown in Fig.(V.3.3.2).

$$E_2 = \frac{H_{aa} - H_{ab}}{1 - S}$$

$$E_1 = \frac{H_{aa} + H_{ab}}{1 + S}$$

(a)

(a)   (b)
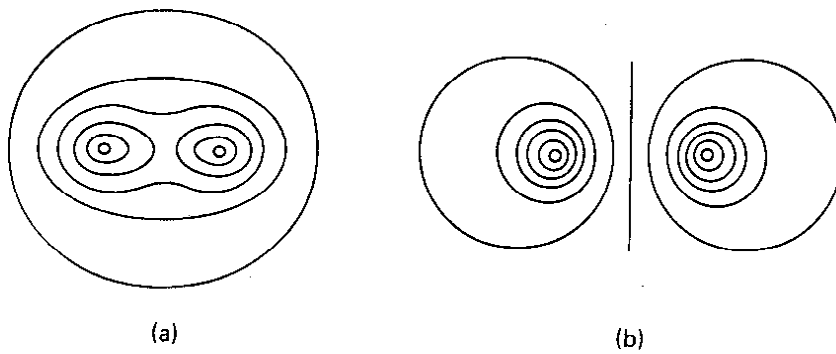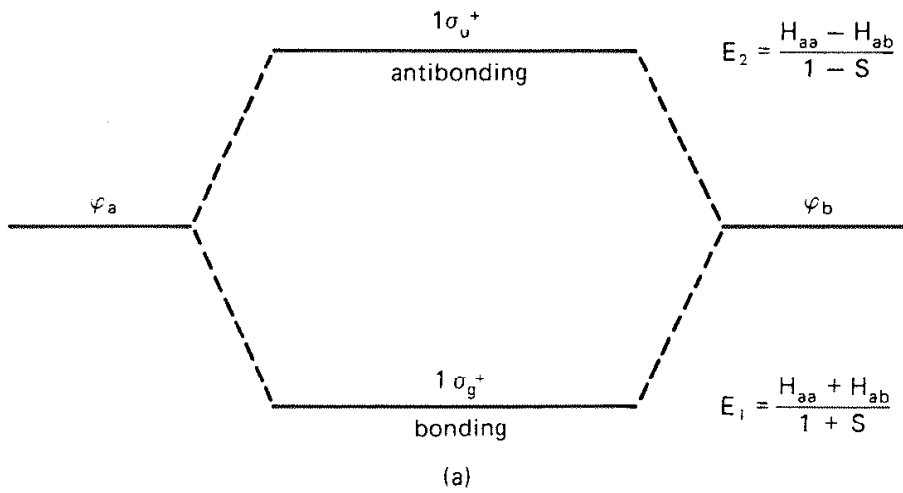
sbluth [4].

Fig. V.2: Charge distribution in Ψ_+ (a) and Ψ_- (b), from Weissbluth [4].

V.3.3.3   Symmetries of MOs in LCAO

(cf. Weissbluth [4] ch. 26.2). This leads to a classification of MOs according to their symmetry under symmetry transformations. The most important classes are the σ **molecular orbitals** which form σ-**bonds**, and the π **molecular orbitals** which form π-**bonds**, cf. Fig.
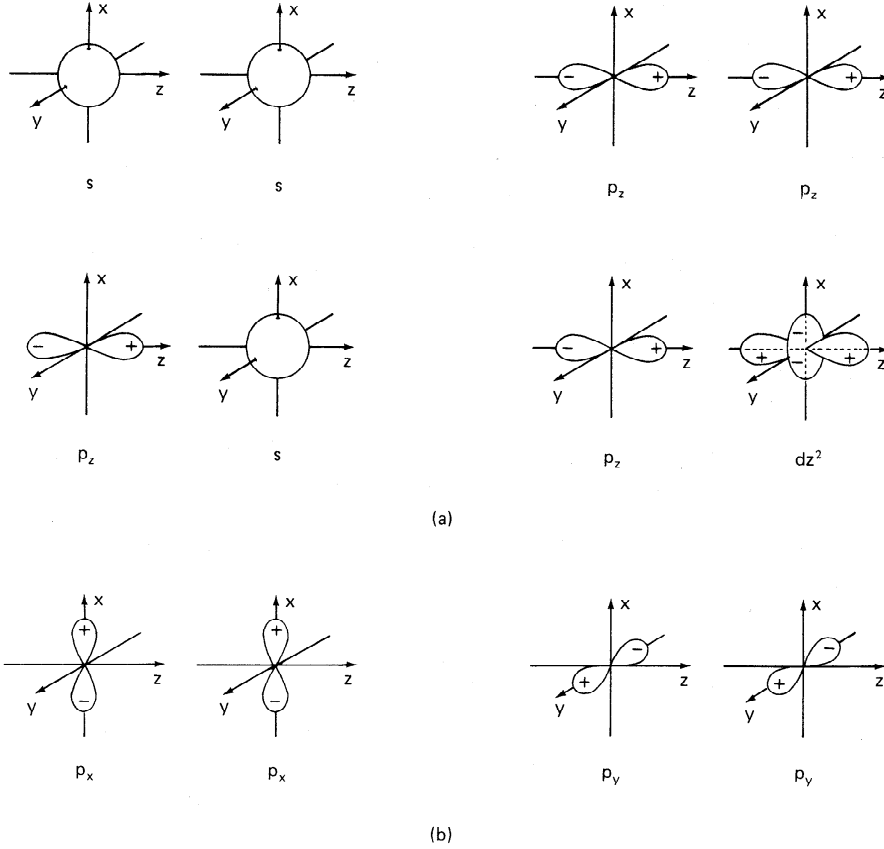
FIG. 26.4 Molecular orbitals: (a) σ type; (b) π type.

Fig. V.3: σ-type and π-type LCAO-MOs, from Weissbluth [4]

V.3.3.4 Molecular Potential Energy

Within BO approximation, the energies $E_\pm(R)$ enter the nuclear Hamiltonian (cf. Eq. (**??**) with $\varepsilon_\alpha = E_\pm$) for the wave functions χ

$$\left[\sum_{i=a,b} \frac{\mathbf{P}_i^2}{2M} + E_\pm(R)\right] \chi_\pm(\mathbf{x}_a, \mathbf{x}_b) = E\chi_\pm(\mathbf{x}_a, \mathbf{x}_b) \tag{V.3.25}$$

of the nuclear system with $R = |\mathbf{x}_a - \mathbf{x}_b|$, cf. Eq. (V.3.1). Clearly, a separation in center-of mass and relative motion is easily done here. The potential energy for the nuclei is given by the function $E_\pm(R)$, cf. Eq. (V.3.22),

$$E_\pm(R) = E_{1s} + \frac{e^2}{4\pi\varepsilon_0 a_0}\left[\frac{1}{R} \mp \frac{j(R) \pm k(R)}{1 \pm S(R)}\right], \tag{V.3.26}$$

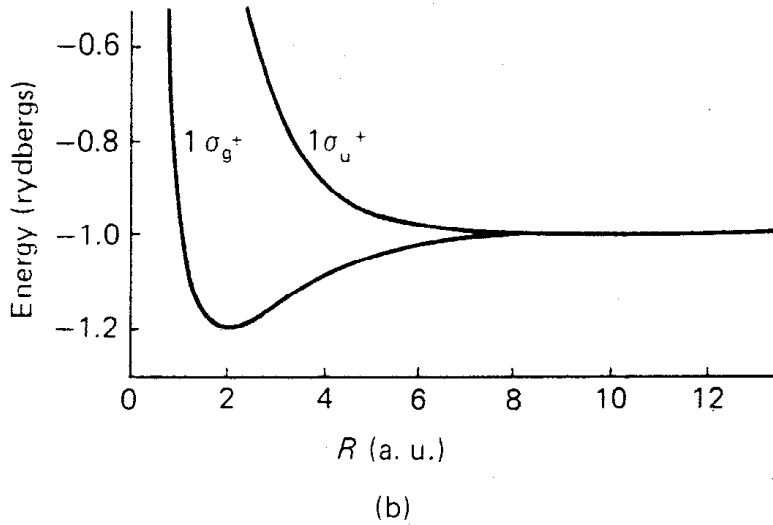**Fig. V.4:** $E_{\pm}(R)$, Eq. (V.3.26), for the H_2^+-ion in Born-Oppenheimer approximation and using the MO-LCAO Rayleigh-Ritz method, from Weissbluth [4].

with the explicit expression for $j(R)$, $k(R)$, $S(R)$, in Eq. (V.3.22). The parametric eigenenergies of the electronic system become the potential for the nuclei, which is the characteristic feature of the BO approximation. The corresponding potential curves are shown in Fig.(V.3.3.4).

- The potential energy $E_+(R)$ of the bonding molecular orbital has a minimum at $R = R_0$. This determines the equilibrium position of the two nuclei. Occupation of the bonding MO helps to bond the nuclei together and thereby form the molecule.

- The potential energy $E_-(R)$ of the antibonding molecular orbital has no local minimum. Therefore, the antibonding state is an excited state in which the molecule dissociates.

V.4 Hartree-Fock for Molecules

We now discuss a method to calculate molecular orbitals within the Hartree-Fock method. Let us start from Eq. (IV.3.27),

$$\left(\hat{H}^0 + \hat{J} - \hat{K}\right)|\nu_j\rangle = \varepsilon_j|\nu_j\rangle \tag{V.4.1}$$

$$\langle\mu|\hat{J}|\nu_j\rangle \equiv \sum_i \langle\mu\nu_i|U|\nu_i\nu_j\rangle, \quad \langle\mu|\hat{K}|\nu_j\rangle \equiv \sum_i \langle\mu\nu_i|U|\nu_j\nu_i\rangle,$$

and assume a **closed shell** situation and a Hamiltonian $\hat{H}^0 + U$ which is diagonal in spin-space, i.e. does not flip the spin. The counter j runs from 1 to $2N$, there are N orbitals with

spin up and N orbitals with spin down. The index j thus runs like

$$j = 1 \uparrow, 1 \downarrow, 2 \uparrow, 2 \downarrow, ..., N \uparrow, N \downarrow .   \tag{V.4.2}$$

We write

$$\psi_{\nu_{j=2k-1}} \equiv \psi_k | \uparrow \rangle, \quad \psi_{\nu_{j=2k}} \equiv \psi_k | \downarrow \rangle,   \tag{V.4.3}$$

because $j = 2k$, $k = 1, ..., N$ corresponds to spin-orbitals with spin $\downarrow$ and $j = 2k - 1$, $k = 1, ..., N$ corresponds to spin-orbitals with spin $\uparrow$. Use the Fock operator

$$\mathcal{F} \equiv \hat{H}^0 + \hat{J} - \hat{K}   \tag{V.4.4}$$

and let us, for example, set $j = 2k - 1$ to obtain

$$\mathcal{F} |\psi_k\rangle \otimes | \uparrow \rangle \;\; = \;\; \varepsilon_{k\uparrow} |\psi_k\rangle \otimes | \uparrow \rangle   \tag{V.4.5}$$

$$\tag{V.4.6}$$

and expand the orbital wave function as

$$(\text{MO}) \quad \psi_k = \sum_{l=1}^{M} c_{lk} \phi_l, \quad (\text{LCAO})   \tag{V.4.7}$$

with $l = 1, ..., M$ given atomic orbitals. Inserting yields

$$\langle \uparrow | \otimes \langle \phi_{l'} | \mathcal{F} | \sum_{l=1}^{M} c_{lk} |\phi_l\rangle \otimes | \uparrow \rangle \;\; = \;\; \varepsilon_{k\uparrow} \sum_{l=1}^{M} c_{lk} \langle \phi_{l'} | \phi_l \rangle$$

$$\sum_{l=1}^{M} \mathcal{F}_{l'l}^{\uparrow\uparrow} c_{lk} \;\; = \;\; \varepsilon_{k\uparrow} \sum_{l=1}^{M} S_{l'l} c_{lk}   \tag{V.4.8}$$

$$S_{l'l} \equiv \langle \phi_{l'} | \phi_l \rangle, \quad \mathcal{F}_{l'l}^{\uparrow\uparrow} \equiv \langle \uparrow | \otimes \langle \phi_{l'} | \mathcal{F} | \phi_l \rangle \otimes | \uparrow \rangle.$$

V.4.1   Roothan Equations

The equations Eq. (V.4.8) are called **Roothan equations** (they are usually written for spin-independent Fock-operator $\mathcal{F}$. We summarize the situation so far:

- We have $l = 1, ..., M$ atomic orbitals (AOs) ϕ_l for $k = 1, ..., N$ molecular orbitals (MOs) expressed as linear combinations (LCAO) of the AOs.

- We define the matrix $\underline{\underline{C}}$ as the matrix of the coefficients, $\underline{\underline{C}}_{lk} = c_{lk}$, $\underline{\underline{S}}$ as the matrix of the overlaps, $\underline{\underline{S}}_{lk} = S_{lk}$, and $\underline{\underline{\mathcal{F}}}$ as the Fock matrix.

- As $\hat{H}^0 + U$ is diagonal in spin-space so is the Fock-operator $\mathcal{F}$ whence there are no mixed terms $\mathcal{F}^{\downarrow\uparrow}$ or $\mathcal{F}^{\uparrow\downarrow}$.

We can then write the Roothan equations as

$$\underline{\underline{\mathcal{F}}}^{\uparrow\uparrow} \underline{\underline{C}} \;\; = \;\; \underline{\underline{S}} \, \underline{\underline{C}} \, \underline{\varepsilon}^{\uparrow}   \tag{V.4.9}$$

$$\underline{\underline{\mathcal{F}}}^{\downarrow\downarrow} \underline{\underline{C}} \;\; = \;\; \underline{\underline{S}} \, \underline{\underline{C}} \, \underline{\varepsilon}^{\downarrow},   \tag{V.4.10}$$

where $\underline{\underline{\varepsilon}}$ are diagonal matrices for the energies ε_k. Now these look like simultaneous linear equations but of course they are not, because the Fock-operator depends on the coefficients c_{kl} that we try to determine: recall $\mathcal{F} \equiv \hat{H}^0 + \hat{J} - \hat{K}$ with

$$
\hat{J}^{\uparrow\uparrow}_{l'l} \equiv \sum_{i=1}^{2N} \langle l'\nu_i|U|\nu_i l\rangle \tag{V.4.11}
$$

$$
\hat{K}^{\uparrow\uparrow}_{l'l} \equiv \sum_{i=1}^{2N} \langle l'\nu_i|U|l\nu_i\rangle \langle \sigma_i| \uparrow\rangle,
$$

where we first considered spin up. The i-sum runs over *spin-orbitals*, i.e. AOs including the spin. We now assume U to be spin-independent.

$$
\hat{J}_{l'l} \equiv \sum_{\sigma=0,1} \sum_{k=1}^{N} \langle l'\nu_{2k-\sigma}|U|\nu_{2k-\sigma}l\rangle = 2\sum_{k=1}^{N} \langle l'\psi_k|U|\psi_k l\rangle
$$

$$
\hat{K}_{l'l} \equiv \sum_{\sigma=0,1} \sum_{k=1}^{N} \langle l'\nu_{2k-\sigma}|U|l\nu_{2k-\sigma}\rangle \langle \sigma| \uparrow\rangle = \sum_{k=1}^{N} \langle l'\psi_k|U|l\psi_k\rangle,
$$

where $\sigma = 0$ corresponds to spin down and $\sigma = 1$ corresponds to spin up, and the orbital part of the spin-orbital $\nu_{2k-\sigma}$ is ψ_k by definition. Now everything is expressed in terms of orbitals only and the spin has just led to the factor of two in front of the direct term!

We now use the LCAO expansion $\psi_k = \sum_m c_{mk}\psi_m$ and thus obtain

$$
\hat{J}_{l'l} = 2\sum_{k=1}^{N} \sum_{m,m'=1}^{M} c^*_{m'k}c_{mk}\langle l'm'|U|ml\rangle = \sum_{m,m'=1}^{M} P_{m'm}\langle l'm'|U|ml\rangle
$$

$$
\hat{K}_{l'l} = \sum_{k=1}^{N} \sum_{m,m'=1}^{M} c^*_{m'k}c_{mk}\langle l'm'|U|lm\rangle = \frac{1}{2}\sum_{m,m'=1}^{M} P_{m'm}\langle l'm'|U|lm\rangle
$$

$$
P_{m'm} \equiv 2\sum_{k=1}^{N} c^*_{m'k}c_{mk}, \quad \text{populations} \tag{V.4.12}
$$

where the populations depend on the c's: it is them who are responsible for the non-linearity (self-consistent character) of the Roothan equations. Summarizing, the matrix elements of the Fock operator are given by

$$
\mathcal{F}^{\uparrow\uparrow}_{l'l} = \left(\hat{H}^0\right)^{\uparrow\uparrow}_{l'l} \tag{V.4.13}
$$

$$
+ \sum_{m,m'=1}^{M} P_{m'm}[\{c_{ij}\}] \left(\langle l'm'|U|ml\rangle - \frac{1}{2}\langle l'm'|U|lm\rangle\right).
$$

VI. TIME-DEPENDENT FIELDS

VI.1 Time-Dependence in Quantum Mechanics

The basis equation is the Schrödinger equation. For a given (time-dependent) Hamiltonian $H(t)$, the time evolution of a Dirac ket is

$$i\hbar\partial_t|\Psi(t)\rangle = H(t)|\Psi(t)\rangle. \qquad (\text{VI.1.1})$$

There are usually two steps in solving a given physical problem

1. find $H(t)$ for the problem at hand.

