7. Atomic spectra and atomic structure

Atomic structure means electronic structure, *i.e.,* distributions of electrons in space and energy. Atomic spectra usually means measurable energies related to electronic transitions.

Spectrum of atomic hydrogen

If ignoring the electron spin, the state of the electron (state of the atom) is defined by three quantum numbers n, ℓ and m_ℓ, as discussed in chapter 3.13. The corresponding state of the electron is denoted as $\psi_{n\ell m_\ell}$ or $|n\ell m_\ell\rangle$ and it is called an *orbital.* The energy eigenvalue depends on the *principal quantum number* n, Eq. (3.66)

$$E_n = -\frac{1}{2}\left(\frac{e^2}{4\pi\varepsilon_o}\right)^2 \frac{\mu}{\hbar^2}\frac{1}{n^2} \; ; n = 1, 2, \dots \; . \tag{7.1}$$

and the *angular momentum quantum number* ℓ and *magnetic quantum number* m_ℓ specify the energy degeneracy.

In spectroscopy the energy is usually written in form

$$E_n = -h\,c\;R_H\frac{1}{n^2}\;;\; R_H = \frac{\mu\,e^4}{8\,\varepsilon_0^2\,h^3\,c}\;, \tag{7.2}$$
$$= 109678 \quad cm^{-1}$$

where R_H is the *Rydberg constant for hydrogen.* It depends on the reduced mass $\mu = m_e\,m_p / (m_e + m_p)$, where m_e and m_p are electron and proton masses. If the nuclear recule (recoil) is ignored (in case of heavy nuclei), then it is used as the *Rydberg constant*

$$R_\infty = (m_e\,e^4) / (8\,\varepsilon_0^2\,h^3\,c) = 109737.31 \text{ cm}^{-1}.$$

Thus,
$$R_H = R_\infty / (1 + m_e/m_p).$$

7.1. Transition energies

Hydrogen spectrum results from transitions between the levels in Eq. (7.2). Thus, the energies are

$$\Delta E = h\,c\;R_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

or *in wave numbers*

$$\bar{\nu} = \frac{\Delta E}{h\,c} = R_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right). \tag{7.3}$$

Spectral lines are grouped according to $n_1 = 1, 2, 3, \dots$ and named after their discoverers as, Lyman-, Balmer-, Paschen-, Brackett-, Pfund- and Humphrey series. With increasing n_2 all series approach to their *series limit*

$$\bar{\nu}_\infty = R_H / n_1^2$$

Substitution $n_1 = 1$ to the series limit gives the ground state *ionisation energy*

$$I = h\,c\,Z^2\,R_H \tag{7.4}$$

This gives $I = 2.179 \times 10^{-18}\,J = 1319$ kJ mol^{-1} = 13.60 eV.
Note, however, that $h\,c\,R_\infty = 13.606$ eV = 1 Ry = 1/2 H.
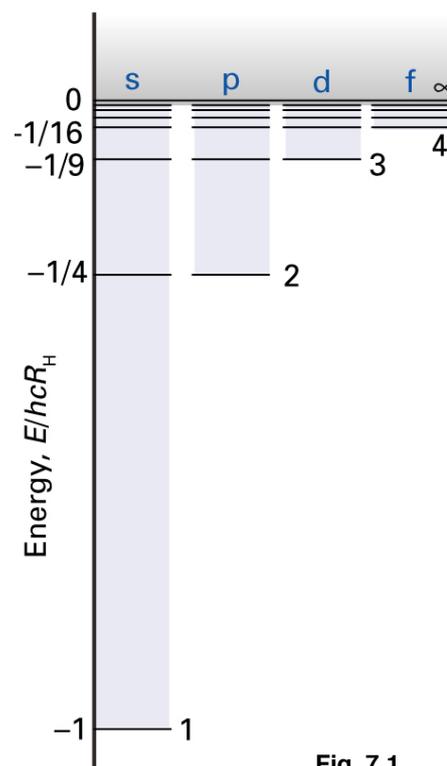
Fig. 7.1

7.2. Selection rules

The interaction hamiltonian of the electric dipole transition is

$$H^{(1)}(t) = -\boldsymbol{\mu} \cdot \mathbf{E}(t),$$

where $\boldsymbol{\mu} = -e\,\mathbf{r}$ is the dipole moment operator, when $\mathbf{r}$ is the position vector of the electron. Thus, the transition rate (intensity) from state $|i\rangle = |\,n_i \ell_i\, m_{\ell i}\rangle$ to state $|f\rangle = |\,n_f \ell_f\, m_{\ell f}\rangle$ is according to the Fermi's golden rule, propotional to the *square of the transition matrix element* $\langle i|H^{(1)}|f\rangle = \boldsymbol{\mu}_{if}\cdot \mathbf{E}(t)$, where

$$\boldsymbol{\mu}_{if} = \langle\, n_i \ell_i\, m_{\ell i}\, |\, \boldsymbol{\mu}\, |\, n_f \ell_f\, m_{\ell f}\rangle \tag{7.5}$$

is the transition dipole moment. From group theory we can infer, that because $\boldsymbol{\mu}$ (or $\mathbf{r}$) is an odd function, also one of the angular momenta ℓ_i or ℓ_f must be odd and the other one even, to make the integrand even: $(-1)^{\ell_i}(-1)(-1)^{\ell_f} = +1$ This is sc. Laporte selection rule:

in the electric dipole transition the parity must change.

On the other hand, by using group theory $\Gamma^{(j_1)} \times \Gamma^{(j_2)} = \Gamma^{(j_1+j_2)} + \Gamma^{(j_1+j_2-1)} + ... + \Gamma^{(|j_1-j_2|)}$ for dipole transition ($\mathbf{r}$: $j = 1$) gives $\Gamma^{(\ell_i)} \times \Gamma^{(1)} = \Gamma^{(\ell_i+1)} + \Gamma^{(\ell_i)} + \Gamma^{(\ell_i-1)}$, of which we already ruled out $\Gamma^{(\ell_i)}$.

By combining these two, we get the selection rule for the *electric dipole transition*

$$\Delta\ell = \pm 1. \tag{7.6a}$$

Alternatively, we can search for the selection rule by considering absorption/emission of the photon, whose spin $s = 1$. Conservation of angular momentum requires that the electron angular momentum (and quantum number) must change by one, which is the same conclusion as above.

The z-component of photon spin s, m_s is called *helicity* σ, which may assume values $\sigma = \pm 1$, while the photon travels in z direction. This gives a further selection rule for Δm_ℓ,

$$\Delta m_\ell = 0, \pm 1. \tag{7.6b}$$

This can be found also directly from the z component $\mu_z = e\,z = e\,r\cos\theta$. Suppose plane polarized photons with the electric field in z direction. Then $\langle n_2 \ell_2 m_{\ell 2}\,|\,e\,z\,|\,n_1 \ell_1 m_{\ell 1}\rangle = e\,\langle n_2 \ell_2\,|\,z\,|\,n_1 \ell_1\rangle\,\langle\, m_{\ell 2}\,|\, m_{\ell 1}\rangle$, where the last factor is

$$\langle m_{\ell i}|m_{\ell f}\rangle = \int_0^{2\pi} e^{-im_{\ell i}\phi}\, e^{im_{\ell f}\phi}\, d\phi = \int_0^{2\pi} e^{i(m_{\ell f}-m_{\ell i})\phi}\, d\phi ,$$

which vanishes, except for $m_{\ell i} = m_{\ell f}$, or $\Delta m_\ell = 0$. Similarly, we get the same result for the x and y polarized light. Thus, in addition, $\Delta m_\ell = \pm 1$.

Thus, the dipole transition selection rules are

$$\Delta n \quad \text{no limitations}$$

$$\Delta\ell \quad = \pm 1$$

$$\Delta m_\ell \quad = 0, \pm 1 \text{ depending on the polarization.}$$

The electric dipole transition is dominant in absorption and spontaneous emission, because the higher order transitions: electric quadrupole ($\langle i|xy|f\rangle$) and magnetic dipole ($\langle i|\ell_z|f\rangle$), quadrupole, etc. are very weak.

Sc. *multiple-quantum transition* selection rules can be considered the same way as the single-quantum transitions, above.

7.3. Orbital and spin magnetic moments

The electron is associated with the electron magnetic moment (charged particle). This magnetic moment couples to the orbital magnetic moment (like the magnetic moments do), which results in the spectral *fine structure.* In case of hydrogen atom the fine structure is weak, but it is the origin of naming levels as: s(harp), p(rincipal), d(iffuse) and f(undamental).

The orbital magnetic moment is $m = (-e/2m_e) \{\ell(\ell+1)\}^{1/2} \hbar$. It can be found by considering a particle with a mass m_e on circular orbit with radius r. Then, in the resulting expression of the magnetic moment the classical angular momentun is replaced by $\{\ell(\ell+1)\}^{1/2}\hbar$.

It is customary to write *the electron orbital magnetic moment* as

$$\mathbf{m} = \gamma_e \, \boldsymbol{\ell}, \quad \text{where} \quad \gamma_e = -e / 2m_e \qquad (7.7)$$

is the *magnetogyric ratio (gyromagneettinen suhde).*

Thus, the orbital magnetic moment has the properties of angular momentum and

$$m_z = m_\ell \, \gamma_e \, \hbar = -\mu_B \, m_\ell \, , \qquad (7.8)$$

where $m_\ell = \ell, \ell-1, ..., -\ell$ and

$$\mu_B = -\gamma_e \, \hbar = e\hbar/2m_e \qquad (7.9)$$

$(= 9.274 \times 10^{-24} \text{ JT}^{-1})$ is sc. *Bohr magneton.*

Electron spin and the related magnetic moment canot be derived classically. It is

$$\mathbf{m}_s = g_e \, \gamma_e \, \mathbf{s}, \quad \text{kun} \quad g_e = 2.002319314,$$

where g_e is sc. *g-factor of the electron.* Now,

$$m_z = -g_e \, \mu_B \, m_s, \quad \text{where} \quad m_s = \pm 1/2. \qquad (7.10)$$

7.4. Spin–orbit coupling

Let us consider hydrogenlike atom with a potential $\phi(r) = Ze/(4\pi\varepsilon_0 r)$ and $V(r) = -e\,\phi(r)$ for an electron giving it an angular momentum ℓ. Then, the interaction energy of the magnetic moments or the spin–orbit hamiltonian is $(-\mathbf{m} \cdot \mathbf{B} = -\mathbf{s} \cdot \mathbf{B} \propto \mathbf{s} \cdot (\mathbf{E} \times \mathbf{v}) \propto \mathbf{s} \cdot (d\phi/dr \, \mathbf{r} \times \mathbf{v}) \propto \mathbf{s} \cdot \boldsymbol{\ell})$, *i.e.* (7.11–13)

$$H_{SO} = \xi(r) \, \mathbf{s} \cdot \boldsymbol{\ell} \, , \qquad (7.14a)$$

where

$$\xi(r) = -\frac{e}{2m_e^2 c^2} \frac{1}{r} \frac{d\phi}{dr} . \qquad (7.14b)$$

Radial average of the coefficient $\xi(r)$ is sc. *spin–orbit coupling constant*

$$hc\zeta_{n\ell} = \hbar^2 \int_0^\infty \xi(r) \, R_{n\ell}^2(r) \, r^2 \, dr . \qquad (7.15)$$

By using the potential $\phi(r) = Ze/(4\pi\varepsilon_0 r)$ and choosing $\ell > 0$,

$$\zeta_{n\ell} = \frac{\alpha^2 R_\infty Z^4}{n^3 \ell(\ell+\frac{1}{2})(\ell+1)} , \qquad (7.16)$$

where

$$\alpha = \frac{e^2}{4\pi\varepsilon_0 \hbar c} = 1 / 137.03604 \qquad (7.19)$$

is sc. *fine-structure constant.*

For example, in case of hydrogen 2p-electron, $\zeta = \alpha^2 R_H / 24 \approx 2.22 \times 10^{-6} R_H$ (hence, the name fine-structure).

7.5. Fine-structure of spectra

Spin–orbit interaction energy depends on coupling $j = \ell \pm s$. According to perturbation theory

$$E_{SO} = \langle n\ell s;jm_j \mid H_{SO} \mid n\ell s;jm_j \rangle = \langle n\ell s;jm_j \mid \xi(r)\, \boldsymbol{\ell} \cdot \mathbf{s} \mid n\ell s;jm_j \rangle. \tag{7.21}$$

Because

$$j^2 = |(\boldsymbol{\ell} + \mathbf{s})|^2 = \ell^2 + s^2 + 2\,\boldsymbol{\ell} \cdot \mathbf{s}, \tag{7.22}$$

we have

$$\boldsymbol{\ell} \cdot \mathbf{s} \mid n\ell s;jm_j \rangle = \tfrac{1}{2}(j^2 - \ell^2 - s^2) \mid n\ell s;jm_j \rangle = \tfrac{1}{2}\hbar^2 \{j(j+1) - \ell(\ell+1) - s(s+1)\} \mid n\ell s;jm_j \rangle \tag{7.23}$$

and

$$E_{SO} = \tfrac{1}{2}\hbar^2 \{j(j+1) - \ell(\ell+1) - s(s+1)\} \langle n\ell s;jm_j \mid \xi(r) \mid n\ell s;jm_j \rangle$$

and with (7.20)

$$E_{SO} = \alpha^2 hcR_\infty Z^4 \frac{j(j+1) - \ell(\ell+1) - s(s+1)}{2n^3\ell(\ell+\frac{1}{2})(\ell+1)}. \tag{7.24}$$

Because the level spacing is the same order of magnitude as R_∞, *i.e.,* 10^5 cm^{-1}, the spin–orbit interaction is only of the order of 1 cm^{-1} (for hydrogen). For heavy atoms, however, it becomes significant, because $E_{SO} \propto Z^4$.

7.6. Term symbols

The *(electronic) configuration* specifies the orbital occupation. A configuration has one or more *terms,* which indicate the symmetry of the wavefunction (angular momentum) and "degeneracy" or *multiplicity.* The terms (singlet, dublet, triplet, ...) are splitted by the spin–orbit interaction to *levels* with different J. For a specific J there are $2J+1$ *states,* which may be separated by external fields.

Hierarchy: configuration — term — level — state.

The term symbol is $^{2S+1}L_J^{M_J}$,

where $L = S, P, D, F, ...$ (orbital angular momentum: 0, 1, 2, 3, ...);
$2S+1 = 1, 2, 3, 4, ...$ (multiplicity: singlet, doublet, ..., if $L \geq S$),
$J = L+S, L+S-1, ..., |L-S|$ (total angular momentum)
and $M_J = J, J-1, ..., -J$ (z component of total angular momentum J).

