CP VIOLATION IN ELEMENTARY PARTICLES AND COMPOSITE SYSTEMS
Advanced School

Molecular orbital theory and e-EDM in molecules

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Contents

Reference books

- Physical Chemistry A Molecular Approach by D. A. McQuarrie & J. D. Simon
- Modern Quantum Chemistry Introductions to Advanced Electronic Structure Theory by A. Szabo, N. S. Ostland
- Molecular Electronic Structure Theory by T. Helgaker, P. Jorgensen, J. Olsen

Quantum Mechanics: time-independent Schrödinger equation

$$\hat{H}\psi = \left(\hat{T} + \hat{V}\right)\psi = E\psi$$

In classical mechanics
（Kinetic energy：T）＋（Potential energy：V）＝Total Energy

In quantum mechanics,

Kinetic energy operator $\hat{T}$ ＋ Potential energy operator $\hat{V}$

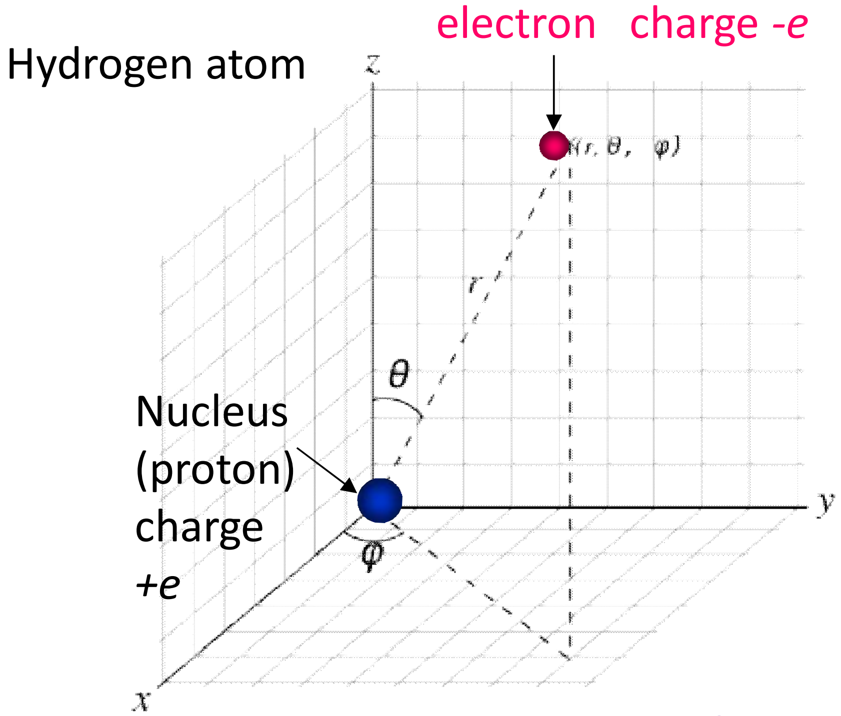
= Hamiltonian operator $\hat{H}$

Energy E is obtained as an eigen value of the Hamiltonian operator.
Eigen function is called as wave function. $\psi : \psi\left(x, y, z\right)$

Schrödinger equation of Hydrogen atom

$$\hat{H}\psi = \left(-\frac{\hbar^2}{2m} \left(\underbrace{\frac{\partial^2}{\partial^2 x} + \frac{\partial^2}{\partial^2 y} + \frac{\partial^2}{\partial^2 z}}_{\nabla^2} \right) + \frac{e^2}{4\pi\varepsilon_0 r} \right) \psi = E\psi$$

$$r = \left| x^2 + y^2 + z^2 \right|$$



Hydrogen atom

electron charge -*e*

Nucleus (proton) charge *+e*

Like the latitude and longitude of earth!