2. solve the corresponding Schrödinger equation.

Depending on the problem, one often has one of the following cases:

$$
\begin{aligned}
H(t) &= H \quad \text{time-independent Hamiltonian} & (\text{VI.1.2}) \\
H(t) &= H(t+T) \quad \text{periodic time-dependence (period } T) & (\text{VI.1.3}) \\
H(t) & \quad\quad \text{arbitrary time-dependence in Hamiltonian} & (\text{VI.1.4})
\end{aligned}
$$

The second case occurs, e.g., in the interaction of atoms with monochromatic electric fields like

$$\mathbf{E}(\mathbf{r}, t) = \mathbf{E}_0 \cos\left(\mathbf{k r} - \omega t\right). \qquad (\text{VI.1.5})$$

An explicit time-dependence in the Hamiltonian usually represents *classical* fields or parameters that can be controlled from the outside and which are *not* quantum variables.

With respect to the interaction between atoms or molecules and light, there are two groups of problems one has to sort out:

1. find the correct Hamiltonian $H(t)$ (in fact not so easy).

2. find appropriate techniques to solve the Schrödinger equation (at least in principle one knows how to do that).

VI.1.1 Time-evolution with time-independent H

(Set $\hbar = 1$ in the following). In this case, the initial value problem

$$i\partial_t|\Psi(t)\rangle = H|\Psi(t)\rangle, \quad |\Psi(t_0)\rangle = |\Psi\rangle_0 \qquad (\text{VI.1.6})$$

is formally solved as

$$|\Psi(t)\rangle = U(t, t_0)|\Psi\rangle_0, \quad U(t, t_0) \equiv e^{-iH(t-t_0)}, \quad t \geq t_0, \qquad (\text{VI.1.7})$$

where we introduced the **time-evolution operator** $U(t, t_0)$ as the exponential of the operator $-iH(t - t_0)$ by the power series

$$e^x = \sum_{n=0}^{\infty} \frac{x^n}{n!}. \tag{VI.1.8}$$

Things are simple, however, when we use the solutions of the stationary Schrödinger equation

$$H|n\rangle = \varepsilon_n|n\rangle, \tag{VI.1.9}$$

where the eigenstates $|n\rangle$ form a complete basis and one has

$$
\begin{aligned}
\langle n|\Psi(t)\rangle &= \sum_m \langle n|e^{-iH(t-t_0)}|m\rangle\langle m|\Psi\rangle_0 \tag{VI.1.10}\\
&= \sum_m \langle n|m\rangle e^{-i\varepsilon_m(t-t_0)}\langle m|\Psi\rangle_0\\
&= \sum_m \delta_{nm} e^{-i\varepsilon_m(t-t_0)}\langle m|\Psi\rangle_0\\
&= e^{-i\varepsilon_n(t-t_0)}\langle n|\Psi\rangle_0\\
&\rightsquigarrow |\Psi(t)\rangle = \sum_n |n\rangle\underline{\langle n|\Psi(t)\rangle} = \sum_n |n\rangle\underline{e^{-i\varepsilon_n(t-t_0)}\langle n|\Psi\rangle_0},
\end{aligned}
$$

where the underlined terms are the expansion coefficients of $|\Psi(t)\rangle$ in the basis $\{|n\rangle\}$.

VI.1.2   Example: Two-Level System

Consider

$$H = \begin{pmatrix} 0 & T_c \\ T_c & 0 \end{pmatrix}. \tag{VI.1.11}$$

We calculate the time-evolution operator $U(t, t_0) \equiv e^{-iH(t-t_0)}$ by two methods:

VI.1.2.1   Power Series

Use

$$
\begin{aligned}
H &= T_c\sigma_x, \quad \sigma_x \equiv \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\\
\sigma_x^0 &= \hat{1}, \quad \sigma_x^1 = \sigma_x, \quad \sigma_x^2 = \hat{1}\\
&\rightsquigarrow e^{\alpha\sigma_x} = \hat{1} + \frac{\alpha}{1!}\sigma_x + \frac{\alpha^2}{2!}\hat{1} + \frac{\alpha^3}{3!}\sigma_x + \frac{\alpha^4}{4!}\hat{1} + ...\\
&= \cosh(\alpha)\hat{1} + \sinh(\alpha)\sigma_x\\
\rightsquigarrow U(t, t_0) &\equiv e^{-iH(t-t_0)} = \cosh(-i(t-t_0)T_c)\hat{1} + \sinh(-i(t-t_0)T_c)\sigma_x\\
&= \cos[(t-t_0)T_c]\hat{1} - i\sin[(t-t_0)T_c]\sigma_x. \tag{VI.1.12}
\end{aligned}
$$

VI.1.2.2 Eigenvectors

We diagonalise H according to

$$H = SDS^{-1}, \tag{VI.1.13}$$

where D is the diagonal matrix of the eigenvalues and S the orthogonal matrix of the eigenvectors. This yields

$$e^{\alpha H} = e^{\alpha SDS^{-1}} = S e^{\alpha D} S^{-1} \tag{VI.1.14}$$

which follows from the definition of the power series (Exercise: CHECK)! For $H = T_c \sigma_x$, we already calculated the EVs in an earlier chapter,

$$\begin{pmatrix} 0 & T_c \\ T_c & 0 \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} \begin{pmatrix} \varepsilon_+ & 0 \\ 0 & \varepsilon_- \end{pmatrix} \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} \tag{VI.1.15}$$

with $\varepsilon_\pm = \pm T_c$. Thus,

$$\begin{aligned}
U(t,t_0) &\equiv e^{-iH(t-t_0)} = S e^{-i(t-t_0)D} S^{-1} \\
&= \frac{1}{2} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} \begin{pmatrix} e^{-i(t-t_0)T_c} & 0 \\ 0 & e^{+i(t-t_0)T_c} \end{pmatrix} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} \\
&= \frac{1}{2} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} \begin{pmatrix} e^{-i(t-t_0)T_c} & e^{-i(t-t_0)T_c} \\ e^{+i(t-t_0)T_c} & -e^{+i(t-t_0)T_c} \end{pmatrix} \\
&= \begin{pmatrix} \cos[(t-t_0)T_c] & -i\sin[(t-t_0)T_c] \\ -i\sin[(t-t_0)T_c] & \cos[(t-t_0)T_c] \end{pmatrix} \\
&= \cos[(t-t_0)T_c]\hat{1} - i\sin[(t-t_0)T_c]\sigma_x. \tag{VI.1.16}
\end{aligned}$$

VI.1.2.3 Quantum Oscillations in Two-Level Systems

We can now easily calculate these: use an initial condition

$$\begin{aligned}
|\Psi\rangle_0 &= \alpha_L |L\rangle + \alpha_R |R\rangle = \begin{pmatrix} \alpha_L \\ \alpha_R \end{pmatrix} \\
\rightsquigarrow |\Psi(t)\rangle &= U(t,t_0)|\Psi\rangle_0 = \left\{ \cos[(t-t_0)T_c]\hat{1} - i\sin[(t-t_0)T_c]\sigma_x \right\} |\Psi\rangle_0 \\
&= \left\{ \alpha_L \cos[(t-t_0)T_c] - i\alpha_R \sin[(t-t_0)T_c] \right\} |L\rangle \\
&+ \left\{ \alpha_R \cos[(t-t_0)T_c] - i\alpha_L \sin[(t-t_0)T_c] \right\} |R\rangle. \tag{VI.1.17}
\end{aligned}$$

Check out a few examples:
$\alpha_L = 1, \alpha_R = 0$ (particle initially in left well): in this case, the probabilities for the particle to be in the left (right) well at time $t \geq t_0$ are

$$\begin{aligned}
|\langle L|\Psi(t)\rangle|^2 &= \cos^2[(t-t_0)T_c] \tag{VI.1.18} \\
|\langle R|\Psi(t)\rangle|^2 &= \sin^2[(t-t_0)T_c] \quad \textbf{quantum-mechanical oscillations}.
\end{aligned}$$

VI.2 Time-dependent Hamiltonians

There are almost no exact analytical solutions when the Hamiltonian, $H(t)$, is time-dependent. A few exceptions do exist, however.

VI.2.1 Spin $\frac{1}{2}$ in Magnetic Field

This case is, for example, extremely important for NMR (nuclear magnetic resonance). Even here the Hamiltonian $\mathcal{H}(t)$ is in general not exactly soluble, its form is

$$
\begin{aligned}
\mathcal{H}(t) &\equiv \mathbf{B}(t)\boldsymbol{\sigma} \equiv B_x(t)\hat{\sigma}_x + B_y(t)\hat{\sigma}_y + B_z(t)\hat{\sigma}_z \\
&\equiv \begin{pmatrix} B_z(t) & B_\parallel^*(t) \\ B_\parallel(t) & -B_z(t) \end{pmatrix}, \quad B_\parallel(t) \equiv B_x(t) + iB_y(t),
\end{aligned}
\tag{VI.2.1}
$$

where the Pauli-matrices are defined as

$$
\hat{\sigma}_x \equiv \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \hat{\sigma}_y \equiv \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \hat{\sigma}_z \equiv \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.
\tag{VI.2.2}
$$

Why is that so difficult? Let us write the Schrödinger equation

$$
\begin{aligned}
i\partial_t|\Psi(t)\rangle &= \mathcal{H}(t)|\Psi(t)\rangle, \quad |\Psi(t)\rangle \equiv \begin{pmatrix} \psi_1(t) \\ \psi_2(t) \end{pmatrix} \\
\rightsquigarrow i\frac{d}{dt}\psi_1(t) &= B_z(t)\psi_1(t) + B_\parallel^*(t)\psi_2(t) \\
i\frac{d}{dt}\psi_2(t) &= B_\parallel(t)\psi_1(t) - B_z(t)\psi_2(t).
\end{aligned}
\tag{VI.2.3}
$$

We assume $B_\parallel \neq 0$ and write (omit the t-dependence for a moment)

$$
\psi_1 = \frac{i\dot{\psi}_2 + B_z\psi_2}{B_\parallel}
\tag{VI.2.4}
$$

$$
\begin{aligned}
i\ddot{\psi}_2 &= \dot{B}_\parallel\psi_1 + B_\parallel\dot{\psi}_1 - \dot{B}_z\psi_2 - B_z\dot{\psi}_2 \\
&= \frac{\dot{B}_\parallel}{B_\parallel}[i\dot{\psi}_2 + B_z\psi_2] - iB_\parallel[B_z\psi_1 + B_\parallel^*\psi_2] - \dot{B}_z\psi_2 - B_z\dot{\psi}_2 \\
&= \frac{\dot{B}_\parallel}{B_\parallel}[i\dot{\psi}_2 + B_z\psi_2] - iB_z[i\dot{\psi}_2 + B_z\psi_2] - iB_\parallel B_\parallel^*\psi_2 - \dot{B}_z\psi_2 - B_z\dot{\psi}_2 \\
&= i\frac{\dot{B}_\parallel}{B_\parallel}\dot{\psi}_2 + \left[\frac{\dot{B}_\parallel}{B_\parallel}B_z - iB_z^2 - i|B_\parallel|^2 - \dot{B}_z\right]\psi_2.
\end{aligned}
\tag{VI.2.5}
$$

This is a second order ODE with time-dependent coefficients, which in general is not solvable in terms of known functions (it can of course be solved numerically quite easily).

VI.2.1.1 Constant $\mathbf{B}$

In this case we must of course recover our usual two-level system:

$$
i\ddot{\psi}_2 = -i[B_z^2 + |B_\parallel|^2]\psi_2 = -i|\mathbf{B}|^2\psi_2
\tag{VI.2.6}
$$

$$
\rightsquigarrow \ddot{\psi}_2 + |\mathbf{B}|^2\psi_2 = 0
\tag{VI.2.7}
$$

$$
\rightsquigarrow \psi_2(t) = \psi_2(0)\cos|\mathbf{B}|t + \frac{\dot{\psi}_2(0)}{|\mathbf{B}|}\sin|\mathbf{B}|t
\tag{VI.2.8}
$$

For constant $\mathbf{B}$, the eigenvalues of the Hamiltonian

$$
\mathcal{H} \equiv \begin{pmatrix} B_z & B_\parallel^* \\ B_\parallel & -B_z \end{pmatrix}
\tag{VI.2.9}
$$

are given by $(B_z - \varepsilon)(-B_z - \varepsilon) - |B_\parallel|^2 = 0$ or $\varepsilon_\pm = \pm\sqrt{B_z^2 + |B_\parallel|^2} = \pm|\mathbf{B}|$. Therefore, Eq. (VI.2.6) describes quantum mechanical oscillations with angular frequency of half the level splitting $2|\mathbf{B}|$ between ground and excited state, in agreement with our specific example $B_z = 0, B_\parallel = T_c$ from section VI.1.2.3.

VI.2.1.2   Rotating Field

This is defined as for constant field in z direction and an oscillating field in the x-y plane,

$$B_z(t) = B_0 = \text{const}, \quad B_\parallel(t) = B_1 e^{i\omega t}. \tag{VI.2.10}$$

Our equation for ψ_2 thus becomes

$$
\begin{aligned}
i\ddot{\psi}_2 &= i\frac{\dot{B}_\parallel}{B_\parallel}\dot{\psi}_2 + \left[\frac{\dot{B}_\parallel}{B_\parallel}B_z - iB_z^2 - i|B_\parallel|^2 - \dot{B}_z\right]\psi_2 \\
&= -\omega\dot{\psi}_2 + i[\omega B_0 - B_0^2 - |B_1|^2]\psi_2 \\
\rightsquigarrow \ddot{\psi}_2 &- i\omega\dot{\psi}_2 + [B_0^2 + |B_1|^2 - \omega B_0]\psi_2 = 0.
\end{aligned}
\tag{VI.2.11}
$$

This can be solved using the exponential ansatz method $\psi_2(t) = ce^{-izt}$ which yields a quadratic equation for z,

$$
\begin{aligned}
z^2 - \omega z + [\omega B_0 - B_0^2 - |B_1|^2] &= 0 \\
z_\pm = \frac{\omega}{2} \pm \frac{1}{2}\sqrt{\omega^2 + 4B_0^2 - 4\omega B_0 + 4|B_1|^2} &= \frac{\omega}{2} \pm \frac{1}{2}\Omega_R \\
\Omega_R \equiv \sqrt{(\omega - 2B_0)^2 + 4|B_1|^2} \quad &\text{Rabi-frequency.}
\end{aligned}
\tag{VI.2.12}
$$

Note that the term $2B_0$ in the Rabi-frequency is determined by the *level-splitting* $\Delta \equiv 2B_0$ in absence of the time-dependent field $B_\parallel(t)$. The solution for $\psi_2(t)$ (from which $\psi_1(t)$ follows immediately) therefore is

$$
\begin{aligned}
\psi_2(t) &= c_1 e^{i\left(\frac{\omega}{2} + \frac{\Omega_R}{2}\right)t} + c_2 e^{i\left(\frac{\omega}{2} - \frac{\Omega_R}{2}\right)t} \\
&= e^{i\frac{\omega}{2}t}\left[c_1' \cos\frac{\Omega_R}{2}t + c_2' \sin\frac{\Omega_R}{2}t\right].
\end{aligned}
\tag{VI.2.13}
$$

We can choose, e.g., the initial condition $\psi_2(0) = 1$ from which follows

$$
\begin{aligned}
\psi_2(t) &= e^{i\frac{\omega}{2}t}\left[\cos\frac{\Omega_R}{2}t + c_2' \sin\frac{\Omega_R}{2}t\right] \\
0 = \psi_1(0) &= \left.\frac{i\dot{\psi}_2 + B_z\psi_2}{B_\parallel}\right\|_{t=0} = \frac{-\frac{\omega}{2} + i\frac{\Omega_R}{2}c_2' + B_0}{B_1} \\
\rightsquigarrow c_2' &= -i\frac{\omega - 2B_0}{\Omega_R}
\end{aligned}
\tag{VI.2.14}
$$

This leads to

$$
\begin{aligned}
|\psi_2(t)|^2 &= \cos^2\frac{\Omega_R}{2}t + \frac{(\omega - 2B_0)^2}{\Omega_R^2}\sin^2\frac{\Omega_R}{2}t \tag{VI.2.15} \\
&= \frac{(\omega - 2B_0)^2}{\Omega_R^2} + \frac{4|B_1|^2}{\Omega_R^2}\cos^2\frac{\Omega_R}{2}t \quad \textbf{Rabi-Oscillations}.
\end{aligned}
$$

Note that the **quantum-mechanical oscillations** at constant $\mathbf{B}$ (e.g., the case $\mathbf{B} = (T_c, 0, 0)$ in Eq. (VI.1.18)) occur for a time-independent Hamiltonian. The **Rabi-oscillations** occur in a time-dependent Hamiltonian containing a time-dependent term ('time-dependent field'). These two often get mixed up in the literature.

VI.2.2   Landau-Zener-Rosen problem

This is another exactly solvable case for a two-level system. To be discussed later in the context of adiabatic and non-adiabatic transitions between energy levels.

