

# 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

The Molecular Hamiltonian

The Hydrogen atom

The Helium atom

$\text{H}_2^+$  and molecular orbitals

Hartree-Fock

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# 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:  $\hat{V}_{eN} = - \sum_{iI} \frac{Z_I}{|r_i - R_I|}$

# The Born-Oppenheimer approximation

- ➊ Electrons are much faster than nuclei, which can be considered “clamped”.
- ➋ Nuclear kinetic energy is neglected, nuclear positions become parameters, the wavefunction is separated.
- ➌ Electronic equation is solved first at fixed (clamped) nuclei.

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

- ➍ Nuclei move in a potential defined by the electronic energy

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

- ➎ Final wavefunction  $\Psi(r, R) = \phi(r; R)\chi(R)$

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The Molecular Hamiltonian

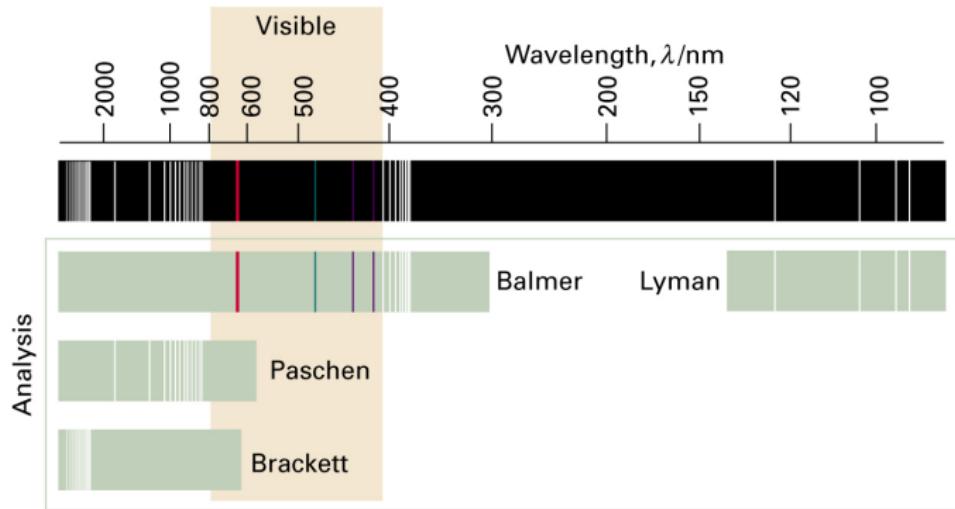
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# The riddle of atomic spectra



- Terms:  $T_n = R_H/n^2$     $R_H = 109677\text{cm}^{-1}$
- Combination rule:  $\nu = T_n - T_m$     $m > n$
- 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:

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

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

$$H_{CM} = \frac{-\nabla_i^2}{2m_{CM}} \quad H_i = T_i + V = \frac{-\nabla_i^2}{2\mu} - \frac{1}{r}$$

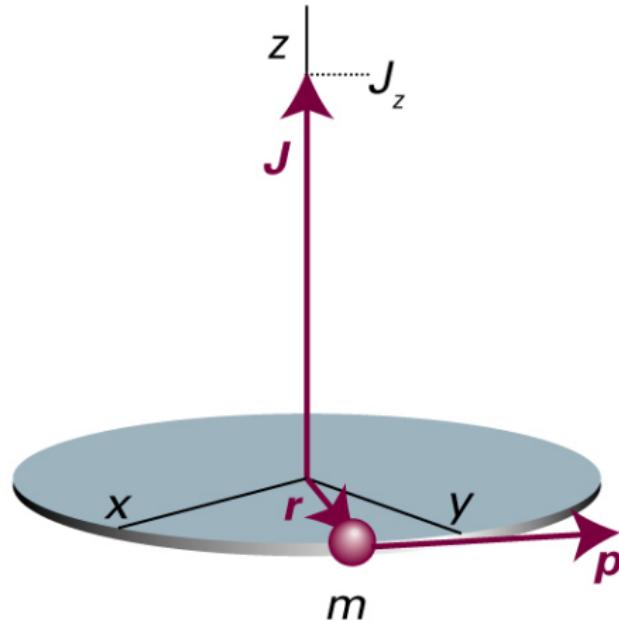
- From cartesian to spherical coordinates:

