Adiabatic or Born-Oppenheimer approximation

Molecular Hamiltonian

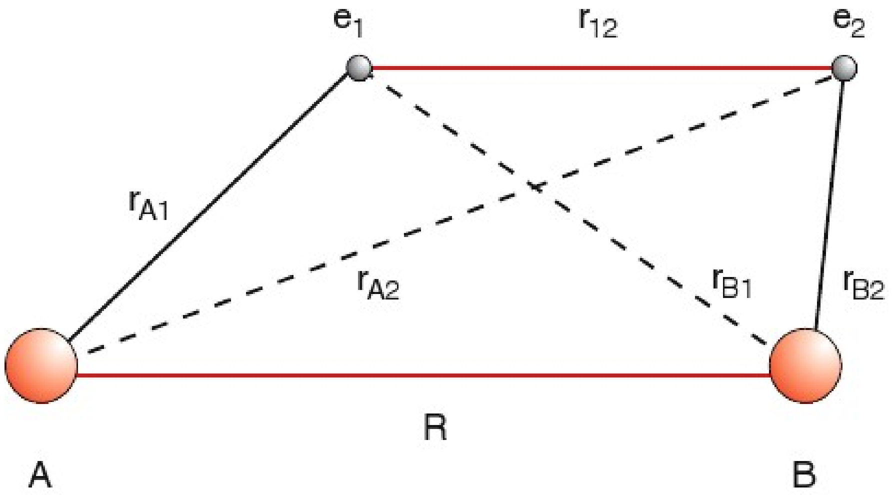
$$\hat{H}=\hat{T}_R+\hat{T}_r+\hat{V}(r,R)$$

R and *r* are vectors
here.
μ, r for electrons
M_j, *R* for nuclei

$$\hat{T}_r=-\frac{\hbar^2}{2\mu}\sum_i^{N_e}\frac{\partial^2}{\partial x_i^2}+\frac{\partial^2}{\partial y_i^2}+\frac{\partial^2}{\partial z_i^2}=-\frac{\hbar^2}{2\mu}\sum_i^{3N_e}\frac{\partial^2}{\partial r_i^2}$$

$$\hat{T}_R=-\sum_j^{N_n}\frac{\hbar^2}{2M_j}\frac{\partial^2}{\partial X_j^2}+\frac{\hbar^2}{2M_j}\frac{\partial^2}{\partial Y_j^2}+\frac{\hbar^2}{2M_j}\frac{\partial^2}{\partial Z_j^2}=-\sum_j^{3N_n}\frac{\hbar^2}{2M_j}\frac{\partial^2}{\partial R_j^2}$$

$$\hat{H}\Psi_{tot}(r,R)=E\Psi_{tot}(r,R)$$



Adiabatic separation

It is difficult to solve the equation

$$\hat{H}\Psi_{tot}(r,R)=E\Psi_{tot}(r,R)$$

An approximation is used. It is based on the fact that electrons move much faster than nuclei.

The kinetic energy term for the nuclear motion is much smaller than the other terms.

$$\hat{H}=\hat{T}_R+\hat{T}_r+\hat{V}(r,R)$$

$$\hat{T}_r=-\frac{\hbar^2}{2\mu}\sum_i\frac{\partial^2}{\partial r_i^2}$$

$$\hat{T}_R=-\sum_j\frac{\hbar^2}{2M_j}\frac{\partial^2}{\partial R_j^2}$$

We separate nuclear and electronic motions and solve the Schrödinger equation for the electronic degrees of freedom at fixed nuclei.

The vibrational part of the Hamiltonian will be treated as a perturbation.

Adiabatic separation

B-O approximation: T_R is small. So, we split H in two parts

$$\hat{H}=\hat{H}_0+\hat{T}_R$$

$$\hat{H}_0=\hat{T}_r+\hat{V}(r,R)$$

And, as a first step, we obtain “adiabatic” molecular states $\varphi_n(R_f,r)$ and energies for fixed R_f

$$\hat{H}_0\varphi_n(R_f,r)=\varepsilon_n(R)\varphi_n(R_f,r)$$

$$n=1,2,\cdots$$

second step: $\Psi_{tot}(r,R)$ is represented as an expansion in the basis of $\varphi_n(R,r)$

$$\Psi^{tot}(r,R)=\sum_n \underset{\text{depend on } R}{c_n}\varphi_n(R,r)=\sum_n \Psi_n(R)\varphi_n(R,r)$$

In a complete form (with continuum states)

$$\Psi^{tot}(r,R)=\sum_n \Psi_n(R)\varphi_n(R,r)+\int \Psi_\epsilon(R)\varphi_\epsilon(R,r)\,d\epsilon$$

Adiabatic separation

$$\Psi^{tot}(r,R)=\sum_n \Psi_n(R)\varphi_n(R,r)+\int \Psi_\epsilon(R)\varphi_\epsilon(R,r)\,d\epsilon$$

discrete continuum states

Using simplified notations

$$\Psi^{tot}(r,R)=\sum_n \Psi_n(R)\left|n(R)\right\rangle$$

Plugging the expansion in the original Schrödinger equation

$$[\hat{H}_0+T_R]\Psi_{tot}(r,R)=E\Psi_{tot}(r,R)$$

multiplying it with <*m*(*R*)| and integrating over *r* we obtain

$$\left[T_R+\varepsilon_m(R)-E\right]\Psi_m(R)=\sum_n \hat{\Lambda}_{mn}\Psi_n(R)$$

where non-adiabatic couplings Λ_{mn} are

$$\hat{\Lambda}_{mn}=\sum_j \frac{\hbar^2}{M_j}\langle m(R)|\frac{\partial}{\partial R_j}|n(R)\rangle\frac{\partial}{\partial R_j}-\langle m(R)|T_R|n(R)\rangle$$

Born-Oppenheimer approximation

$$[\hat{H}_0 + T_R]\Psi_{tot}(r,R) = E\Psi_{tot}(r,R)$$

$$\hat{H}_0\varphi_n(R_f,r) = \varepsilon_n(R)\varphi_n(R_f,r)$$

$$n = 1,2,\cdots$$

$$\Psi^{tot}(r,R) = \sum_n \Psi_n(R)\left|n(R)\right\rangle$$

$$\left[T_R + \varepsilon_m(R) - E\right]\Psi_m(R) = \sum_n \hat{\Lambda}_{mn}\Psi_n(R)$$

$$\hat{\Lambda}_{mn} = \sum_j \frac{\hbar^2}{M_j}\langle m(R)|\frac{\partial}{\partial R_j}|n(R)\rangle\frac{\partial}{\partial R_j} - \langle m(R)|T_R|n(R)\rangle$$

The two above equations are exact if the whole (discrete and continuum) spectrum is included, i.e. a complete basis $\varphi_n(R,r)$ is used.

If Λ_{mn} are small one can truncate the basis. If basis is truncated to one function, it gives the Born-Oppenheimer approximation.

$$\boxed{\left[T_R + \varepsilon_m(R)\right]\Psi^0_{mv} = E^0_{mv}\Psi^0_{mv}}$$

$$\boxed{\hat{H}_0\varphi_n(R_f,r) = \varepsilon_n(R)\varphi_n(R_f,r)}$$

Born-Oppenheimer approximation

$$\boxed{\left[T_R+\varepsilon_m(R)\right]\Psi^0_{mv}=E^0_{mv}\Psi^0_{mv}}$$

$$\boxed{\hat{H}_0\varphi_n(R_f,r)=\varepsilon_n(R)\varphi_n(R_f,r)}$$

Energies E^0_{nv} and states $\Psi^{tot}(r,R)\approx\Psi^0_{nv}(R)\varphi_n(R,r)$

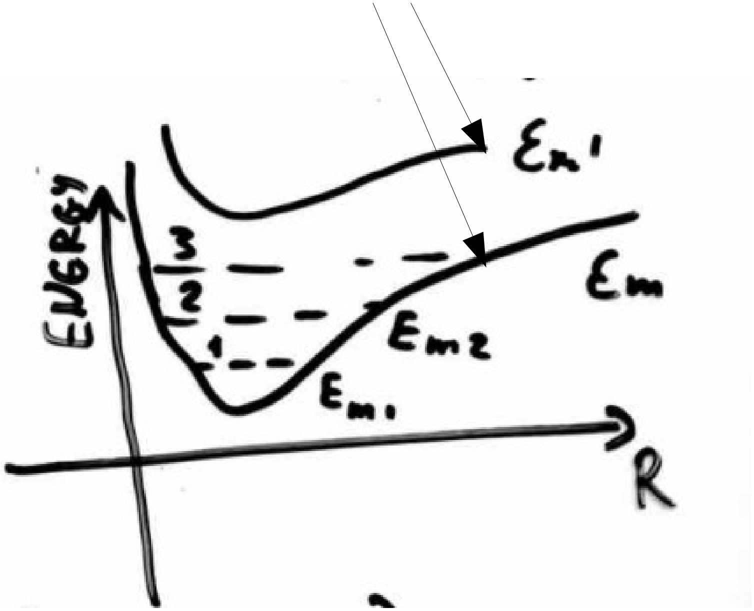
are called adiabatic or Born-Oppenheimer solutions of the molecular Hamiltonian.

The BO approximation is valid only if

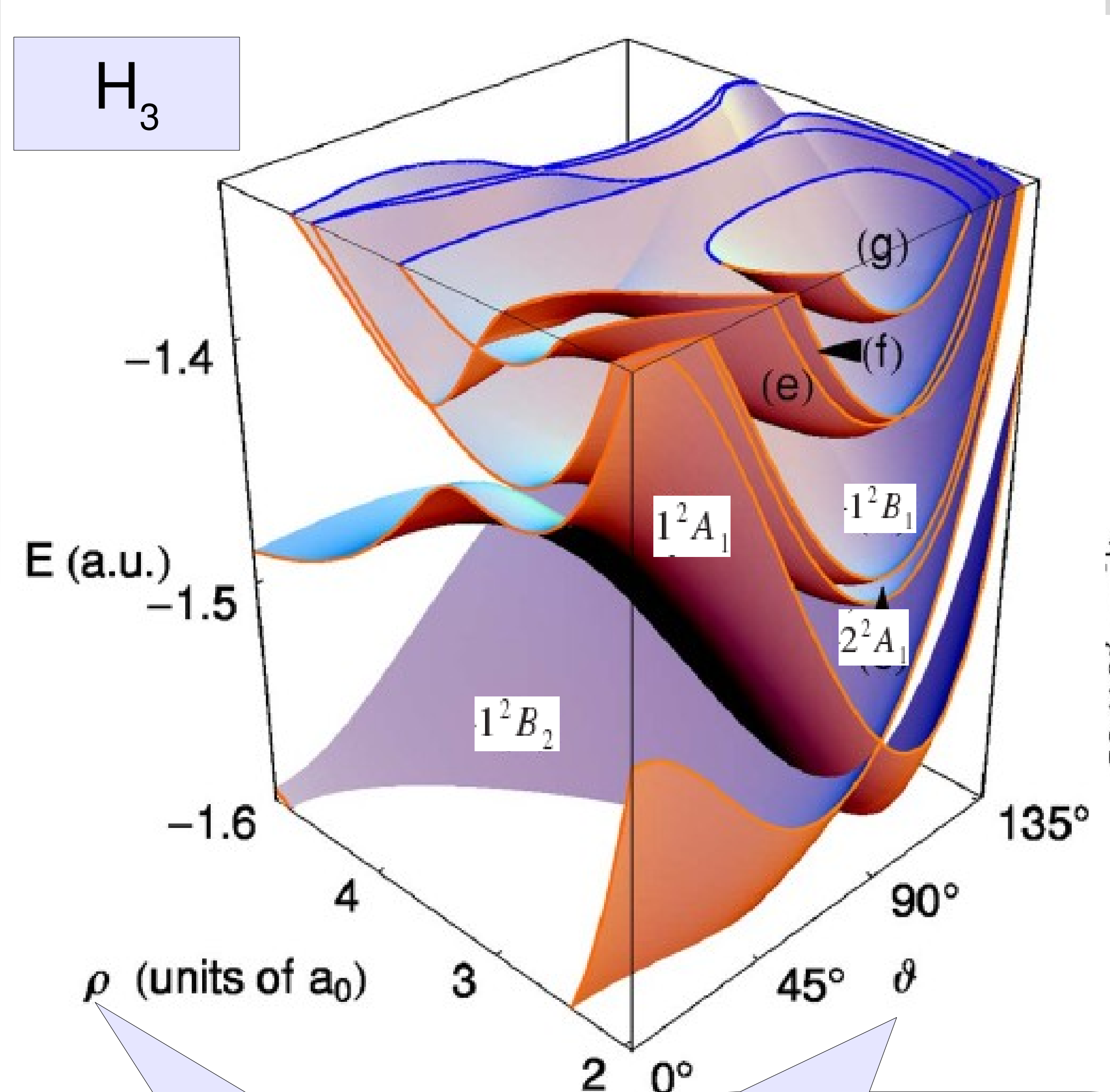
$$\int\Psi^{0*}_{n'v'}\hat{\Lambda}_{mn}\Psi^0_{nv}\,dR\ll\left|E^0_{nv}-E^0_{n'v'}\right|$$

It is similar to the applicability condition for the perturbation theory.