VI.3   Time-Dependent Perturbation Theory

VI.3.1   Model Hamiltonian

This is written in the form

$$H(t) = H_0 + V(t) \tag{VI.3.1}$$

with the time-dependence in the perturbation $V(t)$. The case $H(t) = H_0(t) + V$ with a constant perturbation operator but a time-dependent 'free part' also exists, but is slightly less used.

The term 'time-dependent' perturbation theory, however, primarily refers to perturbation theory for the time-dependence of the wave function and is also used for time-independent *Hamiltonians* $H(t) = H$.

VI.3.2   The Interaction Picture

This is introduced in order to facilitate the solution of the Schrödinger equation

$$\frac{d}{dt}|\Psi(t)\rangle = -iH(t)|\Psi(t)\rangle \tag{VI.3.2}$$

We define

$$|\Psi(t)\rangle_I \equiv e^{iH_0t}|\Psi(t)\rangle \tag{VI.3.3}$$

and derive the new Schrödinger equation for $|\Psi(t)\rangle_I$,

$$
\begin{aligned}
\frac{d}{dt}|\Psi_I(t)\rangle &= iH_0|\Psi_I(t)\rangle + e^{iH_0t}\frac{d}{dt}|\Psi(t)\rangle \\
&= iH_0|\Psi_I(t)\rangle - ie^{iH_0t}\left[H_0 + V(t)\right]e^{-iH_0t}|\Psi_I(t)\rangle \\
&= -ie^{iH_0t}V(t)e^{-iH_0t}|\Psi_I(t)\rangle \equiv -iV_I(t)|\Psi_I(t)\rangle.
\end{aligned}
\tag{VI.3.4}
$$

The Schrödinger equation therefore is transformed into the **interaction picture**

$$
\begin{aligned}
\frac{d}{dt}|\Psi(t)\rangle &= -iH(t)|\Psi(t)\rangle \leftrightarrow \frac{d}{dt}|\Psi_I(t)\rangle = -iV_I(t)|\Psi_I(t)\rangle \\
|\Psi(t)\rangle_I &\equiv e^{iH_0t}|\Psi(t)\rangle, \quad V_I(t) \equiv e^{iH_0t}V(t)e^{-iH_0t}.
\end{aligned}
\tag{VI.3.5}
$$

VI.3.3   First Order Perturbation Theory

This is achieved by doing the first iteration in

$$
\begin{aligned}
\frac{d}{dt}|\Psi_I(t)\rangle &= -iV_I(t)|\Psi_I(t)\rangle \\
\rightsquigarrow |\Psi_I(t)\rangle &= \Psi_I(t_0)\rangle - i\int_{t_0}^t dt' V_I(t')|\Psi_I(t')\rangle \\
&= |\Psi_I(t_0)\rangle - i\int_{t_0}^t dt' V_I(t')|\Psi_I(t_0)\rangle + O(V_I^2).
\end{aligned}
\tag{VI.3.6}
$$

We take $t_0 = 0$ for simplicity and the initial state therefore is $|\Psi_I(0)\rangle = |\Psi(0)\rangle$,

$$|\Psi_I(t)\rangle = |\Psi(0)\rangle - i \int_0^t dt' V_I(t')|\Psi(0)\rangle + O(V_I^2). \tag{VI.3.7}$$

This can be worked out in some more detail by assuming a basis $|n\rangle$ of eigenstates of H_0,

$$H_0|n\rangle = \varepsilon_n|n\rangle, \quad \hat{1} = \sum_{n'} |n'\rangle\langle n'| \rightsquigarrow \tag{VI.3.8}$$

$$\langle n|\Psi_I(t)\rangle = \langle n|\Psi(0)\rangle - i \sum_{n'} \int_0^t dt' \langle n|V_I(t')|n'\rangle\langle n'|\Psi(0)\rangle + O(V_I^2).$$

Let us assume the initial state $|\Psi(0)\rangle = |m\rangle$ is an eigenstate of H_0, then

$$\langle n|\Psi_I(t)\rangle = \delta_{nm} - i \int_0^t dt' \langle n|V_I(t')|m\rangle + O(V_I^2). \tag{VI.3.9}$$

The probability to find the system in state $|n\rangle$ after time t is then a **transition probability**. Use $|\langle n|\Psi(t)\rangle|^2 = |\langle n|\Psi_I(t)\rangle|^2$ (EXERCISE:CHECK!) to find within first order perturbation theory

$$P_{m\to n}(t) = |\langle n|\Psi(t)\rangle|^2 = \left|\int_0^t dt' \langle n|V_I(t')|m\rangle\right|^2 \quad \text{first order}$$

$$|\Psi(0)\rangle \equiv |m\rangle \neq |n\rangle. \tag{VI.3.10}$$

VI.3.3.1   Time-Independent Hamiltonian $V(t) = V$

In this case

$$\langle n|V_I(t')|m\rangle = \langle n|e^{iH_0 t'} V e^{-iH_0 t'}|m\rangle = e^{-i(\varepsilon_n - \varepsilon_m)t'}\langle n|V|m\rangle$$

$$\rightsquigarrow P_{m\to n}(t) = |\langle n|V|m\rangle|^2 \left|\int_0^t dt' e^{-i(\varepsilon_n - \varepsilon_m)t'}\right|^2$$

$$= |\langle n|V|m\rangle|^2 \left|\frac{e^{-i(\varepsilon_n - \varepsilon_m)t} - 1}{\varepsilon_n - \varepsilon_m}\right|^2$$

$$= |\langle n|V|m\rangle|^2 \, 4\frac{\sin^2 \frac{\varepsilon_n - \varepsilon_m}{2}t}{(\varepsilon_n - \varepsilon_m)^2} \tag{VI.3.11}$$

As for the $\sin^2$ function, we now use the representation of the **Dirac Delta-function**,

---

Theorem:
For any integrable, normalised function $f(x)$ with $\int_{-\infty}^{\infty} dx f(x) = 1$,

$$\lim_{\varepsilon \to 0} \frac{1}{\varepsilon} f\left(\frac{x}{\varepsilon}\right) = \delta(x). \tag{VI.3.12}$$

Here, we apply it with $f(x) = \frac{1}{\pi}\frac{\sin^2(x)}{x^2}$

$$\lim_{\varepsilon \to 0} \frac{1}{\varepsilon}\frac{1}{\pi}\frac{\sin^2(x/\varepsilon)}{(x/\varepsilon)^2} = \delta(x), \quad \lim_{t\to\infty}\frac{t}{2\pi}\frac{\sin^2(\Delta E t/2)}{(\Delta E t/2)^2} = \delta(\Delta E)$$

$$\rightsquigarrow \lim_{t\to\infty}\frac{1}{t}P_{m\to n}(t) = \lim_{t\to\infty}|\langle n|V|m\rangle|^2 \, 2\pi\frac{t}{2\pi}\frac{\sin^2\frac{\varepsilon_n - \varepsilon_m}{2}t}{[(\varepsilon_n - \varepsilon_m)t/2]^2}$$

$$= 2\pi|\langle n|V|m\rangle|^2 \, \delta(\varepsilon_n - \varepsilon_m). \tag{VI.3.13}$$

This is an extremely important result, and we therefore highlight it here again, introducing the **transition rate** $\Gamma_{m \to n}$,

$$\Gamma_{m \to n} \equiv \lim_{t \to \infty} \frac{1}{t} P_{m \to n}(t) = \frac{2\pi}{\hbar^2} \left| \langle n|V|m \rangle \right|^2 \delta(\varepsilon_n - \varepsilon_m) \qquad \text{(VI.3.14)}$$

The **total transition rate** into *any* final state $|n\rangle$ is, within first order perturbationtheory in V, given by the sum over all n,

$$\Gamma_m \equiv \frac{2\pi}{\hbar^2} \sum_n \left| \langle n|V|m \rangle \right|^2 \delta(\varepsilon_n - \varepsilon_m)$$

Fermi's Golden Rule. $\qquad$ (VI.3.15)

VI.3.4 Higher Order Perturbation Theory

(This is also discussed in Merzbacher [2] though with a slightly different notation.
    We start from the time-dependent Schrödinger equation

$$i\partial_t |\Psi(t)\rangle = H(t)|\Psi(t)\rangle. \qquad \text{(VI.3.16)}$$

The state $|\Psi(t)\rangle$ at time t is obtained from the state $|\Psi(t_0)\rangle$ at time t_0 by application of the *time evolution operator* $U(t, t_0)$ via

$$|\Psi(t)\rangle = U(t, t_0)|\Psi(t_0)\rangle. \qquad \text{(VI.3.17)}$$

If $H(t) = H$ is time-independent, we have

$$U(t, t_0) = e^{-iH(t - t_0)}, \quad \text{time-independent Hamiltonian.} \qquad \text{(VI.3.18)}$$

For arbitrary $H(t)$, we have

$$i\partial_t U(t, t_0) = H(t)U(t, t_0), \quad U(t_0, t_0) = 1. \qquad \text{(VI.3.19)}$$

We now assume a form

$$H(t) = H_0 + V(t). \qquad \text{(VI.3.20)}$$

We solve this differential equation by introducing the *interaction picture* time-evolution operator $\tilde{U}(t, t_0)$,

$$
\begin{aligned}
\tilde{U}(t, t_0) &= e^{iH_0 t} U(t, t_0) e^{-iH_0 t_0} & \text{(VI.3.21)} \\
i\partial_t \tilde{U}(t, t_0) &= -H_0 \tilde{U}(t, t_0) + i(-i)e^{iH_0 t} H(t) U(t, t_0) e^{-iH_0 t_0} \\
&= -H_0 \tilde{U}(t, t_0) + e^{iH_0 t}[H_0 + V(t)]e^{-iH_0 t} e^{iH_0 t} U(t, t_0) e^{-iH_0 t_0} \\
&= -H_0 \tilde{U}(t, t_0) + e^{iH_0 t}[H_0 + V(t)]e^{-iH_0 t} \tilde{U}(t, t_0) \\
&= \tilde{V}(t)\tilde{U}(t, t_0) & \text{(VI.3.22)} \\
\tilde{V}(t) &= e^{iH_0 t} V(t) e^{-iH_0 t}. & \text{(VI.3.23)}
\end{aligned}
$$

VI.3.5 States

Using Eq. (VI.3.3), in the interaction picture

$$
\begin{aligned}
|\Psi(t)\rangle_I &\equiv e^{iH_0 t}|\Psi(t)\rangle = e^{iH_0 t} U(t, t_0)|\Psi(t_0) \\
&= e^{iH_0 t} e^{-iH_0 t} \tilde{U}(t, t_0) e^{iH_0 t_0}|\Psi(t_0)\rangle \\
&= \tilde{U}(t, t_0)|\Psi(t_0)\rangle_I. & \text{(VI.3.24)}
\end{aligned}
$$

VI.3.5.1 Successive Interation

We can obtain the time-evolution operator $\tilde{U}(t, t_0)$ in the interaction picture by successive iteration:

$$
\begin{aligned}
i\partial_t \tilde{U}(t, t_0) &= \tilde{V}(t)\tilde{U}(t, t_0) & \text{(VI.3.25)}\\
\rightsquigarrow \tilde{U}(t, t_0) &= 1 - i\int_{t_0}^{t} dt_1 \tilde{V}(t_1)\tilde{U}(t_1, t_0)\\
&= 1 - i\int_{t_0}^{t} dt_1 \tilde{V}(t_1) + (-i)^2 \int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2 \tilde{V}(t_1)\tilde{V}(t_2) + ...\\
&= 1 + \sum_{n=1}^{\infty} (-i)^n \int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2 ... \int_{t_0}^{t_{n-1}} dt_n \tilde{V}(t_1)...\tilde{V}(t_n).
\end{aligned}
$$

There is a compact notation that slightly simplifies things here: **time-ordered** products of operators are defined with the **time-ordering operator** T which orders a product of operators $\tilde{V}(t_1)...\tilde{V}(t_n)$ with arbitrary times $t_1,...,t_n$ such that the 'earliest' operator is left and the 'latest' operator is right. For example,

$$
T[\tilde{V}(t_1)\tilde{V}(t_2)] = \theta(t_1 - t_2)\tilde{V}(t_1)\tilde{V}(t_2) + \theta(t_2 - t_1)\tilde{V}(t_2)\tilde{V}(t_1), \qquad \text{(VI.3.26)}
$$

where

$$
\theta(t \geq 0) = 1, \quad \theta(t < 0) = 0. \qquad \text{(VI.3.27)}
$$

Using the time-ordering operator, one can then show

$$
\begin{aligned}
\tilde{U}(t, t_0) &= 1 + \sum_{n=1}^{\infty} \frac{(-i)^n}{n!} \int_{t_0}^{t} dt_1 \int_{t_0}^{t} dt_2 ... \int_{t_0}^{t} dt_n T[\tilde{V}(t_1)...\tilde{V}(t_n)]\\
&\equiv T\exp\left[-i\int_{t_0}^{t} dt' \tilde{V}(t')\right]. & \text{(VI.3.28)}
\end{aligned}
$$

Note that now the upper limit of all integrals is the same t and that there is the additional $1/n!$ in front of each term.

VII. INTERACTION WITH LIGHT

VII.1 Electromagnetic Fields and Maxwells Equations

Literature here: R. Loudon 'The Quantum Theory of Light' [6] and C. Cohen-Tannoudji, J. Dupont-Roc, G. Grynberg 'Atom-Photon Interactions' [7].

Electromagnetism brings in the notion of *fields* as described by Maxwell's equations

$$\nabla \cdot \mathbf{B} = 0 \qquad\qquad (VII.1.1)$$

$$\nabla \times \mathbf{E} + \frac{\partial \mathbf{B}}{\partial t} = 0 \qquad\qquad (VII.1.2)$$

$$\varepsilon_0 \nabla \cdot \mathbf{E} = \rho \qquad\qquad (VII.1.3)$$

$$\nabla \times \mathbf{B} - \frac{1}{c^2}\frac{\partial \mathbf{E}}{\partial t} = \mu_0 \mathbf{j} \qquad\qquad (VII.1.4)$$

in a shorthand notation where $\mathbf{B} = \mathbf{B}(\mathbf{r}, t)$ etc. The transversal parts of $\mathbf{E}$ and $\mathbf{B}$ are *dynamical variables*:

VII.1.1 Longitudinal and transversal parts

Helmholtz' theorem: $\mathbf{E}$ and $\mathbf{B}$ can be decomposed into

$$\mathbf{E} = \mathbf{E}_\parallel + \mathbf{E}_\perp, \quad \mathbf{B} = \mathbf{B}_\parallel + \mathbf{B}_\perp \qquad\qquad (VII.1.5)$$

$$\nabla \times \mathbf{E}_\parallel = \nabla \times \mathbf{B}_\parallel = 0, \quad \nabla \cdot \mathbf{E}_\perp = \nabla \cdot \mathbf{B}_\perp = 0. \qquad\qquad (VII.1.6)$$

This becomes clearer in Fourier space, e.g.

$$\hat{\mathbf{E}}(\mathbf{k}) = \hat{\mathbf{E}}_\parallel(\mathbf{k}) + \hat{\mathbf{E}}_\perp(\mathbf{k}) \qquad\qquad (VII.1.7)$$

$$\hat{\mathbf{E}}_\parallel(\mathbf{k}) = [\mathbf{k} \cdot \hat{\mathbf{E}}(\mathbf{k})]\mathbf{k}/k^2, \quad \hat{\mathbf{E}}_\perp(\mathbf{k}) = [\mathbf{k} \times \hat{\mathbf{E}}(\mathbf{k})] \times \mathbf{k}/k^2. \qquad\qquad (VII.1.8)$$

VII.1.1.1 Longitudinal $\mathbf{E}$ and $\mathbf{B}$ are 'trivial'

For the magnetic field, one has

$$0 = \nabla \cdot \mathbf{B} \rightsquigarrow 0 = \mathbf{k} \cdot \hat{\mathbf{B}}(\mathbf{k}) \rightsquigarrow \hat{\mathbf{B}}_\parallel(\mathbf{k}) = 0 \rightsquigarrow \mathbf{B}_\parallel = 0, \qquad\qquad (VII.1.9)$$

which means that the magnetic field is purely transversal, i.e. $\mathbf{B} = \mathbf{B}_\perp$.

For the electric field, one has

$$\varepsilon_0 \nabla \cdot \mathbf{E} = \rho, \quad \varepsilon_0 i\mathbf{k} \cdot \hat{\mathbf{E}}(\mathbf{k}) = \rho(\mathbf{k}) \rightsquigarrow \hat{\mathbf{E}}_\parallel(\mathbf{k}, t) = -\frac{i\mathbf{k}}{\varepsilon_0 k^2}\rho(\mathbf{k}, t), \qquad (VII.1.10)$$

at all times t the longitudinal electric field is determined by the charge distribution at the same time (no retardation effects).

Therefore, the longitudinal fields are no independent variables; they are either zero for the magnetic field ($\mathbf{B}_\parallel = 0$) or just given by the charge in the case of the electric field. By contrast, the transverse fields are independent variables.

VII.1.2 Potentials

The Maxwell equations are a system of *first order* PDEs that can be transformed into second order equations by introduction of *potentials*.

- This facilitates quantization of the em field by the analogy with harmonic oscillators in Newtons equations.