$$\Psi(x, y, z) \rightarrow R(r) \cdot Y(\phi, \theta)$$

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

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

# Angular momentum operators



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

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

$$L_x = yp_z - zp_y = -i\hbar(y \frac{d}{dz} - z \frac{d}{dy})$$

$$L_y = zp_x - xp_z = -i\hbar(z \frac{d}{dx} - x \frac{d}{dz})$$

$$L_z = xp_y - yp_x = -i\hbar(x \frac{d}{dy} - y \frac{d}{dx})$$

## Linear and angular motion: a comparison

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

# Cartesian, polar and spherical coordinates

- Cartesian coordinates:  $x, y, z$

$$dV = dx dy dz$$

- Cylindrical coordinates:  $r, \phi, z$

$$r^2 = x^2 + y^2 \quad x = r \cos \phi$$

$$\phi = \arctan(y/x) \quad y = r \sin \phi$$

$$dV = r dr d\phi dz$$

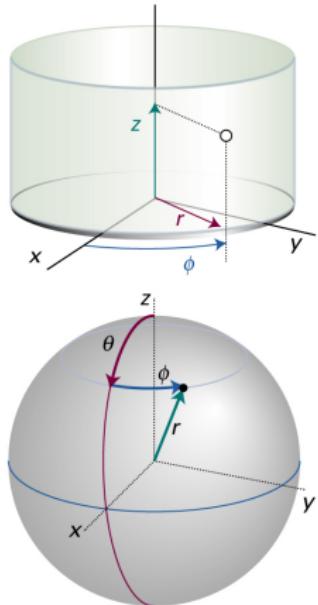
- Spherical coordinates:  $r, \phi, \theta$

$$r^2 = x^2 + y^2 + z^2 \quad x = r \cos \phi \sin \theta$$

$$\phi = \arctan(y/x) \quad y = r \sin \phi \sin \theta$$

$$\theta = \arccos(z/r) \quad z = r \cos \theta$$

$$dV = r^2 dr \sin \theta d\theta d\phi$$



## Particle on a ring

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

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

- Eigenfunctions:

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

## 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

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

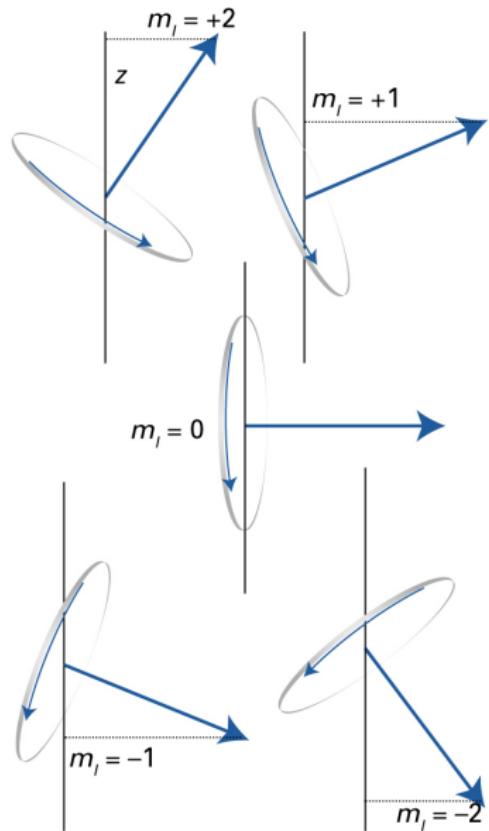
$$L_y = zp_x - xp_z = -i\hbar \left( z \frac{d}{dx} - x \frac{d}{dz} \right)$$

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

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

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

# Angular momentum: eigenvalues



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

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

$$L_z Y_{m_l}^l(\phi, \theta) = \hbar m_l Y_{m_l}^l(\phi, \theta)$$

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

# Angular momentum: eigenfunctions

**Table 8.2** The spherical harmonics

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

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

$$\int_0^\pi \int_0^{2\pi} Y_{l,m_l}(\theta, \phi)^* Y_{l',m'_l}(\theta, \phi) \sin \theta d\theta d\phi = \delta_{ll'} \delta_{m_l m'_l}$$