Selection rules for the electric dipole transition

$$\Delta J = 0, \pm 1 \qquad (J_i + J_f \geq 1)$$
$$\Delta L = \pm 1, 0$$
$$\Delta \ell = \pm 1$$
$$\Delta S = 0.$$

7.7. Detailed spectrum of hydrogen atom
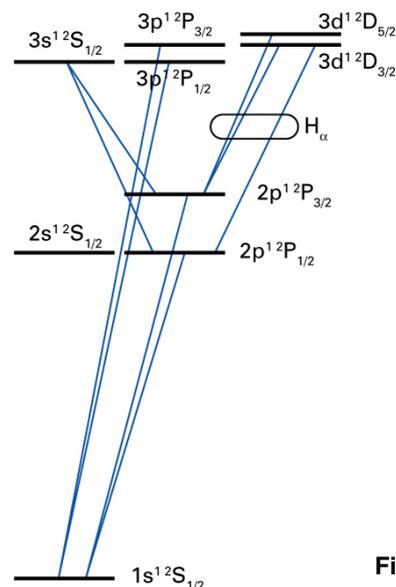
Fig. 7.7.

Closed shells and coupling of holes

Total angular momenta of closed shells of atoms ns^2, np^6, nd^{10}, nf^{14}, ... vanish, and therefore, do not contribute to spectral terms. Thus, to find $^{2S+1}L_J$ it is sufficient to consider the occupations of open shells, only. The ground state term of noble gas atoms is $^1S_0$. Also, for this reason the total angular momentum can be found by coupling those of holes, *i.e.,* the missing electrons wrt. fully occupied shells. Thus, the configurations $1s^2\,2p^1$ and $1s^2\,2p^5$ both give the term $^2P_{1/2,3/2}$.

Alkali metal atoms Li, Na, K, ... have one electron outside the inner closed shells. This single sc. *valence electron,* which "orbits" in outer part of the atom, experiences the nuclear Coulomb potential screened by the sc. *core electrons.*

Structure of helium

7.8. Helium atom

The helium atom is composed of a nucleus with the charge $Z = +2e$, and two electrons 1 and 2, whose positions wrt. the nucleus are $\mathbf{r}_1$ and $\mathbf{r}_2$. Then, the distances are $r_1 = |\mathbf{r}_1|$ and $r_2 = |\mathbf{r}_2|$. Denoting the distance between the electrons as $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$, we can write the hamiltonian

$$H = -\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{1}{4\pi\varepsilon_0}\frac{2e^2}{r_1} - \frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{1}{4\pi\varepsilon_0}\frac{2e^2}{r_2} + \frac{1}{4\pi\varepsilon_0}\frac{e^2}{r_{12}},$$

where ∇_i^2 stands for derivatives wrt. $\mathbf{r}_i$.   (7.26a)

There are no analytical solutions to the corresponding Schrödinger equation

$$H\,\psi(\mathbf{r}_1,\mathbf{r}_2) = E\,\psi(\mathbf{r}_1,\mathbf{r}_2) \tag{7.29}$$

in this case. Therefore, we use the perturbation theory, as follows

$$H = H^{(0)} + H^{(1)}, \quad H^{(0)} = H_1 + H_2$$

$$H_i = -\frac{\hbar^2}{2m_e}\nabla_i^2 - \frac{1}{4\pi\varepsilon_0}\frac{2e^2}{r_i}$$

$$H^{(1)} = \frac{1}{4\pi\varepsilon_0}\frac{e^2}{r_{12}}, \tag{7.30}$$

where H_i is the hamiltonian of hydrogen like atoms, whose eigenfunctions are

$$\psi_{1s}(\mathbf{r}_i) = \left(\frac{Z^3}{\pi a_0^3}\right)^{1/2} e^{-Zr_i/a_0}.$$

Because H_1 depends only on r_1 and H_2 on r_2, the reference state Schrödinger equation is $H^{(0)}\psi(\mathbf{r}_1,\mathbf{r}_2) = E_0\,\psi(\mathbf{r}_1,\mathbf{r}_2)$ and can be separated by a trial

$$\psi(\mathbf{r}_1,\mathbf{r}_2) = \psi_a(\mathbf{r}_1)\,\psi_b(\mathbf{r}_2) = |a\rangle\,|b\rangle = |ab\rangle, \tag{7.31a}$$

where $a \leftrightarrow n_a\,\ell_a\,m_{\ell_a}$ and $b \leftrightarrow n_b\,\ell_b\,m_{\ell_b}$, and the corresponding energies are

$$E_0 = -4\,hc\,R_\infty\,(1/n_a^2 + 1/n_b^2), \tag{7.31b}$$

because $Z^2 = 2^2 = 4$. This is the energy of the helium atom, if interactions between the electrons are ignored. The electron–electron interaction energy from the perturbation operator $H^{(1)}$ is

$$E^{(1)} = \langle ab | H^{(1)} | ab \rangle = J(ab), \tag{7.32}$$

which is sc. *Coulomb integral*

$$J(ab) = \frac{e^2}{4\pi\varepsilon_0}\int |\psi_a(\mathbf{r}_1)|^2 \frac{1}{r_{12}} |\psi_b(\mathbf{r}_2)|^2 \, d\mathbf{r}_1\, d\mathbf{r}_2. \tag{7.33}$$

The Coulomb integral is a classical Coulomb energy of two "orbital charges" $e |\psi_a(\mathbf{r}_1)|^2$ and $e |\psi_b(\mathbf{r}_2)|^2$. It is also called "direct" integral and denoted by $J(a,b) = F_0(a,b) = R_0(a,b;a,b)$. [Slater]

Let us consider the ground state $1s^2$ ($^1S_0$), where both electrons occupy 1s-orbital, *i.e.* $a = b = 1s$ ja $E_0 = 2 E_{1s}$. Then,

$$E(1s^2) = 2 E(1s) + J(1s,1s),$$

where $J(1s,1s) = \langle 1s\, 1s | e^2/(4\pi\varepsilon_0 r_{12}) | 1s\, 1s \rangle$. This can be calculated from Eq. (7.33) as

$$J(1s,1s) = 5/8\, (e^2/4\pi\varepsilon_0)(Z/a_0) = 5/4\, (e^2/4\pi\varepsilon_0 a_0),$$

when $Z = 2$. Numerical value is $J(1s,1s) \approx 5.45 \times 10^{-18}$ J $= 34.0$ eV, and with $E(1s) \approx -54.4$ eV, we obtain $E(1s^2) \approx -74.8$ eV $= -7220$ kJ/mol. Experimentally this is observed to be -79.0 eV $= -7619$ kJ/mol.

The agreement is pretty good, and in particular considering that the "perturbation" $E^{(1)} \approx 34.0$ eV is relatively large compared with the reference state energy $E^0 \approx -108.8$ eV.

7.9. Excited states of helium

Let us consider next an excited state $|ab\rangle$, where $a = 1s$ ja $b \neq 1s$. Because electrons are identical and indistinguishable, in addition to the state $|ab\rangle = \psi_a(\mathbf{r}_1)\,\psi_b(\mathbf{r}_2)$, we need to consider also the state $|ba\rangle = \psi_b(\mathbf{r}_1)\,\psi_a(\mathbf{r}_2)$. This will be crucial in the description of this state.

We consider this state to be degenerate: both wavefunctions $|ab\rangle$ and $|ba\rangle$, correspond to the energy $E = E(a) + E(b)$. So, we can use the perturbation theory presented in section 6.1 or 6.4.

For perturbation theory we write the matrix elements

$$H_{11} = \langle ab | \{H_1 + H_2 + H^{(1)}\} | ab \rangle = E(a) + E(b) + J(ab)$$

$$H_{22} = \langle ba | \{H_1 + H_2 + H^{(1)}\} | ba \rangle = E(b) + E(a) + J(ba) = H_{11}$$

$$H_{12} = \langle ab | \{H_1 + H_2 + H^{(1)}\} | ba \rangle = \langle ab | H_1 | ba \rangle + \langle ab | H_2 | ba \rangle + \langle ab | H^{(1)} | ba \rangle$$

$$= E(b) \langle ab | ba \rangle + E(a) \langle ab | ba \rangle + K(ab) = K(ab), \text{ because } \langle ab | ba \rangle = \langle a | b \rangle \langle b | a \rangle = 0.$$

Now, H_{12} is sc. *exchange integral* (vaihtointegraali)

$$K(ab) = \frac{e^2}{4\pi\varepsilon_0} \int \psi_a^*(\mathbf{r}_1)\,\psi_b^*(\mathbf{r}_2)\,\frac{1}{r_{12}}\,\psi_b(\mathbf{r}_1)\,\psi_a(\mathbf{r}_2)\,d\mathbf{r}_1\,d\mathbf{r}_2 . \qquad (7.35)$$

The exchange integral is also denoted as $K(a,b) = G_0(a,b) = R_0(a,b;b,a)$. [Slater]

Because $H_{21} = K(ba) = K^*(ab) = H_{12}$, the secular equation for $E = E(ab)$ takes the form

$$\begin{vmatrix} H_{11} - E\,S_{11} & H_{12} - E\,S_{12} \\ H_{21} - E\,S_{21} & H_{22} - E\,S_{22} \end{vmatrix} = 0 ,$$

and further, because $S_{ab} = \langle a | b \rangle = \delta_{ab}$, $\qquad (7.36a)$

$$\begin{vmatrix} E(a) + E(b) + J - E & K \\ K & E(a) + E(b) + J - E \end{vmatrix} =$$

$$= \{E(a) + E(b) + J - E\}^2 - K^2 = 0. \qquad (7.36b)$$

Solutions to the secular equation are

$$E = E_\pm(ab) = E(a) + E(b) + J(ab) \pm K(ab) \qquad (7.37)$$

and the corresponding wavefunctions

$$\psi_\pm(\mathbf{r}_1, \mathbf{r}_2) = |\pm\rangle = (1/2)^{1/2} \{ |ab\rangle \pm |ba\rangle \} = (1/2)^{1/2} \{ \psi_a(\mathbf{r}_1)\,\psi_b(\mathbf{r}_2) \pm \psi_b(\mathbf{r}_1)\,\psi_a(\mathbf{r}_2) \}, \qquad (7.38)$$

because

$$1/2 \{ \langle ab | \pm \langle ba | \} (H_1 + H_2 + H^{(1)})\{ |ab\rangle \pm |ba\rangle \} = \ldots = E_\pm(ab).$$

Thus, we have found the proper wavefunction and energies of the helium excited state configuration "ab" by using hydrogen like orbitals with $Z = 2$ as a basis $\psi_n(r) = |n\rangle$.

The function $|+\rangle = |ab\rangle + |ba\rangle$ is *symmetric* with respect to electron exchange,

$$\psi_+(\mathbf{r}_2, \mathbf{r}_1) = (1/2)^{1/2} \{ |ba\rangle + |ab\rangle \}$$
$$= (1/2)^{1/2} \{ |ab\rangle + |ba\rangle \} = \psi_+(\mathbf{r}_1, \mathbf{r}_2),$$

whereas $|-\rangle = |ab\rangle - |ba\rangle$ is *antisymmetric.* This means that exchange of electrons results in change of the wavefunction sign

$$\psi_-(\mathbf{r}_2, \mathbf{r}_1) = (1/2)^{1/2} \{ |ba\rangle - |ab\rangle \} = -(1/2)^{1/2} \{ |ab\rangle - |ba\rangle \} = -\psi_-(\mathbf{r}_1, \mathbf{r}_2).$$

The joint probability density of the two electrons, given by the antisymmetric wavefunction $P_-(\mathbf{r}_1, \mathbf{r}_2) = |\psi_-(\mathbf{r}_1, \mathbf{r}_2)|^2$ vanishes, whenever $\mathbf{r}_1 = \mathbf{r}_2$, because ψ_- vanishes. The resulting minimum (zero) of P_- is called *Fermi or exchange hole* (Fermi- tai vaihtokolo). Its emergence is a pure quantum phenomenon, a consequence of the indistinguishability of particles. In case of symmetric wavefunction, correspondingly a *Fermi heap* emerges (Fermi-kukkula).

Partly for these reasons, the energy of the antisymmetric state is lower than the energy of symmetric state. The difference we found in this case from the lowest order perturbation theory, Eq. (7.37), is 2K.
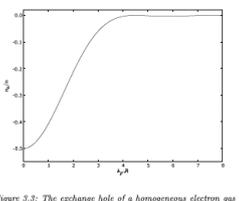
Figure 3.3: The exchange hole of a homogeneous electron gas

Fig. 7.10

7.10. Spectrum of helium

The (experimental) spectrum of helium shows, that not all states assigned with the above terms appear.
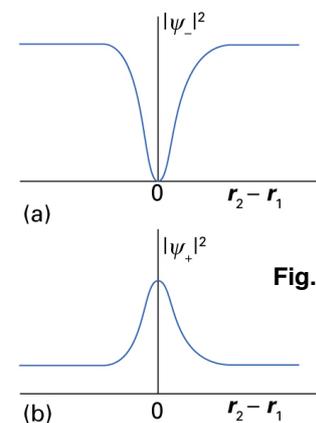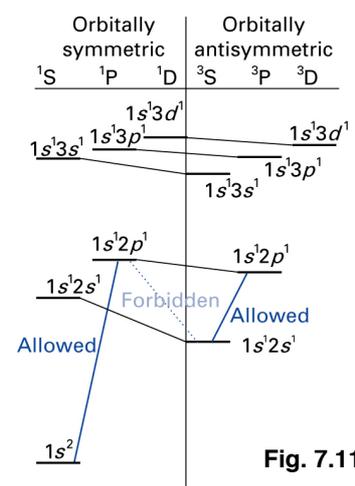
Fig. 7.11

For example the configuration $1s^1 2p^1$ should present terms ${}^1P_1$, ${}^3P_2$, ${}^3P_1$ ja ${}^3P_0$ with both the symmetric and antisymmetric wavefunction, *i.e.,* total of 8 wavefunctions. Interpretation of the experimental spectra finds the terms only once, and furthermore, $|+\rangle$ and $|-\rangle$ assigned to singlet and triplet, respectively.

7.11. The Pauli principle

Pauli explained this observation by writing the total wavefunction as a product of the *orbital and spin-function* and postulating:

The Pauli principle (Paulin periaate)**:**
The total wavefunction of electrons must be antisymmetric
(with respect to exchange of any pair of two electrons).

The particles obeying this principle are called *fermions,* and those obeying the "opposite" requirement, the total wavefunction must be symmetric, are called *bosons.*

The four spin functions of an electron pair, given in section 4.12 are, one antisymmetric (singlet) and three symmetric (triplet). By using these we can write four antisymmetric total wavefunctions

$$(1/2)^{1/2} \quad \psi_+ \ (\alpha\beta - \beta\alpha)$$

$$(1/2)^{1/2} \ \begin{bmatrix} \psi_- & \alpha\alpha \\ \psi_- & (\alpha\beta + \beta\alpha) \\ \psi_- & \beta\beta \ . \end{bmatrix}$$

with notations $\alpha_1\beta_2 = \alpha(1)\beta(2) = \alpha\beta$ and $\beta_1\alpha_2 = \beta(1)\alpha(2) = \beta\alpha$, see sec. 4.12, pp. 58–59.