Molecular terms

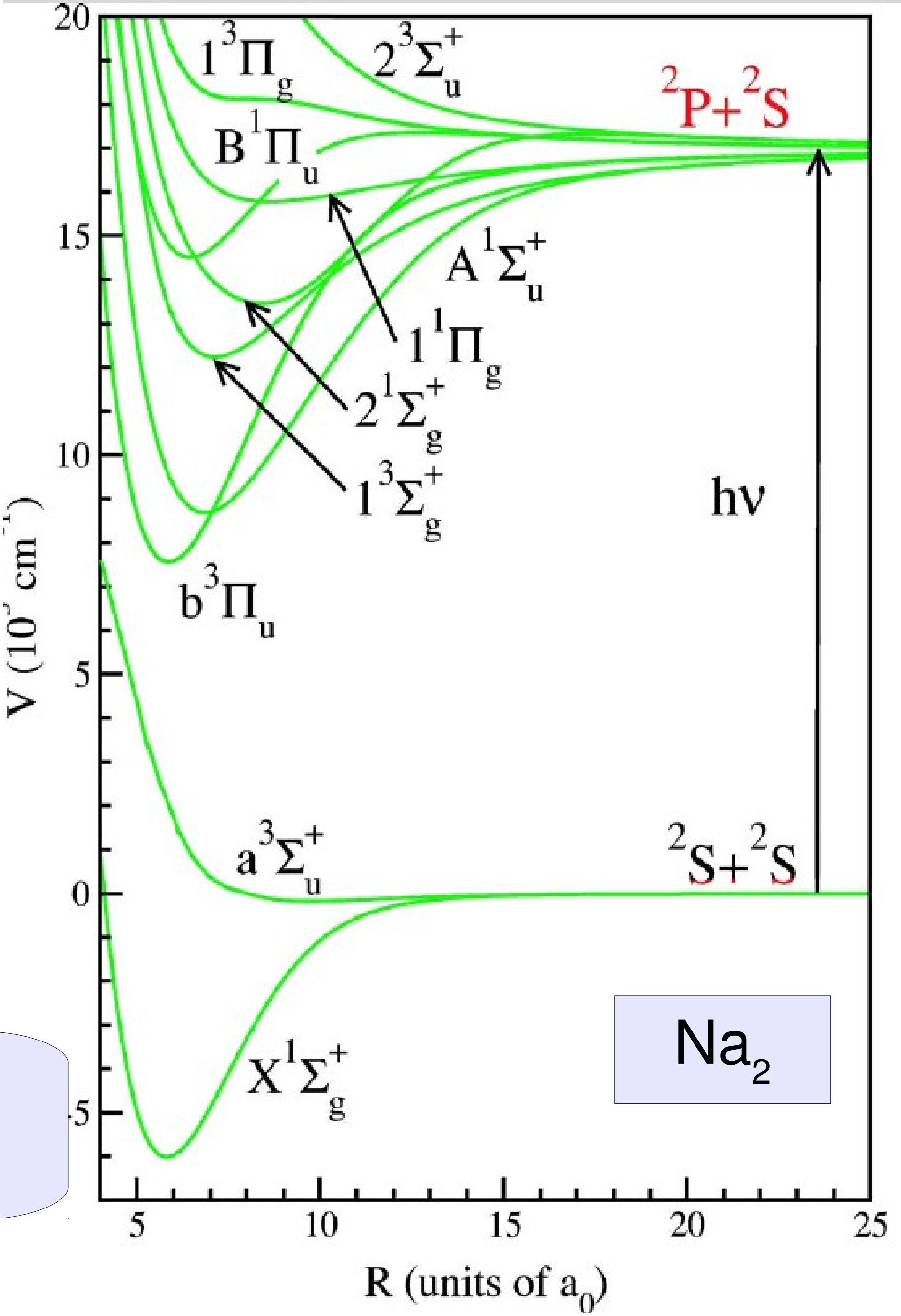


Example of potential surfaces



Symmetric stretching coordinate

asymmetric stretching coordinate



How to obtain vibrational levels for a given potential energy surface?

$$\left[T_R+\varepsilon_m(R)\right]\Psi_{mv}^{0}=E_{mv}^{0}\Psi_{mv}^{0}$$

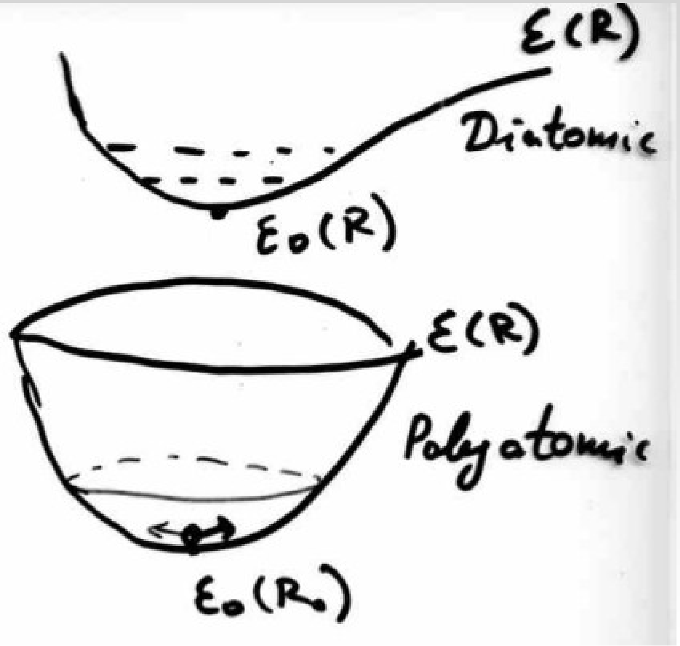
Normal coordinates

Normal mode and harmonic oscillator approximation:

Near a minimum a miltidimensional surface can be approximated by a paraboloid.

Consider ε($\boldsymbol{R}$) near it minimum $\boldsymbol{R}_0$. New coordinates $\boldsymbol{x}=\boldsymbol{R}-\boldsymbol{R}_0$

Near $\boldsymbol{x}=0$ we use the Taylor series for ε($\boldsymbol{R}$)



$$\varepsilon_m(\vec{x}) = \varepsilon_m(0) + \frac{1}{2}\sum_{ij}\frac{\partial^2 \varepsilon}{\partial x_i \partial x_j} x_i x_j = \varepsilon_m(0) + \frac{1}{2}\sum_{ij} k_{ij} x_i x_j$$

and for T_R

$$T_R = \frac{1}{2}\sum_{ij} m_{ij}\frac{d x_i}{dt}\frac{d x_j}{dt} = \frac{1}{2}\sum_{ij} m_{ij}\dot{x}_i \dot{x}_j$$

with $m_{ij}=m_{ji}$

$$T_R = \frac{1}{2}\left(\frac{d\vec{x}}{dt}\right)^T G^{-1}\left(\frac{d\vec{x}}{dt}\right)$$

where $\boldsymbol{G}=\boldsymbol{M}^{-1}$

Normal coordinates

The classical Hamilton function for vibrational motion: *H=T+V*:

$$H_{vib}=T_R+V=\varepsilon_m(0)+\frac{1}{2}\sum_{ij}\left(m_{ij}\dot{x}_i\dot{x}_j+k_{ij}x_ix_j\right)$$

New coordinates ***Q*** $\vec{x}=L\vec{Q}$

such that

$$T_R=\frac{1}{2}\left(\frac{d\vec{Q}}{dt}\right)^T\left(\frac{d\vec{Q}}{dt}\right)$$

diagonal matrix

and

$$\varepsilon_m(\vec{x})=\varepsilon_m(0)+\frac{1}{2}\sum_r\lambda_rQ^2=\varepsilon_m(0)+\frac{1}{2}\vec{Q}^T\Lambda\vec{Q}$$

$$T_R=\frac{1}{2}\left(\frac{d\vec{x}}{dt}\right)^TG^{-1}\left(\frac{d\vec{x}}{dt}\right) \quad \Rightarrow \quad L^TG^{-1}L=I$$

$$\varepsilon_m(\vec{x})=\varepsilon_m(0)+\frac{1}{2}\sum_{ij}x_ik_{ij}x_j=\varepsilon_m(0)+\frac{1}{2}(\vec{x})^TK\vec{x} \quad \Rightarrow \quad L^TKL=\Lambda$$

Classical Hamilton function

After some manipulations

$$L^T G^{-1} L = I \qquad L^T = L^{-1} G$$

$$\Downarrow$$

$$L^T K L = \Lambda \qquad L^{-1} G K L = \Lambda$$

$$\Downarrow$$

$$G K L = L \Lambda$$

we end up with the eigenvalue problem for matrix *GK=A*: $A L = L \Lambda$

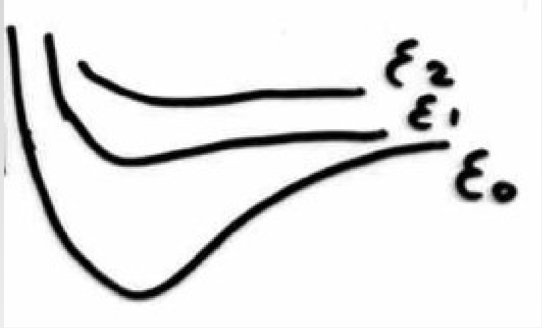
$$A \vec{l} = \lambda \vec{l}$$

$$H_{cl} = \varepsilon_m(0) + \frac{1}{2} \sum_r \left[\left(\frac{d Q_r}{dt} \right)^2 + \lambda_r Q_r^2 \right] = \varepsilon_m(0) + \frac{1}{2} \sum_r \left[p_r^2 + \lambda_r Q_r^2 \right]$$

$$H_q = \varepsilon_m(0) + \frac{1}{2} \sum_r \left[p_r^2 + \lambda_r Q_r^2 \right]$$

Near equilibrium

In “normal” conditions, molecules are in their ground electronic BO state $\varphi_o(R,r)$ and vibrational state can be approximated by a harmonic oscillator state.



Close to the equilibrium, we can use normal coordinates and write

$$\varepsilon_m(R)=\varepsilon_m(R_0)+\frac{1}{2}\sum_r \omega_r^2 Q_r^2$$

We can also neglect rotation of the molecule. Then $\hat{T}_R=-\sum_r \frac{\hbar^2}{2}\frac{\partial^2}{\partial Q_r^2}$ and the Hamiltonian becomes

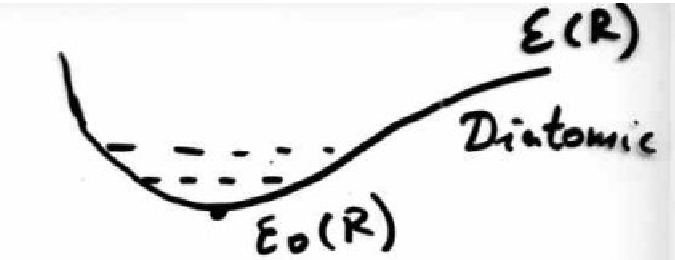
$$H\approx\frac{1}{2}\sum_r\left(\omega_r^2 Q_r^2-\hbar^2\frac{\partial^2}{\partial Q_r^2}\right)+\varepsilon_m(R_0)$$

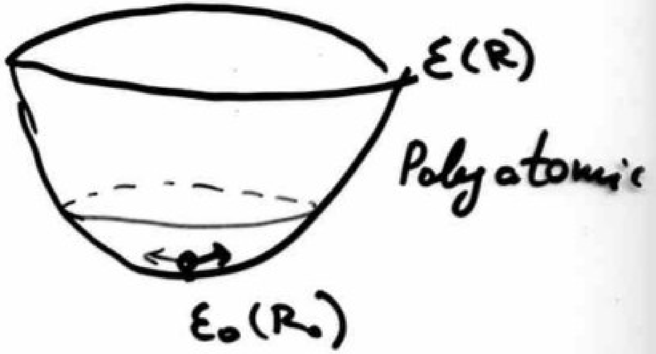
where **Q_s** are normal coordinates. Energies are

$$E_{0(n_1,n_2\cdots)}=\varepsilon_m+\hbar\sum_{r=1}\omega_r\left(n_r+\frac{1}{2}\right)$$

and wave functions

$$|m;n_1,n_2\cdots\rangle=\varphi_m(R_{0,r})\prod_r \Psi_{n_r}(Q_r)$$





Molecular symmetry considerations

Time-independent observables

Observables evolving in time:

$$O(t)=<\psi(t)|\mathbf{O}|\psi(t)>$$

$$\psi(t)=\psi_o\exp(-iEt/\hbar) \text{ with } H\psi_o=E\psi_o$$

We need **O** independent on *t*. If

$$\mathbf{O}\psi_o=\omega\psi_o \text{ then } O(t)=<\psi_o|\mathbf{O}|\psi_o>$$

and it is constant in time. It is equivalent to $[\mathbf{O},H]=0$.

Each state ψ_o is then characterized by *E* and ω (good or conserved quantum numbers).

If the system (molecule) has a certain geometrical symmetry, each symmetry operation (that does not change energy, $[\mathbf{O},H]=0$) can be considered as an operator **O** → it gives an additional good quantum number ω.

Symmetry of a diatomic molecule

R (internuclear distance) is fixed.

Symmetry of electronic wave functions:

(1) Translation in space.

O=**T**; ω=***p*** (linear momentum)

(2) Rotation in space.

O=**R**; ω=***L*** ($L = \sum l_i$)

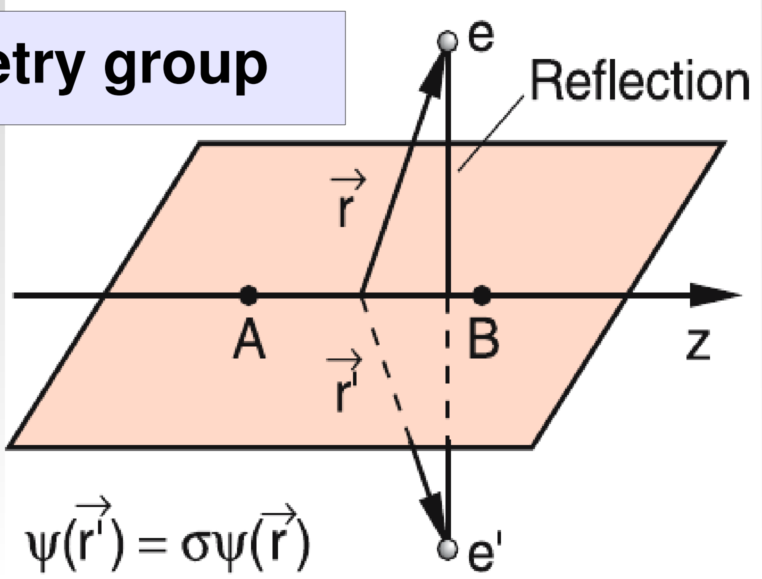
(3) Rotation about the molecular *Z* axis.

O=$\mathbf{R_z}$; ω=Λ (projection of angular momentum on *Z*)

(4) Reflection through a plane containing *Z*.

O=**σ**; ω=+/– (sign of electr. state)

$C_{\infty v}$ symmetry group



(1-4) correspond to the coordinate part of the symmetry group

(5) Symmetry with respect to exchange of electrons – total spin *S*.

$$S = \sum s_i$$

Standard notations

$^{2S+1}\Lambda^{+/-}$

Molecular term

Examples $^1\Sigma^+$, $^3\Pi^-$

Homonuclear molecule

R (internuclear distance) is fixed.

Symmetry of electronic wave functions:

(1) Translation in space.

O=**T**; ω=***p*** (linear momentum)

(2) Rotation in space.

