A quantum chemical journey: from molecules to atoms and back again

compiled by Luca Frediani from his own observations during several years of teaching Quantum Chemistry

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Summary

Summary

The Molecular Hamiltonian

"Bezene is a Cathedral of electrons!"
Prof. R. Moccia, Theoretical Chemistry Course, Pisa 1999.

$$\hat{H} = \hat{T}_N + \hat{T}_e + \hat{V}_N + \hat{V}_e + \hat{V}_{eN}$$

- Nuclear kinetic energy: $\hat{T}_N = \sum_I \frac{-\hbar^2 \Delta_I}{2m_I}$
- Electronic kinetic energy: $\hat{T}_e = \sum_i \frac{-\hbar^2 \Delta_i}{2m_e}$
- Nuclear repulsion: $\hat{V}_N = \sum_{I>J} \frac{Z_I Z_J}{R_{IJ}}$
- Electronic repulsion: $\hat{V}_e = \sum_{i>j} \frac{1}{r_{ij}}$
- Nuclear electronic attraction: $\hat{V}_e = -\sum_{iI} \frac{Z_I}{|r_i - R_I|}$

The Born-Oppenheimer approximation

1. Electrons are much faster than nuclei, which can be considered "clamped".
2. Nuclear kinetic energy is neglected, nuclear positions become parameters, the wavefunction is separated.
3. Electronic equation is solved first at fixed (clamped) nuclei.

$$(T_e + V_{ee} + V_{eN} + V_{NN})\phi(r; R) = E_e(R)\phi(r; R)$$

4. Nuclei move in a potential defined by the electronic energy

$$(T_N + E_e(R))\chi(R) = E\chi(R)$$

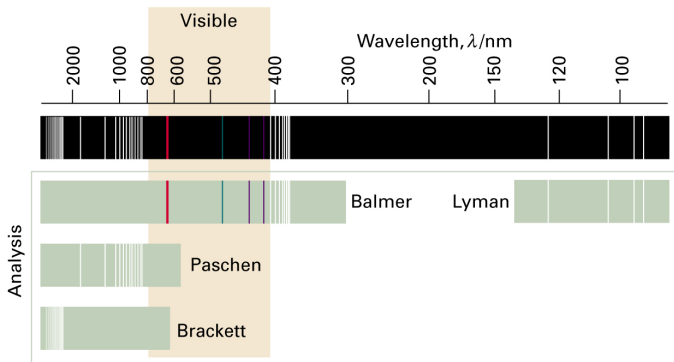5. Final wavefunction $\Psi(r, R) = \phi(r; R)\chi(R)$

Summary

The riddle of atomic spectra

- Terms: $T_n = R_H / n^2 \quad R_H = 109677\,cm^{-1}$
- Combination rule: $\nu = T_n - T_m \quad m > n$
- What are these terms? Energy levels!

The Hamiltonian

- Two particles: electron and nucleus
- Six variables: $x_e, y_e, z_e, x_N, y_N, z_N$
- No external potential
- One interaction (SI): $V(r) = -Ze^2/4\pi\epsilon_0 r$

Hamiltonian (SI):

$$H = T_e + T_N + V = \frac{-\hbar^2}{2m_e}\nabla_e^2 + \frac{-\hbar^2}{2m_N}\nabla_N^2 - \frac{Ze^2}{4\pi\epsilon_0 r}$$

Hamiltonian (a.u. $\hbar = 1, e = 1, 4\pi\epsilon_0 = 1$):

$$H = T_e + T_N + V = \frac{-\nabla_e^2}{2} + \frac{-\nabla_N^2}{2m_N} - \frac{Z}{r}$$

$$r = \sqrt{(x_e - x_N)^2 + (y_e - y_N)^2 + (z_e - z_N)^2}$$

Separation of variables

- From electron and nucleus to center of mass and internal motion:

$$x_{CM} = \frac{m_e x_e + m_N x_N}{m_e + m_N} \simeq x_N \quad m_{CM} = m_e + m_N \simeq m_N$$

$$x_i = x_e - x_N \qquad \mu = \frac{m_e m_N}{m_e + m_N} \simeq m_e$$

$$H_{CM} = \frac{-\nabla_i^2}{2m_{CM}} \quad H_i = T_i + V = \frac{-\nabla_i^2}{2\mu} - \frac{1}{r}$$
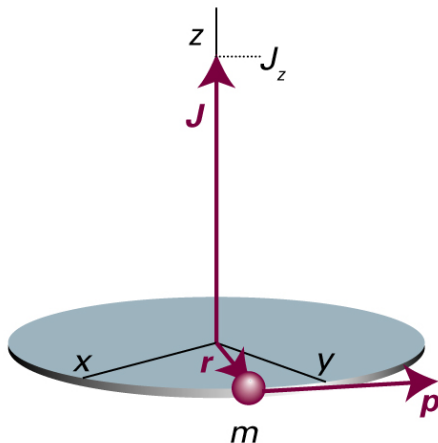
- From cartesian to spherical coordinates:
$\Psi(x,y,z) \rightarrow R(r) \cdot Y(\phi,\theta)$

$$\Lambda^2(\theta,\phi) Y_{m_l}^l(\phi,\theta) = -l(l+1) Y_{m_l}^l(\phi,\theta)$$

$$-\frac{1}{2\mu} \frac{\mathrm{d}^2 u(r)}{\mathrm{d}r^2} + V_{eff} u(r) = E u(r) \quad u(r) = rR(r)$$