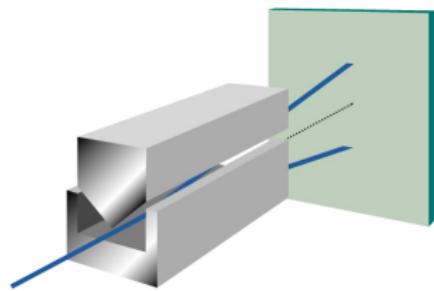
An important 'triple integral' is

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

$$= 0 \quad \text{unless} \quad m''_l = m'_l + m_l$$

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).

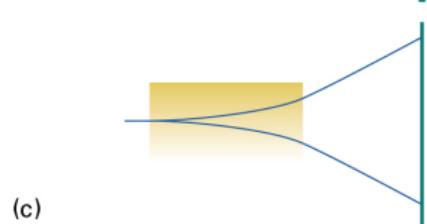
# Spin: the Stern-Gerlach experiment



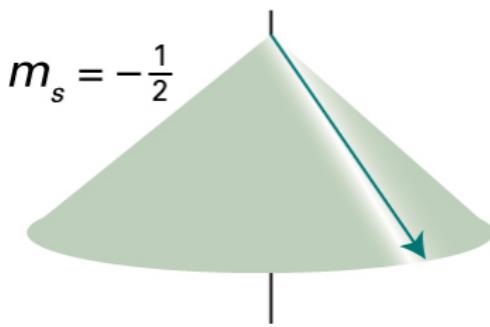
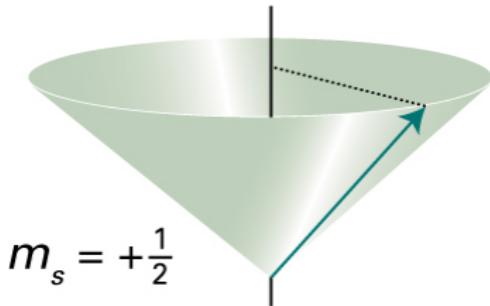
(a)



(b)



(c)



## Spin: general considerations

- The spin is an angular momentum:

$$S^2 \sigma_{m_s}^s = \hbar^2 s(s+1) \sigma_{m_s}^s$$

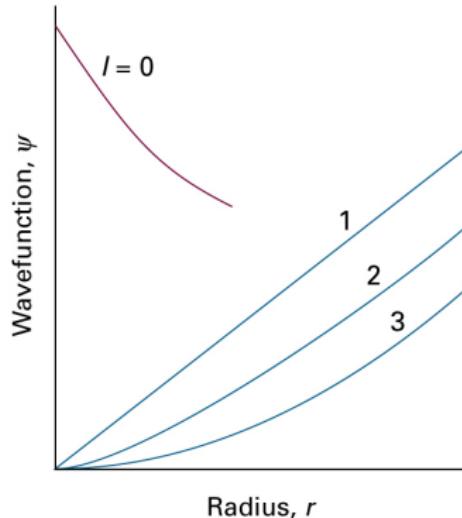
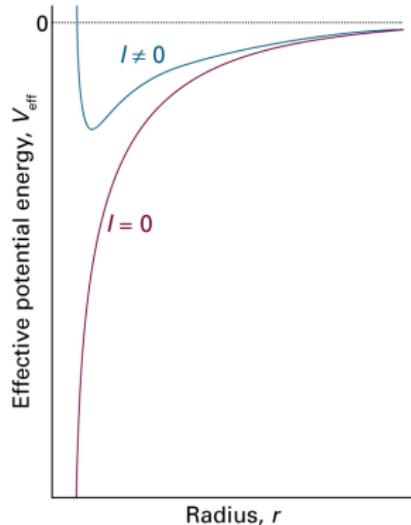
$$S_z \sigma_{m_s}^s = \hbar m_s \sigma_{m_s}^s$$