- This also is in analogy with classical mechanics, where one tries to work with potentials instead of forces which often simplifies things.

One has

$$\mathbf{E} = -\nabla\phi - \partial_t\mathbf{A}, \quad \mathbf{B} = \nabla\times\mathbf{A} \tag{VII.1.11}$$

with the scalar potential ϕ and the vector potential $\mathbf{A}$. In Fourier space,

$$\begin{aligned} \hat{\mathbf{E}}(\mathbf{k}) &= -i\mathbf{k}\phi(\mathbf{k}) - \partial_t\hat{\mathbf{A}}(\mathbf{k}) \rightsquigarrow \hat{\mathbf{E}}_\perp(\mathbf{k}) = -\partial_t\hat{\mathbf{A}}_\perp(\mathbf{k}) & \text{(VII.1.12)} \\ \hat{\mathbf{B}}(\mathbf{k}) &= i\mathbf{k}\times\hat{\mathbf{A}}(\mathbf{k}) = i\mathbf{k}\times\hat{\mathbf{A}}_\perp(\mathbf{k}). & \text{(VII.1.13)} \end{aligned}$$

The 'non-trivial' transverse components of the field are therefore determined only by the *transverse component $\hat{\mathbf{A}}_\perp$ of the vector potential.*

VII.1.2.1 Gauge Transformations

The potentials are not uniquely determined by the fields which are left invariant under a gauge transformation

$$\mathbf{A}' = \mathbf{A} + \nabla f, \quad \phi' = \phi - \partial_t f. \tag{VII.1.14}$$

Again in Fourier space,

$$\hat{\mathbf{A}}'(\mathbf{k}) = \hat{\mathbf{A}}(\mathbf{k}) + i\mathbf{k}f(\mathbf{k}) \rightsquigarrow \hat{\mathbf{A}}'_\perp(\mathbf{k}) = \hat{\mathbf{A}}_\perp(\mathbf{k}). \tag{VII.1.15}$$

The important transverse component of the vector potential, from which the transverse components $\hat{\mathbf{E}}_\perp(\mathbf{k})$ and $\hat{\mathbf{B}}(\mathbf{k})$ are derived via Eq. (VII.1.12), is therefore left invariant under a gauge transformation.

VII.1.2.2 Coulomb Gauge

In the Coulomb gauge one sets

$$\mathbf{A}_\parallel = 0 \rightsquigarrow \mathbf{k}\hat{\mathbf{A}}(\mathbf{k}) = 0 \rightsquigarrow \nabla\cdot\mathbf{A} = 0. \tag{VII.1.16}$$

The vector potential $\mathbf{A} = \mathbf{A}_\perp$ is purely transverse in the Coulomb gauge. We then have

$$\begin{aligned} \hat{\mathbf{E}}(\mathbf{k}) &= -i\mathbf{k}\phi(\mathbf{k}) - \partial_t\hat{\mathbf{A}}(\mathbf{k}) \rightsquigarrow \\ \mathbf{k}\hat{\mathbf{E}}(\mathbf{k}) &= -i\mathbf{k}\mathbf{k}\phi(\mathbf{k}) - \partial_t\mathbf{k}\hat{\mathbf{A}}(\mathbf{k}) = -i\mathbf{k}\mathbf{k}\phi(\mathbf{k}) & \text{(VII.1.17)} \\ \rightsquigarrow -i\rho(\mathbf{k})/\varepsilon_0 &= -i\mathbf{k}\mathbf{k}\phi(\mathbf{k}) \rightsquigarrow \nabla^2\phi(\mathbf{r},t) = -\rho(\mathbf{r},t)/\varepsilon_0, & \text{(VII.1.18)} \end{aligned}$$

which is the Poisson equation.

VII.2 Gauge invariance in single-particle non-relativistic QM

Here, we follow Merzbacher [2].

We now look at the interaction between charges and the electromagnetic field. The first step is to find the Hamiltonian, which is done via the sequence 'classical Lagrangian - classical Hamiltonian - QM Hamiltonian'. For a particle of mass m with charge q in an electromagnetic field described by potentials $(\phi, \mathbf{A})$, the classical Hamiltonian is

$$\mathcal{H} = H(t) + H_{\rm rad}, \quad H(t) \equiv \frac{1}{2m}\left(\mathbf{p} - q\mathbf{A}\right)^2 + q\phi \tag{VII.2.1}$$

$$H_{\rm rad} = \frac{1}{2}\int d\mathbf{r}\left[\varepsilon_0 \mathbf{E}_\perp^2 + \mu_0^{-1}\mathbf{B}^2\right]. \tag{VII.2.2}$$

The em field are still treated classically here. The replacement of the momentum $\mathbf{p}$ by

$$\mathbf{p} \to \mathbf{p} - q\mathbf{A} \tag{VII.2.3}$$

is called *minimal coupling*. The term $H_{\rm rad}$ is the energy of the electromagnetic field.

VII.2.1 Local Gauge Transformation

If we change

$$\mathbf{A}' = \mathbf{A} + \nabla f, \quad \phi' = \phi - \partial_t f, \tag{VII.2.4}$$

the Hamiltonian in the new gauge becomes ($H_{\rm rad}$ is not changed)

$$H'(t) \equiv \frac{1}{2m}\left(\mathbf{p} - q\mathbf{A}'\right)^2 + q\phi' \tag{VII.2.5}$$

The time-dependent Schrödinger equations in the old and the new gauge are

$$i\partial_t \psi = H(t)\psi, \quad i\partial_t \psi' = H'(t)\psi'. \tag{VII.2.6}$$

They should describe the same physics which is the case if

$$\psi'(\mathbf{r}, t) = U\psi(\mathbf{r}, t), \quad U = e^{iqf(\mathbf{r},t)/c}. \tag{VII.2.7}$$

This can be seen by

$$\begin{aligned}
i\partial_t \psi' &= i\partial_t U\psi = (i\partial_t U)\psi + iU\partial_t \psi = (i\partial_t U)\psi + iUH\psi = \left[(i\partial_t U) + UH\right]\psi \\
&= \left[(i\partial_t U) + UH\right]U^\dagger U\psi = \left[(i\partial_t U) + UH\right]U^\dagger \psi' = H'\psi' \\
&\leftrightarrow \quad H' = (i\partial_t U)U^\dagger + UHU^\dagger,
\end{aligned} \tag{VII.2.8}$$

which means

$$H' = (i\partial_t U)U^\dagger + UHU^\dagger, \quad \psi'(\mathbf{r}, t) = U\psi(\mathbf{r}, t) \quad \leftrightarrow \quad \text{same physics.}$$

The transformation from H to H' and correspondingly ψ to ψ' is completely arbitrary and works for any Hamiltonian and transformation (operator) U. In the context we are discussing it here, U is a phase and thus an element of the group $U(1)$. The transformation $U = e^{iqf(\mathbf{r},t)/c}$ is a local gauge transformation as it involves a $\mathbf{r}$-dependent phase.

VII.2.1.1 Example: spatially constant electric field, zero magnetic field

We choose a gauge (set $c = 1$)

$$\phi = 0, \mathbf{A} = -\int_{-\infty}^{t} dt' \mathbf{E}(t'). \tag{VII.2.9}$$

We transform to a new gauge

$$
\begin{aligned}
\mathbf{A}' &= \mathbf{A} + \nabla f = 0, \quad \phi' = \phi - \partial_t f = -\partial_t f \\
&\rightsquigarrow \nabla f = -\mathbf{A}, \quad f(\mathbf{r}, t) = \mathbf{r} \int_{-\infty}^{t} dt' \mathbf{E}(t') \rightsquigarrow \phi'(\mathbf{r}, t) = -\mathbf{r}\mathbf{E}(t) \\
&\rightsquigarrow i\partial_t \psi' = H'(t)\psi' \quad \text{with} \quad H'(t) = \frac{p^2}{2m} - q\mathbf{r}\mathbf{E}(t).
\end{aligned}
\tag{VII.2.10}
$$

VII.3 Gauge invariance for many charges in non-relativistic QM

We follow Woolley [8]. Things become a little bit more complicated now.

VII.3.1 Charge and current densities, polarization and magnetization

The charge and current density for N charges q_n at positions $\mathbf{r}_n$ are

$$\rho(\mathbf{r}) = \sum_n q_n \delta(\mathbf{r}_n - \mathbf{r}), \quad \mathbf{j}(\mathbf{r}) = \sum_n q_n \dot{\mathbf{r}}_n \delta(\mathbf{r}_n - \mathbf{r}) \tag{VII.3.1}$$

These can be expressed in terms of polarization fields $\mathbf{P}$ (electric polarization) and $\mathbf{M}$ (magnetic polarization or magnetization) via

$$\rho = -\nabla \cdot \mathbf{P}, \quad \mathbf{j} = \frac{d\mathbf{P}}{dt} + \nabla \times \mathbf{M}. \tag{VII.3.2}$$

In some traditional formulations of electromagnetism, one distinguishes between 'bound' and 'free' charges which, however, from a fundamental point of view is a little bit artificial. The above definition of $\mathbf{P}$ and $\mathbf{M}$ thus refers to the total charge and current charge densities without such separation.

   The interesting thing now is the fact that $\mathbf{P}$ and $\mathbf{M}$ are not uniquely defined by Eq. (VII.3.2). They are arbitrary in very much the same way as the potentials ϕ and $\mathbf{A}$ are arbitrary. Note that only the longitudinal part of $\mathbf{P}$ is uniquely determined from Eq. (VII.3.2) and given by the charge density,

$$
\begin{aligned}
\rho &= -\nabla \cdot \mathbf{P} \rightsquigarrow i\mathbf{k}\mathbf{P}(\mathbf{k}) = \rho(\mathbf{k}) \\
&\rightsquigarrow \mathbf{P}_\parallel(\mathbf{k}) \equiv [\mathbf{k}\mathbf{P}(\mathbf{k})]\mathbf{k}/k^2 = -i\rho(\mathbf{k})\mathbf{k}/k^2.
\end{aligned}
\tag{VII.3.3}
$$

One can transform $\mathbf{P}$ and $\mathbf{M}$ according to

$$\mathbf{P} \to \mathbf{P}' = \mathbf{P} + \nabla \times \mathbf{U}, \quad \mathbf{M} \to \mathbf{M}' = \mathbf{M} - \frac{d\mathbf{U}}{dt} + \nabla u, \tag{VII.3.4}$$

with $\mathbf{P}'$ and $\mathbf{M}'$ still fulfilling Eq. (VII.3.2). Following Woolley, this arbitraryness is related to charge conservation (I think this interpretation can be carried over to QM and be linked to U(1) invariance of QED). In the classical theory it is the *divergence* operator playing the

central role ($\varepsilon_0 \nabla \cdot \mathbf{E} = \rho$, Gauss' law) and the central object in this discussion therefore is the Greens function $\mathbf{g}(\mathbf{r}, \mathbf{r}')$ in

$$\nabla_{\mathbf{r}} \cdot \mathbf{g}(\mathbf{r}, \mathbf{r}') = -\delta(\mathbf{r} - \mathbf{r}'). \tag{VII.3.5}$$

Fourier transformation yields

$$\begin{aligned} - i\mathbf{k}\mathbf{g}(\mathbf{k}) = -1 \rightsquigarrow \mathbf{g}_{\parallel}(\mathbf{k}) & \equiv \ [\mathbf{k}\mathbf{g}(\mathbf{k})]\mathbf{k}/k^2 = -i\mathbf{k}/k^2 \\ \mathbf{g}_{\perp}(\mathbf{k}) & \qquad \text{arbitrary.} \end{aligned} \tag{VII.3.6}$$

In other words, all the arbitraryness (all the fuss about gauge invariance) sits in the transversal part of the Greens function $\mathbf{g}(\mathbf{r}, \mathbf{r}')$ of the divergence operator.

The polarization is now expressed by $\mathbf{g}(\mathbf{r}, \mathbf{r}')$ that solves $\rho = -\nabla \cdot \mathbf{P}$, i.e.

$$\mathbf{P}(\mathbf{r}) = \int d\mathbf{r}' \mathbf{g}(\mathbf{r}, \mathbf{r}') \rho(\mathbf{r}'). \tag{VII.3.7}$$

VII.3.2   The Hamiltonian

This has to be worked out in detail, starting from the Lagrangian, which is described in Woolley [8]. The result is

$$\begin{aligned} \mathcal{H}(t) & = \ H(t) + H_{\text{rad}} \\ H_{\text{rad}} & = \ \frac{1}{2} \int d\mathbf{r} \left[\varepsilon_0 \mathbf{E}_{\perp}^2 + \mu_0^{-1} \mathbf{B}^2 \right] \\ H(t) & = \ \sum_n \frac{1}{2m_n} [\mathbf{p}_n - q_n \mathbf{A}(\mathbf{r}_n, t)] + V_{\text{Coul}} + V_{\mathbf{EP}} + V_{\mathbf{gg}} \\ V_{\text{Coul}} & \equiv \ \frac{1}{2} \sum_{n,m} \frac{q_n q_m}{4\pi\varepsilon_0 |\mathbf{r}_n - \mathbf{r}_m|} \\ V_{\mathbf{EP}} & \equiv \ -\sum_n q_n \int d\mathbf{r} \mathbf{E}_{\perp} \cdot \mathbf{g}(\mathbf{r}, \mathbf{r}_n) = -\int d\mathbf{r} \mathbf{E}_{\perp} \mathbf{P}_{\perp} \\ V_{\mathbf{gg}} & \equiv \ \frac{1}{2\varepsilon_0} \sum_{n,m} q_n q_m \int d\mathbf{r} \mathbf{g}_{\perp}(\mathbf{r}, \mathbf{r}_n) \mathbf{g}_{\perp}(\mathbf{r}, \mathbf{r}_m). \end{aligned} \tag{VII.3.9}$$

Up to here everything is completely classical (just classical charges and fields). Quantization of the charge degrees of freedom is done canonically via $\mathbf{p}_n \to \hat{\mathbf{p}}_n = -\frac{i}{\hbar}\nabla_n$.

VII.3.2.1   Coulomb Gauge

The Coulomb gauge theory is obtained with the choice

$$\mathbf{g}_{\perp}(\mathbf{r}, \mathbf{r}') = 0, \quad \nabla \cdot \mathbf{A} = 0. \tag{VII.3.10}$$

The Hamiltonian in the Coulomb gauge then is

$$\begin{aligned} \mathcal{H}_{\text{Coul}}(t) & = \ H(t) + H_{\text{rad}} \\ H_{\text{rad}} & = \ \frac{1}{2} \int d\mathbf{r} \left[\varepsilon_0 \mathbf{E}_{\perp}^2 + \mu_0^{-1} \mathbf{B}^2 \right] \tag{VII.3.11} \\ H(t) & = \ \sum_n \frac{1}{2m_n} [\mathbf{p}_n - q_n \mathbf{A}(\mathbf{r}_n, t)] + V_{\text{Coul}}, \quad \nabla \cdot \mathbf{A} = 0. \tag{VII.3.12} \end{aligned}$$

without the polarization terms $V_{\mathbf{EP}}$ and $V_{\mathbf{gg}}$.

VII.3.3   Power-Zienau-Woolley Transformation

One can now show that the Coulomb gauge Hamiltonian $\mathcal{H}_{\text{Coul}}(t)$ can be transformed into a Hamiltonian $\mathcal{H}(t)$ in any other gauge as specified by $\mathbf{g}_\perp$ and given by Eq. (VII.3.8). This is achieved by the so-called *Power-Zienau-Woolley Transformation* which is a unitary transformation of the Coulomb gauge Hamiltonian $\mathcal{H}_{\text{Coul}}(t)$,

$$\mathcal{H}(t) = \Lambda^{-1}\mathcal{H}_{\text{Coul}}(t)\Lambda, \quad \Lambda \equiv \exp\left[i\int d\mathbf{r}\mathbf{A}(\mathbf{r},t)\mathbf{P}(\mathbf{r})\right]. \tag{VII.3.13}$$

A relation can be derived between $\mathbf{A}$ and $\mathbf{A}_{\text{Coul}}$, cf. Woolley [8],

$$\mathbf{A}(\mathbf{r},t) = \mathbf{A}_{\text{Coul}}(\mathbf{r},t) - \nabla \cdot \int d\mathbf{r}'\mathbf{A}_{\text{Coul}}(\mathbf{r}',t)\mathbf{g}_\perp(\mathbf{r}',\mathbf{r}). \tag{VII.3.14}$$

If this is inserted into $\mathcal{H}(t)$, Eq. (VII.3.8), one obtains

$$\begin{aligned}
\mathcal{H}(t) &= H(t) + H_{\text{rad}} \\
H_{\text{rad}} &= \frac{1}{2}\int d\mathbf{r}\left[\varepsilon_0\mathbf{E}_\perp^2 + \mu_0^{-1}\mathbf{B}^2\right] \\
H(t) &= \sum_n \frac{\mathbf{p}_n^2}{2m_n} + V_{\text{Coul}} + V_{\mathbf{EP}} + V_{\mathbf{PP}} + \text{magnetic terms} \\
V_{\text{Coul}} &\equiv \frac{1}{2}\sum_{n,m}\frac{q_n q_m}{4\pi\varepsilon_0|\mathbf{r}_n - \mathbf{r}_m|} \\
V_{\mathbf{EP}} &\equiv -\int d\mathbf{r}\mathbf{E}_\perp\mathbf{P}_\perp \\
V_{\mathbf{PP}} &\equiv \frac{1}{2\varepsilon_0}\int d\mathbf{r}\mathbf{P}_\perp(\mathbf{r})^2.
\end{aligned}$$

$$\tag{VII.3.15}$$
$$\tag{VII.3.16}$$

Basically, apart from the magnetic terms the **pA** coupling is transformed away and one has instead a coupling not to the vector potential, but to the electric field $\mathbf{E}_\perp$. As a slight warning, here things can again get a little bit confusing: compare the discussion in Cohen-Tannoudji, Dupont-Roc and Grynberg [7], and the lecture notes by K.P. Marzlin, http://qis.ucalgary.ca/ pmarzlin/lectures/al0203/ who gives more detailed derivations. In fact, one has to interpret the field in the transformed Hamiltonian as a displacement field $D_\perp$ rather than the electric field $E_\perp$.