Angular momentum operators

$$\boldsymbol{L} = \boldsymbol{r} \times \boldsymbol{p}$$

$$\boldsymbol{L} = I\boldsymbol{\omega} \quad I = mr^2 \quad \omega = \frac{\mathrm{d}\theta}{\mathrm{d}t}$$

$$L_x = yp_z - zp_y = -i\hbar(y\,\mathrm{d}/\,\mathrm{d}z - z\,\mathrm{d}/\,\mathrm{d}y)$$
$$L_y = zp_x - xp_z = -i\hbar(z\,\mathrm{d}/\,\mathrm{d}x - x\,\mathrm{d}/\,\mathrm{d}z)$$
$$L_z = xp_y - yp_x = -i\hbar(x\,\mathrm{d}/\,\mathrm{d}y - y\,\mathrm{d}/\,\mathrm{d}x)$$

Linear and angular motion: a comparison

mass	m	mom. of inertia	$I = mr^2$
position	x	angle	θ
velocity	$v = \mathrm{d}x/\mathrm{d}t$	ang. velocity	$\omega = \mathrm{d}\theta/\mathrm{d}t$
momentum	$p = mv$	ang. mom.	$L = I\omega$
kin. energy	$p^2/2m$	kin. energy	$L^2/2I$

Cartesian, polar and sperical coordinates

- Cartesian cordinates: x, y, z
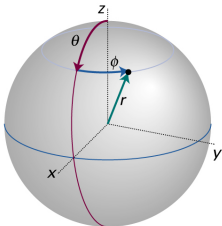
$$\mathrm{d}v = \mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z$$
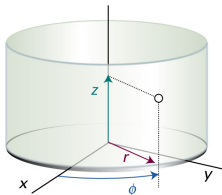
- Cylindrical coordiates: r, ϕ, z

$$r^2 = x^2 + y^2 \qquad x = r\cos\phi$$
$$\phi = \arctan(y/x) \quad y = r\sin\phi$$
$$\mathrm{d}v = r\,\mathrm{d}r\,\mathrm{d}\phi\,\mathrm{d}z$$

- Spherical coordinates: r, ϕ, θ

$$r^2 = x^2 + y^2 + z^2 \qquad x = r\cos\phi\sin\theta$$
$$\phi = \arctan(y/x) \qquad y = r\sin\phi\sin\theta$$
$$\theta = \arccos(z/r) \qquad z = r\cos\theta$$
$$\mathrm{d}v = r^2\,\mathrm{d}r\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi$$

Particle on a ring

- Energy: $E = L^2/2I = L_z^2/2I$
- angular momentum: $L_z = -i\hbar\, \mathrm{d}/\,\mathrm{d}\phi$
- Hamiltonian:

$$H = \frac{L_z^2}{2I} = -\frac{\hbar^2}{2I}\frac{\mathrm{d}^2}{\mathrm{d}\phi^2}$$

- Eigenfunctions:

$$\Psi(\phi) = e^{im_l\phi}$$

Particle on a sphere

- Energy: $E = L^2/2I = (L_x^2 + L_y^2 + L_z^2)/2I$
- The Hamiltonian operator:

$$H = \frac{p^2}{2m} = \frac{L^2}{2I}$$

- Eigenfunctions of H are eigenfunctions of L^2.
- Eigenfunctions of L^2 with the same eigenvalue are degenerate.

Angular momentum: operators and commutators

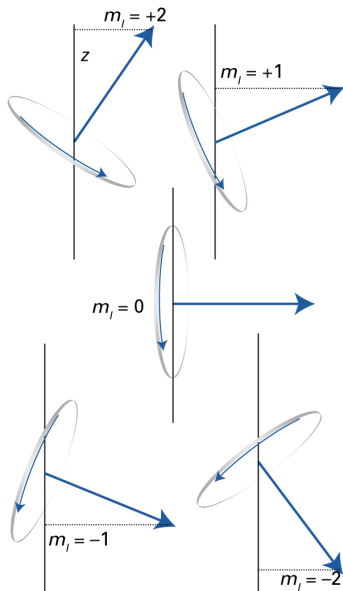$$L_x = yp_z - zp_y = -i\hbar \left(y\frac{\mathrm{d}}{\mathrm{d}z} - z\frac{\mathrm{d}}{\mathrm{d}y} \right)$$

$$L_y = zp_x - xp_z = -i\hbar \left(z\frac{\mathrm{d}}{\mathrm{d}x} - x\frac{\mathrm{d}}{\mathrm{d}z} \right)$$

$$L_z = xp_y - yp_x = -i\hbar \left(x\frac{\mathrm{d}}{\mathrm{d}y} - y\frac{\mathrm{d}}{\mathrm{d}x} \right)$$