O=**R**; ω=***L*** (angular momentum)

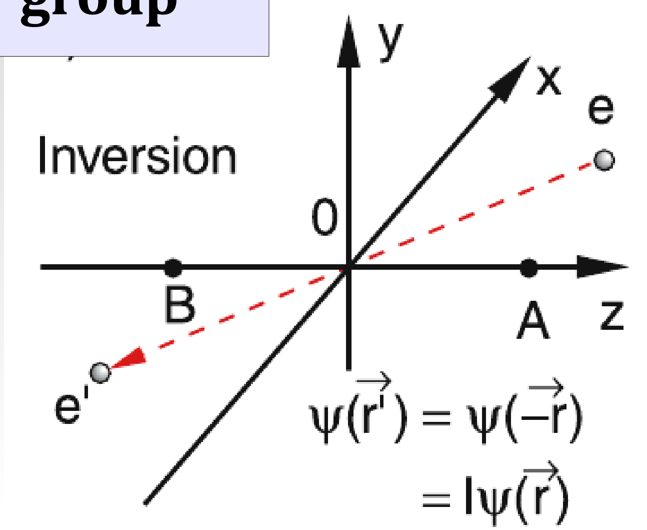
(3) Rotation about the molecular *Z* axis.

O=$\mathbf{R_z}$; ω=Λ (projection of angular momentum on *Z*)

(4) Reflection through a plane containing *Z*.

O=**σ**; ω=+/− (sign of electronic state)

$D_{\infty h}$ symmetry group



(5) Inversion of electronic state

O=**I**; ω=g/u

(1-5) corresponds to the coordinate part of the symmetry group

(6) Total spin *S*.

Standard notations

$^{2S+1}\Lambda_{g/u}^{+/-}$

Molecular term

Examples $^1\Sigma_g^+$, $^3\Pi_u^-$

Symmetry of a diatomic molecule

If the interaction between spin and orbital ang. momentum is strong.

(1) Translation in space.

O=**T**; ω=p (linear momentum)

(2) Rotation in space.

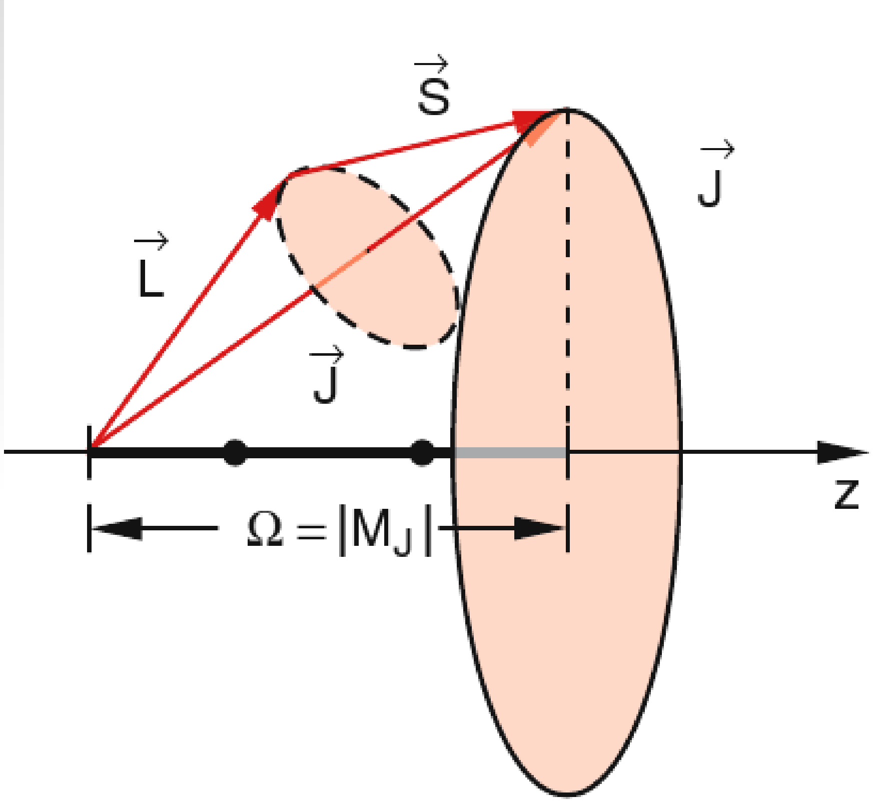
O=**R**; ω=J (total angular momentum, $J=L+S$)

(3) Rotation about the molecular Z axis.

O=$\mathbf{R}_z$; ω=Ω (projection Ω=Λ+Σ of angular momentum J on Z)

(4) Reflection through a plane containing Z.

O=**σ**; ω=+/− (sign of electr. state)



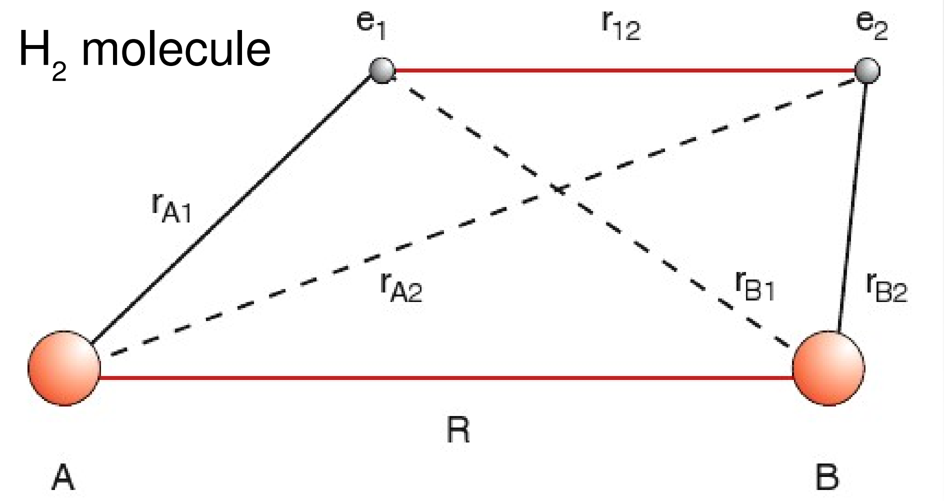
Standard notations

$\Omega^{+/-}$ or $\Omega_{g/u}^{+/-}$

Diatomic molecule: H_2 example

We will use the Born-Oppenheimer approximation

$$\hat{H}^{el} = -\frac{\hbar^2}{2m}\left(\nabla_1^2+\nabla_2^2\right)+ e^2\left(-\frac{1}{r_{A1}}-\frac{1}{r_{B1}}-\frac{1}{r_{A2}}-\frac{1}{r_{B2}}+\frac{1}{r_{12}}+\frac{1}{R}\right)$$



1. LCAO-MO approximate adiabatic states

$$\Phi_s(1)=\frac{1}{\sqrt{2+2S_{AB}}}\left(\phi_A(1)+\phi_B(1)\right)$$

$$\Phi_s(2)=\frac{1}{\sqrt{2+2S_{AB}}}\left(\phi_A(2)+\phi_B(2)\right)$$

First electron
Second electron

Overlap integral

Atomic orbital on atom A

Atomic orbital on atom B

LCAO-MO means linear combination of atomic orbitals

LCAO-MO can represent (but overestimates) the possibility for dissociation to H^-+H^+.

$$\Phi(\boldsymbol{r}_1,\boldsymbol{r}_2,s_1,s_2)=\Phi_s(\boldsymbol{r}_1)\cdot\Phi_s(\boldsymbol{r}_2) \times\left[\chi^+(1)\chi^-(2)-\chi^+(2)\chi^-(1)\right]$$

Electron spin functions

S=0 (singlet) state,

Improvement:

$$\Phi_s^{MO}=\frac{1}{2+2S_{AB}} \times\left[a(1)a(2)+b(1)b(2)+a(1)b(2)+a(2)b(1)\right]$$

$$\Downarrow$$

$$\Phi_s(\boldsymbol{r}_1,\boldsymbol{r}_1)=c_3\left[a(1)b(2)+a(2)b(1)\right] +\lambda\left[a(1)a(2)+b(1)b(2)\right]$$

Variational parameter

Diatomic molecule: H_2 example

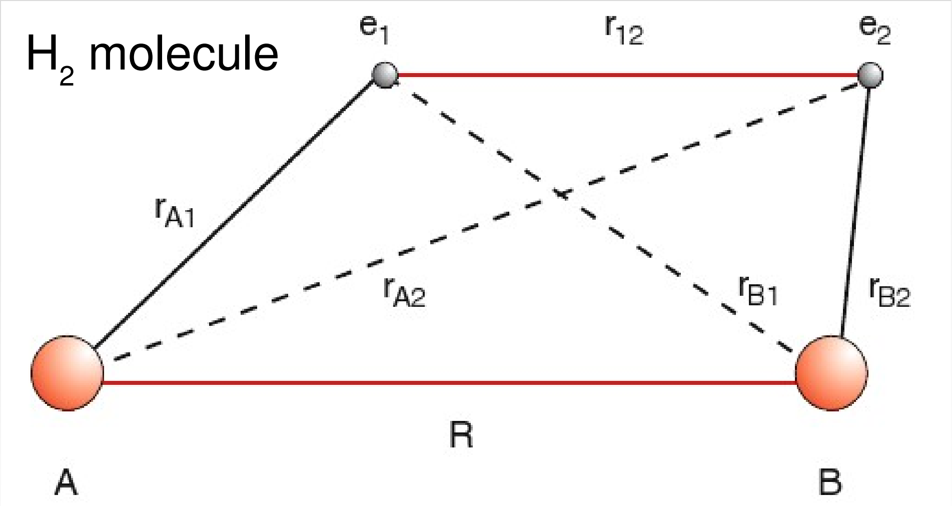
2. Heitler-London approx. adiabatic states

$$\Phi_{a,s} = c\left(\phi_A(1)\phi_B(2) \pm \phi_A(2)\phi_B(1)\right)$$

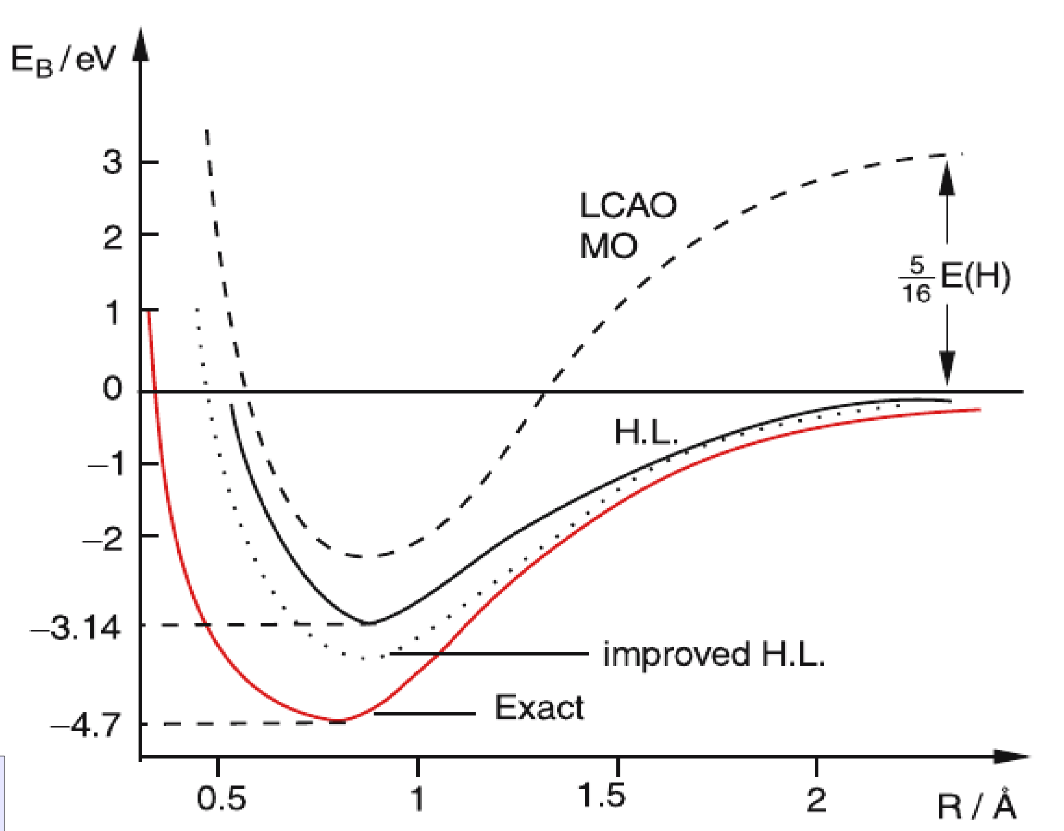
$$c = \left[2\left(1 \pm S_{AB}^2\right)\right]^{-1/2}$$

Overlap integral

Normalization constant



- ∗H-L approximation describes well the H+H dissociation but not H^-+H^+.
- ∗The term for H^-+H^+, in principle, can explicitly be added (with parameter λ) into the total wave function. At this stage, the two approximations become equivalent.
- ∗Further improvements: include more atomic states (2-100 or more)



LCAO-MO

$$\Phi(\boldsymbol{r}_1, \boldsymbol{r}_2) = \Phi(\boldsymbol{r}_1)\Phi(\boldsymbol{r}_2) \qquad \Phi(\boldsymbol{r}_i) = \sum_{k=1}^{N} c_k \phi_k$$

H.-L.