Invert "Cartesian coordinate x, y, z" to "polar coordinate *r, □, □*"

$$x = r \sin\theta \cos\varphi$$

$$y = r \sin\theta \sin\varphi$$

$$z = r \cos\theta$$

Schrödinger equation of Hydrogen atom

$$\hat{H}\psi = \left(-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial^2 x} + \frac{\partial^2}{\partial^2 y} + \frac{\partial^2}{\partial^2 z} \right) + \frac{e^2}{4\pi\varepsilon_0 r} \right)\psi = E\psi$$

$$r = \left| x^2 + y^2 + z^2 \right|$$

$$\psi(r,\theta,\varphi) = R(r)\Theta(\theta)\Phi(\varphi) = R(r)Y(\theta,\varphi)$$

$$\Rightarrow \begin{cases} -\dfrac{\hbar^2}{2m_e r^2}\dfrac{d}{dr}\left(r^2 \dfrac{dR}{dr} \right) + \left[\dfrac{\hbar^2 \beta}{2m_e r^2} - \dfrac{e^2}{4\pi\varepsilon_0 r} - E \right] R(r) = 0 \\ \sin\theta \dfrac{\partial}{\partial\theta}\left(\sin\theta \dfrac{\partial Y}{\partial\theta} \right) + \dfrac{\partial^2 Y}{\partial\phi^2} = \beta \sin^2\theta Y(\theta,\phi) \end{cases}$$

We can solve *R(r)*, *□ □□□□, □ □□)* independently.

Schrödinger equation of Hydrogen atom

$$\sin\theta \frac{\partial}{\partial\theta}\left(\sin\theta \frac{\partial Y}{\partial\theta}\right) + \frac{\partial^2 Y}{\partial\phi^2} = \beta \sin^2\theta Y(\theta,\phi)$$

$$\Rightarrow \quad Y_l^m(\theta,\varphi) = \left[\frac{(2l+1)}{4\pi}\frac{(l-|m|)!}{(l+|m|)!}\right]^{1/2} \boxed{P_l^{|m|}(\cos\theta)e^{im\phi}}$$

$$\beta = l(l+1)$$

Associated Legendre polynomials

Spherical harmonics

$$-\frac{\hbar^2}{2m_e r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \left[\frac{\hbar^2 l(l+1)}{2m_e r^2} - \frac{e^2}{4\pi\varepsilon_0 r} - E\right]R(r) = 0$$

$$\Rightarrow \quad R_{nl}(r) = -\left\{\frac{(n-l-1)!}{2n[(n+l)!]^3}\right\}^{1/2}\left(\frac{2}{na_0}\right)^{l+3/2} r^l e^{-r/na_0} \boxed{L_{n+l}^{2l+1}\left(\frac{2r}{na_0}\right)}$$

Radial function

Associated Laguerre polynomials

Schrödinger equation of Hydrogen atom

Three integers come up when solving Schrödinger equation of H atom.

n:prinsiple quantum number (n = 0, 1, 2, …)
l: angular momentum quantum number (l = 0, …, n)
m: magnetic quantum number (m= -l, -l+1, …, l-1, l)

$$\psi_{n,l,m}(r,\theta,\varphi)=R_{nl}(r)Y_l^m(\theta,\varphi)$$

Radial functions depend on n and l.
Spherical harmonics depend on l and m.

$$E_n=-\frac{m_e e^4}{32\pi^2\varepsilon_0^2\hbar^2 n^2}=-\frac{m_e e^4}{8\pi\varepsilon_0 a_0 n^2}$$

Bohr radius

$$a_0=\frac{4\pi\varepsilon_0\hbar^2}{m_e e^2}$$

Energy only depends on n quantum numbers.

Schrödinger equation of Hydrogen atom

Examples

$$\psi_{1,0,0}(r,\theta,\varphi)=\frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\exp\left(-\frac{Zr}{a_0}\right)$$

… 1s orbital

$$\psi_{2,0,0}(r,\theta,\varphi)=\frac{1}{\sqrt{32\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(2-\left(\frac{Zr}{a_0}\right)\right)\exp\left(-\frac{Zr}{2a_0}\right)$$

… 2s orbital

$$\psi_{2,1,0}(r,\theta,\varphi)=\frac{1}{\sqrt{32\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(\frac{Zr}{a_0}\right)\exp\left(-\frac{Zr}{2a_0}\right)\cos\theta$$

… 2p_0 orbital

$$\psi_{2,1,\pm1}(r,\theta,\varphi)=\frac{1}{\sqrt{64\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(\frac{Zr}{a_0}\right)\exp\left(-\frac{Zr}{2a_0}\right)\boxed{\sin\theta\exp(\pm i\phi)}$$

… 2p_1, 2p_{-1} orbital

p_1, p_{-1} orbitals are complex functions.