VII.3.4   Some Remarks on Fields

- fields as stupid book-keeping tool? Cf. Feynman's Nobel Prize speech. Do you really understand what a field is?

- but there is modern point of view: EM as U(1) gauge theory. Automatically brings in the concept of a field. Or can one do gauge theories without fields.

- retardation is a key point: if retardation is neglected: Breit-formula (Landau-Lifshitz Vol. IV) as $c \to \infty$ limit.

- QED Lagrange density just contains minimal coupling to vector potential, no explicit interaction between particles. *Coulombs law* follows as first term in an expansion in $1/c$, cf. (Landau-Lifshitz Vol. IV).

VIII. ROTATIONS AND VIBRATIONS OF MOLECULES

VIII.1 Vibrations and Rotations in Diatomic Molecules

Here, we follow Weissbluth [4] ch. 27, and Landau-Lifshitz III [1].

VIII.1.1 Hamiltonian

Before deriving the Hamiltonian, a short excursion to classical mechanics of two particles:

VIII.1.1.1 Angular Momentum of Two Particles

If two particles have positions $\mathbf{r}_1$ and $\mathbf{r}_2$ and momenta $\mathbf{p}_1$ and $\mathbf{p}_2$, the angular momentum of the total system of the two particles is

$$\mathbf{L} \;=\; \mathbf{r}_1 \times \mathbf{p}_1 + \mathbf{r}_2 \times \mathbf{p}_2. \tag{VIII.1.1}$$

We introduce center-of-mass and relative coordinates according to

$$\mathbf{R} \;=\; \frac{m_1\mathbf{r}_1 + m_2\mathbf{r}_2}{m_1 + m_2}, \quad \mathbf{r} = \mathbf{r}_2 - \mathbf{r}_1, \tag{VIII.1.2}$$

and furthermore momenta

$$\mathbf{P} \;=\; \mathbf{p}_1 + \mathbf{p}_2 \tag{VIII.1.3}$$

$$\mathbf{p} \;=\; \frac{m_1\mathbf{p}_2 - m_2\mathbf{p}_1}{m_1 + m_2}. \tag{VIII.1.4}$$

Note that the *relative momentum* $\mathbf{p}$ is not just the difference of the individual momenta. It is rather defined such that in terms of

$$\mu \equiv \frac{m_1 m_2}{m_1 + m_2} \quad \text{reduced mass}, \tag{VIII.1.5}$$

one has

$$\mu\dot{\mathbf{r}} = \mu(\dot{\mathbf{r}}_2 - \dot{\mathbf{r}}_1) = \mu\left(\frac{\mathbf{p}_2}{m_2} - \frac{\mathbf{p}_1}{m_1}\right) = \mathbf{p}. \tag{VIII.1.6}$$

Using these definitions, one checks

$$\mathbf{L} \;=\; \mathbf{r}_1 \times \mathbf{p}_1 + \mathbf{r}_2 \times \mathbf{p}_2 \tag{VIII.1.7}$$

$$\;=\; \mathbf{R} \times \mathbf{P} + \mathbf{r} \times \mathbf{p}. \tag{VIII.1.8}$$

This is the sum of a center-of-mass angular momentum, $\mathbf{R} \times \mathbf{P}$, and a relative angular momentum, $\mathbf{r} \times \mathbf{p}$.

VIII.1.1.2 Born-Oppenheimer Approximation

We recall the Born-Oppenheimer Approximation for the total wave function $\Psi(q, X)$ of a molecule, cf. Eq. (V.2.15),

$$\Psi(q, X) = \sum_\alpha \phi_\alpha(X)\psi_\alpha(q, X), \tag{VIII.1.9}$$

where q stands for the electronic, X for the nuclear coordinates, and the sum is over a complete set of adiabatic electronic eigenstates with electronic quantum numbers α. This form leads to the Schrödinger equation in the adiabatic approximation Eq. (V.2.17),

$$\left[\langle\psi_\alpha|\mathcal{H}_\mathrm{n}|\psi_\alpha\rangle_e + E_\alpha(X)\right]|\phi_\alpha\rangle_n = \mathcal{E}|\phi_\alpha\rangle_n. \tag{VIII.1.10}$$

Here, $E_\alpha(X)$ is the potential acting on the nuclei. We now specify the kinetic energy of the nuclear part for a diatomic molecule,

$$\mathcal{H}_\mathrm{n} = \frac{\mathbf{P}^2}{2M} + \frac{\mathbf{p}^2}{2\mu}. \tag{VIII.1.11}$$

Exercise Check that $\mathcal{H}_\mathrm{n} = \frac{\mathbf{p}_1^2}{2m_1} + \frac{\mathbf{p}_2^2}{2m_2}$.

The effective nuclear Hamiltonian corresponding to an electronic eigenstate α thus is

$$\mathcal{H}_{\mathrm{n},\alpha} = \langle\psi_\alpha|\frac{\mathbf{P}^2}{2M}|\psi_\alpha\rangle + \langle\psi_\alpha|\frac{\mathbf{p}^2}{2\mu}|\psi_\alpha\rangle + E_\alpha(r), \tag{VIII.1.12}$$

which is a sum of a center-of-mass Hamiltonian and a Hamiltonian for the relative motion of the two nuclei. Only the latter is interesting because it contains the potential $E_\alpha(r)$. Note that both center-of-mass and relative Hamiltonian still contain the geometrical phase terms, cf. Eq. (E.5.2), which however we will neglect in the following.

VIII.1.2 Angular Momentum

Neglecting the geometric phase terms, Eq. (E.5.2), we have in three spatial dimensions

$$\begin{aligned}
\mathcal{H}_{\mathrm{n},\alpha}^{\mathrm{rel}} &= \frac{\mathbf{p}^2}{2\mu} + E_\alpha(r) = -\frac{\hbar^2}{2\mu}\Delta_\mathbf{r} + E_\alpha(r) \\
&= -\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right) + \frac{\mathbf{J}^2}{2\mu r^2} + E_\alpha(r),
\end{aligned} \tag{VIII.1.13}$$

where $\mathbf{J}$ is the *relative* angular momentum operator of the nuclei. We have a three-dimensional problem which however due to the radial symmetry of $E_\alpha(r)$ is reduced to a one-dimensional radial eqaution, very much as for the case of the hydrogen atom! We could write the eigenfunctions of $\mathcal{H}_{\mathrm{n},\alpha}^{\mathrm{rel}}$ as

$$\Psi(\mathbf{r}) = R(r)Y_{JM}(\theta, \phi) \tag{VIII.1.14}$$

with the corresponding angular quantum numbers J and M of the nuclear relative motion separated off in the spherical harmonics.

Instead of dealing with the angular momentum operator of the nuclei, one would rather descrive rotations of the whole molecule by the *total* angular momentum $\mathbf{K}$ of the molecule

$$\mathbf{K} = \mathbf{J} + \mathbf{L} + \mathbf{S}, \tag{VIII.1.15}$$

where $\mathbf{L}$ is the total angular momentum of all electrons and $\mathbf{S}$ is the total spin.

VIII.1.2.1 Spin $\mathbf{S} = 0$

This is the simplest case. The total angular momentum of the nuclei is then

$$\mathbf{J} = \mathbf{K} - \mathbf{L}. \tag{VIII.1.16}$$

Since we have neglected geometric phase terms, we can replace $\Delta_{\mathbf{r}}$ by its expectation value in the electronic state α under consideration,

$$\Delta_{\mathbf{r}} = \langle\psi_\alpha|\Delta_{\mathbf{r}}|\psi_\alpha\rangle \tag{VIII.1.17}$$
$$\rightsquigarrow \mathbf{J}^2 = \langle\psi_\alpha|\mathbf{J}^2|\psi_\alpha\rangle = \langle\psi_\alpha|(\mathbf{K}-\mathbf{L})^2|\psi_\alpha\rangle. \tag{VIII.1.18}$$

This allows one to express everything in terms of total angular quantum numbers K as follows: We first write

$$\mathbf{J}^2 = \langle\psi_\alpha|(\mathbf{K}-\mathbf{L})^2|\psi_\alpha\rangle \tag{VIII.1.19}$$
$$= \langle\psi_\alpha|\mathbf{K}^2|\psi_\alpha\rangle - 2\langle\psi_\alpha|\mathbf{K}\mathbf{L}|\psi_\alpha\rangle + \langle\psi_\alpha|\mathbf{L}^2|\psi_\alpha\rangle.$$

First, $\mathbf{K}^2$ is conserved and can be replaced by its eigenvalue $K(K+1)$ whence

$$\langle\psi_\alpha|\mathbf{K}^2|\psi_\alpha\rangle = K(K+1). \tag{VIII.1.20}$$

Second, $\langle\psi_\alpha|\mathbf{L}^2|\psi_\alpha\rangle$ only depends on the electronic degrees of freedom and can therefore be simply added to the potential $E_\alpha(r)$.

Finally, we assume that the electronic state α is an eigenstate of the z component L_z with eigenvalue Λ of the electronic angular momentum. Then,

$$\langle\psi_\alpha|\mathbf{K}\mathbf{L}|\psi_\alpha\rangle = \mathbf{K}\langle\psi_\alpha|\mathbf{L}|\psi_\alpha\rangle = \mathbf{K}e_z\Lambda. \tag{VIII.1.21}$$

On the other hand, we have $\mathbf{J}e_z = 0$ since the angular momentum of the two nuclei is perpendicular to the molecule axis $\mathbf{e}_z \propto \mathbf{r}$, thus

$$(K_z - L_z) = 0 \rightsquigarrow K_z = L_z \tag{VIII.1.22}$$

and

$$\langle\psi_\alpha|\mathbf{K}\mathbf{L}|\psi_\alpha\rangle = \mathbf{K}e_z\Lambda = L_z\Lambda \tag{VIII.1.23}$$
$$= \langle\psi_\alpha|L_z|\psi_\alpha\rangle\Lambda = \Lambda^2.$$

Summarizing, we now have for the radial part

$$-\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right) + \frac{K(K+1)}{2\mu r^2} \underline{- \frac{2\Lambda^2}{2\mu r^2} + \frac{\langle\psi_\alpha|\mathbf{L}^2|\psi_\alpha\rangle}{2\mu r^2} + E_\alpha(r)}$$
$$\equiv -\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right) + \frac{K(K+1)}{2\mu r^2} + U_\alpha(r).$$

Thus we have finally arrived at the form for the effective potential energy,

$$\frac{K(K+1)}{2\mu r^2} + U_\alpha(r). \tag{VIII.1.24}$$

The first term $\frac{K(K+1)}{2\mu r^2}$ is the centrifugal energy as in the hydrogen problem. Since $K_z = L_z$ with fixed eigenvalue Λ for the given state α, the eigenvalues of the total angular momentum must fulfill

$$K \geq \Lambda. \tag{VIII.1.25}$$

VIII.1.3 Radial SE

Our SE for the radial motion of the two nuclei has the form

$$\left[-\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} \right) + \frac{K(K+1)}{2\mu r^2} + U_\alpha(r) \right] R_{\alpha;Kv}(r) = \varepsilon_{\alpha;Kv} R_{\alpha;Kv}(r). \quad \text{(VIII.1.26)}$$

We therefore have two sets of quantum numbers K and v that describe the rotational and vibrational and state of the molecule for a given electronic state α. Setting

$$R_{\alpha;Kv}(r) = \frac{1}{r} P_{\alpha;Kv}(r) \quad \text{(VIII.1.27)}$$

leads to a standard one-dimensional SE with a 'proper' $\frac{d^2}{dr^2}$ kinetic energy term,

$$\left[-\frac{1}{2\mu}\frac{d^2}{dr^2} + U_\alpha(r) + \frac{K(K+1)}{2\mu r^2} \right] P_{\alpha;Kv}(r) = \varepsilon_{\alpha;Kv} P_{\alpha;Kv}(r), \quad r \geq 0. \quad \text{(VIII.1.28)}$$

VIII.1.3.1 Harmonic Approximation

The rotation term $\frac{K(K+1)}{2\mu r^2}$ is assumed as small, and the potential $U_\alpha(r)$ is expanded around a minimum r_α,

$$U_\alpha(r) = U_\alpha(r_\alpha) + \frac{1}{2}\frac{d^2}{dr^2}U_\alpha(r = r_\alpha)(r - r_\alpha)^2 + \dots \quad \text{(VIII.1.29)}$$

Here, r_α can be considered as the equilibrium distance of the two nuclei which clearly still depends on the electronic quantum number α. If the higher order terms in the Taylor expansion are neglected, and $\frac{K(K+1)}{2\mu r^2}$ replaced by $\frac{K(K+1)}{2\mu r_\alpha^2}$, the approximate SE becomes

$$\left[-\frac{1}{2\mu}\frac{d^2}{dr^2} + \frac{K(K+1)}{2\mu r_\alpha^2} + U_\alpha(r_\alpha) + \frac{1}{2}\mu\omega_\alpha^2(r - r_\alpha)^2 \right] P_{\alpha;Kv}^{\text{harm}}(r)$$

$$= \varepsilon_{\alpha;Kv} P_{\alpha;Kv}^{\text{harm}}(r), \quad \omega_\alpha^2 = \frac{1}{\mu}\frac{d^2}{dr^2}U_\alpha(r = r_\alpha). \quad \text{(VIII.1.30)}$$

This is the equation of a linear harmonic oscillator apart from the fact that $r \geq 0$. However, $|r - r_\alpha|$ has been assumed to be small anyway and within this approximation, the energy levels are therefore those of a linear harmonic oscillator shifted by $\frac{K(K+1)}{2\mu r_\alpha^2} + U_\alpha(r_\alpha)$,

$$\varepsilon_{\alpha;Kv}^{\text{harm}} = \frac{K(K+1)}{2\mu r_\alpha^2} + U_\alpha(r_\alpha) + \omega_\alpha\left(v + \frac{1}{2} \right). \quad \text{(VIII.1.31)}$$

VIII.1.3.2 The Energy Spectrum

The structure of the energy spectrum is determined by the magnitude of the three terms $\frac{K(K+1)}{2\mu r_\alpha^2}$, $U_\alpha(r_\alpha)$, and $\omega_\alpha\left(v + \frac{1}{2} \right)$. These differ strongly due to their dependence on the relative nuclei mass μ. In terms of the small dimensionless parameter m/μ (where m is the electron mass), we have

$$U_\alpha = O(1), \quad \text{electronic part} \quad \text{(VIII.1.32)}$$

$$\omega_\alpha\left(v + \frac{1}{2} \right) = O(m/\mu)^{1/2}, \quad \text{vibrational part} \quad \text{(VIII.1.33)}$$

$$\frac{K(K+1)}{2\mu r_\alpha^2} = O(m/\mu), \quad \text{rotational part.} \quad \text{(VIII.1.34)}$$

In spectroscopic experiments, one determined energy differences δE which therefore are broadly determined by

$$\delta E_{\text{el}} \gg \delta E_{\text{vib}} \gg \delta E_{\text{rot}}. \tag{VIII.1.35}$$

VIII.1.4 Spin S > 0

Things get a little bit more complicated for $\mathbf{S} > 0$ which leads to the so-called *Hund's cases a, b, c and d.* For more details cf. Landau-Lifshitz III [1], or Atkins-Friedman.

VIII.1.5 Beyond the Harmonic Approximation

The harmonic approximation has to break down somewhere. A diatomic molecule with its two nuclei harmonically bound would never be able to dissociate into two individual atoms or ions.

One way is to introduce phenomenological potentials with fitting parameters, e.g. the **Morse potential**

$$U_\alpha(r) \to U_\alpha^{\text{Morse}}(r) \equiv D_\alpha \left[1 - e^{-\beta_\alpha(r-r_\alpha)}\right]^2, \tag{VIII.1.36}$$

where D_α is the depth of the minimum below the asymptote and represents the dissociation energy of the molecule.