The triplet spin state of two electrons with parallel spins is symmetric and appears with the antisymmetric space wavefunction, where the electrons avoid each other (Fermi hole). This is called as *spin correlation,* which implies lower Coulomb repulsion and lower energy than that of the singlet state.

The Pauli principle also implies

Pauli exclusion principle:
The quantum numbers of two electrons in a system can not be the same.

In case all the quantum numbers were the same, exchange of the two electrons would not change the wavefunction, and therefore, for an antisymmetric wavefunction $\psi = -\psi = 0$, *i.e.,* the wavefunction would vanish.

The ground state $1s^2$ (${}^1S_0$) antisymmetric wavefunction of helium atom can be written now as

$$\psi(\mathbf{r}_1, \mathbf{r}_2) \quad = \psi_{1s}(\mathbf{r}_1) \, \psi_{1s}(\mathbf{r}_2) \, \{ (1/2)^{1/2} \, (\alpha_1\beta_2 - \beta_1\alpha_2) \}$$

$$= (1/2)^{1/2} \{ \psi_{1s}(\mathbf{r}_1) \, \alpha_1 \, \psi_{1s}(\mathbf{r}_2) \, \beta_2 \ - \ \psi_{1s}(\mathbf{r}_1) \, \beta_1 \, \psi_{1s}(\mathbf{r}_2) \, \alpha_2 \}$$

$$= (1/2)^{1/2} \begin{vmatrix} \psi_{1s}(\mathbf{r}_1) \, \alpha_1 & \psi_{1s}(\mathbf{r}_1) \, \beta_1 \\ \psi_{1s}(\mathbf{r}_2) \, \alpha_2 & \psi_{1s}(\mathbf{r}_2) \, \beta_2 \end{vmatrix} .$$

This representation of an antisymmetric wavefunction is called *Slater determinant* and its elements, which can also be denoted as $\psi_{1s}(\mathbf{r}_1) \, \alpha_1 = \psi_{1s}{}^\alpha (\mathbf{r}_1) = |1s\, \alpha \rangle = 1s\, \alpha$, are called *spin–orbitals.*

Many-electron atoms

7.12. Central-field and orbital approximations

The orbitals in the spherical Coulombic central-field are hydrogenic orbitals with the same hydrogenic quantum numbers. This is the *orbital approximation* of atoms, because in many-electron atoms the Coulombic field is not exactly spherical or "central-field", but

$$V(\mathbf{r}_j) = 1/4\pi\varepsilon_0\{ -Ze^2 / r_j + \Sigma_i' e^2 / r_{ij} \}. \tag{7.39}$$

However, **in average** the potential of electrons is **spherical** and hydrogenic. Therefore, the hydrogenic quantum numbers remain practical also for "orbitals" in many-electron atoms.

The outer electrons feel the nuclear charge screened by the inner electrons. Thus, it is proper to use sc. *screened nuclear charge*

$$Z_{eff} = Z - \sigma, \tag{7.40}$$

for the outer electrons, where σ is sc. *nuclear screening constant.* This is also called as *shielding.* However, the outer electron orbital may penetrate through the inner core orbitals close to the nucleus making the shape of the orbitals and distance from the nucleus essential factors in shielding.

From E. Clementi and D.L. Raimondi (IBM. 1963).

Table 7.3 Values of $Z_{eff} = Z - \sigma$ for neutral ground-state atoms

	H							He
$1s$	1							1.6875
	Li	Be	B	C	N	O	F	Ne
$1s$	2.6906	3.6848	4.6795	5.6727	6.6651	7.6579	8.6501	9.6421
$2s$	1.2792	1.9120	2.5762	3.2166	3.8474	4.4916	5.1276	5.7584
$2p$			2.4214	3.1358	3.8340	4.4532	5.1000	5.7584

7.13. Periodic table of elements

Definition of configuration can be started from the pricipal quantum number or *shell* K, L, M, N, ... ($n = 1, 2, 3, 4, ...$) and then with the *(sub)shell or orbital* s, p, d, f, ... ($\ell = 0, 1, 2, 3, ...$). The two more quantum numbers are the magnetic $m_\ell = \ell, \ell-1, ..., -\ell$ and $m_s = \pm 1/2$. Note, that for all electrons always $s = 1/2$. Thus, for atomic orbitals there are four quantum numbers.

In a neutral atom the number of electrons is Z, neutralizing the nuclear charge, according to the *aufbau principle* the orbitals are filled from the lowest energy to higher obeying the Pauli exclusion principle.

Occupation of the outermost orbital determines the chemical properties of an atom. Therefore, the properties appear periodically and the elements can be ordered accordingly.

Ionization energy is the minimum energy needed to remove one electron from an atom. For a neutral this is called as *the first ionization energy,* for removing the next electron from the positive ($+1$) ion it is *the second ionization energy,* etc.

The ionization energies vary periodically following the periodic table of elements.

The energy released in adding an electron to a neutral atom is *electron affinity.*

7.14. Slater atomic orbitals

The atomic orbitals can be approximated by simplifying the hydrogenic orbital

$$\psi_{n\ell m_\ell}(r,\theta,\phi) = N\, R_{n\ell}(r)\, Y_{\ell m_\ell}(\theta,\phi).$$

The *shielding* can be taken into account by using the *effective nuclear charge* Z_{eff} $(\leq Z)$ and *effective principal quantum number* n_{eff} $(\leq n)$. Thus, we can write the sc. *Slater type atomic obitals,* whose radial part $R_{n\ell}(r)$ is a simplified Laguerre associated polynomials, p. 40.

(1) $\psi_{n\ell m_\ell}(r,\theta,\phi) = N\, r^{n_{eff}-1}\, e^{-Z_{eff}\,\rho/n_{eff}}\, Y_{\ell m_\ell}(\theta,\phi)$, where $\{n, \ell, m_\ell\}$ are quantum numbers,   (7.41)

   N is the normalization constant, $\rho = r/a_0$ and $Y_{\ell m_\ell}$ is spherical harmonic. Further,

(2) the effective principal quantum number n_{eff} relates to the principal quantum number as

and the

n	1	2	3	4	5	6
n_{eff}	1	2	3	3.7	4.0	4.2

(3) effective nuclear charge Z_{eff} relates to Z as $Z_{eff} = Z - \sigma$, where σ is the *shielding constant*. It is obtained by grouping the orbitals as
     1s;   2s, 2p;   3s, 3p, 3d;   4s, 4p; 4d;   4f;   5s,5p;   5d;
   and by calculating the shieldings groupwise accordingly as
          $\sigma = \sum_a \sigma_a + \sum_b \sigma_b + \sum_c \sigma_c$, where
   (a) electrons in inner groups: $\sigma_a = 1.00$, except for $\sigma_a = 0.85$ for the next inner group, if the considered electron is s or p electron,
   (b) electrons in the same group: $\sigma_b = 0.35$, except for 1s: $\sigma_b^{1s} = 0.30$ and
   (c) electrons in an outer group: $\sigma_c = 0$.

Slater type orbitals (STO) are used as basis functions. Such approximate orbitals can also be used for approximation of matrix elements, like expectation values and transition probabilities.

Example Write the Slater type orbitals for nitrogen $_7$N 1s, 2s, $2p_x$ and $2p_z$ electrons.

7.15. Slater determinants

By using the notation $\psi(1, 2) = \psi(\mathbf{r}_1, \mathbf{r}_2)$, the ground state wavefunction of helium is written as

$$\psi(1,2) = (1/2)^{1/2} \begin{vmatrix} \psi_{1s}\,\alpha(1) & \psi_{1s}\,\beta(1) \\ \psi_{1s}\,\alpha(2) & \psi_{1s}\,\beta(2) \end{vmatrix} = (1/2)^{1/2} \begin{vmatrix} 1s\,\alpha & 1s\,\beta \\ 1s\,\alpha & 1s\,\beta \end{vmatrix}$$

$$= (1/2)^{1/2} \det |\, 1s\alpha\ 1s\beta\,| = (1/2)^{1/2} \|\, 1s\alpha\ 1s\beta\,\| .$$

Similarly, the antisymmetric wavefunction of N electrons can be written with spin–orbitals φ as N×N Slater determinant

$$\psi(1,2,...,N) = (1 / N!)^{1/2} \begin{vmatrix} \varphi_a(1) & \varphi_b(1) & ... & \varphi_N(1) \\ \varphi_a(2) & \varphi_b(2) & ... & \varphi_N(2) \\ \vdots & \vdots & & \vdots \\ \vdots & \vdots & & \vdots \\ \varphi_a(N) & \varphi_b(N) & ... & \varphi_N(N) \end{vmatrix} = (1 / N!)^{1/2} \det |\, \varphi_a(1)\ \varphi_b(2)\ ...\ \varphi_N(N)\,| ,$$

$$(7.42)$$

where the latter form lists the diagonal elements, only.

The determinant form includes the Pauli principles: Exchange of two electrons correponds to exchange of two rows, which will change the sign. Occupation of the same quantum state by two electrons means two identical columns in the determinat leading vanishing wavefunction.

7.16. Self-consistent fields

For quantitative and precise description the Slater atomic orbitals are not sufficient but the wavefunctions need to obtained from the Schrödinger equation. Because analytical solutions do not exist, numerical methods are needed, and even then approximations are necessary. The conventional method for atoms is the *Hartree–Fock self–consistent–field* (HF–SCF) approach, which is based on the *one–electron model* (one–electron model ⇐ central–field model).

Each of the electrons is moving in the *central-field* of nucleus and all other electrons (central–field model). As a starting point some trial potential is chosen, *e.g.* one from the Slater orbitals. Then, all orbitals are calculated from the Scrödinger equation and used to create a new better potential. Then again, all orbitals are recalculated from the Scrödinger equation and used to create again a new better potential, etc. This *iteration* will be continued until the potential and solutions converge and become stable. This situation is called as *self-consistent* (SCF).

For the numerical solution the atomic hamiltonian can be written as

$$H = \sum_i h_i + \frac{1}{2} \sum_i \sum_{j \neq i} \frac{1}{4\pi\varepsilon_0} \frac{e^2}{r_{ij}} , \qquad (7.46)$$

where h_i is the hydrogenic one-electron hamiltonian Eq. (7.30), and the double sum is the Coulomb repulsion of all electrons i and j. The factor $1/2$ is to avoid "double counting" of interactions.

For simplicity, considering an atom with closed shells, writing the whole wavefunction in form of Slater determinant, and then, the expectation value of the hamiltonian (7.46), *i.e.,* the total energy. Now, conditions for minimization of the total energy wrt. each orbital ψ_s leads to sc. *Hartree–Fock equations*

$$\left\{ h_1 + \sum_r (2J_r - K_r) \right\} \psi_s(1) = \varepsilon_s \, \psi_s(1) \,, \tag{7.47a}$$

one for each ψ_s. These are explicit differential equations for all ψ_s , sc. *one-electron equations,* where the *Coulomb operator* J_r is defined as

$$J_r \, \psi_s(1) = \left\{ \int \psi_r^*(2) \frac{e^2}{4\pi\varepsilon_0 \, r_{12}} \psi_r(2) \, d2 \right\} \psi_s(1) \tag{7.47b}$$

and *exchange operator* or *Fock operator* K_r as

$$K_r \, \psi_s(1) = \left\{ \int \psi_r^*(2) \frac{e^2}{4\pi\varepsilon_0 \, r_{12}} \psi_s(2) \, d2 \right\} \psi_r(1) \tag{7.47c}$$

The Coulomb operator J_r is the average electrostatic potential, sc. *Hartree potential,* of the orbital r. Similarly, the *Fock–operator* includes spin correlation.

Due to the central-field approximation, solutions to Hartree–Fock equations ψ_s contain the spherical harmonics as the angular part with quantum numbers ℓ and m_ℓ. The radial part must fit to the boundary conditions, which leads to certain discrete values of ε_s , only. This is taken care of by the basis fuctions or the numerical (finite-difference) algorithm.

The H–F equations are eigenvalue equations, which determine both the eigenfunctions and eigenenergies of orbitals s.

The orbital energies can also be written as expectation values of H–F equations (7.47a) as

$$\varepsilon_s = E_s + \sum_r (2J_{sr} - K_{sr}), \tag{7.48a}$$

where $E_s = \langle s \, | \, h_1 \, | \, s \rangle$ is sc. *one-electron integral,* (Note, $h_1 = h_s$)

$$J_{sr} = \langle s \, | \, J_r \, | \, s \rangle = \langle sr \, | \, 1/4\pi\varepsilon_0 \, e^2/r_{12} \, | \, sr \rangle \tag{7.48b}$$

is the Coulomb energy between orbitals s and r, *cf.* the equation (7.33)) and

$$K_{sr} = \langle s \, | \, K_r \, | \, s \rangle = \langle sr \, | \, 1/4\pi\varepsilon_0 \, e^2/r_{12} \, | \, rs \rangle \tag{7.48c}$$

is the corresponding exchange energy, *cf.* equation (7.35)). Note, that $J_{rr} = K_{rr}$.

Thus, the orbital energy ε_s comprises the one-electron integral $\langle s \, | \, h_1 \, | \, s \rangle$ and interaction energies of all other electrons r and s. Now, because all orbitals are occupied by 2 electrons, the sum of all orbital energies is $2 \sum_s \varepsilon_s$. However, this sum includes all interactions twice, which is called *double counting.* Therefore, the total energy is

$$E = 2 \sum_s \varepsilon_s - \sum_s \sum_r (2J_{sr} - K_{sr}) \tag{7.49}$$

for an atom with closed shells occupied by two electrons.

For a helium atom, *e.g.,*

$$\varepsilon_{1s} = E_{1s} + (2J_{1s,1s} - K_{1s,1s}) = E_{1s} + J_{1s,1s}$$

and the total energy becomes correctly as

$$E = 2\,\varepsilon_{1s} - (2J_{1s,1s} - K_{1s,1s}) = 2\,(E_{1s} + J_{1s,1s}) - J_{1s,1s} = 2\,E_{1s} + J_{1s,1s}.$$

It is the orbital energy, which is needed to remove the electron from an atom assuming that the energies of other electrons do not change. However, the other electrons, of course, "relax" as a response the removal. Their orbital energies shift slightly downwards.

The shift of energies of other electrons contribute to lowering the ionization potential of the removed one. For removal of the outermost electrons these relaxation effects may be negligible, and then,

$$I_r \approx \varepsilon_r \qquad (7.50)$$

This assumption is called *Koopmans' theorem:* The ionization energy of the outermost electron is roughly its orbital energy (with opposite sign).

7.17. Restricted and unrestricted Hartree–Fock approach

Above, while considering atomic orbitals we assumed closed shells, each occupied with 2 electrons with opposite spins. Implicitly, we also assumed the same spatial orbital form for each of these electron pairs. Of course, in case of odd number of electrons, at least one open shell with single occupation occurs, but there is only one spatial form for each shell. This is called *restricted Hartree–Fock* (RHF) method.