- 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

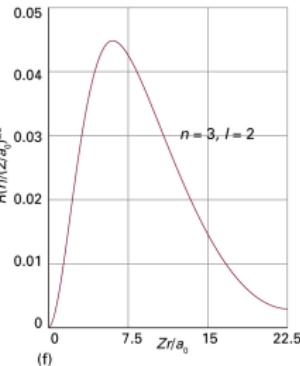
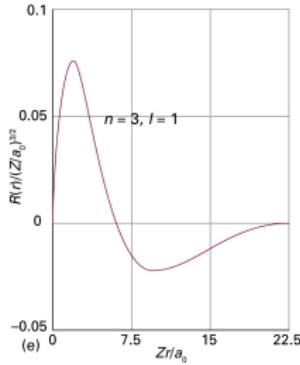
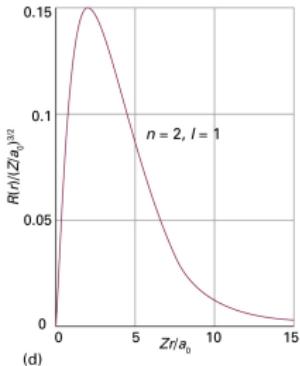
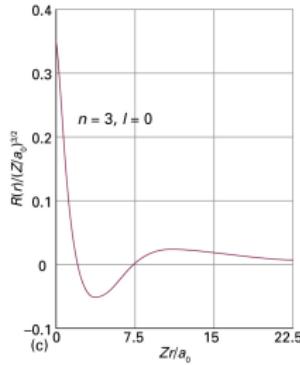
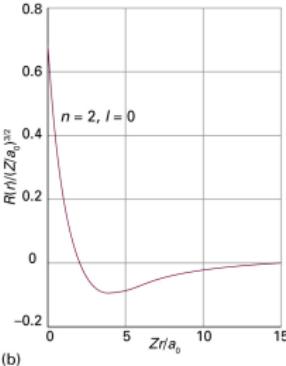
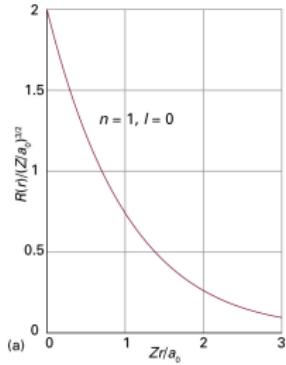
$$-\frac{1}{2\mu} \frac{d^2 u(r)}{dr^2} + V_{\text{eff}}(r) = E u(r) \quad u(r) = r R(r)$$

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



# 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

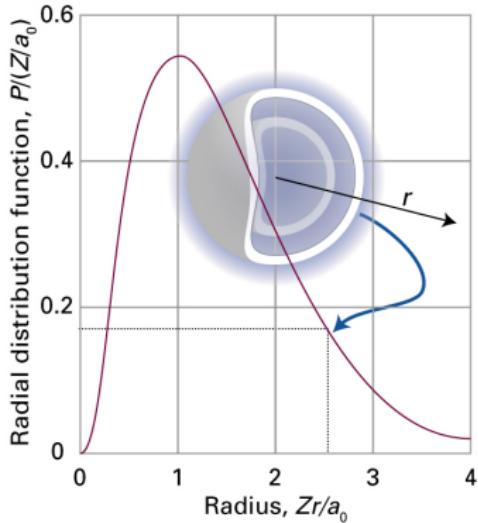
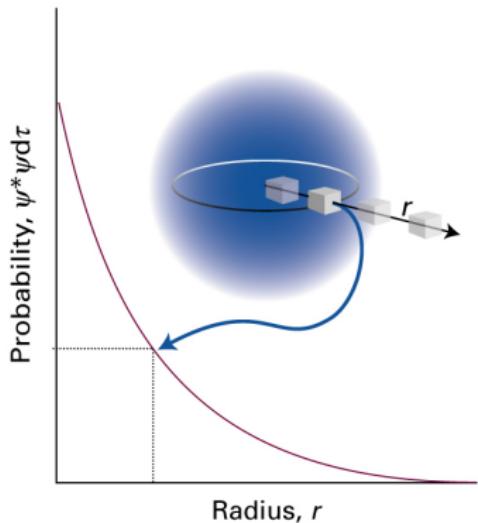
$n$	$l$	$R_{n,l}$
1	0	$2 \left( \frac{Z}{a} \right)^{3/2} e^{-\rho/2}$
2	0	$\frac{1}{8^{1/2}} \left( \frac{Z}{a} \right)^{3/2} (2 - \rho) e^{-\rho/2}$
2	1	$\frac{1}{24^{1/2}} \left( \frac{Z}{a} \right)^{3/2} \rho e^{-\rho/2}$
3	0	$\frac{1}{243^{1/2}} \left( \frac{Z}{a} \right)^{3/2} (6 - 6\rho + \rho^2)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