VIII.2 Selection Rules

VIII.2.1 Dipole Approximation

Assume system of charges q_n localised around a spatial position $\mathbf{r}_0 = 0$. The coupling to an electric field $\mathbf{E}(\mathbf{r}, t)$ within dipole approximation is then given by

$$H_{\text{dip}}(t) = -\mathbf{d}\mathbf{E}(t), \quad \mathbf{d} \equiv \sum_n q_\alpha \mathbf{r}_\alpha, \tag{VIII.2.1}$$

where $\mathbf{E}(t) \equiv \mathbf{E}(\mathbf{r}_0, t)$ is the electric field at $\mathbf{r}_0 = 0$. The dipole approximation is valid if the spatial variation of $\mathbf{E}(\mathbf{r}, t)$ around $\mathbf{r}_0$ is important only on length scales l with $l \gg a$, where a is the size of the volume in which the charges are localised. For a plane wave electric field with wave length λ one would have $l \sim \lambda$.

VIII.2.2 Pure Rotation

Pure rotational transitions are between states where only rotational quantum numbers are changed,

$$|Km_K, v, \alpha\rangle \to |K'm_K', v, \alpha\rangle \tag{VIII.2.2}$$

leaving the vibrational quantum number(s) v and the electronic quantum number(s) α unchanged. Such transitions then depend on matrix elements of the dipole operator,

$$\langle Km_K|\mathbf{d}|K'm_K'\rangle. \tag{VIII.2.3}$$

The calculation of this matrix element, using spherical harmonics, yields the purely rotational selection rules

$$\Delta K = \pm 1, \quad \Delta m_K = 0, \pm 1. \tag{VIII.2.4}$$

Writing the rotational part of the energy as

$$\varepsilon_{\text{rot}}(K) = BK(K+1) \tag{VIII.2.5}$$
$$\rightsquigarrow \quad \Delta \varepsilon_{\text{rot}}(K) \equiv B(K+1)(K+2) - BK(K+1) = 2B(K+1).$$

The distance between the corresponding spectral lines is constant, $\Delta \varepsilon_{\text{vib}}(K+1) - \Delta \varepsilon_{\text{vib}}(K) = 2B$.

VIII.2.3   Pure Vibration

In this case, we have to deal with the harmonic oscillator.

VIII.2.3.1   Recap of the Harmonic Oscillator

The Hamiltonian of the harmonic oscillator

$$\hat{H}_{\text{osc}} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2 \hat{x}^2 \tag{VIII.2.6}$$

can be re-written using the ladder operators

$$a \equiv \sqrt{\frac{m\omega}{2\hbar}}\hat{x} + \frac{i}{\sqrt{2m\hbar\omega}}\hat{p}, \quad a^\dagger \equiv \sqrt{\frac{m\omega}{2\hbar}}\hat{x} - \frac{i}{\sqrt{2m\hbar\omega}}\hat{p} \tag{VIII.2.7}$$

$$\hat{x} = \sqrt{\frac{\hbar}{2m\omega}}\left(a + a^\dagger\right), \quad \hat{p} = -i\sqrt{\frac{m\hbar\omega}{2}}\left(a - a^\dagger\right), \tag{VIII.2.8}$$

as

$$\hat{H}_{\text{osc}} = \hbar\omega\left(a^\dagger a + \frac{1}{2}\right). \tag{VIII.2.9}$$

The commutation relation is

$$[\hat{x}, \hat{p}] = i\hbar, \quad [a, a^\dagger] = 1. \tag{VIII.2.10}$$

The eigenfunctions of the harmonic oscillator are n-phonon states,

$$\hat{H}_{\text{osc}}|n\rangle = \varepsilon_n|n\rangle, \quad \varepsilon_n = \hbar\omega\left(n + \frac{1}{2}\right), \quad n = 0, 1, 2, ...$$

$$|n\rangle \leftrightarrow \psi_n(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4}\frac{1}{\sqrt{n!2^n}}H_n\left(\sqrt{\frac{m\omega}{\hbar}}x\right)e^{-\frac{m\omega}{2\hbar}x^2}, \tag{VIII.2.11}$$

where H_n are the Hermite polynomials.

The ladder operators are also called creation ($a^\dagger$) and annihiliation (a) operators. They act on the states $|n\rangle$ as

$$a^\dagger|n\rangle = \sqrt{n+1}|n+1\rangle, \quad a|n\rangle = \sqrt{n}|n-1\rangle, \quad a|n\rangle = 0. \tag{VIII.2.12}$$

The state $|0\rangle$ is called ground state.

VIII.2.3.2 Pure Vibrational Dipole Transitions

Pure vibrational transitions are between states where only vibrational quantum numbers are changed,

$$|Km_K, v, \alpha\rangle \rightarrow |Km_K, v', \alpha\rangle. \tag{VIII.2.13}$$

Such transitions then depend on matrix elements of the dipole operator,

$$\langle v|\mathbf{d}_\alpha|v'\rangle, \tag{VIII.2.14}$$

where $|v\rangle$ is an harmonic oscillator eigenstate (we write v instead of n now), and

$$\mathbf{d}_\alpha = \langle\alpha|\mathbf{d}|\alpha\rangle \tag{VIII.2.15}$$

is the diagonal matrix element of the dipole operator between the adiabatic electronic eigenstates $|\alpha\rangle$.

Remember that the harmonic potential came from the Taylor expansion of the Born-Oppenheimer energy,

$$
\begin{aligned}
U_\alpha(r) &\approx U_\alpha(r_\alpha) + \frac{1}{2}\frac{d^2}{dr^2}U_\alpha(r = r_\alpha)(r - r_\alpha)^2 \\
\leadsto \hat{H}_{\mathrm{osc}} &= \frac{\hat{p}^2}{2\mu} + \frac{1}{2}m\omega_\alpha^2\hat{x}^2 = \hbar\omega_\alpha\left(a^\dagger a + \frac{1}{2}\right) \tag{VIII.2.16} \\
\omega_\alpha^2 &= \frac{1}{\mu}\frac{d^2}{dr^2}U_\alpha(r = r_\alpha) \tag{VIII.2.17}
\end{aligned}
$$

where the harmonic oscillator coordinate $x = r - r_\alpha$.

The dipole moment operator $\mathbf{d}_\alpha$ depends on the electronic wave functions α and thus parametrically on the coordinate x that describes the internuclear separation. We Taylor-expand

$$\mathbf{d}_\alpha(x) = \mathbf{d}_\alpha(0) + \mathbf{d}'_\alpha(0)x + O(x^2). \tag{VIII.2.18}$$

For transitions between v and $v' \neq v$, one therefore has to linear approximation

$$
\begin{aligned}
\langle v|\mathbf{d}_\alpha|v'\rangle &= \mathbf{d}'_\alpha(0)\langle v|x|v'\rangle = \mathbf{d}'_\alpha(0)\sqrt{\frac{\hbar}{2\mu\omega}}\langle v|a + a^\dagger|v'\rangle \\
&= \mathbf{d}'_\alpha(0)\sqrt{\frac{\hbar}{2\mu\omega}}\left(\delta_{v+1,v'}\sqrt{v+1} + \delta_{v-1,v'}\sqrt{v}\right). \tag{VIII.2.19}
\end{aligned}
$$

The vibrational selection rule thus is

$$\Delta v = \pm 1. \tag{VIII.2.20}$$

The corresponding energy differences determine the transition frequency,

$$\Delta\varepsilon_{\mathrm{vib}}(v) = \hbar\omega_\alpha, \tag{VIII.2.21}$$

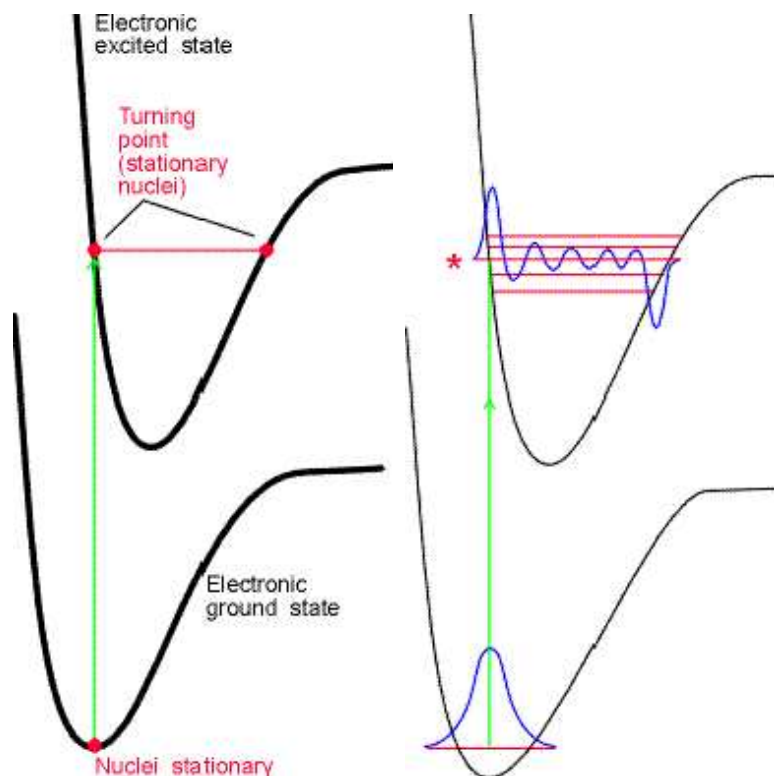which means that a purely vibrational, harmonic spectrum just consists of a single spectral line!

Fig. VIII.1: Franck-Condon-Principle. **Left:** Classical picture, **right:** quantum-mechanical picture. From Prof. Ed Castner's lecture http://rutchem.rutgers.edu/.

VIII.2.4 Vibration-Rotation Spectra

Vibrational and Rotational transitions are coupled, and one now has to discuss the various transition possibilities. This leads to a description in terms of **P-, Q-, and R-branch** for the allowed transitions in diatomic molecules. For further reading, cf. Atkins/Friedman [5] ch. 10.11 or Weissbluth [4] ch. 27.2

VIII.3 Electronic Transitions

Transitions between two molecular states in general involve all quantum numbers: electronic, vibrational, and rotational, i.e.

$$|Km_K, v, \alpha\rangle \rightarrow |K'm'_K, v', \alpha'\rangle. \tag{VIII.3.1}$$

VIII.3.1 The Franck-Condon Principle

Here, a good description is in Atkins/Friedman ch. 11.4.

For simplicity, we leave out the rotations here and just discuss electronic and vibrational transitions. In a classical picture (with respect to the large mass nuclear motion), one considers the two potential curves $U_\alpha(r)$ and $U_{\alpha'}(r)$ and argues that the electronic transition occurs so fast that the nuclear system has no time to react: before and after the transition, the nuclear coordinate X is the same. This, however, means that the distance $|x'| \equiv |X - r_{\alpha'}|$ from the equilibrium position $r_{\alpha'}$ after the transition and the distance $|x| \equiv |X - r_\alpha|$ from the equilibrium position r_α before the transition are not the same: when the nuclei are in equilibrium before

the transition $(X = r_\alpha, x = 0)$, their new coordinate x' *relative to the new equilibrium $r_{\alpha'}$* is $x' \equiv X - r_{\alpha'} = r_\alpha - r_{\alpha'} \neq 0$ after the transition.

The total dipole moment operator is a sum of electronic and nuclear dipole moment,

$$\mathbf{d} = -e \sum_i \mathbf{q}_i + e \sum_s Z_s \mathbf{X}_s = \mathbf{d}_e + \mathbf{d}_n. \tag{VIII.3.2}$$

The transition matrix element in Born-Oppenheimer approximation is $(\alpha \neq \alpha')$

$$
\begin{aligned}
\langle \alpha' v' | \mathbf{d}_e + \mathbf{d}_n | \alpha v \rangle & = \int dq\, dX\, \psi^*_{\alpha'}(qX) \phi^*_{\alpha',v'}(X) (\mathbf{d}_e + \mathbf{d}_n) \phi_{\alpha,v}(X) \psi_\alpha(qX) \\
& = \int dX\, \phi^*_{\alpha',v'}(X) \left[\int dq\, \psi^*_{\alpha'}(qX) \mathbf{d}_e \psi_\alpha(qX) \right] \phi_{\alpha,v}(X) \\
& + \int dX\, \phi^*_{\alpha',v'}(X) \phi_{\alpha,v}(X) \mathbf{d}_n \int dq\, \psi^*_{\alpha'}(qX) \psi_\alpha(qX) \\
& = \int dX\, \phi^*_{\alpha',v'}(X) \left[\int dq\, \psi^*_{\alpha'}(qX) \mathbf{d}_e \psi_\alpha(qX) \right] \phi_{\alpha,v}(X) + 0 \\
& \approx \langle \alpha' | \mathbf{d}_e | \alpha \rangle S(v, v'), \quad S(v, v') \equiv \langle v' | v \rangle. \tag{VIII.3.3}
\end{aligned}
$$

Here it was assumed that the integral

$$\int dq\, \psi^*_{\alpha'}(qX) \mathbf{d}_e \psi_\alpha(qX) \approx \langle \alpha' | \mathbf{d}_e | \alpha \rangle \tag{VIII.3.4}$$

does not depend on the nuclear coordinates X.

The transition between two electronic levels α and α' is therefore determined by the dipole matrix element $\langle \alpha' | \mathbf{d}_e | \alpha \rangle$ and the **Franck-Condon factors** $S(v, v')$, which are the overlap integrals of the corresponding vibronic states. As these states belong to different electronic states α and α', the overlaps are not zero, and there is also no selection rule for Δv.

IX. INTERACTION BETWEEN MOLECULES

IX.1 From microscopic to macroscopic

IX.1.1 Introduction

Often one wants to replace a fully microscopic theory by a more manageable, effective theory. This can be done in two steps as follows:

First step: divide the system under consideration into constituent entities (subsystems).

Second step: find a description in terms of effective potentials between the constituent entities while trying to stay as close as possible to the full microscopic theory.

Example 1: Two molecules of size a at distance $R \gg a$. Full system = all electrons and all nuclei together. Subsystems: the two molecules. This is a 'good description' as long as each molecule is recognizable as one unity. *Separation of a) length and b) energy scales* is important here: a) $R \gg a$; b) the force between the molecules is not strong enough to destroy them, e.g. by ripping out electrons.

Example 2: Nuclear physics. Underlying microscopic theory is QCD. Use effective description of system (nucleus) in terms of effective potentials between constituent nucleons (neutrons and protons).

Example 3: (classical or quantum) statistical mechanics, e.g. calculation of the free energy of a system of atomsor a system of molecules (gas/liquid/solid).

3a) Cohesive energy of solids, cf. Ashcroft/Mermin 'Solid State Physics' [9] ch. 20.

3b) Dispersion forces in colloids, cf. Mahanty/Ninham 'Dispersion Forces' [10].

IX.1.2 General considerations

In the following, the system under consideration is a system of interacting charges (electrons and nuclei) as described by a non-relativistic Schrödinger equation. We are mostly interested in the case where the subsystems are molecules (or atoms). Key questions are the following: what are the forces between the molecules? What are the interactions among the molecules? What kind of *effective potentials* does one need to describe a system of N molecules ?

IX.2 Effective Potentials

IX.2.1 Electrostatics: multipole expansions

This is the simplest case: each of the N subsystems (molecules) is considered as a distribution of charges with charge density $\rho_n(\mathbf{x})$. The total charging energy is

$$E \;=\; \frac{1}{2} \sum_{nn'} \int \int d\mathbf{x} d\mathbf{x}' \frac{\rho_n(\mathbf{x})\rho_{n'}(\mathbf{x}')}{|\mathbf{x} - \mathbf{x}'|}. \tag{IX.2.1}$$

We assume the molecules well separated with their center of mass at $\mathbf{R}_n$. We first consider the contribution from two different molecules, $n \neq n'$, and thus write

$$\mathbf{x} = \mathbf{R}_n + \xi, \quad \mathbf{x}' = \mathbf{R}_{n'} + \xi' \tag{IX.2.2}$$

and expand $\frac{1}{|\mathbf{x}-\mathbf{x}'|}$ for each pair n, n', using the Taylor expansion

$$\begin{aligned}
\frac{1}{|\mathbf{R} + \mathbf{a}|} &= \frac{1}{R}\left(1 + \frac{\mathbf{a}^2 + 2\mathbf{R}\mathbf{a}}{R^2}\right)^{-1/2} \tag{IX.2.3}\\
&= \frac{1}{R}\left(1 - \frac{1}{2R^2}(\mathbf{a}^2 + 2\mathbf{R}\mathbf{a}) + \frac{3}{8R^4}(\mathbf{a}^2 + 2\mathbf{R}\mathbf{a})^2 + ...\right)
\end{aligned}$$

$$\tag{IX.2.4}$$

with $\mathbf{R} = \mathbf{R}_{nn'} \equiv \mathbf{R}_n - \mathbf{R}_{n'}$ and $\mathbf{a} = \xi - \xi'$. We assume *uncharged* molecules, i.e.

$$\int d\mathbf{x}\rho_n(\mathbf{x}) = 0. \tag{IX.2.5}$$

This yields

$$\begin{aligned}
\int\int & d\mathbf{x}d\mathbf{x}'\frac{\rho_n(\mathbf{x})\rho_{n'}(\mathbf{x}')}{|\mathbf{x} - \mathbf{x}'|} = \\
&= \int\int d\xi d\xi'\rho_n(\xi)\rho_{n'}(\xi')\frac{1}{R}\Big(1 - \frac{1}{2R^2}([\xi - \xi']^2 + 2\mathbf{R}[\xi - \xi']) \\
&+ \frac{3}{8R^4}([\xi - \xi']^2 + 2\mathbf{R}[\xi - \xi'])^2 + ...\Big) \\
&= \int\int d\xi d\xi'\rho_n(\xi)\rho_{n'}(\xi')\frac{1}{R}\Big(0 + 2\frac{1}{2R^2}\xi\xi' + 0 + \frac{3}{8R^4}4(\mathbf{R}[\xi - \xi'])(\mathbf{R}[\xi - \xi']) + ...\Big) \\
&= \int d\xi d\xi'\rho_n(\xi)\rho_{n'}(\xi')\frac{1}{R}\Big(\frac{1}{R^2}\xi\xi' - \frac{3}{R^4}(\mathbf{R}\xi)(\mathbf{R}\xi') + ...\Big) \\
&= \frac{\mathbf{d}_n\mathbf{d}_{n'}}{|\mathbf{R}_{nn'}|^3} - 3\frac{(\mathbf{R}_{nn'}\mathbf{d}_n)(\mathbf{R}_{nn'}\mathbf{d}_{n'})}{|\mathbf{R}_{nn'}|^5} + ..., \quad \mathbf{R}_{nn'} \equiv \mathbf{R}_n - \mathbf{R}_{n'} \tag{IX.2.6}
\end{aligned}$$

Here, the dipole moments are defined as

$$\mathbf{d}_n = \int d\mathbf{x}\,\mathbf{x}\rho_n(\mathbf{x}), \tag{IX.2.7}$$

and the remaining terms are dipole-quadrupole, quadrupole-quadrupole etc interaction energies which decay faster with increasing R. Usually the dipole-dipole interaction terms are dominant over the higher multipoles for the interaction between molecules.