$$\Phi(\boldsymbol{r}_1, \boldsymbol{r}_2) = \sum_{i,k} c_i \phi_i(1)\phi_k(2)$$

Singlet states, for simplicity

More advanced methods

In modern calculations, one uses more advanced methods such as

∗Hartree-Fock method-HF or self-consistent field - SCF,

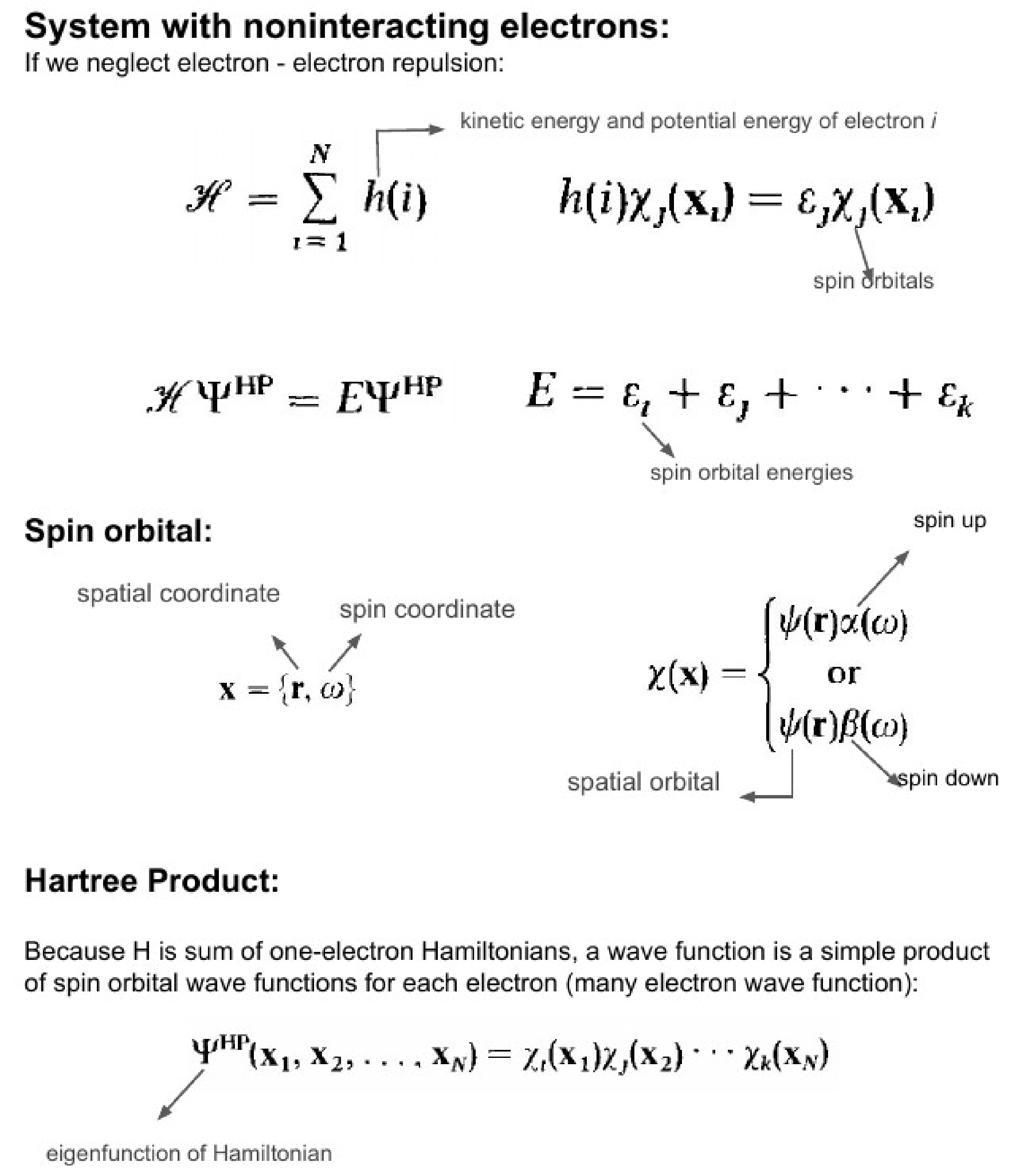
∗Multi-reference configuration interaction (MRCI),

∗Coupled-cluster methods - CCSDT, CCSD(D),

∗Density-functional theory - DFT

∗Møller–Plesset perturbation theory - MP2, MP3,

∗others.



System with noninteracting electrons:

If we neglect electron - electron repulsion:

kinetic energy and potential energy of electron *i*

$$\mathscr{H} = \sum_{i=1}^{N} h(i) \qquad h(i)\chi_j(\mathbf{x}_i) = \varepsilon_j\chi_j(\mathbf{x}_i)$$

spin orbitals

$$\mathscr{H}\Psi^{HP} = E\Psi^{HP} \qquad E = \varepsilon_i + \varepsilon_j + \cdots + \varepsilon_k$$

spin orbital energies

Spin orbital:

spatial coordinate

spin coordinate

$$\mathbf{x} = \{\mathbf{r}, \omega\}$$

spin up

$$\chi(\mathbf{x}) = \begin{cases} \psi(\mathbf{r})\alpha(\omega) \\ \text{or} \\ \psi(\mathbf{r})\beta(\omega) \end{cases}$$

spatial orbital

spin down

Hartree Product:

Because H is sum of one-electron Hamiltonians, a wave function is a simple product of spin orbital wave functions for each electron (many electron wave function):

$$\Psi^{HP}(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) = \chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2)\cdots\chi_k(\mathbf{x}_N)$$

eigenfunction of Hamiltonian

Slater determinants

The Hartree product does not satisfy the Pauli antisymmetry principle.

The way to make the wave functions to be antisymmetric:

$$\Psi_{12}^{\mathrm{HP}}(\mathbf{x}_1, \mathbf{x}_2) = \chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2)$$

$$\Psi_{21}^{\mathrm{HP}}(\mathbf{x}_1, \mathbf{x}_2) = \chi_i(\mathbf{x}_2)\chi_j(\mathbf{x}_1)$$

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = 2^{-1/2}(\chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2) - \chi_j(\mathbf{x}_1)\chi_i(\mathbf{x}_2))$$

The wave function vanishes if both electrons occupy the spin orbital. The wave function is antisymmetric with respect to the interchange of the coordinates of the two electrons.

Antisymmetric wave function can be written as a determinant:

spin orbitals

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = 2^{-1/2}\begin{vmatrix} \chi_i(\mathbf{x}_1) & \chi_j(\mathbf{x}_1) \\ \chi_i(\mathbf{x}_2) & \chi_j(\mathbf{x}_2) \end{vmatrix} = 2^{-1/2}(\chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2) - \chi_j(\mathbf{x}_1)\chi_i(\mathbf{x}_2))$$

normalization factor

spatial orbital

spin up

$$\chi(\mathbf{x}) = \begin{cases} \psi(\mathbf{r})\alpha(\omega) \\ \text{or} \\ \psi(\mathbf{r})\beta(\omega) \end{cases}$$

spin down

$$\mathbf{x} = \{\mathbf{r}, \omega\}$$

N-electron system

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) = (N!)^{-1/2} \begin{vmatrix} \chi_i(\mathbf{x}_1) & \chi_j(\mathbf{x}_1) & \cdots & \chi_k(\mathbf{x}_1) \\ \chi_i(\mathbf{x}_2) & \chi_j(\mathbf{x}_2) & & \chi_k(\mathbf{x}_2) \\ \vdots & \vdots & & \vdots \\ \chi_i(\mathbf{x}_N) & \chi_j(\mathbf{x}_N) & \cdots & \chi_k(\mathbf{x}_N) \end{vmatrix}$$

N electrons occupying *N* spin orbitals without specifying which electron is in which orbital

rows: electrons
columns: spin orbitals

normalization factor

Another notation that only shows diagonal elements of the determinant:

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) = |\chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2) \cdots \chi_k(\mathbf{x}_N)\rangle$$

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) = |\chi_i\chi_j \cdots \chi_k\rangle$$

$$|\cdots \chi_m \cdots \chi_n \cdots\rangle = -|\cdots \chi_n \cdots \chi_m \cdots\rangle$$

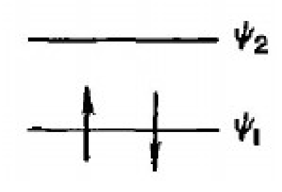
$$\mathbf{x} = \{\mathbf{r}, \omega\}$$

Ground HF state

For two-electron system:

$$|\Psi_0\rangle = |\chi_1\chi_2\rangle$$

$$|\Psi_0\rangle = |\psi_1\bar{\psi}_1\rangle = |1\bar{1}\rangle$$



$$\chi_1(\mathbf{x}) = \psi_1(\mathbf{r})\alpha(\omega)$$

$$\chi_2(\mathbf{x}) = \psi_1(\mathbf{r})\beta(\omega)$$

with α spin

$\chi_1 \equiv \psi_1$

with β spin

$\chi_2 \equiv \bar{\psi}_1$

For *N*-electron system:

$$|\Psi_0\rangle = |\chi_1\chi_2\cdots\chi_a\chi_b\cdots\chi_N\rangle$$

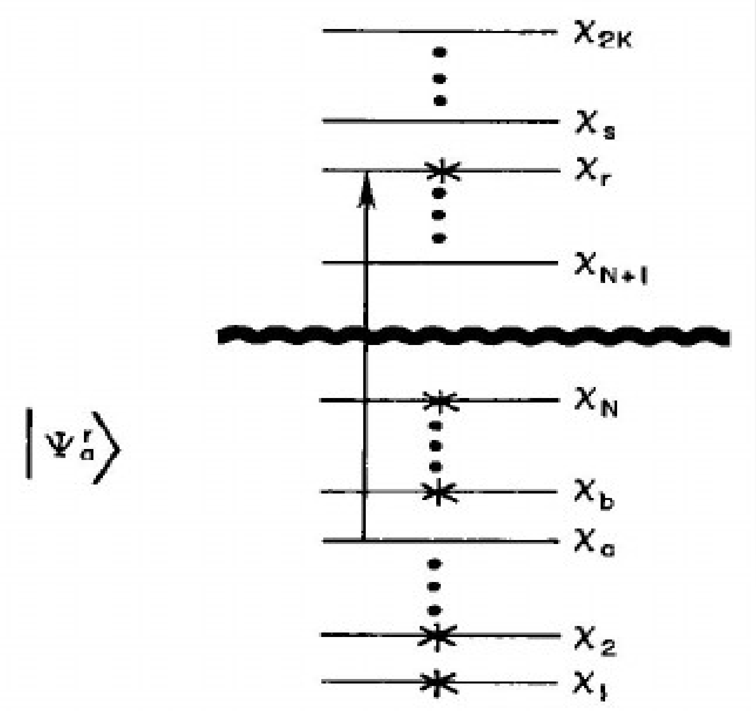
The number of different single determinants that one can form from *N* electrons and 2*K* spin orbitals: (the HF ground state is just one of these)

$$\binom{2K}{N} = \frac{(2K)!}{N!(2K-N)!}$$

$$\mathbf{x} = \{\mathbf{r}, \omega\}$$

Excited HF state

A singly excited determinant is the one in which an electron occupying the χ_a spin-orbital in the HF ground state is *promoted* to a *virtual* spin orbital χ_r :



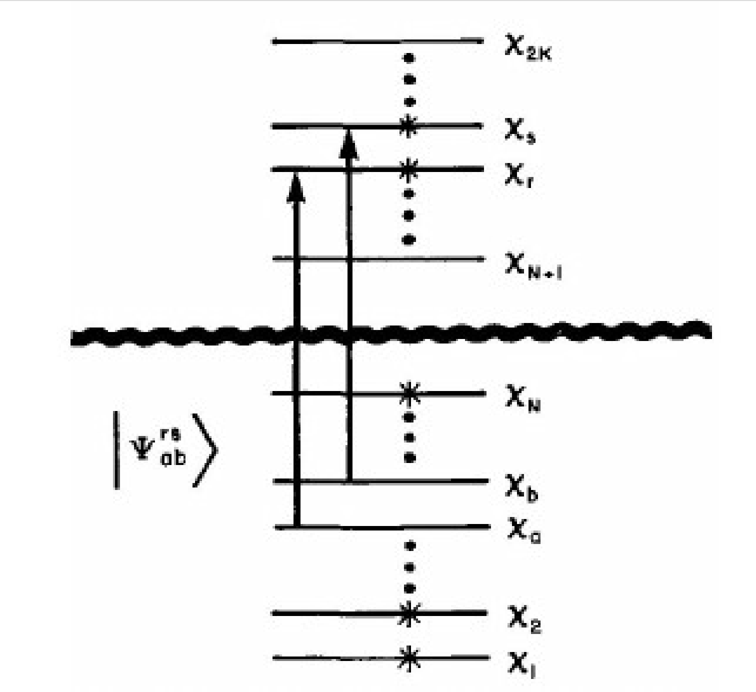
$$|\Psi_0\rangle = |\chi_1\chi_2\cdots\chi_a\chi_b\cdots\chi_N\rangle \longrightarrow |\Psi_a^r\rangle = |\chi_1\chi_2\cdots\chi_r\chi_b\cdots\chi_N\rangle$$

$$\mathbf{x} = \{\mathbf{r}, \omega\}$$

How to solve the electronic part of the equation?

$$\hat{H}_0 \varphi_n(R_f, r) = \varepsilon_n(R) \varphi_n(R_f, r)$$

Doubly-excited HF state

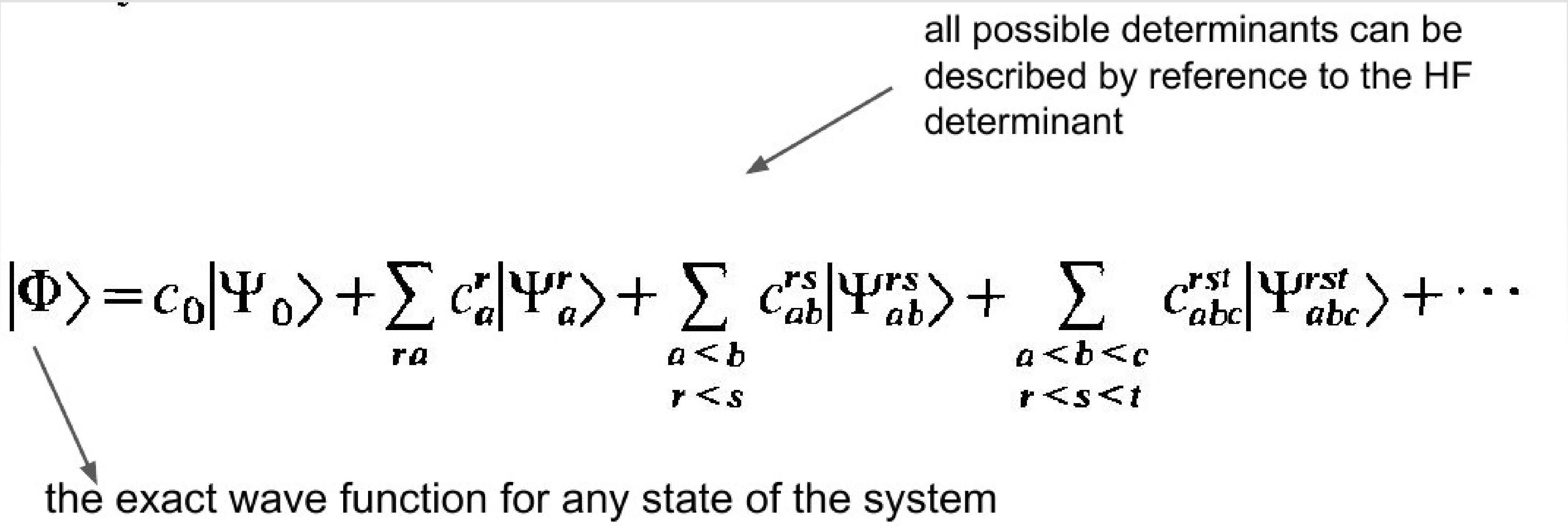


$$|\Psi_0\rangle = |\chi_1\chi_2\cdots\chi_a\chi_b\cdots\chi_N\rangle \longrightarrow |\Psi_{ab}^{rs}\rangle = |\chi_1\chi_2\cdots\chi_r\chi_s\cdots\chi_N\rangle$$

All C_{2K}^{N} determinants can thus be classified as either the HF ground state or singly, doubly, triply, … , *m*-tuply excited states.