$$L^2 = L_x^2 + L_y^2 + L_z^2$$

- $[L_x, L_y] = i\hbar L_z$
- $[L^2, L_z] = 0$

Angular momentum: eigenvalues

$$L^2 Y^l_{m_l}(\phi, \theta) = \hbar^2 l(l+1) Y^l_{m_l}(\phi, \theta)$$

$$l = 0, 1, 2 \ldots$$

$$L_z Y^l_{m_l}(\phi, \theta) = \hbar m_l Y^l_{m_l}(\phi, \theta)$$

$$m_l = -l, -l+1, \ldots 0 \ldots l-1, l$$

Angular momentum: eigenfunctions

Table 8.2 The spherical harmonics

l	m_l	$Y_{l,m_l}(\theta,\phi)$
0	0	$\left(\dfrac{1}{4\pi}\right)^{1/2}$
1	0	$\left(\dfrac{3}{4\pi}\right)^{1/2}\cos\theta$
	±1	$\mp\left(\dfrac{3}{8\pi}\right)^{1/2}\sin\theta\,\mathrm{e}^{\pm i\phi}$
2	0	$\left(\dfrac{5}{16\pi}\right)^{1/2}(3\cos^2\theta-1)$
	±1	$\mp\left(\dfrac{15}{8\pi}\right)^{1/2}\cos\theta\sin\theta\,\mathrm{e}^{\pm i\phi}$
	±2	$\left(\dfrac{15}{32\pi}\right)^{1/2}\sin^2\theta\,\mathrm{e}^{\pm 2i\phi}$
3	0	$\left(\dfrac{7}{16\pi}\right)^{1/2}(5\cos^3\theta-3\cos\theta)$
	±1	$\mp\left(\dfrac{21}{64\pi}\right)^{1/2}(5\cos^2\theta-1)\sin\theta\,\mathrm{e}^{\pm i\phi}$
	±2	$\left(\dfrac{105}{32\pi}\right)^{1/2}\sin^2\theta\cos\theta\,\mathrm{e}^{\pm 2i\phi}$
	±3	$\mp\left(\dfrac{35}{64\pi}\right)^{1/2}\sin^3\theta\,\mathrm{e}^{\pm 3i\phi}$

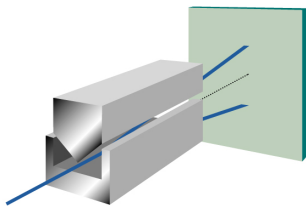The spherical harmonics are orthogonal and normalized in the following sense:

$$\int_0^\pi\int_0^{2\pi} Y_{l',m_{l'}}(\theta,\phi)^* Y_{l,m_l}(\theta,\phi)\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi = \delta_{l'l}\delta_{m_{l'}m_l}$$
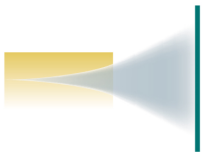
An important 'triple integral' is

$$\int_0^\pi\int_0^{2\pi} Y_{l'',m_{l''}}(\theta,\phi)^* Y_{l',m_{l'}}(\theta,\phi) Y_{l,m_l}(\theta,\phi)\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi$$

$$= 0 \qquad \text{unless} \qquad m_l'' = m_l' + m_l$$

and we can form a triangle with sides of lengths l'', l', and l (such as 1, 2, and 3 or 1, 1, and 1, but not 1, 2, and 4).
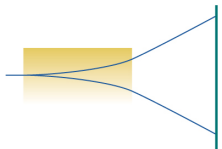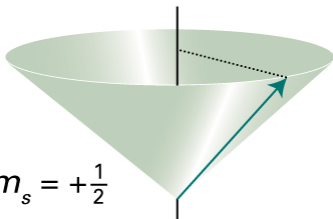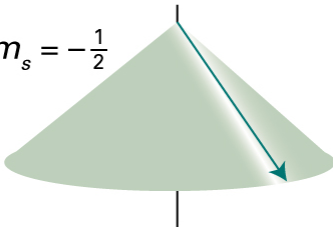
Spin: the Stern-Gerlach experiment

(a)

(b)

(c)

$$m_s = +\tfrac{1}{2}$$

$$m_s = -\tfrac{1}{2}$$

Spin: general considerations

- The spin is an angular momentum:

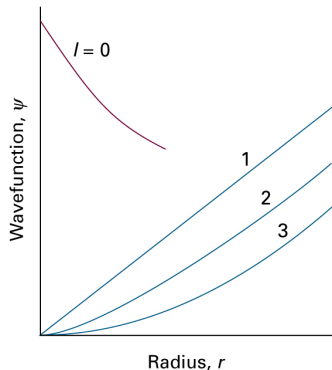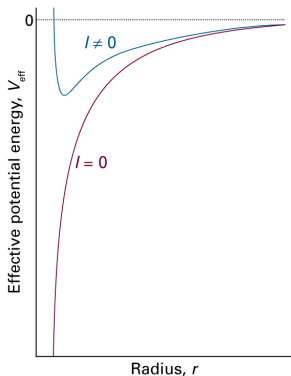$$S^2 \sigma^s_{m_s} = \hbar^2 s(s+1) \sigma^s_{m_s}$$
$$S_z \sigma^s_{m_s} = \hbar m_s \sigma^s_{m_s}$$