Summarizing, we have

$$\begin{aligned}
E &= \frac{1}{2}\sum_n E_n^{\text{self}} + \frac{1}{2}\sum_{nn'}\left(E_{nn'}^{\text{d}-\text{d}} + E_{nn'}^{\text{higher multipoles}}\right) \tag{IX.2.8}\\
E_n^{\text{self}} &= \int\int d\mathbf{x}d\mathbf{x}'\frac{\rho_n(\mathbf{x})\rho_n(\mathbf{x}')}{|\mathbf{x} - \mathbf{x}'|} \\
E_{nn'}^{\text{d}-\text{d}}(\mathbf{R}_{nn'}) &= \frac{\mathbf{d}_n\mathbf{d}_{n'}}{|\mathbf{R}_{nn'}|^3} - 3\frac{(\mathbf{R}_{nn'}\mathbf{d}_n)(\mathbf{R}_{nn'}\mathbf{d}_{n'})}{|\mathbf{R}_{nn'}|^5}, \quad \mathbf{R}_{nn'} \equiv \mathbf{R}_n - \mathbf{R}_{n'}.
\end{aligned}$$

Exercise: Derive the expression for $E_{nn'}^{\text{d}-\text{d}}$

IX.2.1.1 Remark on Dipole-Dipole Interaction

The interaction energy of two dipoles with distance vector $\mathbf{R}$,

$$E^{\mathrm{d-d}}(\mathbf{R}) \quad = \quad \frac{\mathbf{d}_1\mathbf{d}_2}{|\mathbf{R}|^3} - 3\frac{(\mathbf{R}\mathbf{d}_1)(\mathbf{R}\mathbf{d}_2)}{|\mathbf{R}|^5} \tag{IX.2.9}$$

can alternatively be written as

$$E^{\mathrm{d-d}}(\mathbf{R}) \quad = \quad -\mathbf{d}_1\mathbf{E}_2^{\mathrm{dip}} = -\mathbf{d}_2\mathbf{E}_1^{\mathrm{dip}}, \tag{IX.2.10}$$

where $\mathbf{E}_2^{\mathrm{dip}}$ is the electric field generated by dipole 2 at the position of dipole 1, and vice versa.

IX.2.2 Effective Interaction between Molecules

IX.2.2.1 From Classical to Quantum

So far everything is still completely classical. We obtain an effective Hamiltonian for N molecules by writing

$$\mathcal{H}_{\mathrm{eff}} \quad \equiv \quad \mathcal{H}_0 + V, \quad \mathcal{H}_0 = \sum_n H_0^{(n)} \tag{IX.2.11}$$

$$V \quad = \quad \frac{1}{2}\sum_{nn'} E_{nn'}^{\mathrm{d-d}}, \tag{IX.2.12}$$

with $H_0^{(n)}$ the individual Hamiltonian of molecule n, and V the interaction between all the molecules.

From the Hamiltonian $\mathcal{H}_{\mathrm{eff}}$, Eq. (IX.2.11), a semi-classical theory can be constructed as follows: for given internal states of the molecules, we derive effective classical interaction potentials that eventually lead to a classical dynamics of the molecule positions $\mathbf{R}_n$ and momenta $\hat{\mathbf{P}}_n$ in the phase space of the $(\hat{\mathbf{P}}_n, \mathbf{R}_n)$ of the molecules.

If V is regarded as a small perturbation, the interaction potentials are obtained most easily by calculating the T-**matrix** of the system of N molecules with respect to the decomposition Eq. (IX.2.11).

IX.2.2.2 The T-Matrix

For the following, Economou's 'Green's functions in quantum physics' [11] is a useful reference.
We perform perturbation theory for a Hamiltonian

$$H = H_0 + V \tag{IX.2.13}$$

by defining two Green's functions (resolvents) of H and H_0 as the operators

$$G(z) = (z - H)^{-1}, \quad G_0(z) = (z - H_0)^{-1}. \tag{IX.2.14}$$

We have

$$G = (z - H_0 - V)^{-1} = (G_0^{-1} - V)^{-1} = (1 - G_0 V)^{-1}G_0 \tag{IX.2.15}$$

and by expanding in V we obtain the **Dyson equation**

$$G = G_0 + G_0 V G_0 + G_0 V G_0 V G_0 + ... = G_0 + G_0 V G. \tag{IX.2.16}$$

We can express the full Green's function G in terms of the free Green's function G_0 and the T-matrix,

$$
\begin{aligned}
G &= G_0 + G_0 V G_0 + G_0 V G_0 V G_0 + G_0 V G_0 V G_0 V G_0 + \dots \\
&= G_0 + G_0 \left[V + V G_0 V + V G_0 V G_0 V + \dots \right] G_0 \equiv G_0 + G_0 T G_0 \\
T(z) &\equiv V + V G_0(z) V + V G_0(z) V G_0(z) V + \dots
\end{aligned}
\tag{IX.2.17}
$$

We recognize that $T(z)$ plays the role of an effective, z-dependent potential, the knowledge of which is sufficient to calculate the full Green's function G.

IX.2.2.3   Two molecules

(Reading assigment: revision of statistical density operator).

We assume the unperturbed state (no interaction) of the two molecules described by a (quantum statistical) density operator

$$
\hat{\rho} = \sum_{kk'} P_{kk'} |kk'\rangle\langle kk'|,
\tag{IX.2.18}
$$

where the undashed indices refer to molecule 1 and the dashed ones to molecule 2. We call the unperturbed eigenvalues of $\mathcal{H}_0$

$$
E_{kk'} \equiv E_k + E_{k'}
\tag{IX.2.19}
$$

and define the effective interaction as

$$
\begin{aligned}
V_{\text{eff}} &\equiv \sum_{kk'} p_{kk'} \langle kk' | T(E_{kk'}) | kk' \rangle
\tag{IX.2.20} \\
&= \sum_{kk'} P_{kk'} \langle kk' | V | kk' \rangle + \sum_{kk'} P_{kk'} \langle kk' | V G_0(E_{kk'}) V | kk' \rangle + \dots \\
&\equiv V_{\text{eff}}^{(1)} + V_{\text{eff}}^{(2)} + \dots
\tag{IX.2.21}
\end{aligned}
$$

We write the interaction potential operator V

$$
V = \sum_i v_i \otimes v_i'
\tag{IX.2.22}
$$

as a sum over products of operators belonging to molecule 1 and molecule 2. We furthermore assume uncorrelated classical probabilities

$$
P_{kk'} = p_k p_{k'}.
\tag{IX.2.23}
$$

IX.2.3   First oder term: static dipole-dipole interaction

The first order term in V_{eff} in our expansion Eq. (IX.2.20) is

$$
V_{\text{eff}}^{(1)} = \sum_i \sum_k p_k \langle k | v_i | k \rangle \sum_{k'} p_{k'} \langle k' | v_i' | k' \rangle = \sum_i \langle v_i \rangle \langle v_i' \rangle.
\tag{IX.2.24}
$$

This is just given by the expectation value of the terms that make up the interaction potential $= \sum_i v_i \otimes v_i'$, Eq. (IX.2.22). For the dipole-dipole interaction, this gives

$$
V_{\text{eff}}^{(1)}(\mathbf{R}) = \frac{\langle \mathbf{d} \rangle \langle \mathbf{d}' \rangle}{|\mathbf{R}|^3} - 3 \frac{(\mathbf{R}\langle \mathbf{d} \rangle)(\mathbf{R}\langle \mathbf{d}' \rangle)}{|\mathbf{R}|^5}.
\tag{IX.2.25}
$$

Since the first order is *linear* in the interaction potential operator V, the effective $V_{\text{eff}}^{(1)}$ is essential just the V with all operators replaced by their expectation values. This is the *static dipole-dipole interaction* between the molecules. The corresponding force between the two dipoles is

$$\mathbf{F}_{\text{eff}}^{(1)}(\mathbf{R}) = -\nabla V_{\text{eff}}^{(1)}(\mathbf{R}). \tag{IX.2.26}$$

Its form is just as in the classical dipole-dipole interaction. However, this interaction is zero if one of the expectation values of the dipole moment operators vanishes. Such molecules are said to have no static dipole moment.

IX.2.4 Second oder term: (London) dispersion forces (van-der-Waals forces)

This is a much more interesting case.

IX.2.4.1 Physical Picture

The second order term becomes important if the first order term is zero, i.e. when the molecules have no static dipole moment. Quantum mechanically, the expectation value of the dipole moment is zero, but there can be quantum fluctuations as with any expectation value. These fluctuations ('fluctuating dipoles') generate fluctuating electric fields that eventually lead to an attractive interaction between the molecules. In quantum chemistry, the resulting forces are called dispersion forces, in physics they are often called van-der-Waals forces. They can be derived from quantum field theory (quantum electrodynamics), which establishes their close relation to the *Casimir effect* and also accounts for retardation effects due to the finite propagation velocity of interaction (speed of light). If these retardation effects are neglected, we can derive the van-der-Waals forces from our second order perturbation theory, which was based on semi-classical considerations. This is essentially the derivation that was first given by F. London.

IX.2.4.2 Derivation from Second Order Term

We have

$$
\begin{aligned}
V_{\text{eff}}^{(2)} &\equiv \sum_{kk'} p_k p_{k'} \langle kk'|V G_0(E_{kk'})V|kk'\rangle \\
&= \sum_{kk'nn'} p_k p_{k'} \frac{\langle kk'|V|nn'\rangle \langle nn'|V|kk'\rangle}{E_k + E_{k'} - E_n - E_{n'}},
\end{aligned}
\tag{IX.2.27}
$$

where we have inserted $\hat{1} = \sum_{nn'} |nn'\rangle\langle nn'|$ twice and used

$$\langle nn'|G_0(z)|mm'\rangle = \frac{\delta_{nm}\delta_{mm'}}{z - E_{nn'}}. \tag{IX.2.28}$$

Exercise: verify these expressions.

IX.2.4.3   Matrix Elements

We recall the form of the interaction operator,

$$V = E^{\mathrm{d-d}}(\mathbf{R}) \;\;=\;\; \frac{\mathbf{dD}}{|\mathbf{R}|^3} - 3\frac{(\mathbf{Rd})(\mathbf{RD})}{|\mathbf{R}|^5}, \tag{IX.2.29}$$

where we now write $\mathbf{d}$ for $\mathbf{d}_1$ and $\mathbf{D}$ for $\mathbf{d}_2$. Choosing

$$\mathbf{R} = R\mathbf{e}_z \tag{IX.2.30}$$

in z-direction, we can write the interaction operator as a quadratic form,

$$V = \mathbf{d}\underline{\underline{M}}\mathbf{D}, \quad \underline{\underline{M}} = \frac{1}{R^3}\mathrm{diag}(1,1,-2). \tag{IX.2.31}$$

We abbreviate the matrix elements of the dipole moment components as

$$\langle k|\mathbf{d}_\alpha|n\rangle \equiv d_\alpha^{kn}, \quad \langle k|\mathbf{D}_\alpha|n\rangle \equiv D_\alpha^{kn}, \quad \alpha = x, y, z. \tag{IX.2.32}$$

This allows us to write the square in the numerator of Eq. (IX.2.27) as

$$\begin{aligned}
\langle kk'|V|nn'\rangle\langle nn'|V|kk'\rangle \;\;&=\;\; \langle kk'|\mathbf{d}\underline{\underline{M}}\mathbf{D}|nn'\rangle\langle nn'|\mathbf{d}\underline{\underline{M}}\mathbf{D}|kk'\rangle \tag{IX.2.33}\\[4pt]
&=\;\; \sum_{\alpha\beta\gamma\delta} d_\alpha^{kn} M_{\alpha\beta} D_\beta^{k'n'} d_\gamma^{nk} M_{\gamma\delta} D_\delta^{n'k'}\\[4pt]
&=\;\; \sum_{\alpha\gamma} d_\alpha^{kn} d_\gamma^{nk} D_\alpha^{k'n'} D_\gamma^{n'k'} M_{\alpha\alpha} M_{\gamma\gamma}.
\end{aligned}$$

For simplicity, we now assume spherical symmetry for both molecules (which is OK if they are 1-atom molecules, i.e. atoms, but not very realistic otherwise although the following calculations can be generalised to that case as well.) The following property of products of dipole moment operators then holds:

$$d_\alpha^{kn} d_\beta^{nk} = \frac{1}{3}\delta_{\alpha\beta}\mathbf{d}^{kn}\mathbf{d}^{nk}, \quad D_\alpha^{kn} D_\beta^{nk} = \frac{1}{3}\delta_{\alpha\beta}\mathbf{D}^{kn}\mathbf{D}^{nk}. \tag{IX.2.34}$$

Then,

$$\begin{aligned}
\langle kk'|V|nn'\rangle\langle nn'|V|kk'\rangle \;\;&=\;\; \frac{1}{9}\mathbf{d}^{kn}\mathbf{d}^{nk}\mathbf{D}^{k'n'}\mathbf{D}^{n'k'} \sum_{\alpha\beta} M_{\alpha\beta} M_{\alpha\beta}\\[4pt]
&=\;\; \frac{1}{9}\mathbf{d}^{kn}\mathbf{d}^{nk}\mathbf{D}^{k'n'}\mathbf{D}^{n'k'} \sum_{\alpha} M_{\alpha\alpha} M_{\alpha\alpha}\\[4pt]
&=\;\; \frac{2}{3}\frac{1}{R^6}\mathbf{d}^{kn}\mathbf{d}^{nk}\mathbf{D}^{k'n'}\mathbf{D}^{n'k'}. \tag{IX.2.35}
\end{aligned}$$

The effective interaction therefore is

$$V_{\mathrm{eff}}^{(2)}(R) \;\;\equiv\;\; \frac{2}{3}\frac{1}{R^6} \sum_{kk'nn'} p_k p_{k'} \frac{\mathbf{d}^{kn}\mathbf{d}^{nk}\mathbf{D}^{k'n'}\mathbf{D}^{n'k'}}{E_k + E_{k'} - E_n - E_{n'}}. \tag{IX.2.36}$$

If the two molecules are in their groundstates labeled as $k = 0$ and $k' = 0'$, this becomes

$$V_{\mathrm{eff}}^{(2),\mathrm{GS}}(R) \;\;\equiv\;\; \frac{2}{3}\frac{1}{R^6} \sum_{nn'} \frac{\mathbf{d}^{kn}\mathbf{d}^{nk}\mathbf{D}^{k'n'}\mathbf{D}^{n'k'}}{E_0 + E_{0'} - E_n - E_{n'}}. \tag{IX.2.37}$$

The interaction potential therefore is negative, corresponding to an attractive **dispersion force**, and falls of as R^{-6}.

IX.2.5 Polarizabilities, Linear Response Theory

IX.2.5.1 Static Fields

A molecule in a static electric field $\mathbf{E}$ acquires the additional energy (dipole interaction)

$$V = -\mathbf{d}\mathbf{E}, \quad \mathbf{d} = \sum_i q_i \mathbf{r}_i, \tag{IX.2.38}$$

where $\mathbf{d}$ denotes the dipole moment operator and q_i the ith charge. As a result of the interaction with the electric field, the average dipole moment of the molecule changes from its value $\langle \mathbf{d} \rangle_0$ at zero electric field,

$$\langle \mathbf{d} \rangle = \langle \mathbf{d} \rangle_0 + \underline{\underline{\alpha}}\mathbf{E} + \text{higher order in } \mathbf{E}. \tag{IX.2.39}$$

The **polarization tensor** $\underline{\underline{\alpha}}$ ($d \times d$ matrix, where d is the dimension of the system, i.e. usually $d = 3$) can be obtained from second order perturbation theory.