Now, in many cases and, in particular, in the presence of open shells and/or presence of imbalance of spins the two electrons with different spins have different interaction potential. Therefore, the spatial parts of orbitals for different spins will find different spatial form in self-consistency, if not restricted but allowed. This is called *unrestricted Hartree–Fock* (UHF) method.

7.18. Density functionals

An alternative approach to the electronic structure calculations is to consider the electron density, instead of the wavefunction, as a starting point. Later in chapter 9, we will learn, that all the properties of any system of electrons in the ground state can be derived from its density function $\rho(\mathbf{r})$, alone. Let us consider the homogeneous electron gas (HEG) in infinite space as an example.

With the Thomas–Fermi theory it can be shown that for the HEG the kinetic energy per electron is a functional of ρ as

$$T[\rho] = C \int \rho^{5/3}(\mathbf{r}) \, d\mathbf{r}, \qquad (7.53)$$

where $C = 3^{5/3}\pi^{4/3}/10 \approx 2.871$. For the electron–nucleus interaction we can write

$$V_{eN}[\rho] = -Z/4\pi\varepsilon_0 \int \rho(\mathbf{r})/r \, d\mathbf{r} \qquad (7.54)$$

and for the electron–electron interaction, the Hartree energy, as

$$V_{ee}[\rho] = 1/2 \, Z/4\pi\varepsilon_0 \int \rho(\mathbf{r}_1)\rho(\mathbf{r}_2) / |\mathbf{r}_1-\mathbf{r}_2| \, d\mathbf{r}_1 \, d\mathbf{r}_2. \qquad (7.55)$$

Thus, the Thomas–Fermi total energy functional becomes as

$$E_{TF}[\rho] = T[\rho] + V_{eN}[\rho] + V_{ee}[\rho]. \qquad (7.56)$$

This total energy lacks the excahange interaction between electrons. P.A.M. Dirac showed that the exchange interaction per electron in HEG is proportinal to $\rho^{4/3}$. Therefore, the exchange functional becomes as

$$K[\rho] = C_{ex} \int \rho^{4/3}(\mathbf{r}) \, d\mathbf{r}, \qquad (7.68)$$

where $C_{ex} = 3/2/4\pi\varepsilon_0 \, (3/\pi)^{1/3} \approx 1.477$. This is called the Thomas–Fermi–Dirac method.

7.19. Term symbols of many-electron atoms

See the chapter 7.6.on pages 115–116.

7.20. Hund's rules

Hund's rules are empirical "laws" for the order of energy levels and states of terms. As an example consider configuration np^2, which gives terms $^1D_2$, $^3P_{2,1,0}$ and $^1S_0$. These remain from terms of np $n'p$ configuration $^3D_{3,2,1}$, $^3P_{2,1,0}$, $^3S_1$, $^1D_2$, $^1P_1$ and $^1S_0$ after applying Pauli exclusion principle for $n = n'$.

Rule 1:
The term with maximum multiplicity lies lowest in energy. This is a consequence of spin correlation. For the np^2 configuration this implies $E(^3P) < E(^1D), E(^1S)$.

Rule 2:
For a given multiplicity, the term with the highest L lies lowest in energy. With larger L the electrons orbit further away from each other (and to same direction) leading to lower Coulombin repulsion. Thus, for np^2 configuration it implies that $E(^1D) < E(^1S)$.

Rule 3:
For a given multiplicity and L, the level with lowest J lies lowest in energy for less than half-filled shell, and vice versa. This can be understood as a consequence of spin–orbit interaction. Thus, for configuration np^2

$$E(^3P_0) < E(^3P_1) < E(^3P_2) < E(^1D) < E(^1S).$$

Correspondingly, for the configuration np^4

$$E(^3P_2) < E(^3P_1) < E(^3P_0) < E(^1D) < E(^1S).$$

7.21. LS- and jj-coupling

The coupling scheme presented earlier is useful, in case the Coulomb interactions dominate. There, the orbital angular momenta of electrons ℓ_i are coupled to give L, and the spins s_i to give S, and then coupling of L and S is considered. This scheme is called *LS- or Russell–Saunders-coupling,* which is good for, light atoms. The spectral terms presented earlier naturally describe this scheme.

In case of heavy atoms, the spin–orbit interaction may dominate, and therefore it is naural to first couple s and ℓ of each electron to yield j, and then, these can be further coupled to form J. This is called *jj-coupling.*

Atoms in external fields

7.22. Normal Zeeman effect

Through coupling to the magnetic moments the external magnetic field **B** effects on the energy states of electrons, which can be seen in atomic spectra. This is called the *Zeeman effect.*

Fig. 7.22

Consider the $^1P_1$ level, where $S = 0$ and $L = J = 1$, and thus, only L contributes to **m**. Then, $\mathbf{M} = \gamma_e \mathbf{L}$, where γ_e is the magnetogyric ratio, and the interaction hamiltonian is

$$H^{(1)} = -\mathbf{M} \cdot \mathbf{B} = -\gamma_e \mathbf{L} \cdot \mathbf{B} = -\gamma_e L_z B. \tag{7.71}$$
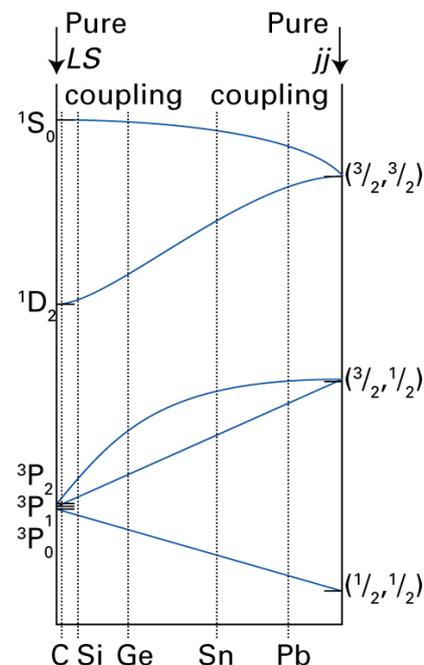
Now, the term $^1P_1$ comprises states $M_L = M_J = 0, \pm 1$, which implies that $\mathbf{L} \cdot \mathbf{B} = L_z\, B = \hbar\, M_L\, B$ and the corresponding energy is

$$E^{(1)} = \langle\, ^1P^{M_L}\, |\, H^{(1)}\, |\, ^1P^{M_L}\,\rangle = -\gamma_e\, \hbar\, M_L\, B = \mu_B\, M_L\, B, \qquad (7.72)$$

where $M_L = -1, 0, 1$; and μ_B is Bohr magneton. Now, consider transition $^1P \to {}^1S$, where the final state is not effected by the magnetic field, because $S = L = 0$, with the presence of magnetic field instead of one line, three lines appear, with separation $\mu_B\, B$, see Fig. 7.23.
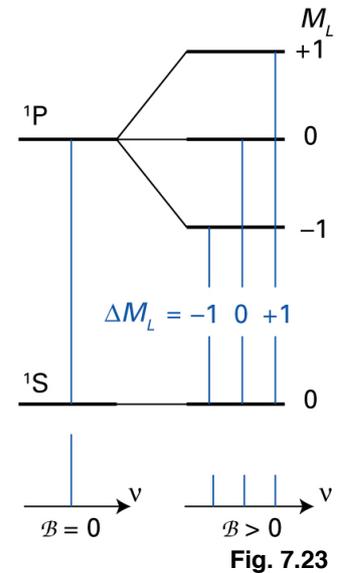
This splitting of a singlet level (and spectral line) to three is called as *normal Zeeman effect.* The central line is called π-line (linearly polarized) and the other two σ-lines (circularly polarized).

Fig. 7.26

7.23. Anomalous Zeeman effect

A more general case than "splitting of a singlet level", where levels of higher multiplicity contribute is called *anomalous Zeeman effect,* see Fig. 7.26.

Note, the selection rules in transitions.

$\Delta M_L = -1\ \ 0\ +1$

Fig. 7.23
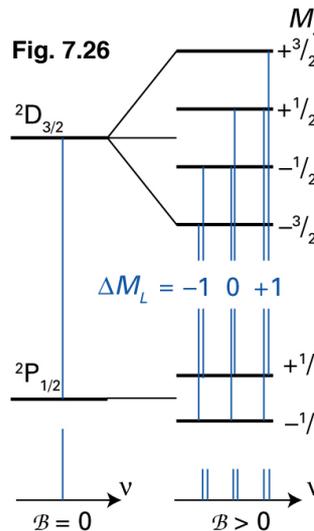
7.24. Stark effect

Effects from the electric field on the energy states of electrons and spectra is called *Stark effect.* The strongest, though even then relatively weak, the sc. *linear Stark effect,* which is observed from the hydrogenlike atoms. This is due to the polarization.

The hamiltonian is

$$H^{(1)} = -\boldsymbol{\mu} \cdot \boldsymbol{\mathcal{E}} = -\mu_z\, \mathcal{E} = e\, z\, \mathcal{E}, \qquad (7.77)$$

where $\boldsymbol{\mu} = e\, \mathbf{r}$ is the dipole moment of the electron.

The hydrogenlike orbitals are not eigenfunctions of this operator. The selection rules of dipole transition allow non-zero matrix elements between such states as 2s- and $2p_z$. The perturbation operator $H^{(1)} = e\, z\, \mathcal{E}$ is said to mix the states, and according to perturbation theory, sec. 6.1,

$$\langle 2p_z\, |\, H^{(1)}\, |\, 2s \rangle = 3\, e\, a_0\, \mathcal{E} \qquad (7.78)$$

The mixed state wave functions are $(s + p) / \sqrt{2}$ and $(s - p) / \sqrt{2}$, which are illustrated in Fig 7.28. The energy separation of these states depends linearly on the electric field, as seen in Eqs. above.

Very strong field can rip the electron off from the atom. This means tunneling as illustrated in Fig. 7.29. This is one example of a state with finite lifetime, which is seen as broadening in the corresponding spectral line.

Fig. 7.28

Fig. 7.29

Energy due to externally applied potential

Total potential energy

Coulomb potential energy

ψ
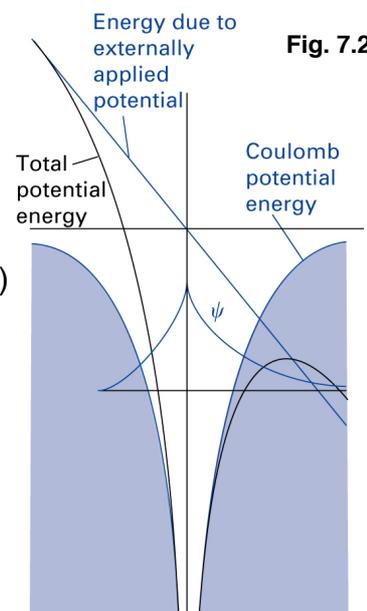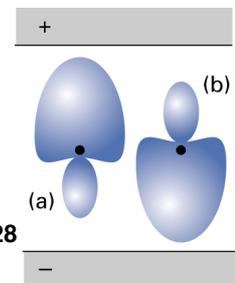
8. Molecular structure

Molecular structure comprises the conformation by its atoms (spatial configuration) and electronic structure, *i.e.,* distributions in space and energy. Molecular structure lays basis for chemical properties and reactions, and can be experimentally measured by spectroscopies.

Traditionally, the electronic structure has been considered with *molecular orbital theory* or *valence bond theory,* which both are using the atomic orbitals as starting point.

Born–Oppenheimer approximation

The complete Schrödinger equation of a molecule includes the kinetic and interaction energies of all particles: electrons and nuclei. The simplest molecule H_2^+ consists of three particles, electron and two protons, only, but there are no exact analytical solutions to its Schrödinger equation.

In practice, the nuclear dynamics is conventionally separated from that of the electrons: The electronic structure is calculated by keeping the nuclei in fixed positions, giving their Coulomb potential for electrons, only. This is called *Born–Oppenheimer approximation.*

The total energies of such nuclear conformations of a molecule define the sc. *potential energy (hyper)surface* (PES) for nuclear dynamics. For a diatomic molecule the PES reduces to a *potential energy curve.*
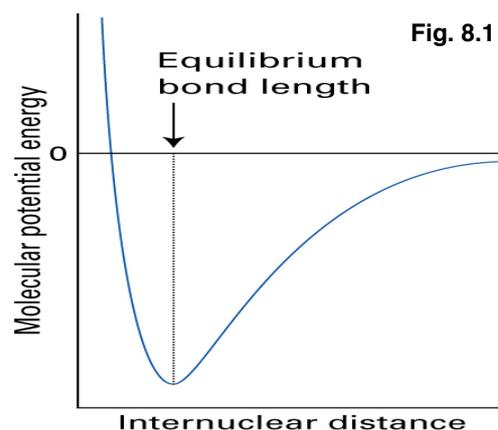
Fig. 8.1

8.1. Formulation of Born–Oppenheimer approximation

The Born–Oppenheimer (BO) approximation is motivated by the large difference of masses of electrons and nuclei. Therefore, the electrons are considered to adapt to the nuclear motions without delay and without exchange of energy, *i.e., adiabatically.* Thus, the momentary nuclear conformation only creates a "time-independent" external potential to the Schrödinger equation of electrons. The total energy of electrons and potential energy of nuclei together define the PES, where the nuclear dynamics can be considered classically or quantum mechanically, if relevant. The minimum energy point of PES is called *equilibrium conformation.*

In practice, the above means approximate separation of the wavefunction as

$$\Psi(\overline{\overline{R}},\overline{\overline{r}}) = \psi_{Nrovib}(\overline{\overline{r}};\overline{\overline{R}})\ \psi(\overline{\overline{R}};\overline{\overline{r}}). \tag{8.3}$$

From now on, we will consider the latter part, the electronic wavefunction, only.

8.2. Hydrogen molecule ion

Within the B–O approximation, only the simplest molecule, H_2^+, can be treated exactly (in ellipsoidal coordinates). The hamiltonian is

Fig. 8.3

$$H = -\frac{\hbar^2}{2m_e}\nabla^2 + \frac{e^2}{4\pi\varepsilon_0}\left(-\frac{1}{r_a} - \frac{1}{r_b} + \frac{1}{R}\right). \tag{8.9}$$

Let us consider the energy eigenstates of the electron as a function of the distance of protons R. The exact solutions are illustrated in the Figs. 8.5 and 8.6.
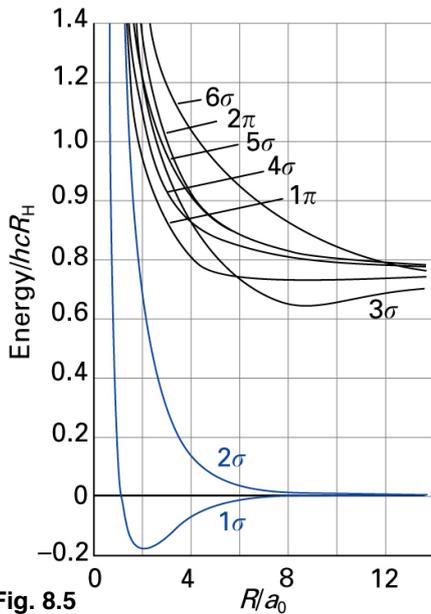
Fig. 8.5

The bond of the molecule is formed by minimization of the energy, which happens only with the lowest (and negative) eigenenergy and certain distance of the protons, see Fig. 8.5. Therefore, the corresponding eigenfunction 1σ is called as the *"bonding" molecular orbital,* for which it is typical to bring the electronic charge in between the nuclei. The minimum energy distance of the nuclei is called as *(equilibrium) bond length.* For H_2^+ it is $R_e = 1.06$ Å, corresponding to the binding energy 2.648 eV.