$$\mathbf{x} = \{\mathbf{r}, \omega\}$$

The use of excited determinants as *N*-electron basis functions:



all possible determinants can be described by reference to the HF determinant

$$|\Phi\rangle = c_0|\Psi_0\rangle + \sum_{ra} c_a^r|\Psi_a^r\rangle + \sum_{\substack{a<b\\ r<s}} c_{ab}^{rs}|\Psi_{ab}^{rs}\rangle + \sum_{\substack{a<b<c\\ r<s<t}} c_{abc}^{rst}|\Psi_{abc}^{rst}\rangle + \cdots$$

the exact wave function for any state of the system

Configuration interaction – CI.

$$H\Phi = E\Phi$$

Full CI
Multi-reference CI – MRCI

*M*x*M* eigenvalue problem

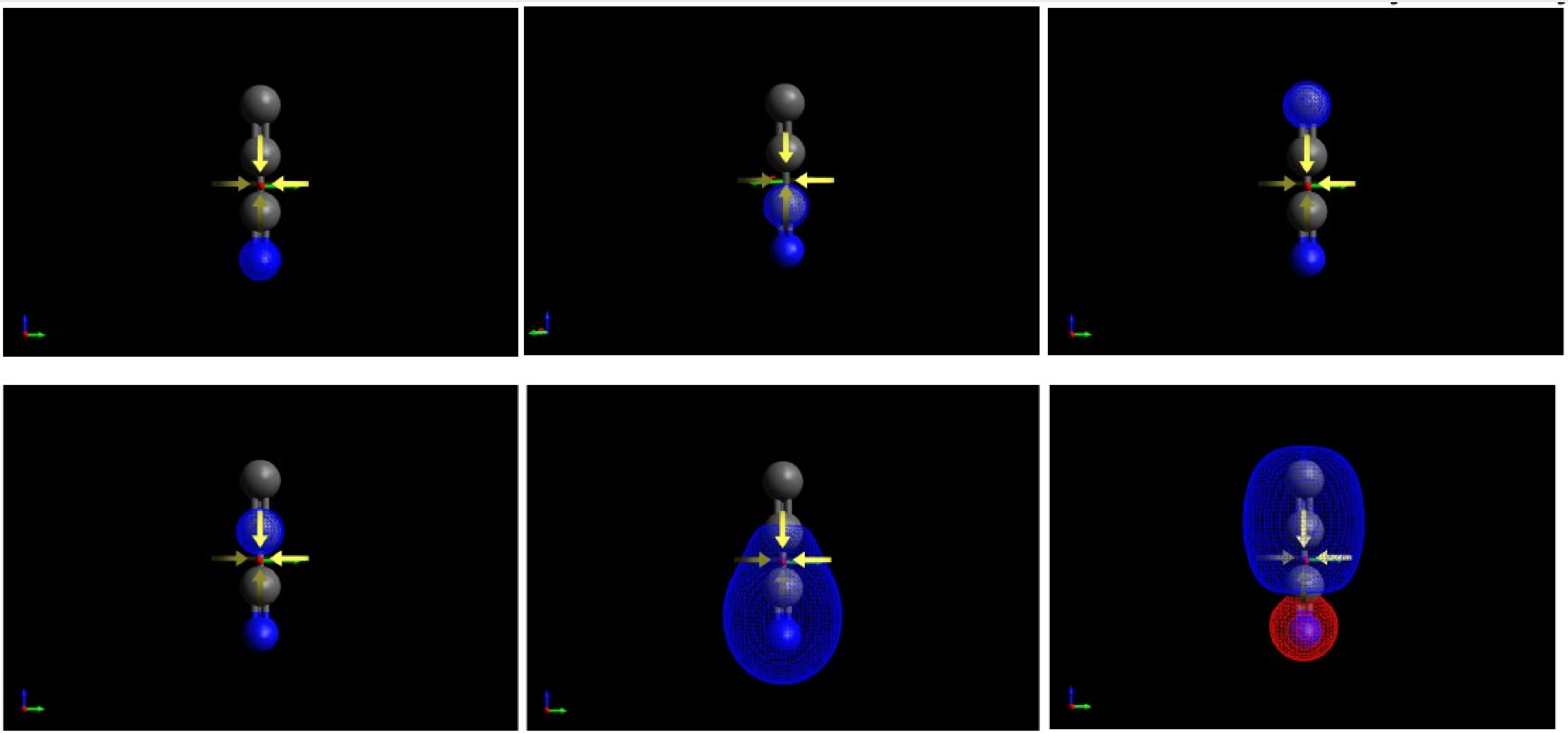
$$H\vec{c} = E\vec{c}$$

$$\mathbf{x} = \{\mathbf{r}, \omega\}$$

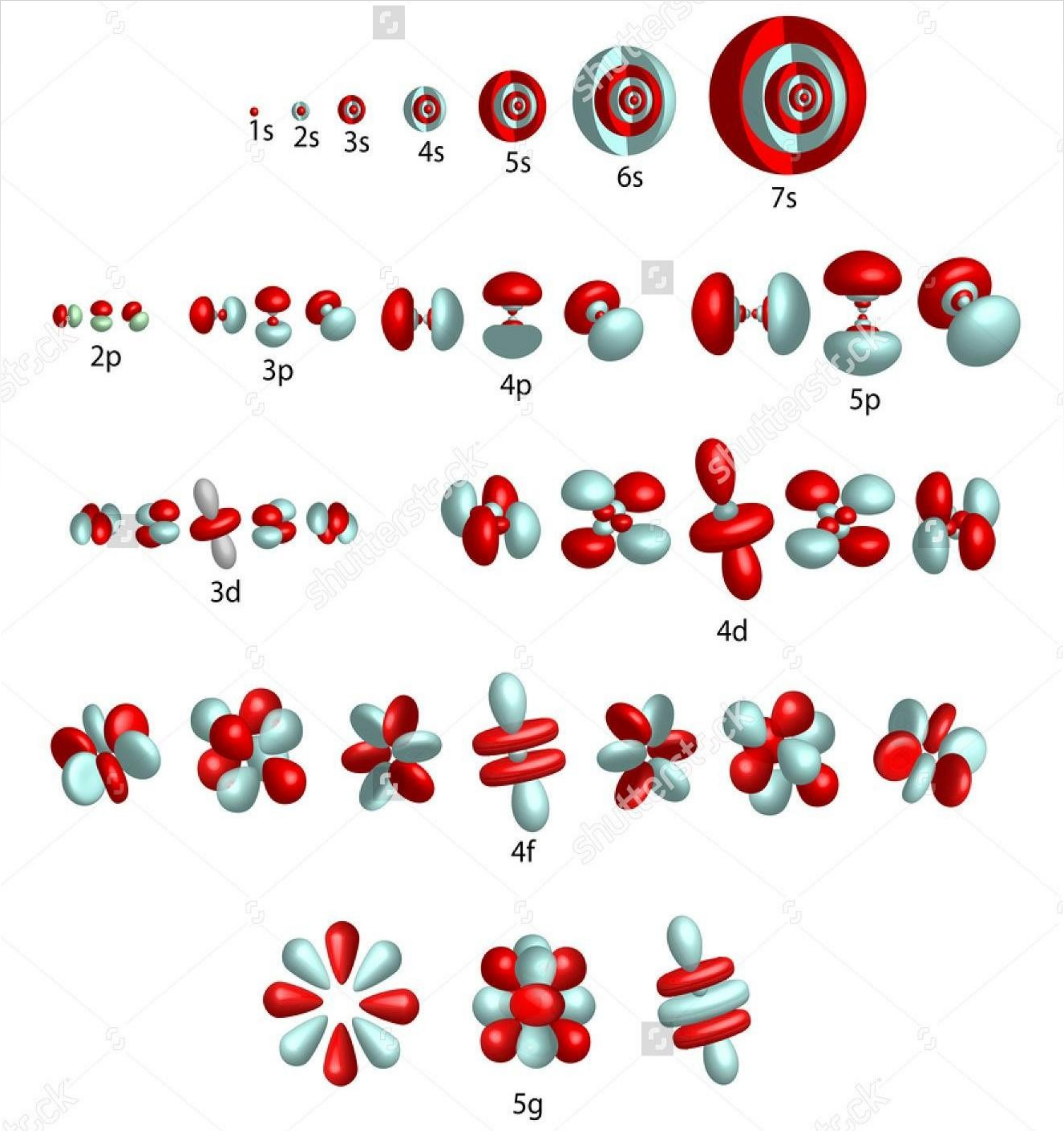
Example: HF orbitals of C_3N^-

σ^+ HF orbitals

occupied in the ground state

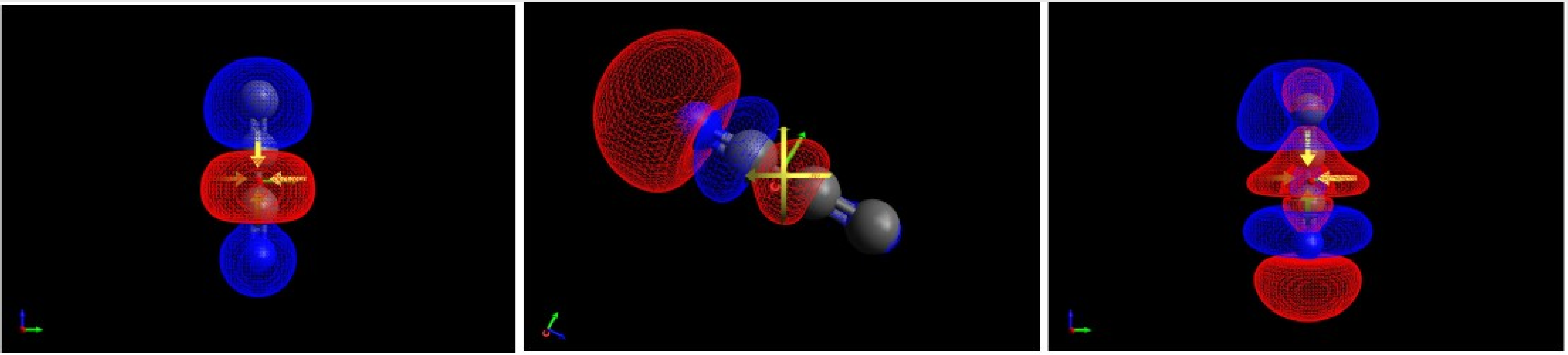


Atomic orbitals for comparison

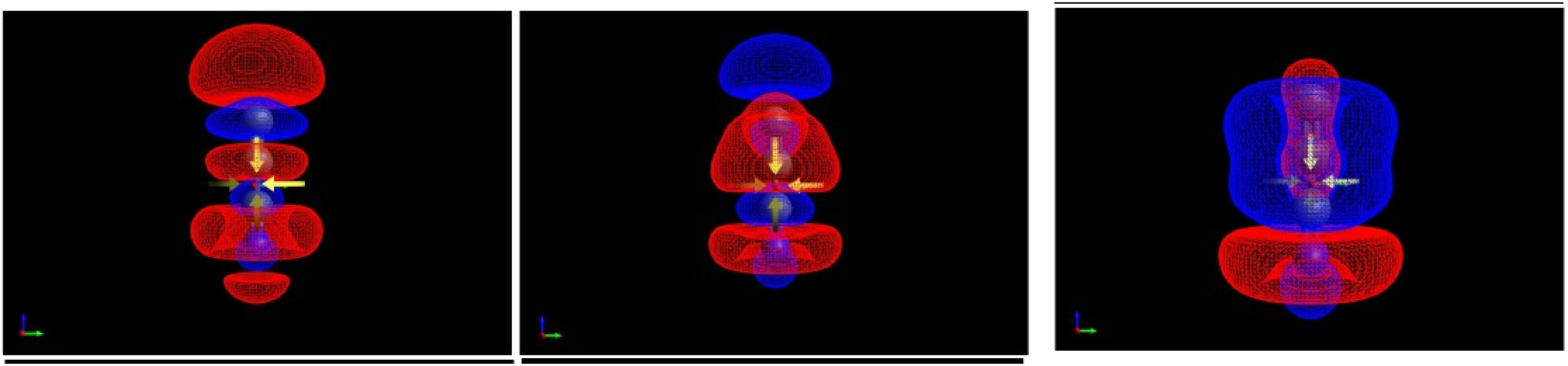


Example: HF orbitals of C_3N^-

σ^+ HF orbitals, occupied in the ground state



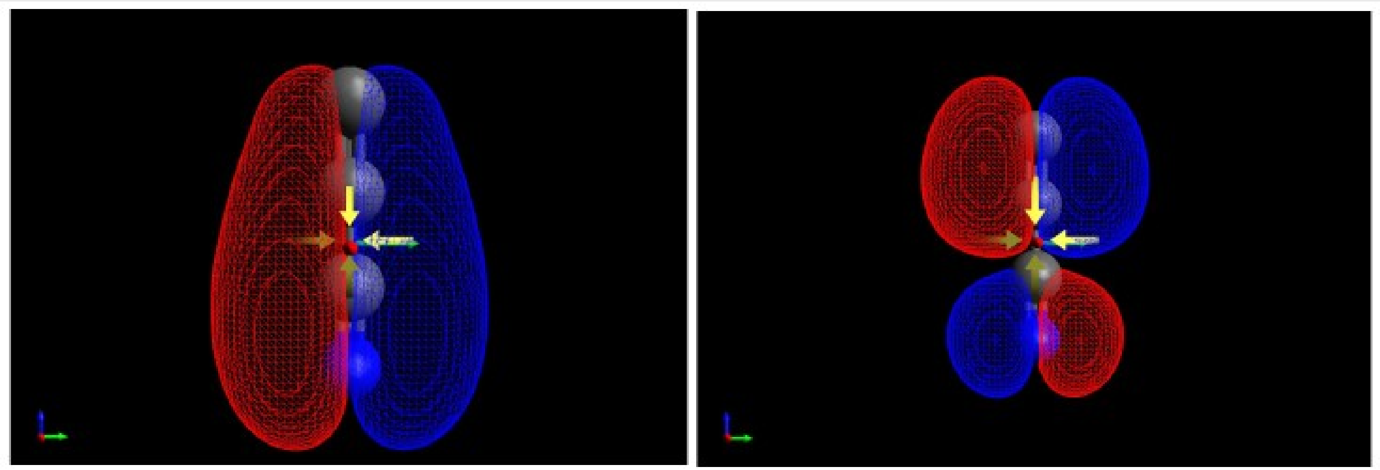
unoccupied in the ground state



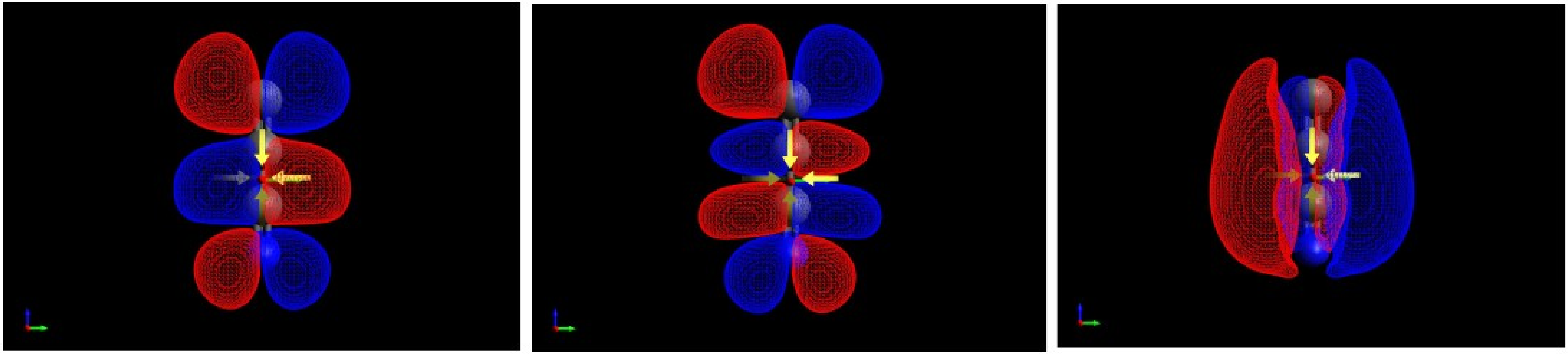
Example: HF orbitals of C_3N^-

π HF orbitals, doubly-degenerate

occupied in the ground state



unoccupied in the ground state



C_3N^- ground state slater determinant

$$\Psi_0 = \left| \begin{array}{cccccccccc} \overset{\text{With } \alpha \text{ spin}}{\uparrow} & \overset{\text{With } \beta \text{ spin}}{\nearrow} & & & & & & & & \\ \psi_{1.1}(r_1) & \bar{\psi}_{1.1}(r_1)\ldots\psi_{9.1}(r_1) & \bar{\psi}_{9.1}(r_1) & \psi_{1.2}(r_1).. & \psi_{2.2}(r_1) & \bar{\psi}_{2.2}(r_1) & \psi_{1.3}(r_1) & \bar{\psi}_{1.3}(r_1) & \psi_{2.3}(r_1) & \bar{\psi}_{2.3}(r_1) \\ \psi_{1.1}(r_2) & \bar{\psi}_{1.1}(r_2)\ldots\psi_{9.1}(r_2) & \bar{\psi}_{9.1}(r_2) & \psi_{1.2}(r_2).. & \psi_{2.2}(r_2) & \bar{\psi}_{2.2}(r_2) & \psi_{1.3}(r_2) & \bar{\psi}_{1.3}(r_2) & \psi_{2.3}(r_2) & \bar{\psi}_{2.3}(r_2) \\ \vdots & & & & & & & & & \\ \psi_{1.1}(r_{26}) & \bar{\psi}_{1.1}(r_{26})\ldots\psi_{9.1}(r_{26}) & \bar{\psi}_{9.1}(r_{26}) & \psi_{1.2}(r_{26}) & \psi_{2.2}(r_{26}) & \bar{\psi}_{2.2}(r_{26}) & \psi_{1.3}(r_{26}) & \bar{\psi}_{1.3}(r_{26}) & \psi_{2.3}(r_{26}) & \bar{\psi}_{2.3}(r_{26}) \end{array} \right|$$

MRCI calculations