# Quantum numbers and eigenvalues

- Principal quantum number:  $n = 1, 2, 3 \dots$
- Angular quantum number:  $l = 0, 1, 2, \dots n - 1$
- Magnetic quantum number:  $m = 0, \pm 1, \pm 2, \dots \pm l$
- 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:  $P(r) = r^2 R(r)^2 = u(r)^2$



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# The Hamiltonian operator

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

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

- 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):  
 $V_{Ne_1} = -Ze^2/|R_N - r_{e_1}|, V_{Ne_2} = V_{e_1 e_2} = -Ze^2/|R_N - r_{e_2}|$
- 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):

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

- 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 ( $\mathbf{r} = (x, y, z)$ ) and spin ( $s$ ). We define  $\mathbf{x} = (x, y, z, s)$
- 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

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

- Electron 1 in the  $1s$  orbital with spin  $\alpha$  and electron 2 in the  $1s$  orbital with spin  $\beta$ .
- 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.

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = -\Psi(\mathbf{x}_2, \mathbf{x}_1)$$

## The ground state of He revisited

- Our original  $1s^2$  wavefunction 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:

$$(\alpha(s_1)\beta(s_2) - \beta(s_1)\alpha(s_2)) / \sqrt{2}$$

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

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

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

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

- 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:

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

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

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

$$\Psi_t = \frac{1s(\mathbf{r}_1) 2s(\mathbf{r}_2) - 2s(\mathbf{r}_1) 1s(\mathbf{r}_2)}{\sqrt{2}} \left\{ \begin{array}{l} \frac{\alpha(s_1) \alpha(s_2)}{\sqrt{2}} \\ \frac{\alpha(s_1) \beta(s_2) + \beta(s_1) \alpha(s_2)}{\sqrt{2}} \\ \beta(s_1) \beta(s_2) \end{array} \right.$$

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## Molecular-Orbital theory for H<sub>2</sub><sup>+</sup>

- 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:

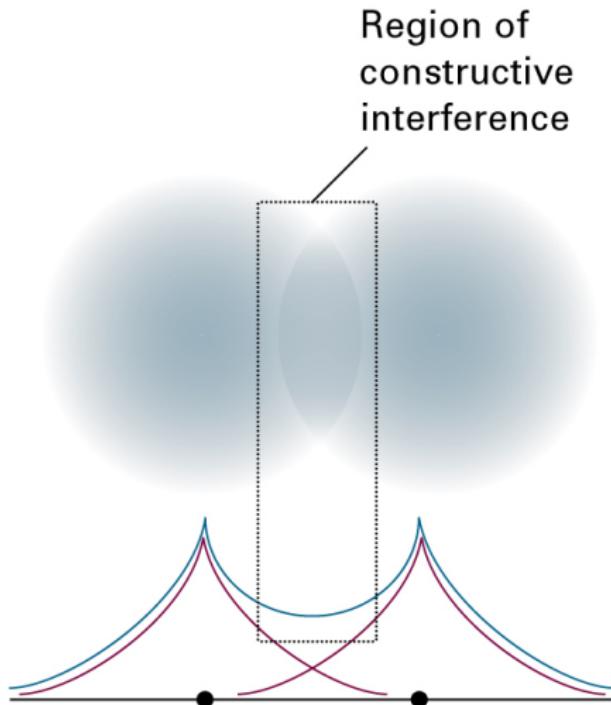
$$\Phi_{\pm} = N_{\pm}(1s_A \pm 1s_B)$$

- Normalization coefficient:

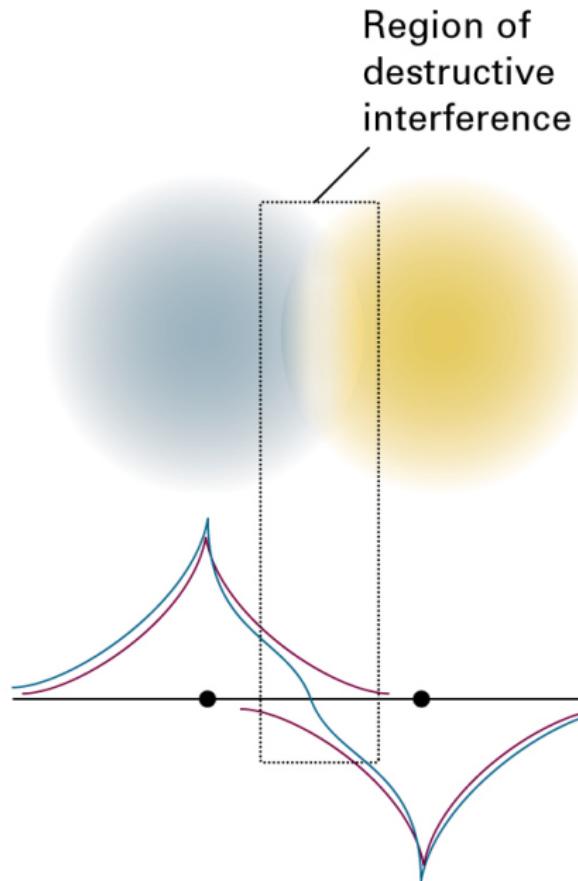
$$N_{\pm} = \frac{1}{2 + 2S}$$

- $S$  is the so called overlap integral.

# The bonding orbital of $\text{H}_2^+$



# The antibonding orbital of $\text{H}_2^+$



## The orbital energies of $\text{H}_2^+$

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

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

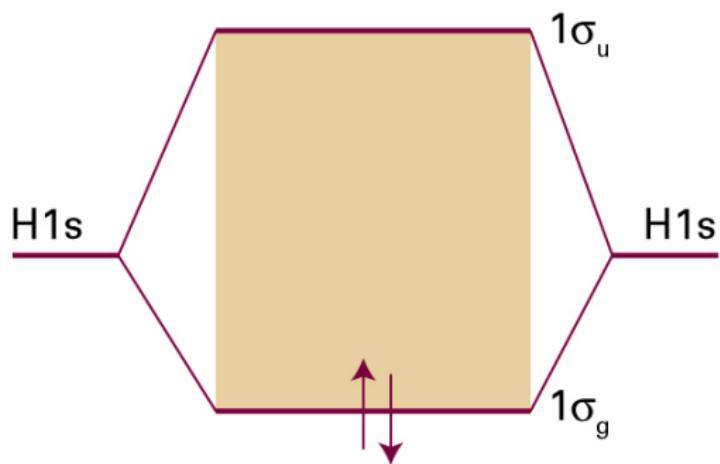
- Both  $j$  and  $k$  are positive: the bonding orbital is lower in energy than the antibonding one.
- Interaction of electron  $s_A$  with nucleus  $B$

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

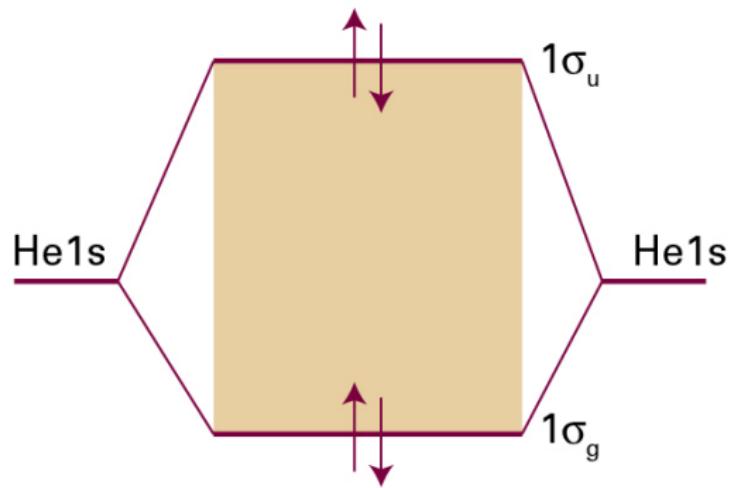
- Interaction of the overlap density  $s_A s_B$  with nucleus  $A$  (or  $B$ )