Schrödinger equation of Hydrogen atom

p_1 and p_{-1} are energetically degenerated.
Besides, they have same probability density function.

$$\left|Y_1^1(\theta,\varphi)\right|^2 = \left|Y_1^{-1}(\theta,\varphi)\right|^2 = \frac{3}{8\pi}\sin^2\theta$$

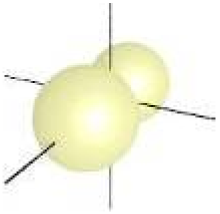
Take linear combinations of p_1 and p_{-1} as bellow.

$$p_x \equiv \frac{1}{\sqrt{2i}}\left(Y_1^1 + Y_1^{-1}\right) = \left(\frac{3}{4\pi}\right)^{1/2} \sin\theta\cos\phi$$

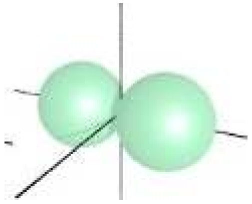
$$p_y \equiv \frac{1}{\sqrt{2i}}\left(Y_1^1 - Y_1^{-1}\right) = \left(\frac{3}{4\pi}\right)^{1/2} \sin\theta\sin\phi$$

p_x, p_y orbitals are now real functions with same eigen energy (but no more than the eigen function of m).

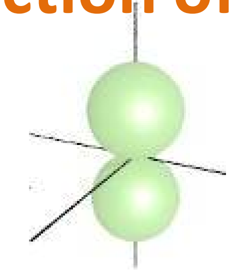
p_x



p_y



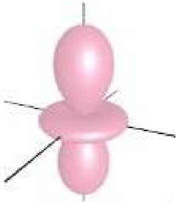
p_z



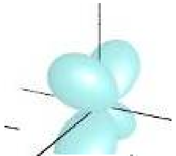
Schrödinger equation of Hydrogen atom

Similarly, we take linear combinations of d orbitals to make real functions as follows,

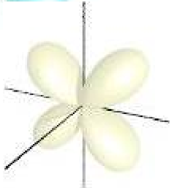
$$d_{z^2} \equiv Y_2^0 = \left(\frac{5}{16\pi}\right)^{1/2}\left(3\cos^2\theta - 1\right)$$



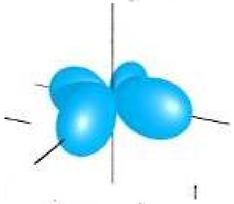
$$d_{xz} \equiv \frac{1}{\sqrt{2}}\left(Y_2^1 + Y_2^{-1}\right) = \left(\frac{15}{4\pi}\right)^{1/2}\sin\theta\cos\theta\cos\phi$$



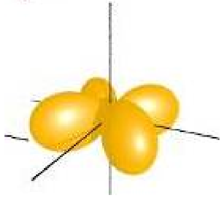
$$d_{yz} \equiv \frac{1}{\sqrt{2}i}\left(Y_2^1 - Y_2^{-1}\right) = \left(\frac{15}{4\pi}\right)^{1/2}\sin\theta\cos\theta\sin\phi$$



$$d_{x^2-y^2} \equiv \frac{1}{\sqrt{2}}\left(Y_2^2 + Y_2^{-2}\right) = \left(\frac{15}{16\pi}\right)^{1/2}\sin^2\theta\cos 2\phi$$



$$d_{xy} \equiv \frac{1}{\sqrt{2}i}\left(Y_2^2 - Y_2^{-2}\right) = \left(\frac{15}{16\pi}\right)^{1/2}\sin^2\theta\sin 2\phi$$