- The spin is an intrinsic property (like mass or charge)
- Some particles have a spin (electrons, some nuclei)
- Nuclear spin can have other values than 1/2.
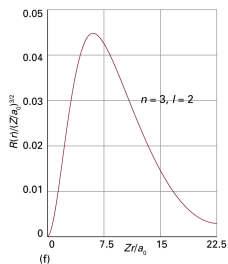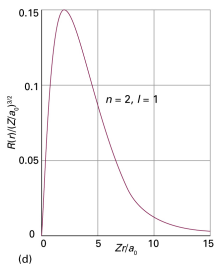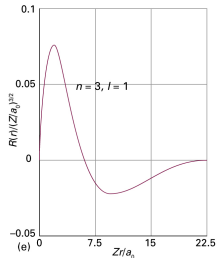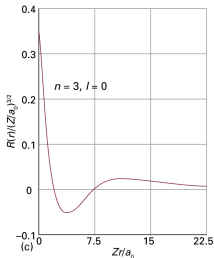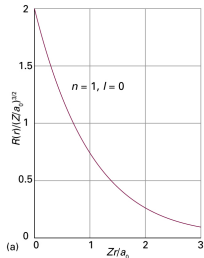
The radial equation

$$-\frac{1}{2\mu}\frac{\mathrm{d}^2 u(r)}{\mathrm{d}r^2} + V_{\text{eff}}u(r) = Eu(r) \quad u(r) = rR(r)$$

$$V_{\text{eff}}(r) = -\frac{1}{r} + \frac{\hbar^2 l(l+1)}{2\mu r^2}$$

The solutions of the radial equation

$$R_{n,l} = N_{n,l}\rho^l L_{n-l-1}^{2l+1}(\rho)e^{-\rho/2} \quad \rho = \frac{2Zr}{ra_0} \quad a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2}$$
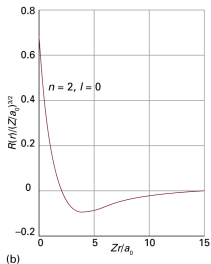
Form of the solutions

n	l	$R_{n,l}$
1	0	$2\left(\dfrac{Z}{a}\right)^{3/2} e^{-\rho/2}$
2	0	$\dfrac{1}{8^{1/2}}\left(\dfrac{Z}{a}\right)^{3/2} (2-\rho)e^{-\rho/2}$
2	1	$\dfrac{1}{24^{1/2}}\left(\dfrac{Z}{a}\right)^{3/2} \rho e^{-\rho/2}$
3	0	$\dfrac{1}{243^{1/2}}\left(\dfrac{Z}{a}\right)^{3/2} (6-6\rho+\rho^2)e^{-\rho/2}$
3	1	$\dfrac{1}{486^{1/2}}\left(\dfrac{Z}{a}\right)^{3/2} (4-\rho)\rho e^{-\rho/2}$
3	2	$\dfrac{1}{2430^{1/2}}\left(\dfrac{Z}{a}\right)^{3/2} \rho^2 e^{-\rho/2}$

Quantum numbers and eigenvalues

- Principal quantum number: $n = 1, 2, 3 \ldots$
- Angular quantum number: $l = 0, 1, 2, \ldots n - 1$
- Magnetic quantum number: $m = 0, \pm 1, \pm 2, \ldots \pm l$
- Energy eigenvalues: $E_n = -\frac{Z^2 \mu e^4}{32\pi^2 \epsilon_0^2 \hbar^2 n^2}$
- Rydberg constant for H: $hcR_H = \frac{\mu_H e^4}{32\pi^2 \epsilon_0^2 \hbar^2}$
- Rydberg constant $R = R_H \cdot \frac{m_e}{\mu_H}$

Probability density and radial probability

- Probability density: $\Psi^*(r, \phi, \theta)\Psi(r, \phi, \theta)$
- Radial probability: $P(r) = r^2 R(r)^2 = u(r)^2$
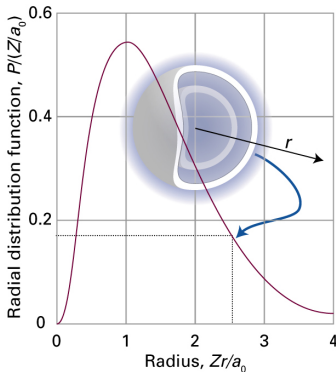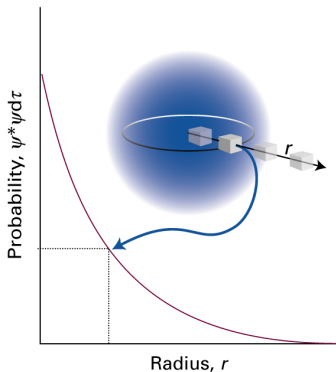
Summary

The Hamiltonian operator

- Helium atom has three particles: one nucleus and two electrons
- Hamiltonian operator:

$$\hat{H} = T_N + T_{e_1} + T_{e_2} + V_{Ne_1} + V_{Ne_2} + V_{e_1 e_2} \qquad (1)$$

- Kinetic energy terms:
  $T_N = \frac{-\hbar^2}{2m_N}\nabla_N^2$, $T_{e_1} = \frac{-\hbar^2}{2m_e}\nabla_{e_1}^2$, $T_{e_2} = \frac{-\hbar^2}{2m_e}\nabla_{e_2}^2$
- Nucleus-electron attraction(s):
  $V_{Ne_1} = -Ze^2/|R_N - r_{e_1}|$, $V_{Ne_2} = V_{Ne_1} = -Ze^2/|R_N - r_{e_2}|$
- Electron-electron repulsion:
  $V_{e_1 e_2} = 1/|r_{e_1} - r_{e_2}|$