$$|\Phi\rangle = c_0|\Psi_0\rangle + \sum_{ra} c_a^r|\Psi_a^r\rangle + \sum_{\substack{a<b\\ r<s}} c_{ab}^{rs}|\Psi_{ab}^{rs}\rangle + \sum_{\substack{a<b<c\\ r<s<t}} c_{abc}^{rst}|\Psi_{abc}^{rst}\rangle + \cdots$$

$$H\vec{c} = E\vec{c}$$

Many codes available to perform quantum chemistry calculations

Bound electronic states:

https://en.wikipedia.org/wiki/List_of_quantum_chemistry_and_solid-state_physics_software

- Molpro
- Columbus
- Gaussian
- *and many others*

Electron-scattering codes:

- UK R-matrix
- Complex-Kohn variational method

Rotational states of molecules

Rotational Hamiltonian

Approximation: Solid body with atoms rigidly fixed – **rigid rotator or a top**

∗Classical kinetic energy: $$T=\frac{1}{2}\sum_{i,k} I_{ik}\Omega_i\Omega_k$$

∗Tensor of inertia $$I_{ik}=\sum m\left(x_l^2\delta_{ik}-x_ix_k\right)$$

∗

∗

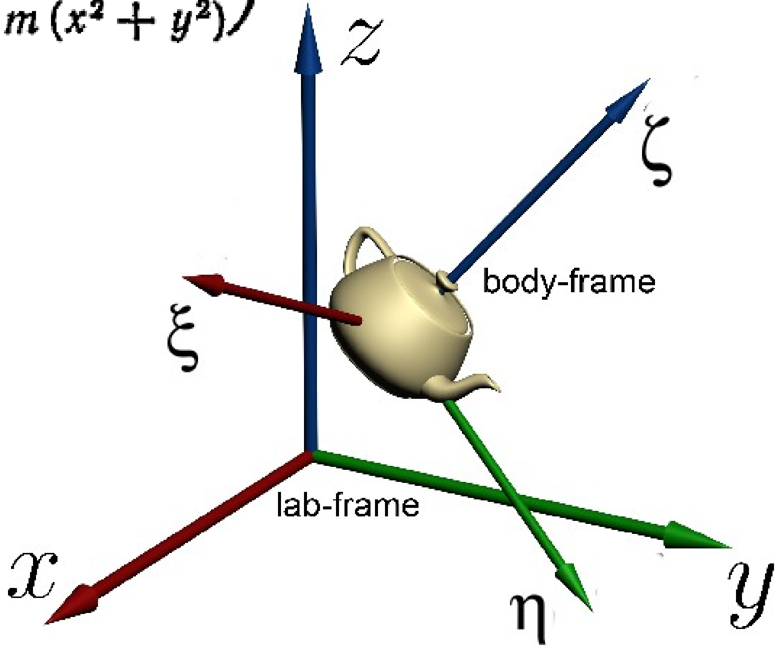
∗

∗

∗

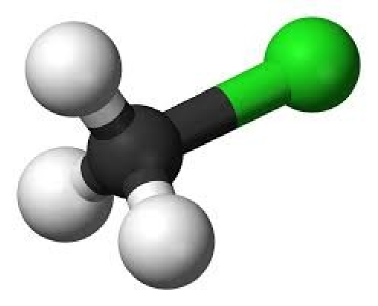
$$I_{ik}=\begin{pmatrix} \sum m\,(y^2+z^2) & -\sum mxy & -\sum mxz \\ -\sum myx & \sum m\,(x^2+z^2) & -\sum myz \\ -\sum mzx & -\sum mzy & \sum m\,(x^2+y^2) \end{pmatrix}.$$

∗Instantaneous angular velocities: Ω_i



Rotational Hamiltonian

- The body-frame axes ξ, η, and ζ are along principal axes of inertia.

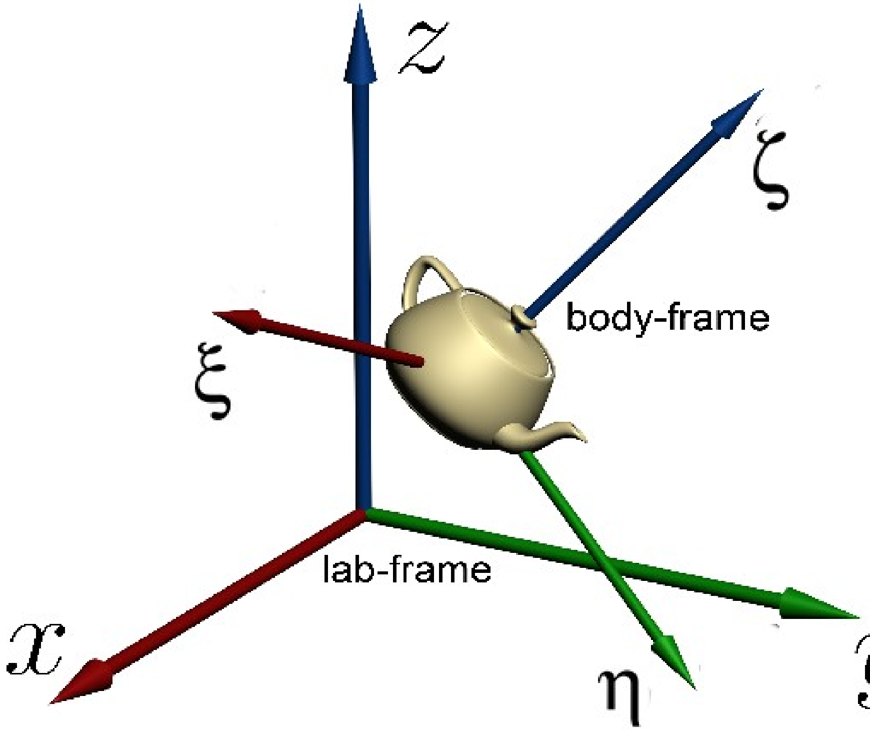


$$T=\frac{1}{2}\left(I_A\Omega_\xi+I_B\Omega_\xi+I_C\Omega_\xi\right)=\frac{1}{2}\left(\frac{J_\xi^2}{I_A}+\frac{J_\eta^2}{I_B}+\frac{J_\zeta^2}{I_C}\right)$$

$$\hat{H}=\frac{\hbar^2}{2}\left(\frac{\hat{J}_\xi^2}{I_A}+\frac{\hat{J}_\eta^2}{I_B}+\frac{\hat{J}_\zeta^2}{I_C}\right)$$

$$\hat{J}_\xi\hat{J}_\eta-\hat{J}_\eta\hat{J}_\xi=-i\hat{J}_\zeta,$$

- Operators J^2, J_z, and J_ζ commute with each other.



Spherical top molecules

$$\hat{H} = \frac{\hbar^2}{2}\left(\frac{\hat{J}_\xi^2}{I_A} + \frac{\hat{J}_\eta^2}{I_B} + \frac{\hat{J}_\zeta^2}{I_C}\right)$$

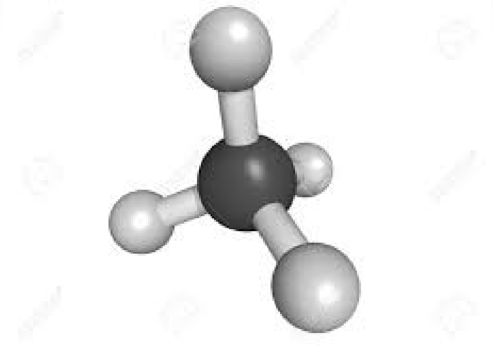
$I_A = I_B = I_C = I$

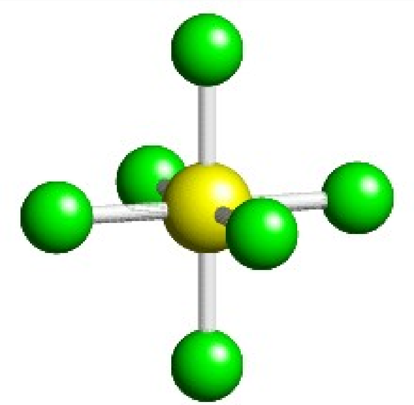
$$\hat{H} = \frac{\hbar^2}{2I}\hat{\mathbf{J}}^2$$

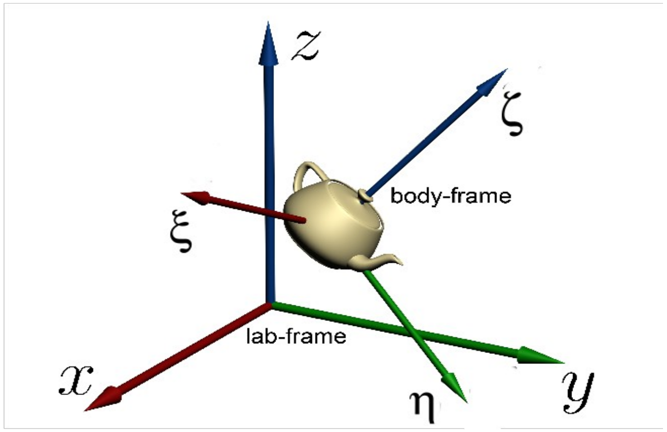
$$E = \frac{\hbar^2}{2I} J(J+1)$$

Examples:
SF_6, CH_4

Each energy is (2*J*+1)-times degenerate over projections *M* on a laboratory axis (say, *z*) and (2*J*+1)-times degenerate over projections *k* on a molecular axis (say, *ζ*).