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

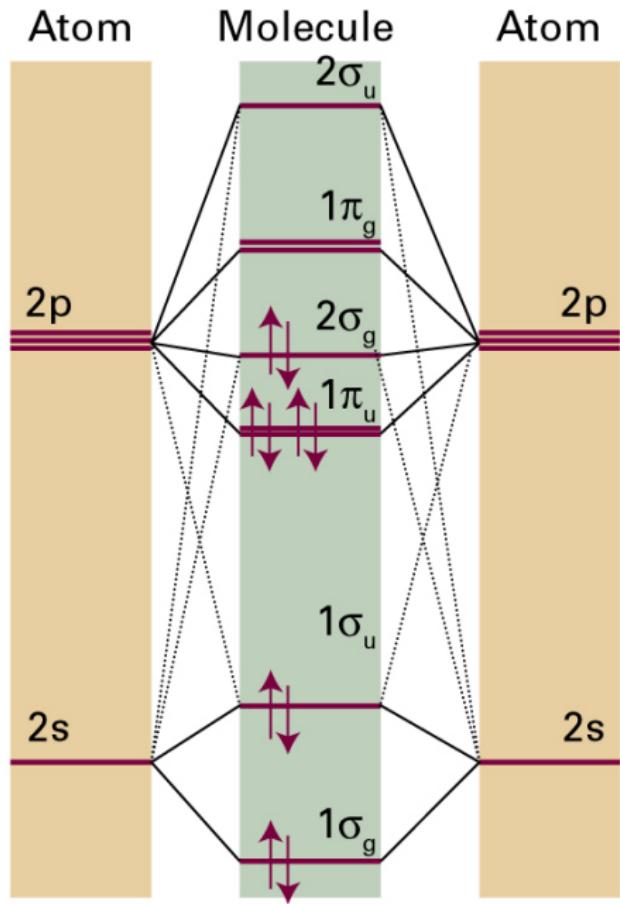
# The MO energy diagram of some diatomics



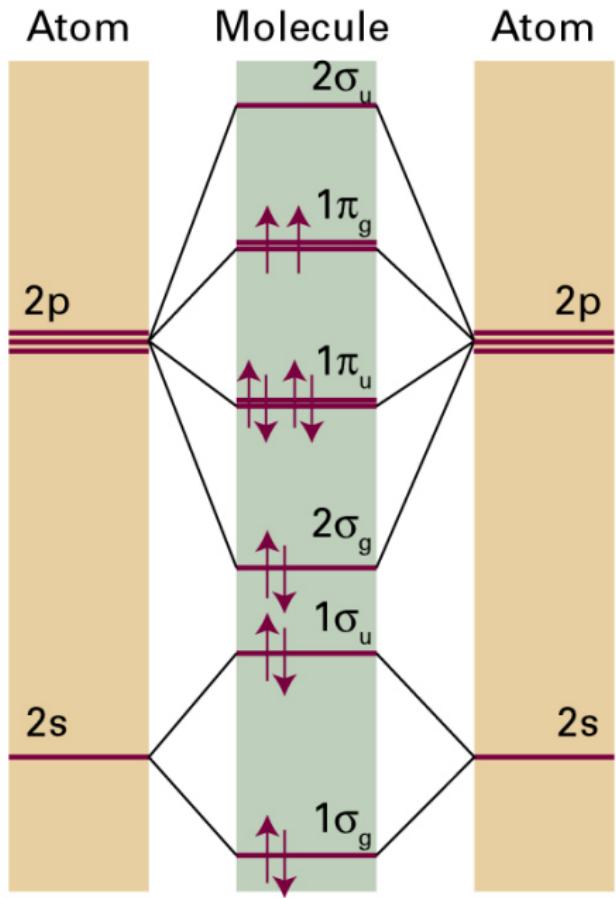
# The MO energy diagram of some diatomics