The orbital approximation

- Simplified Hamiltonian operator (electron-electron repulsion neglected:

$$\hat{H} = T_N + T_{e_1} + T_{e_2} + V_{Ne_1} + V_{Ne_2} \qquad (2)$$

- The electronic coordinates are now separated.
- For each electron the solution is the same as the Hydrogen atom
- The complete (but approximate) solution is the product of two orbitals $\Psi'(\mathbf{x}_1, \mathbf{x}_2) = \phi_1(\mathbf{x}_1)\phi_2(\mathbf{x}_2)$

Introducing the spin

- Each electron has four coordinates: position ($\boldsymbol{r} = (x, y, z)$) and spin ($s$). We define $\boldsymbol{x} = (x, y, z, s)$
- The spin coordinate is just a convenient way to "attach" the spin to an orbital.
- Example: $\phi(x, y, z, s) = 1s(x, y, z)\alpha(s)$
- The ground state of the Helium atom ($1s^2$) might be

$$\Psi'(\boldsymbol{x}_1, \boldsymbol{x}_2) = 1s(\boldsymbol{r}_1)\alpha(s_1)1s(\boldsymbol{r}_2)\beta(s_2)$$

- Electron 1 in the $1s$ orbital with spin α and electron 2 in the $1s$ orbital with spin β.
- Problem: the Pauli principle!

The Pauli principle

- The "chemist" formulation: two electrons cannot have the same set of quantum numbers.
- The "physicist" formulation: the wavefunction of a many-electron system must be antisymmetric.
  $\Psi(\boldsymbol{x}_1, \boldsymbol{x}_2) = -\Psi(\boldsymbol{x}_2, \boldsymbol{x}_1)$

The ground state of He revisited

- Our original $1s^2$ wavefinction was:

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = 1s(x_1, y_1, z_1)\alpha(s_1)1s(x_2, y_2, z_2)\beta(s_2)$$

- There is only one way to make this antisymmetric

$$\Psi'(\mathbf{x}_1, \mathbf{x}_2) = 1s(\mathbf{r}_1)1s(\mathbf{r}_2)\alpha(s_1)\beta(s_2)$$

$$\Psi''(\mathbf{x}_1, \mathbf{x}_2) = 1s(\mathbf{r}_1)1s(\mathbf{r}_2)\beta(s_1)\alpha(s_2)$$

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = (\Psi'(\mathbf{x}_1, \mathbf{x}_2) - \Psi''(\mathbf{x}_1, \mathbf{x}_2))/\sqrt{2}$$

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = 1s(\mathbf{r}_1)1s(\mathbf{r}_2)(\alpha(s_1)\beta(s_2) - \beta(s_1)\alpha(s_2))/\sqrt{2}$$

Symmetric spin functions: the triplet states

- There is only one way to construct an antisymmetric spin function:
$$\left(\alpha(s_1)\beta(s_2) - \beta(s_1)\alpha(s_2)\right)/\sqrt{2}$$

- There are three ways to build a symmetric spin function:

$$\alpha(s_1)\alpha(s_2)$$

$$\left(\alpha(s_1)\beta(s_2) + \beta(s_1)\alpha(s_2)\right)/\sqrt{2}$$

$$\beta(s_1)\beta(s_2)$$

- The first one is the so called *singlet* function. The other three are the three component of the *triplet*.

- Triplet functions are important when electrons are not paired.

Excited states of the Helium atom

- Let us consider the configuration $1s^1 2s^1$
- Our starting point is:

$$\Psi'(\boldsymbol{x}_1 \boldsymbol{x}_2) = 1s(\boldsymbol{r}_1)2s(\boldsymbol{r}_2)\alpha(s_1)\beta(s_2)$$

- Two possibilities: symmetric spacial part with antisymmetric spin part (singlet) or the opposite (triplet).

$$\Psi_s = \frac{1s(\boldsymbol{r}_1)2s(\boldsymbol{r}_2) + 2s(\boldsymbol{r}_1)1s(\boldsymbol{r}_2)}{\sqrt{2}} \cdot \frac{\alpha(s_1)\beta(s_2) - \beta(s_1)\alpha(s_2)}{\sqrt{2}}$$

$$\Psi_t = \frac{1s(\boldsymbol{r}_1)2s(\boldsymbol{r}_2) - 2s(\boldsymbol{r}_1)1s(\boldsymbol{r}_2)}{\sqrt{2}} \begin{cases} \alpha(s_1)\alpha(s_2) \\ \frac{\alpha(s_1)\beta(s_2) + \beta(s_1)\alpha(s_2)}{\sqrt{2}} \\ \beta(s_1)\beta(s_2) \end{cases}$$