The next orbital is $2\sigma^*$, which is *"antibonding",* whose occupation is seen to minimize its positive energy towards zero (the reference energy) by increasing the bond length
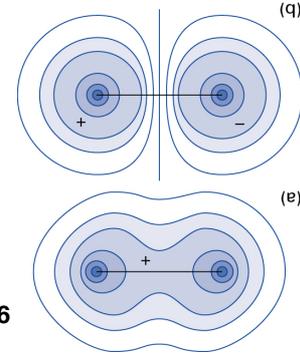
Fig. 8.6

towards infinity. The charge distribution explains why, but also the higher kinetic energy contributes.

Once again, the simple "two degenerate level perturbation theory" can also be used to analyze these two orbitals. Then, we assume that these molecular orbitals are formed from those of two hydrogen 1s orbitals at the two nuclei. The reference system is the two 1s orbital at infinite distance and pertubation is their interaction at the binding distance, *i.e.,* the bond length.

Molecular orbital theory

8.3. Linear combination of atomic orbitals (LCAO)

As shown in the above perturbational treatment, the molecular orbitals can be thought of forming from 1s orbitals of hydrogen atom ϕ_a and ϕ_b or $|\,a\,\rangle$ and $|\,b\,\rangle$. As seen, then

$$1\sigma \approx \phi_a + \phi_b \qquad \text{and} \qquad 2\sigma \approx \phi_a - \phi_b. \qquad (8.11)$$

Similarly, in general molecular orbitals can be described with a linear combination of atomic orbitals *(LCAO).* This is also called as *molecular orbital (MO) method,* or LCAO–MO method. Several kind of atomic orbitals (AO) can be chosen, *e.g.,* HF–SCF–AO or STO.

Hamiltonian of H_2^+ ion is

$$H = -\frac{\hbar^2}{2m_e}\nabla^2 + \frac{e^2}{4\pi\varepsilon_0}\left(-\frac{1}{r_a} - \frac{1}{r_b} + \frac{1}{R}\right). \qquad (8.12)$$

The LCAO trial wavefunction is now

$$\psi = \Sigma_r\, c_r\, \phi_r = \Sigma_r\, c_r\,|\,r\,\rangle, \qquad (8.13)$$

where $\phi_r = |\,r\,\rangle$ are the basis functions and we should determine the coefficients c_r. From the variation method we get the secular equations

$$\Sigma_r\, c_r\,(H_{rs} - E\, S_{rs}) = 0. \qquad (8.14)$$

Now, consider the basis set $\{\,|\,a\,\rangle, |\,b\,\rangle\,\}$, *i.e.,* $r, s = a, b$. Then, evaluation of the matrix elements yields

$H_{aa} = H_{bb} = \langle a \,|\, H \,|\, a \rangle = \alpha$ is sc. Coulomb integral,

$H_{ab} = H_{ba} = \langle a \,|\, H \,|\, b \rangle = \beta$ is sc. resonance integral or "hopping" integral,

$S_{ab} = S_{ba} = \langle a \,|\, b \rangle = S$ is overlap integral and $S_{aa} = S_{bb} = \langle a \,|\, a \rangle = 1$.

Thus, the secular equations (8.14) take the form

$$c_a (\alpha - E) + c_b (\beta - E\,S) = 0$$

$$c_a (\beta - E\,S) + c_b (\alpha - E) = 0$$

and nontrivial solutions exist, if the secular determinant vanishes

$$\begin{vmatrix} \alpha - E & \beta - E\,S \\ \beta - E\,S & \alpha - E \end{vmatrix} = 0. \tag{8.15}$$

This gives the second order equation $(\alpha - E)^2 - (\beta - E\,S)^2 = 0$. The solutions for E are

$$E_\pm = (\alpha \pm \beta) / (1 \pm S) \tag{8.16}$$

From the secular equations we get

$$E_+ : \qquad c_a = c_b \qquad \text{and} \qquad c_a = 1 / \{2(1+S)\}^{1/2}$$

$$E_- : \qquad c_a = - c_b \qquad \text{and} \qquad c_a = 1 / \{2(1-S)\}^{1/2} \tag{8.17}$$

which determine the wavefunctions

$$\psi_\pm = c_a \left(\,|\, a \rangle \pm |\, b \rangle \right), \tag{8.24}$$

where $|\, a \rangle$ and $|\, b \rangle$ are the 1s orbitals of hydrogen atom.

Let us find expressions for α, β and S. The Coulomb integral is

$$\alpha = \langle a \,|\, H \,|\, a \rangle = \langle a \,|\, \left(-\frac{\hbar^2}{2m_e} \nabla^2 - \frac{e^2}{4\pi\varepsilon_0} \frac{1}{r_a} \right) |\, a \rangle + \tag{8.18}$$

$$+ \langle a \,|\, \left(-\frac{e^2}{4\pi\varepsilon_0} \frac{1}{r_b} \right) |\, a \rangle + \frac{e^2}{4\pi\varepsilon_0} \frac{1}{R} \langle a \,|\, a \rangle$$

$$= E_{1s} - j' + \frac{e^2}{4\pi\varepsilon_0} \frac{1}{R}, \tag{8.20}$$

where

$$j' = \frac{e^2}{4\pi\varepsilon_0} \int \frac{\phi_a^2}{r_b} \, d\mathbf{r}_b. \tag{8.19}$$

As $\phi_a(r_a) = \sqrt{\dfrac{Z^3}{\pi a_0^3}}\, e^{-Zr_a/a_0}$, we get $j'(R,Z) = \dfrac{e^2}{4\pi\varepsilon_0} \dfrac{1}{R} \left\{ 1 - \left(1 + \dfrac{ZR}{a_0} \right) e^{-2ZR/a_0} \right\}$. (Example 8.1 in book)

Resonance integral $\beta = \langle a \,|\, H \,|\, b \rangle = \langle a \,|\, \left(-\frac{\hbar^2}{2m_e} \nabla^2 - \frac{e^2}{4\pi\varepsilon_0} \frac{1}{r_b} \right) |\, b \rangle +$

$$+ \langle a \,|\, \left(-\frac{e^2}{4\pi\varepsilon_0} \frac{1}{r_a} \right) |\, b \rangle + \frac{e^2}{4\pi\varepsilon_0} \frac{1}{R} \langle a \,|\, b \rangle \tag{8.21a}$$

$$= \left(E_{1s} + \frac{e^2}{4\pi\varepsilon_0} \frac{1}{R} \right) S - k',$$

where

$$k' = \frac{e^2}{4\pi\varepsilon_0} \int \frac{\phi_a \phi_b}{r_a} \, d\mathbf{r}_a. \tag{8.21b}$$

Also k' is obtained analytically, see the appendix

$$k'(R,Z) = \frac{e^2}{4\pi\varepsilon_0} \frac{1}{a_0} \left(1 + \frac{ZR}{a_0} \right) e^{-ZR/a_0}. \tag{8.22}$$

The overlap integral is (see the example 8.1 in the text book)

$$S(R,Z) = \langle a \,|\, b \rangle = \left\{ 1 + \frac{ZR}{a_0} + \frac{1}{3} \left(\frac{ZR}{a_0} \right)^2 \right\} e^{-ZR/a_0}.$$

Now we write the energy eigenvalues $E_\pm = (\alpha \pm \beta)/(1 \pm S)$ explicitly as:

$$E_+ = E_{1s} + \frac{e^2}{4\pi\varepsilon_0}\frac{1}{R} - \frac{j' + k'}{1 + S} \qquad (8.23a)$$

and

$$E_- = E_{1s} + \frac{e^2}{4\pi\varepsilon_0}\frac{1}{R} - \frac{j' - k'}{1 - S} , \qquad (8.23b)$$

illustrated in Fig. 8.11. Both j' and k' are positive, and thus, E_+ is the energy of bonding orbital and E_- that of antibonding. Note, E_- is more upwards from E_{1s} energy than E_+ is downwards.

As given above, already, the wavefunctions are

$$\psi_\pm = \{2(1-S)\}^{-1/2}\,(\,|\,a\,\rangle \pm |\,b\,\rangle\,) . \qquad (8.24)$$

Fig. 8.11.

By using the above analytical expressions the minimum energy of H_2^+ molecule and the corresponding bond length R_e can be found. We find $R_e = 1.30$ Å and for the dissociation energy $E_{1s} - E_+ = 1.76$ eV (170 kJmol^{-1}). The experimental values are 1.06 Å and 2.60 eV (255 kJmol^{-1}). The deviation is large and the main reason for that is the insufficient basis set: the hydrogen 1s orbitals, only.

Diatomic molecules have cylindrical symmetry. The eigenstates of full symmetry are called as σ-orbitals, cf. the atomic s-orbitals. An antibonding orbital can be denoted with a star (*). In case of homonuclear diatomic the inversion symmetry can be denoted by a subscript: even with g (*gerade*) and odd with u (*ungerade*). Thus, the two lowest energy orbitals are denoted as σ_g and σ_u*. If it is relevant to indicate the relationship to the corresponding atomic orbitals, the origin, the notation can be extended correspondingly to $1s\sigma_g$ and $1s\sigma_u$*. Also, the principal quantum number can be indicated like $1\sigma_g$ and $1\sigma_u$* (or $1\sigma_g$ and $2\sigma_u$*).

8.4. Hydrogen molecule

The electronic configuration of He atom was obtained by occupying the 1s orbital of He with two electrons. Similarly, we now occupy the $1\sigma_g$ orbital of H_2^+ by two electrons to obtain the electronic configuration of H_2 molecule. Thus, we obtain the configuration $1\sigma^2$ ($^1\Sigma_g$). The symmetric orbital part is now $1\sigma_g(1)\,1\sigma_g(2)$, which needs an antisymmetric spin part, cf. sec. 7.11 for helium, which is

$$\psi(1,2) = 1\sigma_g(1)\,1\sigma_g(2)\,(1/2)^{1/2}\,\{\alpha\beta - \beta\alpha\}. \qquad (8.26)$$

Because $1\sigma_g = \{2(1+S)\}^{-1/2}(a+b)$, where $a = \phi_a = |\,a\rangle$, we have

$$\psi(1,2) = \{2(1+S)\}^{-1}\{a(1)+b(1)\}\{a(2)+b(2)\}(1/2)^{1/2}\{\alpha_1\beta_2 - \beta_1\alpha_2\}.$$

The corresponding energy can now be calculated according to the perturbation theory using the hamiltonian

$$H = -\frac{\hbar^2}{2m_e}\left(\nabla_1^2 + \nabla_2^2\right) + \frac{e^2}{4\pi\varepsilon_0}\left(-\frac{1}{r_{1a}} - \frac{1}{r_{1b}} - \frac{1}{r_{2a}} - \frac{1}{r_{2b}} + \frac{1}{r_{12}} + \frac{1}{R}\right), \qquad (8.25)$$

It is a function of R. Thus, the potential energy curve is

$$E = 2E_{1s} + \frac{e^2}{4\pi\varepsilon_0}\frac{1}{R} - \frac{2j' + 2k'}{1 + S} + \frac{j + 2k + m + 4\ell}{2(1 + S)^2} , \qquad (8.27)$$

where the sc. *two-electron integrals* are

$$(8.28)$$

$$j = \frac{e^2}{4\pi\varepsilon_0}\langle ab\,|\,\frac{1}{r_{12}}\,|\,ab\rangle , \quad k = \frac{e^2}{4\pi\varepsilon_0}\langle ab\,|\,\frac{1}{r_{12}}\,|\,ba\rangle , \quad \ell = \frac{e^2}{4\pi\varepsilon_0}\langle aa\,|\,\frac{1}{r_{12}}\,|\,ab\rangle \text{ and } m = \frac{e^2}{4\pi\varepsilon_0}\langle aa\,|\,\frac{1}{r_{12}}\,|\,aa\rangle .$$

This gives the bond length 0.85 Å and binding energy $2\,E_{1s}^H - E_+^{H_2} = 2.70$ eV (260 kJmol^{-1}). Corresponding experimental values are 0.742 Å and 4.48 eV (432 kJmol^{-1}). Thus, the description is reasonable, but not very good.

8.5. Configuration interaction

Valence bond method (VB)

MO-method does not properly describe bond breaking of the hydrogen molecule and its dissociation to two hydrogen atoms, whose "natural" wavefunction would be $a(1) b(2) = | ab \rangle$ = ab. With *valence bond method,* instead, this natural wavefunction is good for describing an **electron pair**, which is taken as the starting concept.

Together with ab the degenerate function ba is as good to start with and the degenerate states perturbation theory (or variational approach) again leads to $\psi_\pm = N_\pm \{ab \pm ba\}$ and ψ_+ is identified as the ground state.

Normalization constant is found from $\langle \psi_\pm | \psi_\pm \rangle = N_\pm^2 \{ \langle ab | ab \rangle \pm \langle ab | ba \rangle \pm \langle ba | ab \rangle + \langle ba | ba \rangle \} = = N_\pm^2 2(1 \pm S^2) = 1$, which gives

$$N_\pm = 1 / \{2(1 \pm S^2)\}^{1/2}.$$

Consider next the expectation value of hamiltonian for the function $\psi_\pm = N_\pm \{| ab \rangle \pm | ba \rangle\}$. We get

$$E_\pm = 2E_{1s} + \frac{e^2}{4\pi\varepsilon_0} \frac{1}{R} - \frac{J \pm K}{1 \pm S^2} ,$$

where $$J = j - 2j' \quad \text{and} \quad K = k - 2k'S.$$

Note, that the integral k corresponds to the helium atom exchange integral K. Also, the now found expressions J and K are called Coulomb and exchange integrals. Both of these are negative, and therefore $E_+ < E_-$. Minimum of E_+ wrt. R gives the equilibrium bond length 0.875 Å and the corresponding binding energy $2 E_{1s}^H - E_+ = 3.14$ eV (303 kJmol^{-1}), which is "better" than what was found with the molecular orbital theory.
[MO: 0.85 Å / 2.70 eV; Exp.: 0.742 Å / 4.48 eV]

Molecular orbital method (MO) and charge correlation

Let us compare the descriptions of H_2 molecule given by the MO and VB methods. Omitting the normalization factors the above given wavefunction of the two can be written as

$$\psi^{VB} = a(1) b(2) + b(1) a(2) \qquad = ab + ba$$

ja

$$\psi^{MO} = a(1)b(2) + b(1)a(2) + a(1)a(2) + b(1)b(2) = ab + ba + aa + bb.$$

The valence bond wavefunction presents the *covalent bond* formed by the pair of electrons coming from atoms a and b. The molecular orbital wavefunction includes the covalent bond, but in addition, the two terms introducing the *ionic bond* of the form H$^+$–H$^-$, which describes the occasion that both of the electrons occupy a or b. Consider dissociation, for example!