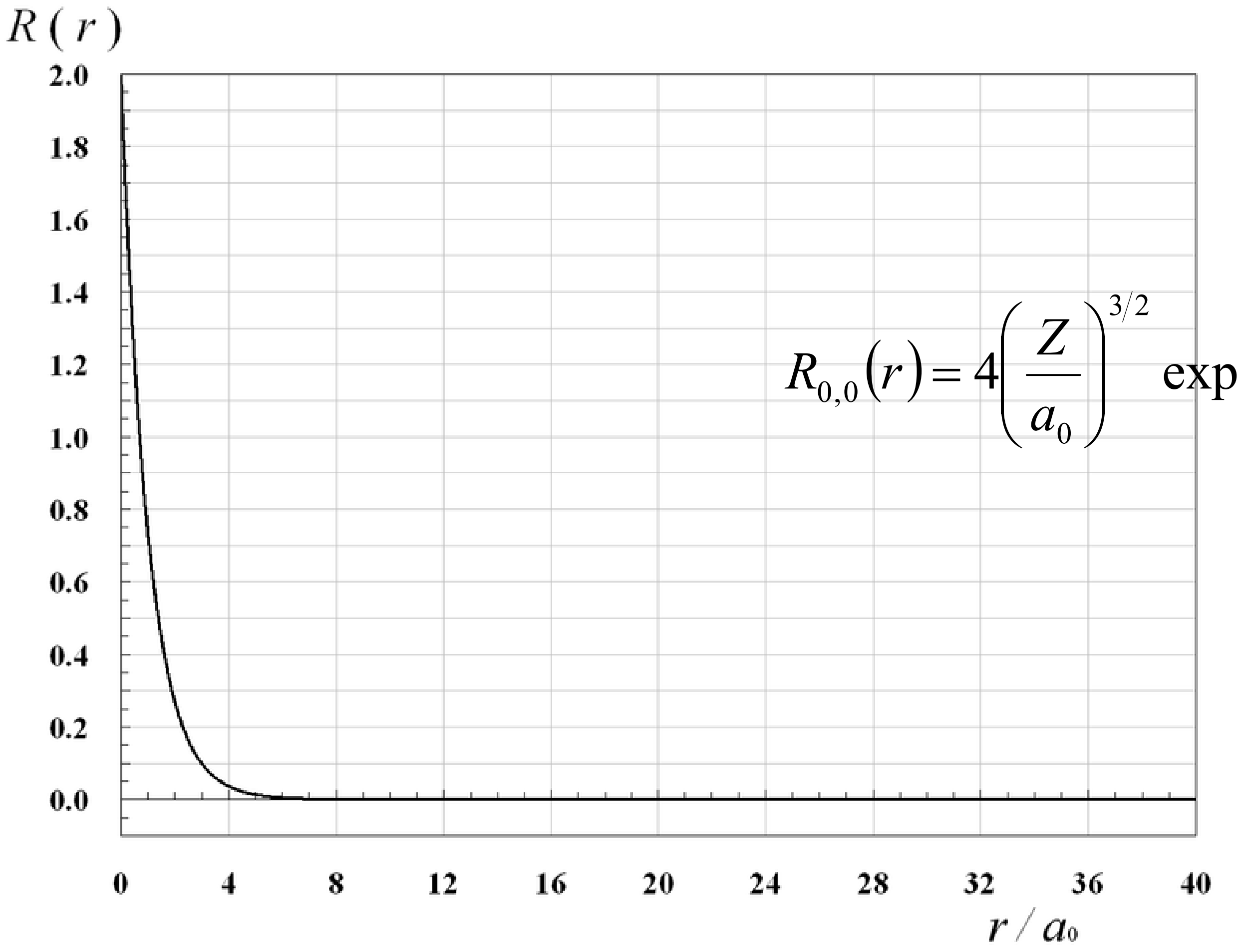


These d functions are real and possible to show as pictures.

Molecular calculations use the real functions as basis sets.