Symmetrical top

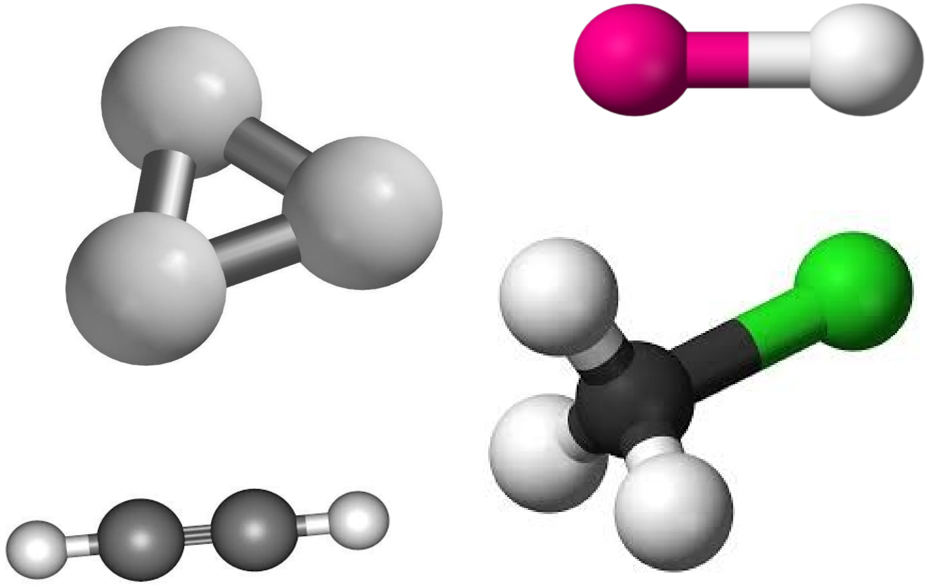
$$\hat{H} = \frac{\hbar^2}{2}\left(\frac{\hat{J}_\xi^2}{I_A} + \frac{\hat{J}_\eta^2}{I_B} + \frac{\hat{J}_\zeta^2}{I_C}\right)$$

$I_A = I_B \neq I_C$

$$\hat{H} = \frac{\hbar^2}{2I_A}\left(\hat{J}_\xi^2 + \hat{J}_\eta^2\right) + \frac{\hbar^2}{2I_C}\hat{J}_\zeta^2 = \frac{\hbar^2}{2I_A}\hat{\mathbf{J}}^2 + \frac{\hbar^2}{2}\left(\frac{1}{I_C} - \frac{1}{I_A}\right)\hat{J}_\zeta^2$$

$$E = \frac{\hbar^2}{2I_A}J(J+1) + \frac{\hbar^2}{2}\left(\frac{1}{I_C} - \frac{1}{I_A}\right)k^2$$

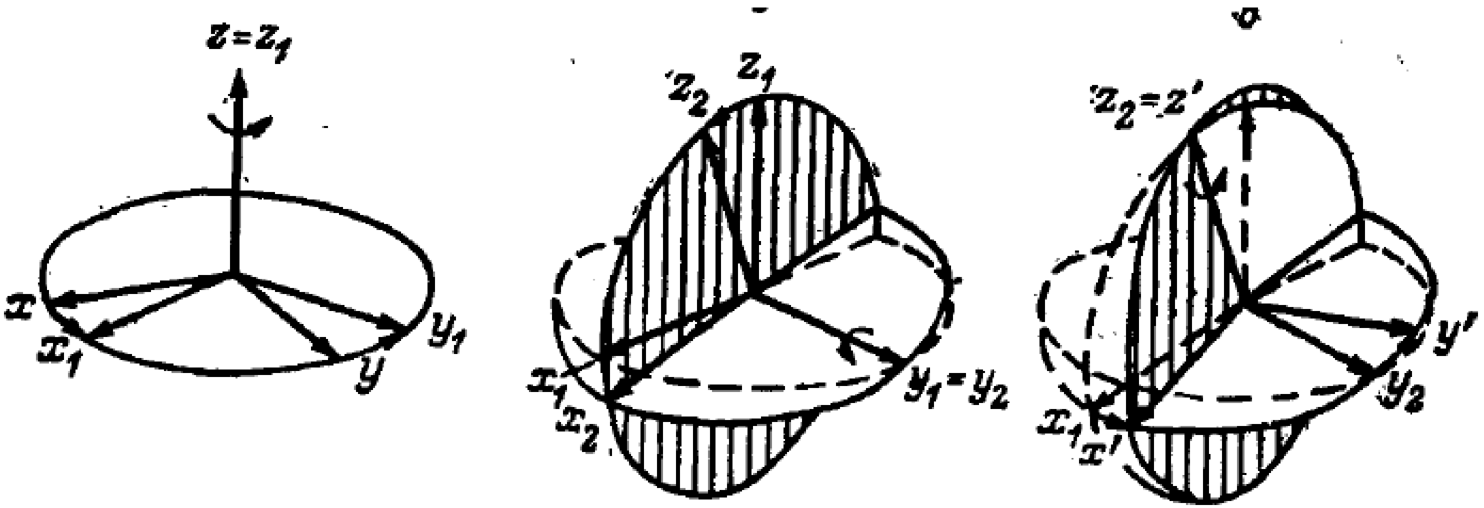
- Each energy is (2*J*+1)-times degenerate over projections *M* on the *z*-axis and degenerate with respect to sign of *k*.
- Each rotational state is characterized by quantum numbers *J, k,* and *M*.



Euler angles

- Any rotation of a coordinate system ($xyz \rightarrow x'y'z'$) can be described by three Euler angles, α, β, and γ.

- α represents a rotation around the z axis,
- β represents a rotation around new y_1 axis,
- γ represents a rotation around new $z_2=z'$ axis.



Rotational Wigner functions

- Suppose, we have an arbitrary state $|JM'\rangle = \Psi_{JM'}(\mathbf{r}')$ having a definite angular momentum J and a definite projection M' of the momentum on an axis z'.
- Suppose we want to write this state in a coordinate system (xyz) rotated with respect to ($x'y'z'$) by the three Euler angles.
- The transformation is written as

$$|JM'\rangle = \sum_{M=-J}^{J} |JM\rangle\langle JM|JM'\rangle$$

$$\Psi_{JM'}(\vartheta', \varphi', \sigma') = \sum_{M=-J}^{J} \Psi_{JM}(\vartheta, \varphi, \sigma)\, D^{J}_{MM'}(\alpha, \beta, \gamma)$$

Wigner functions

$$D^{J}_{MM'}(\alpha, \beta, \gamma) = e^{-iM\alpha} d^{J}_{MM'}(\beta)\, e^{-iM'\gamma}$$

Eigenstates of symmetrical top

- Eigenstates of symmetric top are eigenstates of $\boldsymbol{J}^2$, $\boldsymbol{J}_z$, and $\boldsymbol{J}_\zeta$.
- We can consider these eigenstates in the two coordinate systems, lab frame - *xyz* and molecular frame - ξηζ.

$$\psi_{Jk} = \sum_{M=-J}^{J} \psi_{JM} D^{J}_{Mk}(\alpha\beta\gamma)$$

$$\psi_{JM} = \sum_{k=-J}^{J} \psi_{Jk} \left(D^{J}_{Mk}(\alpha\beta\gamma) \right)^*$$

- The state ψ_{JM} should have a definite *k*, because it is an eigenstate of operator $\boldsymbol{J}_\zeta$.
- Therefore:

$$\psi_{JMk} = \psi_{Jk} \left(D^{J}_{Mk}(\alpha\beta\gamma) \right)^*$$

- And ψ_{Jk} is constant, i.e. it does not depend on Euler angles.

$$\psi_{JMk} = \sqrt{\frac{2J+1}{8\pi^2}} \left(D^{J}_{Mk}(\alpha\beta\gamma) \right)^*$$

Eigenstate of symmetric top molecules

Asymmetrical top

$$\hat{H} = \frac{\hbar^2}{2}\left(\frac{\hat{J}_\xi^2}{I_A} + \frac{\hat{J}_\eta^2}{I_B} + \frac{\hat{J}_\zeta^2}{I_C}\right)$$

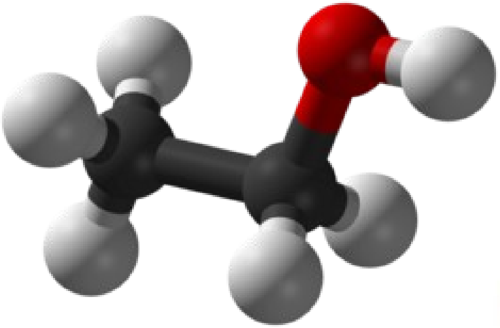
$I_A \neq I_B \neq I_C$

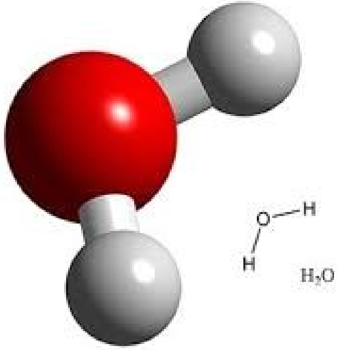
$$\hat{H}\psi_J = E_J\psi_J$$

$$\psi_J = \sum_k c_k \psi_{Jk}$$

$$\sum_{k'} \left(\langle Jk \,|\, H \,|\, Jk' \rangle - E\delta_{kk'}\right) c_{k'} = 0$$

$$\left| \langle Jk \,|\, H \,|\, Jk' \rangle - E\delta_{kk'} \right| = 0$$





Asymmetrical top

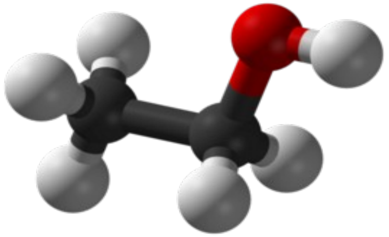
$$\hat{H} = \frac{\hbar^2}{2}\left(\frac{\hat{J}_\xi^2}{I_A} + \frac{\hat{J}_\eta^2}{I_B} + \frac{\hat{J}_\zeta^2}{I_C}\right)$$

$$H_{\text{rot}} = B^{(1)}\hat{N}_1^2 + B^{(2)}\hat{N}_2^2 + B^{(3)}\hat{N}_3^2$$

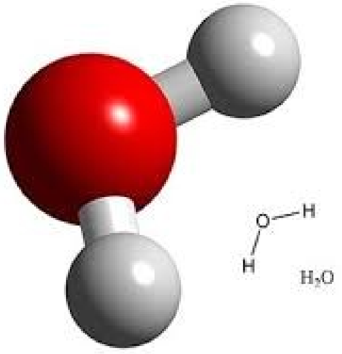
$$H_{\text{rot}} = \frac{B^{(1)} + B^{(2)}}{2}\hat{N}^2 + \left(B^{(3)} - \frac{B^{(1)} + B^{(2)}}{2}\right)\hat{N}_3^2 + \frac{B^{(1)} - B^{(2)}}{4}\left(\hat{N}_+^2 + \hat{N}_-^2\right)$$

where $N_\pm = N_1 \pm \mathrm{i}N_2$ and $\hat{N}^2 = \hat{N}_1^2 + \hat{N}_2^2 + \hat{N}_3^2$

$$\mathscr{R}^{N^+}_{k^+m^+}(\alpha, \beta, \gamma) = \left[\frac{2N^+ + 1}{8\pi^2}\right]^{1/2}\left[D^{N^+}_{m^+,K^+}(\alpha, \beta, \gamma)\right]^*$$

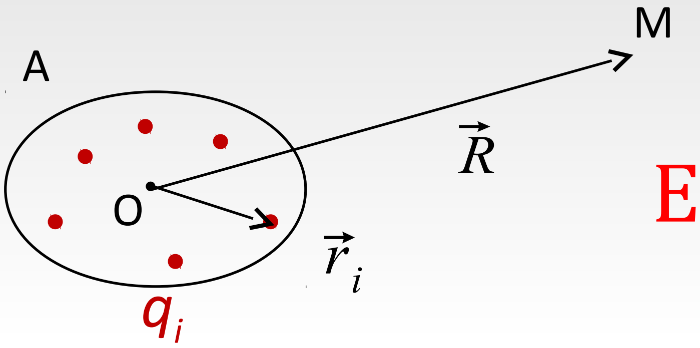


$$\begin{aligned}
\langle N, k, m|\hat{N}^2|N, k, m\rangle &= N(N+1),\\
\langle N, k, m|\hat{N}_3^2|N, k, m\rangle &= k^2,\\
\langle N, k-2, m|\hat{N}_+^2|N, k, m\rangle &= \langle N, k, m|\hat{N}_-^2|N, k-2, m\rangle\\
&= \sqrt{[N(N+1) - (k-1)(k-2)][N(N+1) - k(k-1)]}.
\end{aligned}$$



Long-distance interaction of two charge distributions

Electrostatic potential of a charge distribution



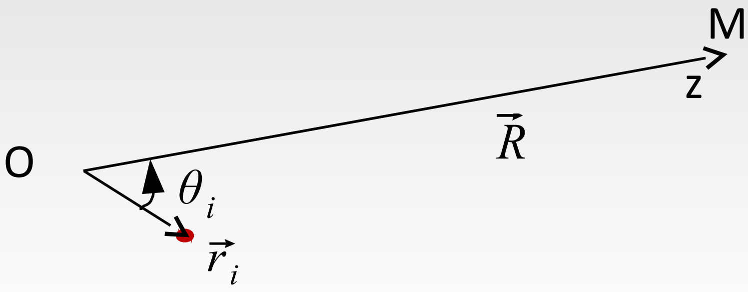
Electrostatic potential at point *M* :

$$\Phi_A\left(\vec{R}\right)=\frac{1}{4\pi\varepsilon_0}\sum_i \frac{q_i}{|\vec{R}-\vec{r}_i|}$$

Assumption: *M* is far from distribution *A*

$$|\vec{R}|>>|\vec{r}_i|$$

Electrostatic potential in a form of multipole moments



Laplace expansion

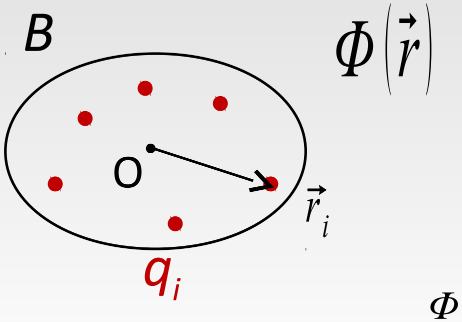
$$\frac{1}{|\vec{R}-\vec{r}_i|}=\frac{1}{R}\sum_L\left(\frac{r_i}{R}\right)^L P_L(\cos\theta_i)$$

$$\Phi_A(R)=\frac{1}{4\pi\varepsilon_0}\left[\frac{1}{R}\underbrace{\sum_i q_i}_{q_{\text{tot}}(A)}+\frac{1}{R^2}\underbrace{\sum_i q_i r_i\cos\theta_i}_{d_z(A)}+\frac{1}{R^3}\underbrace{\sum_i q_i r_i^2\frac{3\cos^2\theta_i-1}{2}}_{\frac{1}{2}Q_{zz}(A)}+\ldots\right]$$

general form of the Laplace expansion

$$\frac{1}{|\mathbf{r}-\mathbf{r}'|}=\sum_{\ell=0}^{\infty}\frac{4\pi}{2\ell+1}\sum_{m=-\ell}^{\ell}(-1)^m\frac{r_<^\ell}{r_>^{\ell+1}}Y_\ell^{-m}(\theta,\varphi)Y_\ell^m(\theta',\varphi')$$

Energy of interaction of two charge distributions



Potential energy of interaction:

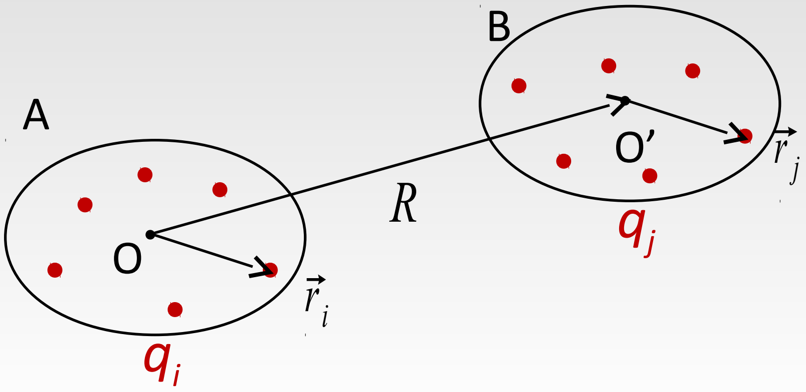
$$V_B=\sum_{i\in B} q_i\Phi\left(\vec r_i\right)$$

$$\Phi_A(R)=\frac{1}{4\pi\varepsilon_0}\left[\frac{1}{R}\sum_i q_i+\frac{1}{R^2}\sum_i q_i r_i\cos\theta_i+\frac{1}{R^3}\sum_i q_i r_i^2\frac{3\cos^2\theta_i-1}{2}+\dots\right]$$