Summary

Molecular-Orbital theory for H_2^+

- The analytic solution for a diatomic system is not known.
- We take individual atomic orbitals (AOs) as starting point
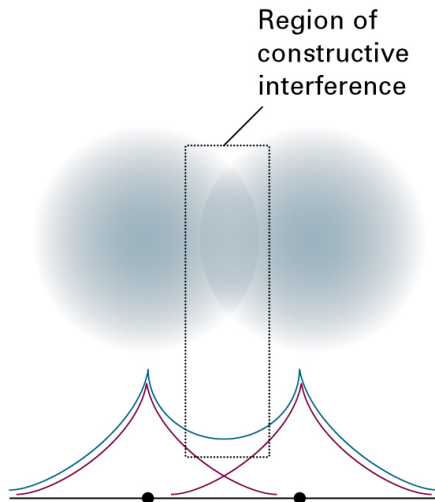- We build molecular orbitals as linear combinations of AOs:

$$\Phi_\pm = N_\pm(1s_A \pm 1s_B)$$

- Normalization coefficient:

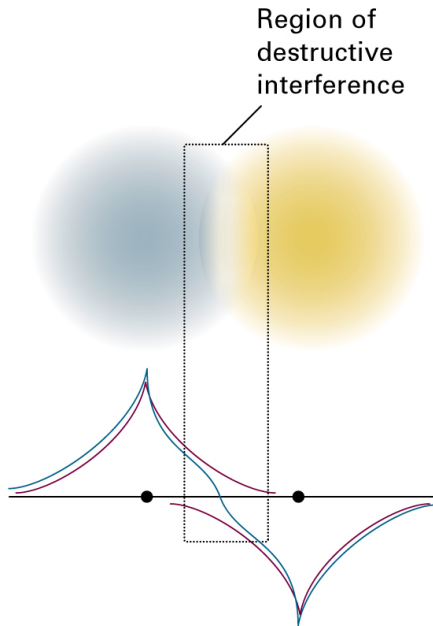$$N_\pm = \frac{1}{2 + 2S}$$

- S is the so called overlap integral.

The bonding orbital of H_2^+

Region of constructive interference

The antibonding orbital of H_2^+

Region of destructive interference

The orbital energies of H_2^+

- The energy is obtained as the expectation value of the Hamiltonian operator

$$E_\pm = E_{1s} + \frac{1}{R} - \frac{j \pm k}{1 \pm S}$$

- Both j and k are positive: the bonding orbital is lower in energy than the antibonding one.

- Interaction of electron s_A with nucleus B

$$j = \int \frac{s_A^2}{|r - r_B|} dr$$

- Interaction of the overlap density $s_A s_B$ with nucleus A (or B)

$$k = \int \frac{s_A s_B}{|r - r_A|} dr$$

The MO energy diagram of some diatomics
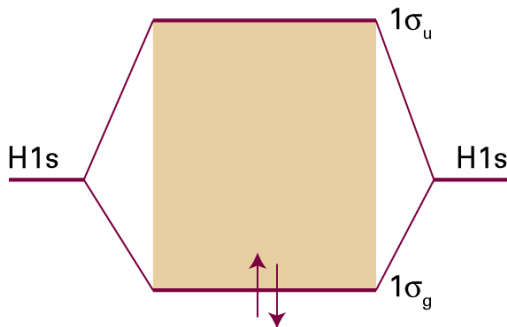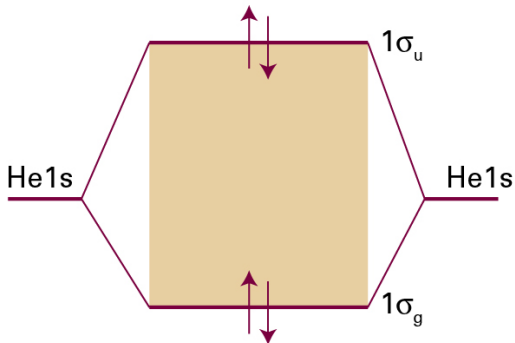
The MO energy diagram of some diatomics

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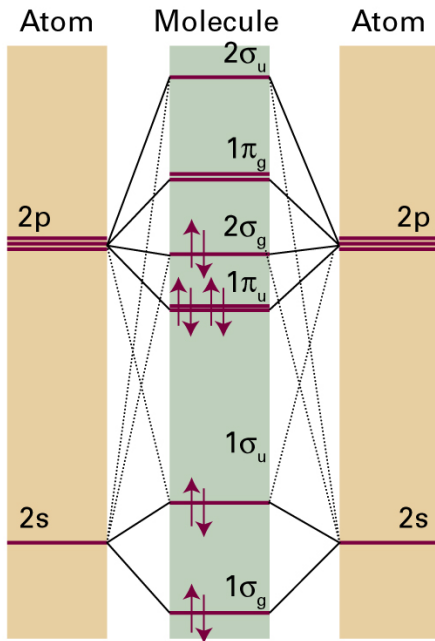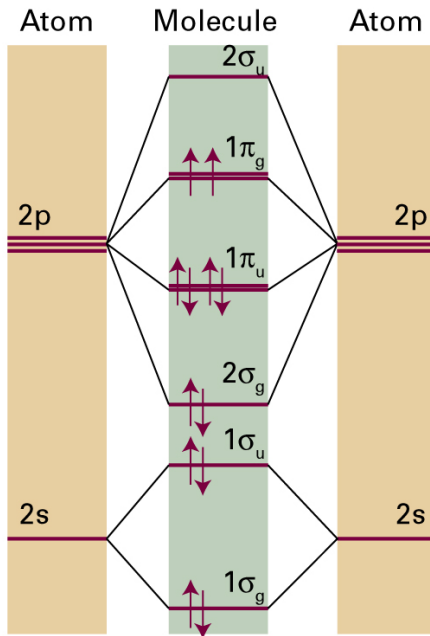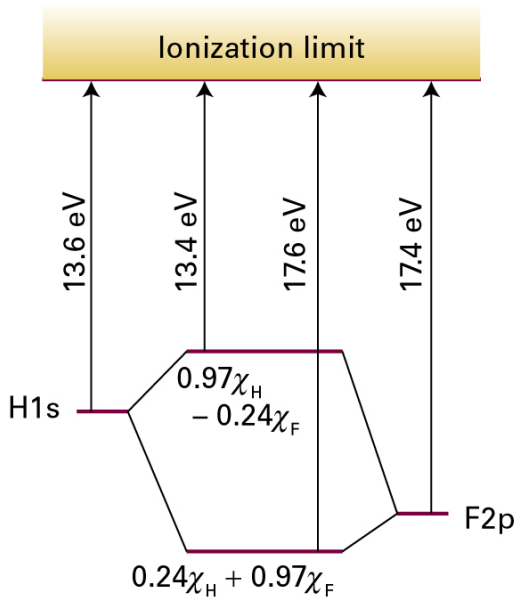