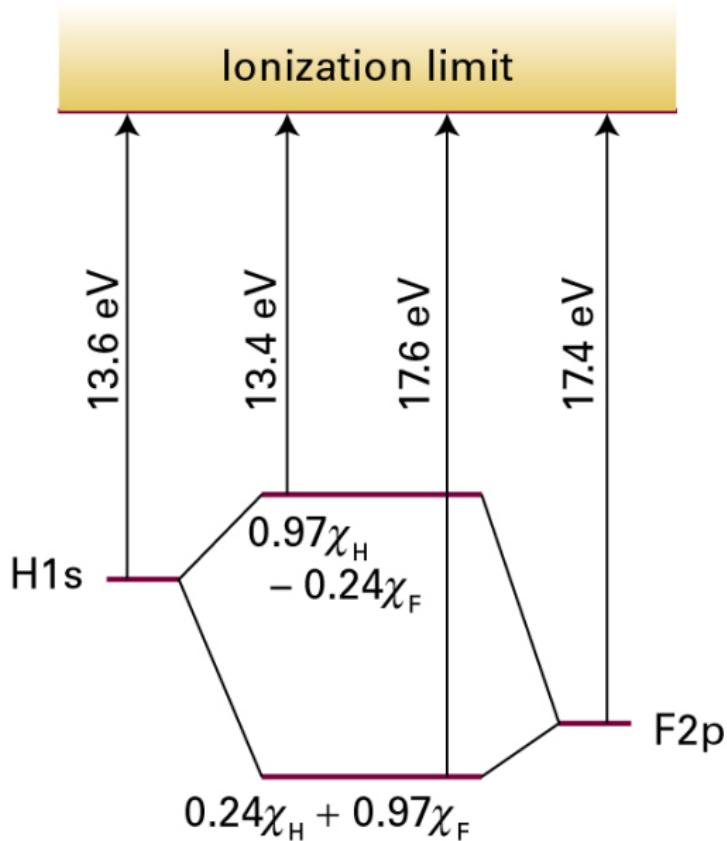
# The MO energy diagram of some diatomics



# The MO energy diagram of some diatomics



# The MO energy diagram of some diatomics



## The variational principle

- A given Hamiltonian  $H$  has a spectrum of eigenfunctions  $\Psi_i$  and eigenvalues  $E_i$ :

$$H\Psi_i = E_i\Psi_i \quad i = 0, 1, 2, 3 \dots$$

- For molecular Hamiltonians the eigenfunctions  $\Psi_i$  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  $\Phi$  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 excited 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:

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

$$\frac{\partial E}{\partial c_1} = \frac{H_{11}c_1 - Ec_1 + H_{12}c_2 - ES_{12}c_2}{c_1^2 + c_2^2 + 2c_1 c_2 S_{12}}$$

- A linear system of equations:

$$H_{11}c_1 - Ec_1 + H_{12}c_2 - ES_{12}c_2 = 0$$

$$H_{21}c_1 - ES_{21}c_1 + H_{22}c_2 - Ec_2 = 0$$

# Summary

The Molecular Hamiltonian

The Hydrogen atom

The Helium atom

$\text{H}_2^+$  and molecular orbitals

Hartree-Fock

# Slater determinant

- Two electrons:

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

- 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:

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

## 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

$$\langle \Phi | \hat{H}^{(1)} | \Phi_i^a \rangle = \langle \phi_i | \hat{h} | \phi_a \rangle$$

- 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

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

- Two-electron operator: single excitation

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

- 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

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

- The Orbital expansion of the 1-RDM:

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

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

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

- 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

$$\Gamma(x_1, x_2; x'_1, x'_2) =$$

$$N(N-1) \int \Psi^*(x_1, x_2, x_3, \dots, x_N) \Psi(x'_1, x'_2, x_3, \dots, x_N) dx_3 \cdots dx_N$$

- 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

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