Simplification: Φ varies weakly near B

$$V_B=\underbrace{\left(\sum_i q_i\right)}_{q_{\text{tot}}(B)}\Phi(0)+\underbrace{\sum_i\left(q_i\vec r_i\cdot\vec\nabla_i\Phi(0)\right)}_{-\vec d(B)\cdot\vec E(0)}+\underbrace{\frac{1}{2}\sum_i q_i\sum_{j,k=x,y,z}x_jx_k\frac{\partial^2}{\partial x_j\partial x_k}\Phi(0)}_{\sum_{j,k=x,y,z}Q_{jk}(B)\,\partial^2_{jk}\Phi(0)}+\dots$$

Electrostatic potential
Multipole moments



$$V_{AB}(R)=\frac{1}{4\pi\varepsilon_0}\sum_{L_A,L_B=0}^{+\infty} V_{L_AL_B}(R)$$

(0,0) : charge-charge interaction is $1/R$

(0,1) : charge-dipole interaction is $1/R^2$

(1,0) : dipole-charge interaction is $1/R^2$

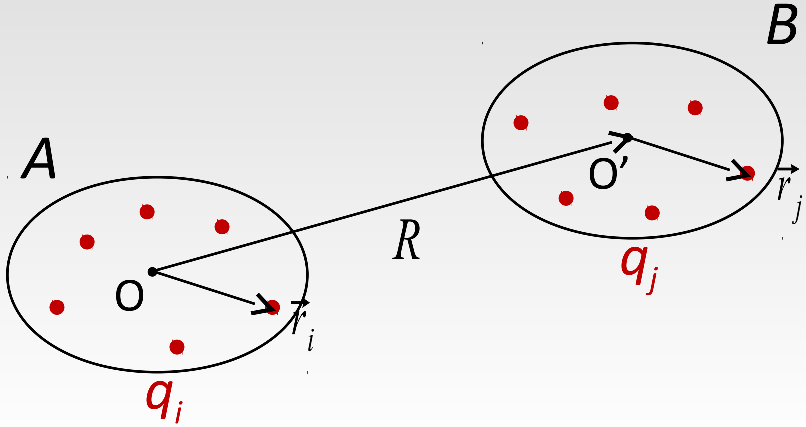
(1,1) : dipole-dipole interaction is $1/R^3$

(0,2) : charge-quadrupole interaction is $1/R^3$

…

(L_A, L_B) : $2^{L_A}-2^{L_B}$ -pole interaction is $R^{-(L_A+L_B+1)}$

Electrostatic potential
Multipole moments



$$V_{AB}=\frac{1}{4\pi\varepsilon_0}\sum_{L_A,L_B=0}^{+\infty}\sum_{M=-L_<}^{+L_<}(-1)^{L_B}\frac{g_M(L_A,L_B)}{R^{1+L_A+L_B}}Q_{L_A}^{M}Q_{L_B}^{-M}$$

tensorial notations: $Q_1^{\pm1}=d_x\pm id_y$

$$L_<=\min(L_A,L_B)$$

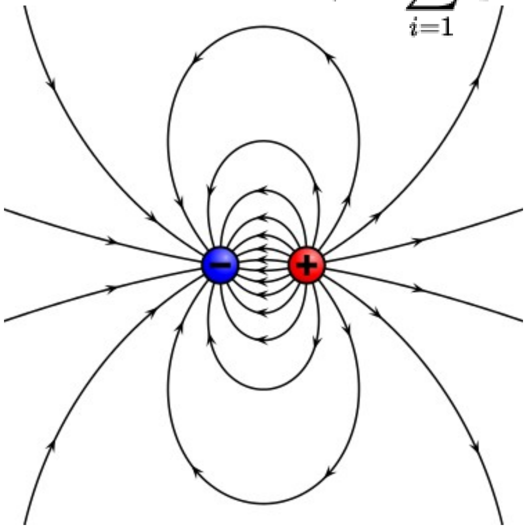
$$g_M(L_A,L_B)=\frac{(-1)^{L}_{B}(L_A+L_B)!}{\sqrt{(L_A-M)!(L_A+M)!(L_B+M)!(L_B-M)!}}$$

Multipole moments

$$V_{AB}=\frac{1}{4\pi\varepsilon_0}\sum_{L_A,L_B=0}^{+\infty}\sum_{M=-L_<}^{+L_<}\left(-1\right)^{L_B}\frac{g_M\left(L_A,L_B\right)}{R^{1+L_A+L_B}}Q_{L_A}^{M}Q_{L_B}^{-M}$$

The field of dipole moment

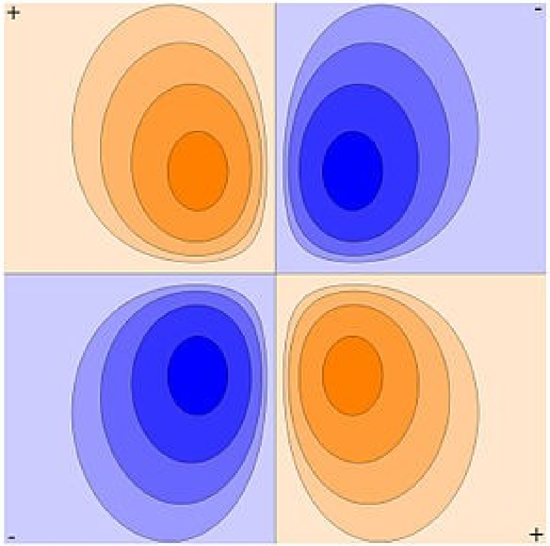
$$\mathfrak{p}=\sum_{i=1}^{N}q_i\,\mathbf{r}_i\,.$$



$$\Phi(\mathbf{r})=\frac{1}{4\pi\varepsilon_0}\frac{\mathbf{p}\cdot\hat{\mathbf{r}}}{r^2}$$

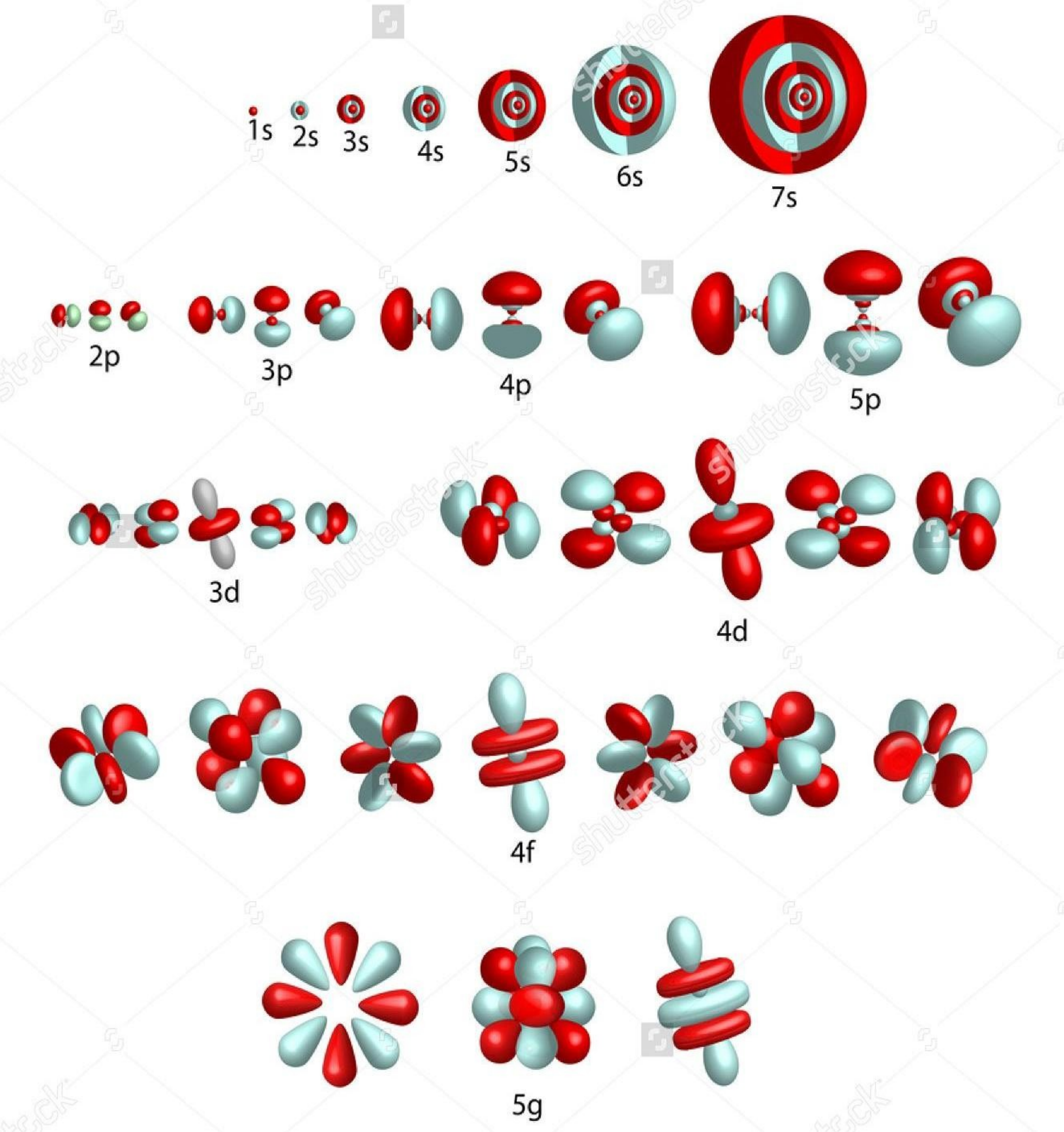
Quadrupole moment

$$Q_{ij}=\sum_l q_l(3r_{il}r_{jl}-\|\overrightarrow{r_l}\|^2\delta_{ij})$$



$$V_q(\mathbf{R})=\frac{k}{|\mathbf{R}|^3}\sum_{i,j}\frac{1}{2}Q_{ij}\,n_in_j\;,$$

Atomic orbitals and multipole moments



Multipole potential as a perturbation

$$E_n = E_{An}^0 + E_{Bn}^0 + E_n^1 + E_n^2 + \dots$$

$$|\Psi_n\rangle = |\Psi_{An}^0\rangle |\Psi_{Bn}^0\rangle + |\Psi_n^1\rangle + |\Psi_n^2\rangle + \dots$$

In the first order, diagonal elements of V_{AB}, i.e. permanent multipole moments of electronic states

$$E^1 = \left\langle \Psi_{An}^0 \Psi_{Bn}^0 \middle| \hat{V}_{AB} \middle| \Psi_{An}^0 \Psi_{Bn}^0 \right\rangle$$

$$\hat{V}_{AB} = \sum_{L_A, L_B = 0}^{+\infty} \sum_{M=-L_<}^{+L_<} \frac{g_M(L_A, L_B)}{R^{1+L_A+L_B}} Q_{L_A}^M Q_{L_B}^{-M}$$

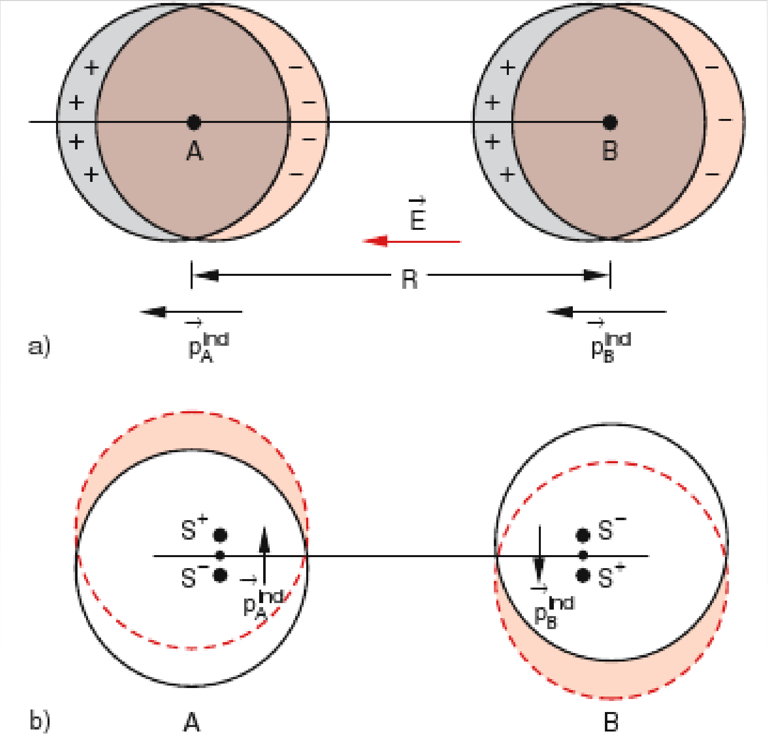
$$g_M(L_A, L_B) = \frac{(-1)^{L}_{B}(L_A + L_B)!}{\sqrt{(L_A - M)!(L_A + M)!(L_B + M)!(L_B - M)!}}$$

example: 2 atoms in a state *S*: $E^1 = 0$

example: 2 atoms in a state *p* : $E^1 = C_3/R^3$

Second-order perturbation

In the second order, non-diagonal elements are always present for dipoles. It corresponds to an interaction of *induced dipole~induced dipole* (L_A=L_B=1)



$$E_n^2 = \sum_{m\neq n} \frac{|\langle \Psi_m^0 | V_{AB} | \Psi_n^0\rangle|^2}{E_n^0 - E_m^0} =$$

$$\frac{1}{R^6}\sum_{m\neq n}\frac{\left|\sum_{M=-1}^{1} g_1(1,1)\langle\Psi_{An}^0|\hat{Q}_1^M|\Psi_{Am}^0\rangle\langle\Psi_{Bn}^0|\hat{Q}_1^{-M}|\Psi_{Bm}^0\rangle\right|^2}{\left(E_{An}^0-E_{Am}^0\right)+\left(E_{Bn}^0-E_{Bm}^0\right)}$$

$$=\frac{C_6}{R^6}$$

van der Waals interaction

Interaction of induced quadrupole~induced dipole: C_8/R^8

Interaction of induced quadrupole~induced quadrupole: C_{10}/R^{10}