IX.2.5.2 Time-dependent Fields

More generally, for time-dependent fields the molecule has a Hamiltonian

$$\mathcal{H}(t) = H_0 + V(t), \quad V(t) \equiv -\mathbf{d}\mathbf{E}(t), \tag{IX.2.40}$$

where H_0 is the 'free' molecule Hamiltonian without the field. As a result of the interaction with the electric field, the average dipole moment now is

$$\langle \mathbf{d} \rangle_t = \langle \mathbf{d} \rangle_0 + \int_{-\infty}^{t} dt' \underline{\underline{\alpha}}(t - t')\mathbf{E}(t') + \text{higher order in } \mathbf{E}, \tag{IX.2.41}$$

where the expectation value

$$\langle \mathbf{d} \rangle_t \equiv \langle \psi(t)|\mathbf{d}|\psi(t) \rangle \tag{IX.2.42}$$

is calculated with the wave function at time t. The **response** of the molecule to the time-dependent electgric field is now a function of time, in fact it is in general a **retarded response** as expressed by the convolution integral over the time-dependent polarisability tensor $\underline{\underline{\alpha}}(t-t')$. The response at time t is only to electric fields at an earlier time $t' < t$ which ensures *causality*: there is no response to fields in the future.

We can calculate the expectation value $\langle \mathbf{d} \rangle_t$ in time-dependent perturbation theory in the interaction picture. We assume that the field is switched on at an early time t_0 and write

$$|\psi(t)\rangle = U(t, t_0)|\psi(t_0)\rangle \tag{IX.2.43}$$

with our time-evolution operator, Eq. (VI.3.17). Using the interaction picture,

$$\begin{aligned}
|\psi_I(t)\rangle &= |\psi_I(t_0)\rangle - i \int_{t_0}^{t} dt' \tilde{V}(t')|\psi_I(t_0)\rangle + ... \\
\langle \psi_I(t)| &= \langle \psi_I(t_0)| + i\langle \psi_I(t_0)| \int_{t_0}^{t} dt' \tilde{V}(t') + ... \\
\rightsquigarrow \langle \psi(t)|\mathbf{d}|\psi(t)\rangle &= \langle \psi_I(t)|\tilde{\mathbf{d}}(t)|\psi_I(t)\rangle = \langle \psi_I(t_0)|\tilde{\mathbf{d}}(t)|\psi_I(t_0)\rangle \\
&\quad - i \int_{t_0}^{t} dt' \langle \psi_I(t_0)|\tilde{\mathbf{d}}(t)\tilde{V}(t') - \tilde{V}(t')\tilde{\mathbf{d}}(t)|\psi_I(t_0)\rangle + ... \\
&= \langle \tilde{\mathbf{d}}(t)\rangle_0 - i \int_{t_0}^{t} dt' \langle [\tilde{\mathbf{d}}(t), \tilde{V}(t')]\rangle_0 + ...,
\end{aligned} \tag{IX.2.44}$$

where we defined

$$\langle ... \rangle_0 \equiv \langle \psi_I(t_0) ... \psi_I(t_0) \rangle. \tag{IX.2.45}$$

We compare this with the original definition

$$
\begin{aligned}
\langle \mathbf{d} \rangle_t &= \langle \mathbf{d} \rangle_0 + \int_{-\infty}^{t} dt' \underline{\underline{\alpha}}(t-t') \mathbf{E}(t') + \text{higher order in } \mathbf{E} \tag{IX.2.46} \\
&= \langle \tilde{\mathbf{d}}(t) \rangle_0 - i \int_{t_0}^{t} dt' \langle [\tilde{\mathbf{d}}(t), \tilde{V}(t')] \rangle_0 + ..., \qquad V(t) \equiv -\mathbf{dE}(t)
\end{aligned}
$$

and send $t_0 \to -\infty$,

$$\underline{\underline{\alpha}}(t-t') = i\langle [\tilde{\mathbf{d}}(t), \tilde{\mathbf{d}}(t')] \rangle_0 \theta(t-t'), \tag{IX.2.47}$$

where the step function $\theta(t-t')$ ensures that $t > t'$. The matrix elements

$$\underline{\underline{\alpha}}_{\alpha\beta}(t-t') = i\langle [\tilde{d}_\alpha(t), \tilde{d}_\beta(t')] \rangle_0 \theta(t-t') \tag{IX.2.48}$$

are the components of the polarisation tensor. They describe the **response** of the molecule to an electric field $\mathbf{E}(t')$ and are expressed in terms of expectation values of products of dipole-operators with respect to the unperturbed wave function $|\psi_I(t_0 \to -\infty)\rangle$.

IX.2.5.3 Response Functions

The polarizabilities are examples of **response functions**: the response of the expectation value of an observable (operator) A to an external perturbation

$$V(t) = -Bf(t), \tag{IX.2.49}$$

(f is a c-function and B an operator), is given by a **dynamical susceptibility**

$$
\begin{aligned}
\chi_{AB}(t-t') &= i\langle [\tilde{A}(t), \tilde{B}(t')] \rangle_0 \theta(t-t') \\
\langle A \rangle_t &= \langle A \rangle_0 + \int_{-\infty}^{\infty} dt' \chi_{AB}(t-t') f(t') + O(f^2). \tag{IX.2.50}
\end{aligned}
$$

In frequency space, the first order correction to the expectation value is

$$\delta \langle A \rangle_\omega^{(1)} = \chi_{AB}(\omega) f(\omega). \tag{IX.2.51}$$

For example, for the polarization of a molecule in an electric field $\mathbf{E}(t)$ we have for the dipole moment component d_α

$$\delta \langle d_\alpha \rangle_\omega^{(1)} = \chi_{d_\alpha d_\beta}(\omega) E_\beta(\omega) \equiv \underline{\underline{\alpha}}_{\alpha\beta}(\omega) E_\beta(\omega). \tag{IX.2.52}$$

X. EXAMPLES

E.1 Two-Level System

Consider the double-well system in the basis of the left state ($|L\rangle$) and the right state ($|R\rangle$). The Hamiltonian is written as

$$\mathcal{H}_{\mathrm{TLS}} \equiv \hat{H}_0 + \hat{H}_1 = \begin{pmatrix} \frac{\varepsilon}{2} & T_c \\ T_c & -\frac{\varepsilon}{2} \end{pmatrix}, \quad \hat{H}_0 = \begin{pmatrix} \frac{\varepsilon}{2} & 0 \\ 0 & -\frac{\varepsilon}{2} \end{pmatrix}, \quad \hat{H}_1 = \begin{pmatrix} 0 & T_c \\ T_c & 0 \end{pmatrix}. \quad \text{(E.1.1)}$$

E.1.1

a) Briefly explain the meaning of ε and T_c.
b) Calculate the eigenvalues of $\mathcal{H}_{\mathrm{TLS}}$.
c) Calculate the eigenvectors for the case $\varepsilon = 0$.
d) Use first order degenerate perturbation theory to calculate eigenvalues and eigenvectors of $\mathcal{H}_{\mathrm{TLS}}$. Compare to the exact result

E.2 Hydrogen Atom

E.2.1

Derive the Darwin term $\hat{H}_{\mathrm{KE}} = -\frac{1}{2mc^2} \left(\frac{\mathbf{p}^2}{2m} \right)^2$ as the relativistic energy correction for the Hamiltonian.

E.2.2

a) Briefly explain the origin of the spin-orbit coupling. Write down the most general form of a spin-orbit Hamiltonian.
b) Sketch the level scheme for $n = 2$ when spin-orbit and relativistic terms are included.

E.3 Bosons and Fermions

E.3.1

a) Write down the wave function for three identical Bosons which are all in the same spin orbital $\psi_\alpha(\xi)$, where $\xi = (\mathbf{r}, \sigma)$ denotes the position and spin coordinate.
b) Write down the wave function for two identical Fermions in spin orbitals $\psi_1(\xi)$ and $\psi_2(\xi)$.

E.3.2

Verify the identity for Slater determinants,

$$\langle \xi_1, ..., \xi_N | \nu_1, ..., \nu_N \rangle_A \equiv \frac{1}{\sqrt{N!}} \sum_p \text{sign}(p) \psi_{\nu_1}(\xi_{p(1)}) ... \psi_{\nu_N}(\xi_{p(N)})$$

$$= \frac{1}{\sqrt{N!}} \sum_p \text{sign}(p) \psi_{\nu_{p(1)}}(\xi_1) ... \psi_{\nu_{p(N)}}(\xi_N). \tag{E.3.1}$$

by explicit calculation for $N = 3$ Fermions.

E.3.3

a) Use the spin-up/spin-down notation and write down the four spin wave functions (triplets and singlet) for two spin $1/2$ particles. Assign total spin S and total spin projection M to each of them.
b) Use the triplets and singlet from a) and briefly explain the meaning of 'entanglement'.
c) Consider the following four spin-orbitals

$$\psi_1(\mathbf{r})| \uparrow \rangle, \quad \psi_1(\mathbf{r})| \downarrow \rangle, \quad \psi_2(\mathbf{r})| \uparrow \rangle, \quad \psi_2(\mathbf{r})| \downarrow \rangle. \tag{E.3.2}$$

(i) For a system of two electrons, explicitly write down the four basis states, i.e. the four Slater determinants (each is an antisymmetric linear combination of products of these spin-orbitals).

(ii) Explicitly write down the single-triplet basis as linear combinations of the basis states from (i).

E.3.4

a) Consider symmetric and anti-symmetric orbital wave functions for two Fermions,

$$\phi_{\alpha\beta}^{\pm}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} \left[\phi_\alpha(\mathbf{r}_1)\phi_\beta(\mathbf{r}_2) \pm \phi_\alpha(\mathbf{r}_2)\phi_\beta(\mathbf{r}_1) \right], \tag{E.3.3}$$

and show that the matrix elements

$$\langle \phi_{\alpha\beta}^+ | \hat{U} | \phi_{\alpha\beta}^- \rangle = \langle \phi_{\alpha\beta}^- | \hat{U} | \phi_{\alpha\beta}^+ \rangle = 0, \quad \hat{U} = U(|\mathbf{r}_1 - \mathbf{r}_2|). \tag{E.3.4}$$

b) Write down the terms

$$\langle \phi_{\alpha\beta}^+ | \hat{U} | \phi_{\alpha\beta}^+ \rangle, \quad \langle \phi_{\alpha\beta}^- | \hat{U} | \phi_{\alpha\beta}^- \rangle = 0 \tag{E.3.5}$$

explicitely as double integrals. Which one is the direct term, which one is the exchange term?
c) Write down the first order correction of the ground state energy of Helium explicitly as double integrals (you don't need to calculate these integrals).

E.4 Hartree-Fock

Consider the Hamiltonian of N electrons interacting via a interaction potential U which is constant and does not depend on the coordinates of the particles,

$$\hat{H} = \hat{\mathcal{H}}_0 + \hat{U} \equiv \sum_{i=1}^N \hat{H}_0^{(i)} + \frac{1}{2} \sum_{i \neq j}^N U. \tag{E.4.1}$$

E.4.1

Let ε_1, ε_2,... be the sequence of the (non-degenerate) eigenvalues of the one-particle Hamiltonians $\hat{H}_0^{(i)}$, with corresponding eigenstates $\Psi_1(\xi)$, $\Psi_2(\xi)$,...
a) Write down the exact expression for the ground state energy E_0 of the total Hamiltonian $\hat{H}$,
    (i) for $U = 0$
    (ii) for $U > 0$.
b) Write down the N-electron ground state wave function of the total Hamiltonian $\hat{H}$ for both cases $U = 0$ and $U > 0$.

E.4.2

The Hartree-Fock equations in the position representation are

$$\left[\hat{H}_0 + \sum_i \int d\mathbf{r}' |\psi_{\nu_i}(\mathbf{r}')|^2 U(|r - r'|) \right] \psi_{\nu_j}(\mathbf{r})$$

$$-\sum_i \int d\mathbf{r}' \psi_{\nu_i}^*(\mathbf{r}') U(|r - r'|) \psi_{\nu_j}(\mathbf{r}') \psi_{\nu_i}(\mathbf{r}) \delta_{\sigma_i \sigma_j} = \varepsilon_j \psi_{\nu_j}(\mathbf{r}). \tag{E.4.2}$$

In this problem, we consider the case where the interaction is constant, U=const.
a) Simplify the Hartree-Fock equations by using the orthonormality of the ψ_{ν_i}.
b) Thus solve the Hartree-Fock equations for the ground state wave function $|\Psi\rangle_{\text{HF}}$ explicitly.
c) Using b), calculate the Hartree-Fock ground state energy

$$E_\Psi = \frac{1}{2} \sum_{i=1}^N \left[\varepsilon_i + \langle \nu_i | \hat{H}_0 | \nu_i \rangle \right]. \tag{E.4.3}$$

d) Compare the Hartree-Fock ground state energy E_Ψ with the exact ground state energy E_0 from the exact solution of the previous problem and briefly discuss your result.

E.5   Molecules

E.5.1

Assume a Hamiltonian

$$\mathcal{H} = \mathcal{H}_e(q, p) + \mathcal{H}_n(X, P) + \mathcal{H}_{en}(q, X) \tag{E.5.1}$$

for the interaction between electrons e and nuclei n in a molecule, where X stands for the nuclear and q for the electronic coordinates.
a) Write down the Schrödinger equation for i) the electronic wave function $\psi_e(q, X)$, and ii) the nuclear wave function $\phi_n(X)$ in the Born-Oppenheimer approximation.
b) Briefly explain the idea of the Born-Oppenheimer approximation.
c) Assuming a basis of electronic states $\psi_\alpha(q, X)$, write the total wave function of a molecule as $\Psi(q, X) = \sum_\alpha \phi_\alpha(X) \psi_\alpha(q, X)$. Hence derive the Schrödinger equation for the nuclear part,

$$\left[-\frac{\hbar^2}{2M} \nabla_X^2 + E_\alpha(X) - \frac{\hbar^2}{2M} G(X) - \frac{\hbar^2}{M} F(X) \right] |\phi_\alpha\rangle_n = \mathcal{E} |\phi_\alpha\rangle_n$$

$$G(X) \equiv \langle \psi_\alpha | \nabla_X^2 \psi_\alpha \rangle, \quad F(X) \equiv \langle \psi_\alpha | \nabla_X \psi_\alpha \rangle \quad , \tag{E.5.2}$$

E.5.2

Consider the Hydrogen molecule ion H_2^+.
a) Write down the Hamiltonian for the electronic part of H_2^+, including the repulsion energy of the protons.
b) Briefly explain (one or two sentences) what LCAO means.
c) Write down the molecular orbitals (MO) for the lowest bonding and antibonding state in H_2^+ in terms of atomic orbitals.
d) Briefly explain the spatial symmetry of the bonding and antibonding MO in H_2^+.
e) Sketch the effective potentials for the nuclei $E_\pm(R)$ as a function of their distance R for the bonding and the antibonding state. Very briefly explain why the bonding state is called 'bonding'.

E.6 Time-Dependence

E.6.1

Consider the Hamiltonian for a particle in a double well potential with both energies left and right $\varepsilon_R = \varepsilon_L = 0$ and tunnel coupling T_c,

$$H = \begin{pmatrix} 0 & T_c \\ T_c & 0 \end{pmatrix}. \tag{E.6.1}$$

Consider an initial state at time $t = 0$,

$$|\Psi(t = 0)\rangle = |L\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}. \tag{E.6.2}$$

a) Calculate the state vector $|\Psi(t)\rangle = \begin{pmatrix} \alpha_L(t) \\ \alpha_R(t) \end{pmatrix}$ for times $t > 0$.
b) Use the result from a) to calculate the probability to find the particle in the left well after time t.

E.6.2

We discuss the interaction picture with respect to a Hamiltonian $H = H_0 + V$ in this problem.
a) Prove that for any given operator M, the interaction picture operator $M_I(t) \equiv e^{iH_0 t} M e^{-iH_0 t}$ fulfills

$$\frac{d}{dt} M_I(t) = i[H_0, M_I(t)], \tag{E.6.3}$$

where $[A, B] \equiv AB - BA$ is the commutator of two operators.
b) Prove the rule $[AB, C] = A[B, C] + [A, C]B$ for any three operators A, B, C.
c) Now consider the harmonic oscillator $H_0 = \omega a^\dagger a$. Use b) and the fundamental relation $[a, a^\dagger] = 1$ to find the interaction picture operator $a_I(t)$ and $a_I^\dagger(t)$.
d) Now consider the time-dependent Hamiltonian of a harmonic oscillator in a damped, oscillating radiation field,

$$H(t) = H_0 + V(t), \quad H_0 = \omega a^\dagger a, \quad V(t) = V_0 e^{-t/\tau} \left[e^{-i\omega_0 t} a^\dagger + e^{i\omega_0 t} a \right]. \tag{E.6.4}$$

i) Use c) to calculate the transition probability from the ground state $|0\rangle$ at $t = 0$ to the first excited state $|1\rangle$ after time $t \to \infty$,

$$P_{0\to1}(t \to \infty) \quad = \quad \left| \int_0^\infty dt' \langle 1|V_I(t')|0\rangle \right|^2 . \tag{E.6.5}$$

Hint: Use $a|0\rangle = 0$ and $a^\dagger|0\rangle = |1\rangle$.
ii) Sketch $P_{0\to1}(t \to \infty)$ as a function of the radiation frequency ω_0.

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