Ionization limit

13.6 eV   13.4 eV   17.6 eV   17.4 eV

H1s

$0.97\chi_H - 0.24\chi_F$

F2p

$0.24\chi_H + 0.97\chi_F$

The variational principle

- A given Hamiltonian *H* has a spectrum of eigenfunctions Ψ_i and eigenvalues E_i:

$$H\Psi_i = E_i\Psi_i \qquad i = 0, 1, 2, 3 \ldots$$

- For molecular Hamiltonians the eigenfunctions Ψ_i cannot be found exactly.
- How can we try to get as close as possible to the exact result?
- The variational principle:
  "*The energy expectation value of any wave function Φ is always greater or equal the ground-state energy. Equality holds only when $\Phi = \Psi_0$*"

$$\frac{\langle \Phi \, | \, H \, | \, \Phi \rangle}{\langle \Phi \, | \, \Phi \rangle} = E_\Phi \geq E_0$$

- The variational principle can be exploited to obtain better approximations to the ground state wave function (and under certain conditions also exciterd states).

The LCAO approximation

- LCAO means Linear Combination of Atomic Orbitals.
- Molecular orbitals are obtained by combining the atomic orbitals of the different atoms:

$$\phi_i = \sum_\alpha c_{i\alpha} \chi_\alpha$$

- The "best" coefficients $c_{i\alpha}$ are obtained by an application of the variational principle.

Variational principle combined with LCAO

- Orbital: $\phi = \sum_\alpha c_\alpha \chi_\alpha$
- Energy $\frac{\langle \phi \, | \, H \, | \, \phi \rangle}{\langle \phi \, | \, \phi \rangle}$
- Energy minimization: $\frac{\partial E}{\partial c_\alpha} = 0$
- For a diatomic system:

$$E = \frac{c_1^2 H_{11} + c_2^2 H_{22} + 2c_1 c_2 H_{12}}{c_1^2 + c_2^2 + 2c_1 c_2 S_{12}}$$

$$\frac{\partial E}{\partial c_1} = \frac{H_{11} c_1 - E c_1 + H_{12} c_2 - E S_{12} c_2}{c_1^2 + c_2^2 + 2c_1 c_2 S_{12}}$$

- A linear system of equations:

$$H_{11} c_1 - E c_1 + H_{12} c_2 - E S_{12} c_2 = 0$$
$$H_{21} c_1 - E S_{21} c_1 + H_{22} c_2 - E c_2 = 0$$

Summary

Slater determinant

- Two electrons:

$$\Psi(x_1, x_2) = \frac{1}{\sqrt{2!}} \begin{vmatrix} \phi_1(x_1) & \phi_2(x_1) \\ \phi_1(x_2) & \phi_2(x_2) \end{vmatrix} = \frac{1}{\sqrt{2}} \Big(\phi_1(x_1)\phi_2(x_2) - \phi_2(x_1)\phi_1(x_2) \Big)$$

- 3 electrons:

$$\Psi(x_1, x_2, x_3) = \frac{1}{\sqrt{3!}} \begin{vmatrix} \phi_1(x_1) & \phi_2(x_1) & \phi_3(x_1) \\ \phi_1(x_2) & \phi_2(x_2) & \phi_3(x_2) \\ \phi_1(x_3) & \phi_2(x_3) & \phi_3(x_3) \end{vmatrix} =$$

$$\phi_1(x_1)\phi_2(x_2)\phi_3(x_3) + \phi_2(x_1)\phi_3(x_2)\phi_1(x_3) + \phi_3(x_1)\phi_1(x_2)\phi_2(x_3)$$

$$-\phi_1(x_1)\phi_3(x_2)\phi_2(x_3) - \phi_2(x_1)\phi_1(x_2)\phi_3(x_3) - \phi_3(x_1)\phi_2(x_2)\phi_1(x_3)$$