We can infer, that the ionic nature of MO-bond is too strong. Due to the Coulomb repulsion the two electrons tend to occupy the two different atoms more than the same. This is called *charge correlation,* or in general, *correlation interaction.* Note the difference between this and the above considered *spin correlation* or *exchange interaction.* The latter is purely quantum mechanical phenomenon, whereas the nature of charge correlation is a classical kind *many–body interaction.*

On the other hand, the VB wavefunction underestimates the ionic nature, because to some extent the two electrons appear also in the same atom. Therefore the VB wavefunction can be improved with a trial wave function

$$\psi^{VB} = ab + ba + \lambda \{aa + bb\}$$

$$= \psi_{cov}^{VB} + \lambda \psi_{ion}^{VB},$$

where we now have a mixing parameterr $\lambda < 1$ to be found.

With the variational method to minimize the total energy we get $\lambda \approx 1/6$. Thus, there is some small ionic bonding present, $\lambda^2 \approx 1/36 \approx 3\%$, instead of 50% suggested by the MO method. This explains why uncorrected VB method describes hydrogen molecule better than the MO method with this simple basis set. With the optimized wavefunction we now get the binding energy 4.10 eV (396 kJmol^{-1}), to be compared with the experimental 4.48 eV (432 kJmol^{-1}).

Molecular orbital method (MO) and charge correlation

The MO wavefunction can also be improved to include correlations or the many-body effects. This can be done by including the sc. *configuration interactions* (CI), as follows. Consider the occupations of molecular orbitals σ_g ja σ_u* spanned by the two 1s orbitals a and b, *i.e.* the different electronic configurations σ_g^2, $\sigma_g \sigma_u$ ja σ_u^2. In more details we have the four configurations $\sigma_g(1) \sigma_g(2)$, $\sigma_g(1) \sigma_u*(2)$, $\sigma_u*(1) \sigma_g(2)$ and $\sigma_u*(1) \sigma_u*(2)$. The second and the third are degenerate and become mixed, and with spin functions can be written as:

$$^1\Sigma_g: \quad \Psi_1 = \sigma_g \sigma_g \ (\alpha \beta - \beta \alpha)$$

$$^1\Sigma_u: \quad \Psi_2 = \{\sigma_g \sigma_u* + \sigma_u* \sigma_g\} \ (\alpha \beta - \beta \alpha)$$

$$^1\Sigma_g: \quad \Psi_3 = \sigma_u* \sigma_u* \ (\alpha \beta - \beta \alpha)$$

$$^3\Sigma_u: \quad \Psi_4 = \{\sigma_g \sigma_u* - \sigma_u* \sigma_g\} \quad \begin{matrix} \alpha \alpha \\ (\alpha \beta + \beta \alpha) \\ \beta \beta \end{matrix}$$

Here, the total molecular symmetry is indicated with the spectral terms $^1\Sigma_g$ or $^3\Sigma_u$, similarly with the case of atoms.

Now, consider the asymptotic behavior of energies of these configurations as the molecule dissociates, *i.e.* R → ∞. We see, that configurations Ψ_1 and Ψ_3 approach to two the 1s^1 atomic configurations as σ_g and σ_u* become degenerate, and then their energies approach to E_+. Also, as these two molecular configurations assume the same symmetry, $^1\Sigma_g$, with the perturbation theory these configurations may be allowed to mix, in order to minimize the total energy. Thus, we can write a trial wavefunction (omitting normalization constant)

$$\psi_{CI}^{MO} = c_1 \Psi_1 + c_3 \Psi_3 \tag{8.29}$$

$$= \{c_1 \sigma_g \sigma_g + c_3 \sigma_u* \sigma_u*\} (\alpha \beta - \beta \alpha) \tag{8.30}$$

$$= c_1 \{\sigma_g \sigma_g + \lambda' \sigma_u* \sigma_u*\} (\alpha \beta - \beta \alpha),$$

where $\lambda' = c_3/c_1$. Now, $\lambda' < 1$, because the lower energy configuration σ_g^2 can be expected to dominate: have more weight than σ_u^2. Substitutions $\sigma_g = a + b$ and $\sigma_u = a - b$, (omitting normalization and spin functions) give

$$\psi_{MO} = a b + b a + \lambda \{a a + b b\},$$

which is exactly the same as the improved ψ^{VB}.

Fig. 8.15

The MO method (plus CI) is more "straightforward", and therefore, more used than VB. In what follows, the concepts and formalism of MO will be used.
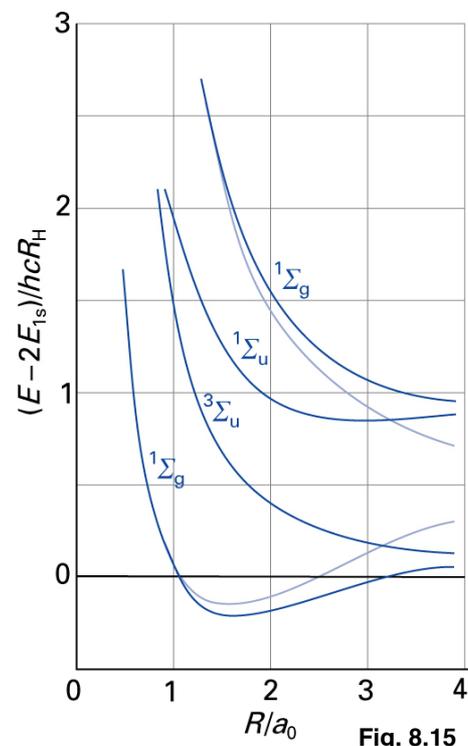
8.6. Diatomic molecules

Now, we consider formation of the electronic configuration of diatomic molecules based on the Bohr aufbau principle and Pauli exclusion principle. First however, let us look at some rules and conditions in formation of molecular orbitals and bonds.

The atomic orbitals forming the bond must have same symmetry wrt. the rotation around the axis of the bond. Such orbitals are *e.g.* atomic s, p_z and d_{zz}, ... orbitals in one set, they have the full rotation symmetry wrt. z-axis (the bond) and they form the highest symmetry molecular orbitals, the sc. σ orbitals.

(a)   (b)

(c)   (d)   **Fig. 8.16**

Atomic p_x and p_y orbitals have lower sc. π symmetry and they form π bonds, together with d_{xz}, d_{yz}, f_{xzz}, f_{yzz} ..., orbitals. Similarly, there are δ, φ, ... symmeries and bonds.

Same symmery requirement follows from the needed overlap of participating atomic orbitals. The measure of this is the overlap integral S. The overlap integral of different symmetry atomic orbitals vanishes.

On the other hand, in case of the same symmetry orbitals, sufficient spatial overlap is needed, i.e. the atomic orbitals should not be too diffuse or localized in different parts in space.
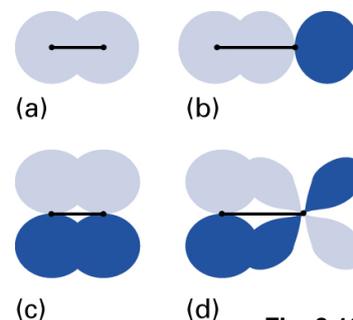
The atomic orbitals forming the molecular orbital should be close in energy. With MO approach the energies are solutions to the secular determinant equation, cf. (6.14) and (8.15)

$$\begin{vmatrix} \alpha_A - E & \beta - E\,S \\ \beta - E\,S & \alpha_B - E \end{vmatrix} = 0, \qquad (8.32)$$

(a)

and in simplest form as, cf. (6.16), Fig. 6.3 and (8.16)

$$E_+ \approx \alpha_A - \beta^2/(\alpha_B - \alpha_A) \quad \text{and} \quad E_- \approx \alpha_B + \beta^2/(\alpha_B - \alpha_A) \qquad (8.33)$$

where $\beta = H_{12}$, and α_A and α_B are the atomic orbital energies. We see that large difference $\alpha_B - \alpha_A$ implies less changes in the energies, small mixing of A and B , and thus, weak binding.

With these rules and principles we can analyze evolution of the molecular electronic configurations of homonuclear diatomic molecules of second row atoms, as shown in Fig. 8.18. Note, that also $2s\sigma^*$ and $2p_z\sigma$ molecular orbitals mix, and as a consequence, change their bonding/antibonding nature.

(b)   **Fig. 8.17**

All this carries a name hybridization, which results in *hybrid orbitals.*

Occupying the 14 electrons of nitrogen molecule N_2 we end up with the configuration

$$N_2: \quad 1s\sigma_g{}^2\ 1s\sigma_u^{*2}\ 2s\sigma_g{}^2\ 2s\sigma_u^{*2}\ 2p\pi_u{}^4\ 2p\sigma_g{}^2 \quad (\,^1\Sigma_g\,),$$
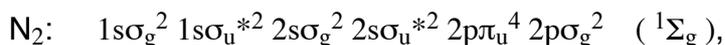
which we can interpret as a triple bond: one σ bond and two π bonds. The triple bond is denoted as N≡N .
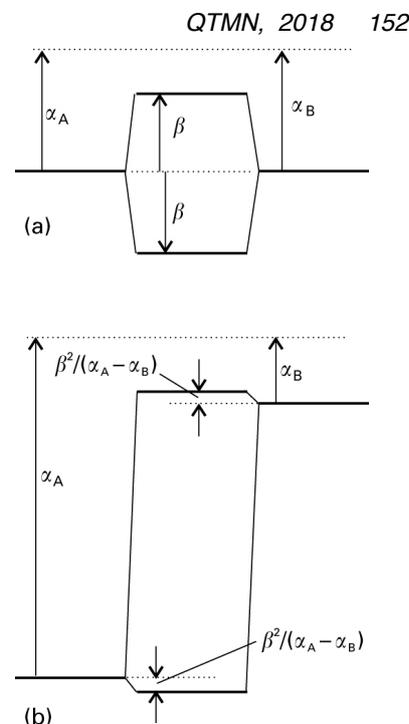
The 16 electrons of oxygen O_2 have the configuration

O_2: $1s\sigma_g^2\ 1s\sigma_u^{*2}\ 2s\sigma_g^2\ 2s\sigma_u^{*2}\ 2p\pi_u^4\ 2p\sigma_g^2\ 2p\pi_g^{*2}$,
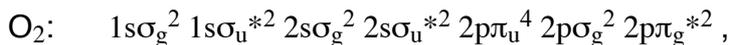
whose possible spectral terms are $^3\Sigma$, $^1\Sigma$ and $^1\Delta$. Applying the reasoning behind Hund's rules for atoms, we can infer, that the ground state is $^3\Sigma$. This makes oxygen gas paramagnetic. By counting the difference of bonding and antibonding orbitals, we can conclude the case of a double bond: O=O.

The bond of fluorine dimer F_2: ... $2p\sigma_g^2\ 2p\pi_g^{*4}$ ($^1\Sigma_g$) is only single F–F and weak: 1.60 eV (cf. N_2: 9.76 eV), and that of Ne_2: ... $2p\sigma_g^2\ 2p\pi_g^{*4}\ 2p\sigma_u^{*2}$ ($^1\Sigma_g$) does not exist at all according to the MO theory. There is however, very weak binding due to the many-body effects in form of the van der Waals interaction.

The configuration of carbon dimer C_2 can be predicted to be according to the scheme ... $2s\sigma_u^{*2}\ 2p\pi_u^4$ ($^1\Sigma_g$), but for the ground state it turns out to be: ... $2s\sigma_u^{*2}\ 2p\pi_u^3\ 2p\sigma_g$ ($^3\Pi_u$). This again, can be explained by Hund's rule reasoning that the triplet state $^3\Pi_u$ is lower in energy than $^1\Sigma_g$ due to the spin correlation.
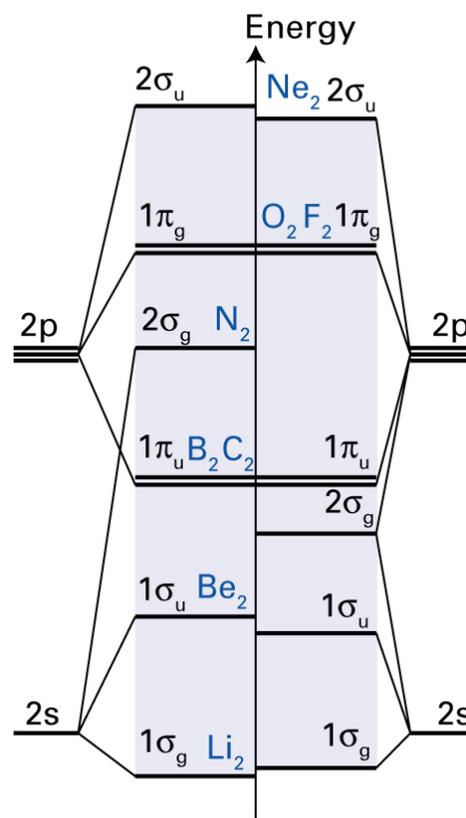
Fig. 8.18

Heteronuclear diatomic molecules

The simplest approximation of molecular orbitals of heteronuclear diatomics is

$$\psi = c_A\,\phi_A + c_B\,\phi_B$$

where contributions from the participating atomic orbitals $|c_A|^2$ and $|c_B|^2$ are not equal as in the case of homonuclear diatomic. As an example consider carbon monoxide

CO: $1\sigma^2\ 2\sigma^2\ 3\sigma^2\ 4\sigma^2\ 1\pi^4\ 5\sigma^2$ ($^1\Sigma^+$).

By looking at the level scheme in Fig. 8.22, we can infer that it is a triple bond, like in case of N_2.
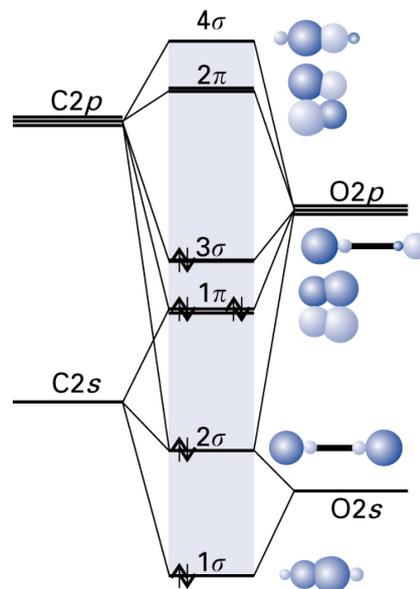
Polyatomic molecules

Generally, within the molecular orbital theory the electronic wavefunctions ψ of polyatomic molecules are sperpositions of atomic orbitals ϕ_i as

$$\psi = \Sigma_i\,c_i\,\phi_i. \tag{8.35}$$

Molecular orbitals can be *delocalized* in the whole molecule or *localized* to some extent or even in one of the atoms of the molecule, only.