- General form:

$$\Psi(x_1, \ldots, x_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(x_1) & \phi_2(x_1) & \cdots & \phi_N(x_1) \\ \phi_1(x_2) & \phi_2(x_2) & \cdots & \phi_N(x_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(x_N) & \phi_2(x_N) & \cdots & \phi_N(x_N) \end{vmatrix}$$

Slater-Condon rules: one-electron operators

- One-electron operator: expectation value

$$\langle \Phi | \hat{H}^{(1)} | \Phi \rangle = \sum_{i=1}^{N} \langle \phi_i | \hat{h} | \phi_i \rangle$$

- One-electron operator: single excitation

$$\langle \Phi | \hat{H}^{(1)} | \Phi \rangle = \sum_{i=1}^{N} \langle \phi_i | \hat{h} | \phi_i \rangle$$

- One-electron operator: double excitation

$$\langle \Phi | \hat{H}^{(1)} | \Phi_{ij}^{ab} \rangle = 0$$

Slater-Condon rules: two-electron operators

- Two-electron operator: expectation value

$$\langle\Phi|\hat{H}^{(2)}|\Phi\rangle = \frac{1}{2}\sum_{i,j}\left(\langle\phi_i\phi_j|\hat{g}|\phi_i\phi_j\rangle - \langle\phi_i\phi_j|\hat{g}|\phi_j\phi_i\rangle\right)$$

- Two-electron operator: single excitation

$$\langle\Phi|\hat{H}^{(2)}|\Phi_i^a\rangle = \sum_{j}\left(\langle\phi_i\phi_j|\hat{g}|\phi_a\phi_j\rangle - \langle\phi_i\phi_j|\hat{g}|\phi_j\phi_a\rangle\right)$$

- Two-electron operator: double excitation

$$\langle\Phi|\hat{H}^{(2)}|\Phi_{ij}^{ab}\rangle = \langle\phi_i\phi_j|\hat{g}|\phi_a\phi_b\rangle - \langle\phi_i\phi_j|\hat{g}|\phi_b\phi_a\rangle$$

One-electron density matrix

- The one-electron Reduced Density Matrix

$$\gamma(x, x') = N \int \Psi^*(x, x_2, \ldots, x_N) \, \Psi(x', x_2, \ldots, x_N) \, dx_2 \cdots dx_N$$

- The Orbital expansion of the 1-RDM:

$$\gamma(x, x') = \sum_{p,q} \gamma_{pq} \, \phi_p(x) \, \phi_q^*(x')$$

- Natural orbitals $\gamma_{pq} = \gamma_{pp}\delta_{pq}$:

$$\gamma(x, x') = \sum_{p} \gamma_{pp} \, \phi_p(x) \, \phi_q^*(x')$$

- The one-electron RDM for a Slater determinant:

$$\gamma(x, x') = \sum_{i=1}^{N} \phi_i(x) \, \phi_i^*(x')$$

Two-electron density matrix

- The two-electron Reduced Density Matrix

$$\Gamma(x_1, x_2; x_1', x_2') =$$
$$N(N-1) \int \Psi^*(x_1, x_2, x_3, \ldots, x_N)\, \Psi(x_1', x_2', x_3, \ldots, x_N)\, dx_3 \cdots dx_N$$

- The Orbital expansion of the 2-RDM:

$$\Gamma(x_1, x_2; x_1', x_2') = \sum_{p,q,r,s} \Gamma_{pq,rs}\, \phi_p(x_1)\phi_q(x_2)\, \phi_r^*(x_1')\phi_s^*(x_2')$$

- The 2-RDM for a Slater determinant:

$$\Gamma(x_1, x_2; x_1', x_2') =$$
$$\sum_{i,j=1}^{N} \left[\phi_i(x_1)\phi_j(x_2)\phi_i^*(x_1')\phi_j^*(x_2') - \phi_i(x_1)\phi_j(x_2)\phi_j^*(x_1')\phi_i^*(x_2') \right]$$

The Hartree-Fock method

- Write the energy of a Slater determinant

$$E[\Phi] = \sum_i^{\text{occ}} \langle \phi_i | \hat{h} | \phi_i \rangle + \frac{1}{2} \sum_{i,j}^{\text{occ}} \left(\langle \phi_i \phi_j | \hat{g} | \phi_i \phi_j \rangle - \langle \phi_i \phi_j | \hat{g} | \phi_j \phi_i \rangle \right)$$

- Add the orthonormality constraints

$$\langle \phi_i | \phi_i \rangle = \delta_{ij}$$

- Lagrangian including orthogonality constraints:

$$L = E - \sum_{ij} \lambda_{ij} \langle \phi_i | \phi_i \rangle - \delta_{ij}$$

The Hartree-Fock equations

- The Fock operator

$$F = h + \sum_j J_j - K_j$$

- The Coulomb operator

$$J\phi_i = \sum_j J_j \phi_i = \int \frac{\phi_j^* \phi_j}{|r - r'|} dr' \phi_i$$

- The Exchange operator

$$K\phi_i = \sum_j K_j \phi_i = \int \frac{\phi_j^* \phi_i}{|r - r'|} dr' \phi_j$$

- The Hartree-Fock equations

$$F\phi_i = \sum_j F_{ij} \phi_j$$