By using group theory and symmetry analysis it is possible to find out, which AOs mix to form molecular orbitals of certain symmetry.

Fig. 8.22

8.7. Symmetry-adapted basis sets

Conformations of water molecule H_2O and ammonia molecule NH_3 can be understood by binding and molecular orbitals, which origin from 2p orbitas. The 1s orbitals of hydrogen contribute to these molecular orbitals by binding to the roughly orthogonal p_x, p_y and p_z orbitals. Therefore, the angles between the bonds are close to 90° (water: 104.5° ja ammonia: 107°).

However, instead of using these as a basis set for LCAO-MO, directly, let us consider the symmetry adapted basis functions.

In case of water we consider 2s, $2p_x$, $2p_y$ and $2p_z$ orbitals of oxygen ans 1s orbitals $1s_A$ and $1s_B$ of hydrogen (oxygen 1s does not contribute). For H_2O in C_{2v} group, this can be done similarly as it was done for NH_3 in chapter 5.
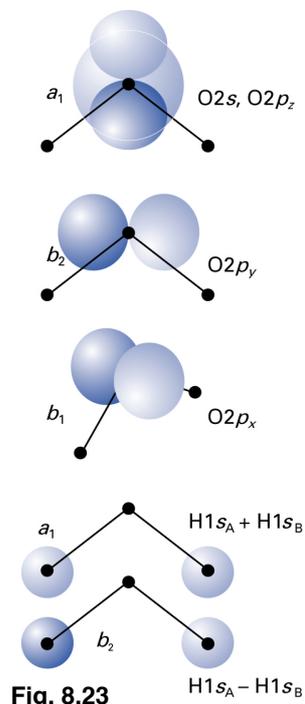
Fig. 8.23

Thus, the six atomic orbitals give six symmetry-adapted basis functions: O2s, $O2p_x$, $O2p_y$, $O2p_z$, $H1s_A+H1s_B$ and $H1s_A-H1s_B$. With these and the hamiltonian the 6×6 matrices can be written, secular equations and the determinat, which gives 6 eigenvalues as the solution.

Because each of the basis functions belong to some symmetry species, the 6×6 matrices reduce to three matrices (3×3, 2×2 and 1×1), each corresponding to different symmetry species. This simplifies the problem as the different symmetry species can be worked out separately. All of the molecular orbitals take the form:

A_1: $a_1 = c_1 (H1s_A+H1s_B) + c_2 (O2p_z) + c_3 (O2s)$

B_1: $b_1 = O2p_x$

B_2: $b_2 = c_1' (H1s_A-H1s_B) + c_2' (O2p_y)$,

where the coefficients c_i and c_i' are obtained from the secular equations.

By occupying the 10 lowest energy spin-orbitals we get the configuration $O1s^2 1a_1^2 1b_2^2 1b_1^2 2a_1^2$ ($^1A_1$), see Fig. 8.24. The total energy of the molecule can be evaluated and its minimization gives the equilibrium conformation of the molecule. By using the HF–SCF method to properly include the electronic interations a relatively good conformation is obtained.
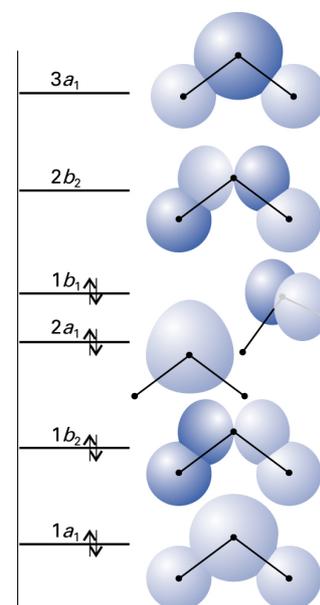
Fig. 8.24

Similarly, the electronic structure of NH_3 molecule in group C_{3v} can be considered, which was done in sec. 5.12 in example 5.9. Thus, with the same notations

$\quad s_N = N2s \quad\quad\quad\quad\quad\quad (a_1)$

$\quad s_1 = H1s_A + H1s_B + H1s_C \quad (a_1)$

$\quad s_2 = 2\,H1s_A - H1s_B - H1s_C \quad (e)$

$\quad s_3 = H1s_B - H1s_C \quad\quad\quad (e)$

In addition, considering the 2p orbitals p_x, p_y ja p_z of nitrogen, one can infer that

$\quad A_1:\ a_1 = c_1\,s_1 + c_2\,s_N + c_3\,p_z\ ,$

$\quad E:\ e = c_1'\,s_2 + c_2'\,p_x\ $ ja

$\quad\quad e = c_1''\,s_3 + c_2''\,p_y\ .$

Now, this leads to 7×7 matrix, which reduces to three: 3×3, 2×2 and 2×2, the two last ones being essentially the same and giving degenerate molecular orbitals. The 7 solutions are illustrated in Fig. 8.26. These can now be occupied by the 10 electrons of NH_3 molecule, which leads to the configuration $N1s^2\ 1a_1^2\ 1e^4\ 2a_1^2\ (^1A_1)$.
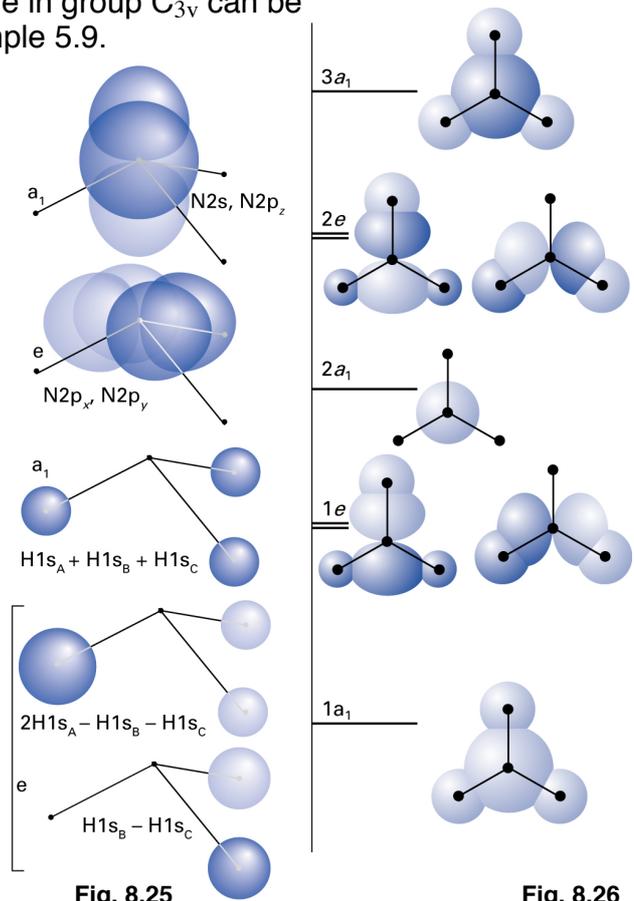
Fig. 8.25

Fig. 8.26

Hybrid orbitals

Appearance of covalent bonds and their orientation can also be described by kind of mixing, sc. *hybridization*. Now, in case of the molecules H_2O and NH_3 we can assume hybridization of the "central" 2s orbital with 2p orbitals in bond formation. Bonds can be thought of formed by the electron pair: one occupying the hybrid and the other occupying hydrogen 1s, cf. VB description.

The two bonds of H_2O are in same plane. Let us consider the hybridization leading to this. The hybrids of 2s, $2p_x$ and $2p_y$ orbitals can be written now

$\quad h_1 = a\,s + b_x\,p_x + b_y\,p_y,$

$\quad h_2 = a\,s - b_x\,p_x + b_y\,p_y\ .$

These are mutually orthogonal, as well as the third one, a perpendicular hybrid h_0, which is occupied by 2 electrons, already, and therefore, it does not participate in bonding.

If only p_x and p_y orbitals are hybridized ($a = 0$, $b_x = b_y = 1$), the angle between the hybrids is $90°$. Then, $h_0 = s$ and occupations $1s^2\ 2p_z^2\ h_0^2\ h_1\ h_2$ projected onto the atomic orbitals give a "configuration" $1s^2\ 2s^2\ 2p_x\ 2p_y\ 2p_z^2$, which can be considered as the occupation of the oxygen in water molecule. This is called p^2-*hybridisation.*
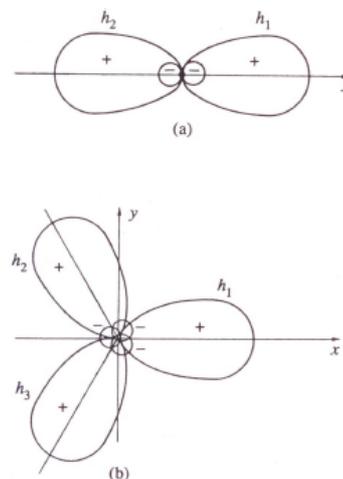
In case only s and p_x orbitals are hybridized ($a = b_x = 1$, $b_y = 0$), the angle between the hybrids h_1 and h_2 is 180°. Then, $h_0 = p_y$ and occupations $1s^2 2p_z^2 h_0^2 h_1 h_2$. This is projected to the "configuration" $1s^2 2s 2p_x 2p_y^2 2p_z^2$, which is called *sp-hybridisation.*

Whereas if the three orbitals 2s, $2p_x$ and $2p_y$ get mixed with equal weights ($a = b_x = b_y = 1$), it is *sp^2-hybridisation,* intermediate of the two above, which yields the bond angle 120°.

The angle between the two bonds in water molecule is observed to be 104.45°, where the contribution of O2s orbital to the bonds ia bout 20%, because $a^2 = 0.20$ ($a = 0.45$ and $b = 0.89$).

Nitrogen atom usually forms three bonds, one with each of its p orbitals. Without hybridization the bond angles would be 90°. However, the bond angles of NH_3 molecule are 107°, for which reason the 2s orbital can be assumed to be hybridized with p orbitals. In fact, hybridization of the 2s orbital can be evaluated to be 80%, which is close to the sc. *sp^3-hybridisation*.

Carbon usually forms four bonds, *e.g.* CH_4, where the bons are oriented as the tetrahedron. Then, the bond angles are 109.47° = arccos(−1/3). The valence orbitals of carbon, 2s , $2p_x$, $2p_y$ and $2p_z$ form the hybrids

$h_1 = s + p_x + p_y + p_z$,

$h_2 = s − p_x + p_y − p_z$,

$h_3 = s + p_x − p_y − p_z$ and

$h_4 = s − p_x − p_y + p_z$.

(c)
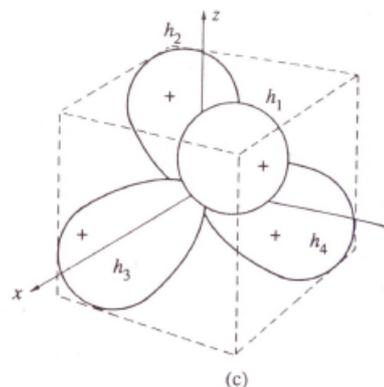
This is how the atomic occupation of orbitals $1s^2 2s^2 2p^2$ transforms to $1s^2 2s 2p^3$, because each of the hybrid orbitals assume 1/4 of s nature and 3/4 of p nature. This is called as *sp^3-hybridisation.* The sp^3-hybridization is also found in many crystal structures.

8.8. Conjugated π-systems and Hückel MO method

The double bond of ethene molecule $H_2C=CH_2$ is composed of a σ bond from sp^2-hybridized s, p_y, p_z –> h_1, h_2, h_3 (120°), and a *π-bond* of the two p_x orbitals of both atoms. This kind of π-bond is torsionally rigid forcing all the H atoms into the same plane.

Consider next the butadiene molecule $CH_2=CH–CH=CH_2$, where each of the carbon atoms initially have four valence electrons ($2s^2 2p^2$) and the hydrogens have one each "for bonding". Thus, we have now σ-bonds from (2s, $2p_z$), as $H_2C–CH–CH–CH_2$. Each of the carbon atoms still have one p electron, perpendicular to the σ-bonds, to form the π-bonds. Separation by symmetry allows us to consider these π-bonds, formed by the orbitals p_1, p_2, p_3 and p_4, independently of σ-bonds.

Fig. 8.27.

Thus, secular equation of π-symmetry is

$$\sum_i c_i \{H_{ij} − E S_{ij}\} = 0 \; ; \quad i = 1, 2, 3, 4,$$

and the energies can be solved from the corresponding secular determinant

$$\det | H_{ij} − E S_{ij} | = 0,$$
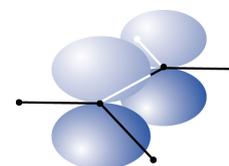
i.e.

$$\begin{vmatrix} H_{11} - E\,S_{11} & H_{12} - E\,S_{12} & H_{13} - E\,S_{13} & H_{14} - E\,S_{14} \\ H_{21} - E\,S_{21} & H_{22} - E\,S_{22} & H_{23} - E\,S_{23} & H_{24} - E\,S_{24} \\ H_{31} - E\,S_{31} & H_{32} - E\,S_{32} & H_{33} - E\,S_{33} & H_{34} - E\,S_{34} \\ H_{41} - E\,S_{41} & H_{42} - E\,S_{42} & H_{43} - E\,S_{43} & H_{44} - E\,S_{44} \end{vmatrix} = 0.$$

Let us solve this by using the *Hückel molecular orbital approximation,* which may also be called as *tight-binding approximation.* These are based on the following approximations:

(1) Nondiagonal overlap integrals are set to zero: $S_{ij} = \delta_{ij}$,

(2) the diagonal hamiltonian matrix elements are the same: $H_{ii} = \alpha$ and

(3) the nondiagonals vanish, except for the neighboring ones, all of which are the same:
$H_{ij} = 0$, if $|i - j| > 1$; and $H_{ij} = \beta$, if $|i - j| = 1$.

With these assumptions the secular determinant simplifies to

$$\begin{vmatrix} \alpha - E & \beta & 0 & 0 \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ 0 & 0 & \beta & \alpha - E \end{vmatrix} = 0.$$

The four roots of this determinant are $E = \alpha \pm 1/2\,(\sqrt{5} \pm 1)\,\beta$ $\approx \{\,\alpha \pm 1.6\,\beta \;\; ja \;\; \alpha \pm 0.6\,\beta\,\}$. The orbital energies and bonding are illustrated in Fig. 8.28. Note, that both the Coulomb integral α and the resonance integral β are negative.

These π-orbitals are *delocalized* in the whole molecule and a systematic wavelike behavior of bonding/antibonding nature can be identified, see Fig. 8.29.

These kind of delocalized π-orbitals from "perpendicular" p orbitals are called *conjugated* π-systems.

Now, we occupy the two lowest levels by four electrons and get two more bonds, one between 1 and 2 and another between 3 and 4. Thus, we can write the molecular formula as $CH_2{=}CH{-}CH{=}CH_2$, though the π-electrons are delocalized in the whole chain of carbon atoms.

$\alpha - 1.618\beta$

$\alpha - 0.618\beta$

$\alpha + 0.618\beta$

$\alpha + 1.618\beta$

Figs. 8.28–29.

The joint energy of these delocalized π-electrons can be written now as

$$2\,(\alpha + 1.6\,\beta) + 2\,(\alpha + 0.6\,\beta) = 4\,\alpha + 4.4\,\beta.$$

Comparing this to the alternative of two localized pairs of bonding electrons with the energy $4\,\alpha + 4\,\beta$, we see, that delocalization lowers the energy by $0.4\,\beta$, where $\beta < 0$. This is called delocalization energy.
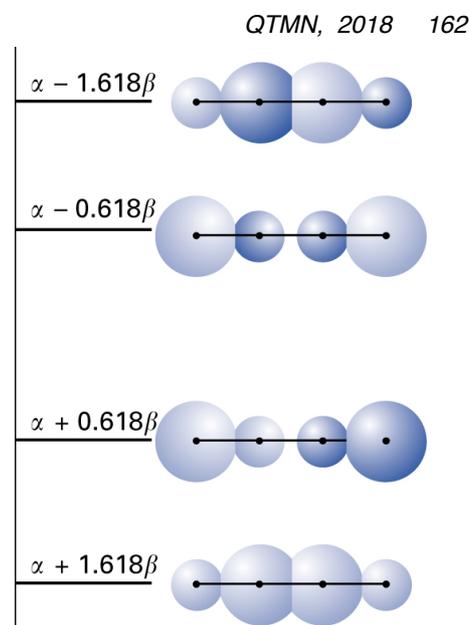
These kind of conjugated bonds constructed from delocalized electrons are common in organic compounds, e.g., aromatic compounds. Generally this kind of bonds are called π-bonds, although the π-symmetry might be somewhat broken, like in benzene. There, the axis of cylindrical symmetry is bent to make a ring.

In Fig. 8.30, the energy levels and delocalized molecular π-orbitals of benzene molecule are illustrated.

It has been developed several other methods improved from the Hückel MO-method by including more interactions between the neighbors, overlap integrals and better basis sets. Often, instead of calculation of the integrals they may be fitted to the experimental properties of molecules. Such methods are called *semi-empirical,* e.g. CNDO and MINDO (complete neglect of differential overlap and modified intermediate neglect of differential overlap).

8.9. Ligand field theory

This is kind of "3-dimensional Hückel method", with which the main features of bonding can be deduced in some 3D cases. One example is the system of a transition metal atom with ligands and some relate to atoms or molecules in voids of crystals.

$\alpha - 2\beta$
b_{2g}

$\alpha - \beta$
e_{2u}

0

$\alpha + \beta$
e_{1g}

$\alpha + 2\beta$
a_{2u}
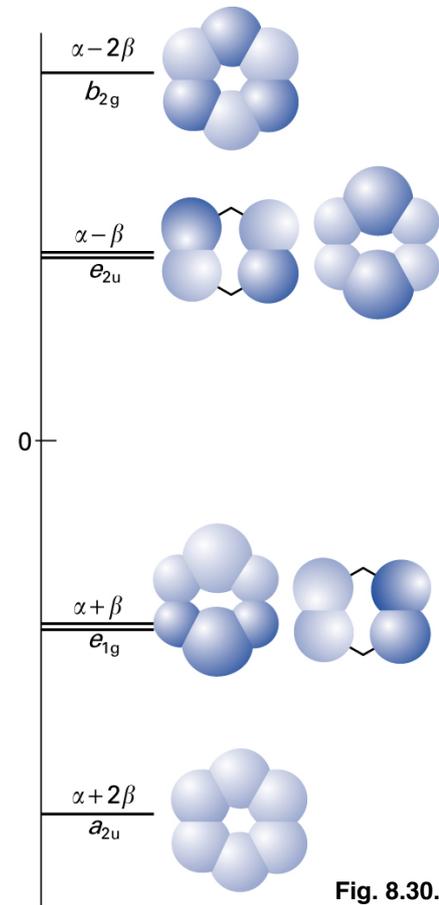
Fig. 8.30.

Band theory of solids

8.10. "Tight-binding"-approximation

Tight-binding-approximation is a Hückel like approach, mostly for conduction and valence bands of electrons in crystals.

In a simple model we assume one s electron from each atom given to a set of joint valence electrons. Like delocalized π electrons, these form the sc. *bands,* see Fig. 8.40.

In the crystal, the quasi-continuous energy bands consist of an infinite number of states.

Depending on the occupation of the states, the crystal is metal, semiconductor or an insulator/dielectric.
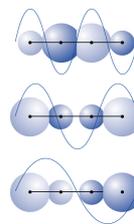
Fig. 8.29.
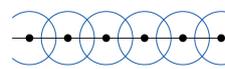
Fig. 8.39.
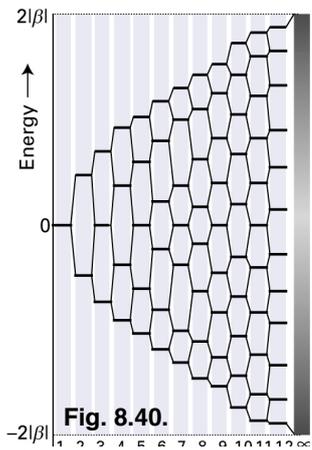
Fig. 8.40.
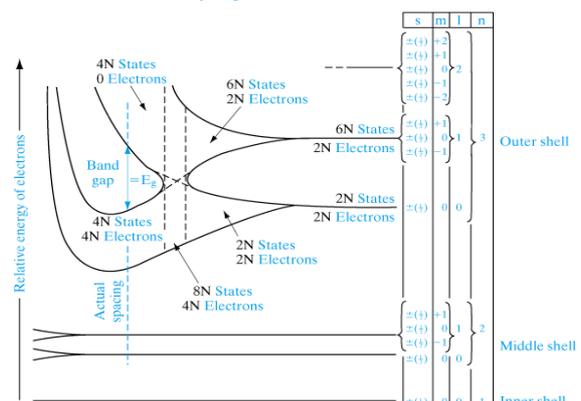
8.11. Electrons in periodic crystal

Let us assume, that conduction electrons feel an average constant potential in a crystal, in 1D or 3D. This is the *free electron model,* whose Schrödinger equation is

$$(-\hbar^2/2m \, \nabla^2 + V) \, \psi \; = \; E \, \psi, \qquad\qquad (8.40)$$

whose solutions are

$$\psi \; = \; A \, e^{i\mathbf{k}\cdot\mathbf{r}} \pm B \, e^{i\mathbf{k}\cdot\mathbf{r}} \quad \text{or} \quad C \, e^{i\mathbf{k}\cdot\mathbf{r} + \delta}. \qquad (8.39a)$$

These are *standing* or *propagating waves.* Here $\mathbf{k}$ is the wavevector, $|\mathbf{k}| = (2mE \, / \, \hbar^2)^{1/2}$ and the energy spectrum of electrons is the free electron parabola, Fig. 8.45.

$$E(k) \; = \; \hbar^2/2m \cdot k^2. \qquad\qquad (8.39b)$$

The *Fermi energy* and *wave vector* are $E_F = \hbar^2 \, k_F^2 \, / \, 2m$ and $k_F = (3\pi^2 \, n)^{1/3}$, where the *electron density* $n = N/V$. The density-of-states in 3D space is $\quad g(E) \; = \; \Omega \, / \, \pi^2\hbar^3 \cdot (2m^3 \, E)^{1/2}, \qquad (7.51)$ where Ω is the atomic volume.
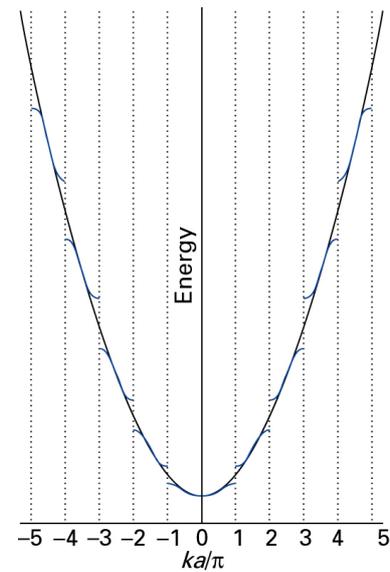
Fig. 8.45.

In general,

$$g(E) \; \propto \; E^{\,d/2 - 1},$$

where $d = 3, 2, 1$ is the dimension of the nanostructure.
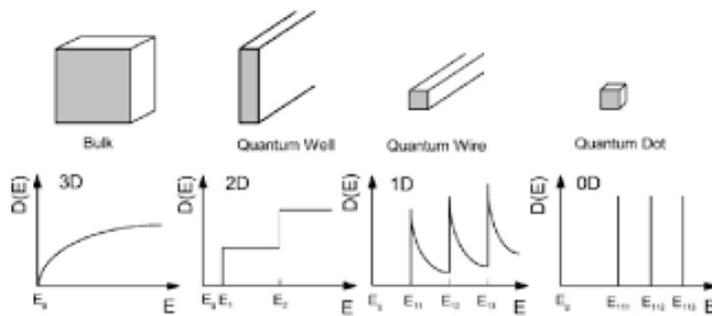
Taking into account the periodicity $\mathbf{a_k}$ in direction $\mathbf{k}$, $V(\mathbf{k},\mathbf{r}+\mathbf{a_k}) = V(\mathbf{k},\mathbf{r})$, the wavefunction takes the form

$$\psi_\mathbf{k}(\mathbf{r}) \; = \; u(\mathbf{k},\mathbf{r}) \, e^{i\mathbf{k}\cdot\mathbf{r}}. \qquad\qquad (8.41)$$

This is the *Bloch theorem:* the wavefunction of an electron is a plane wave modulated by the crystal periodicity. The Kronig–Penney model is a simplified periodic model of crystals.

8.12. Brillouin zones

The band structure of periodic free electron model is presented in Figs. 8.45 and 8.46 in the reciprocal space as a function of $\mathbf{k}$.

Note that $\lambda = h/p = h/(\hbar k) = 2\pi/k$ as $k = 2\pi/\lambda$, where λ is the electron wave length. Compare with the Fig. 8.29, where delocalized π-electrons are illustrated.

Fig. 8.29.

Fig. 8.45.

Fig. 8.46.
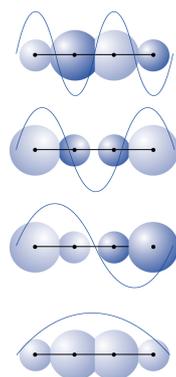
Fermi hole   +   Coulomb hole   =   total hole
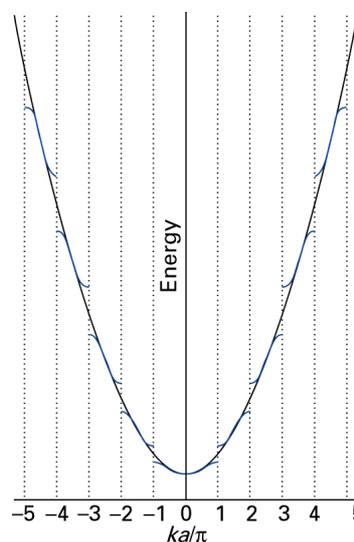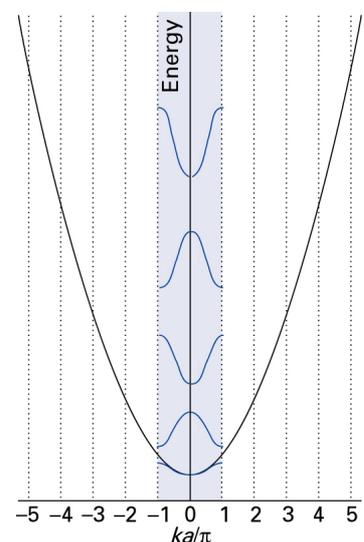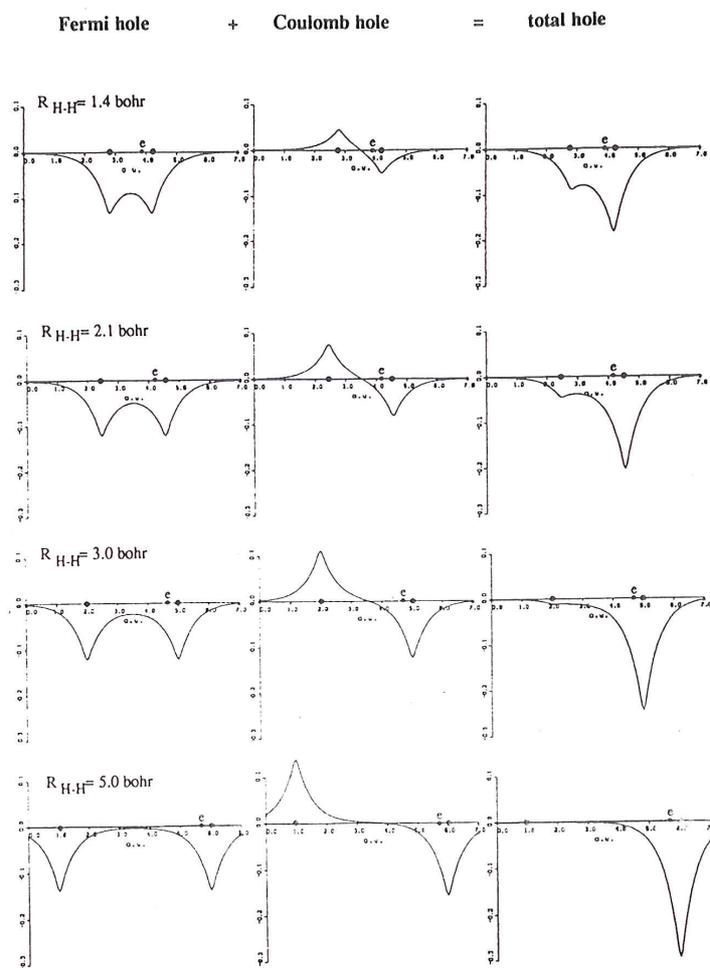
Figure 1. The Fermi hole, Coulomb hole, and total hole in the H₂ molecule at various values of the internuclear distance. In all plots the reference electron is placed 0.3 bohr to the left of the right nucleus. Nuclear positions are indicated with black dots on the axis.