Schrödinger equation of Hydrogen atom

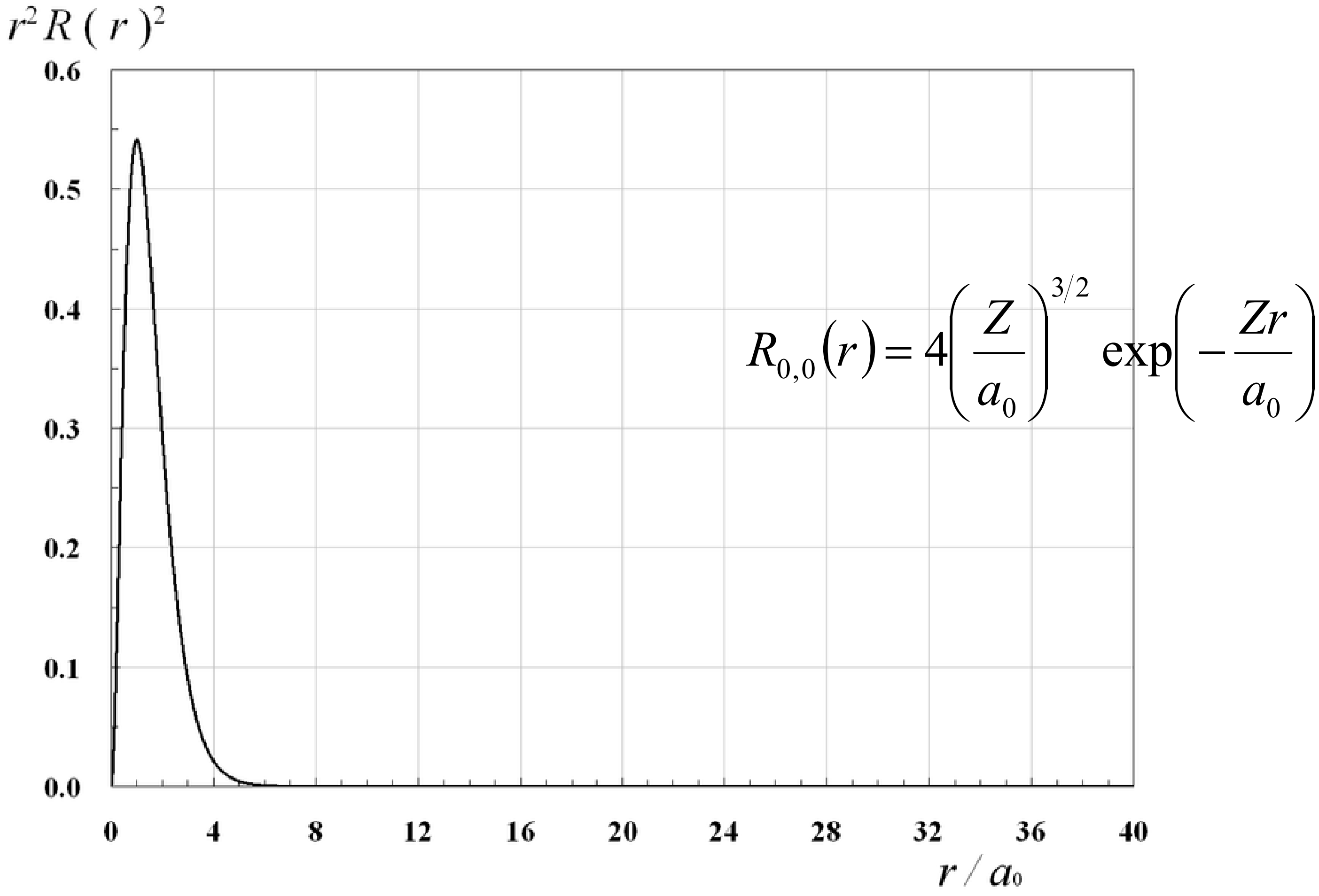
Radial function of 1s orbital



$$R_{0,0}(r) = 4\left(\frac{Z}{a_0}\right)^{3/2} \exp\left(-\frac{Zr}{a_0}\right)$$

Schrödinger equation of Hydrogen atom

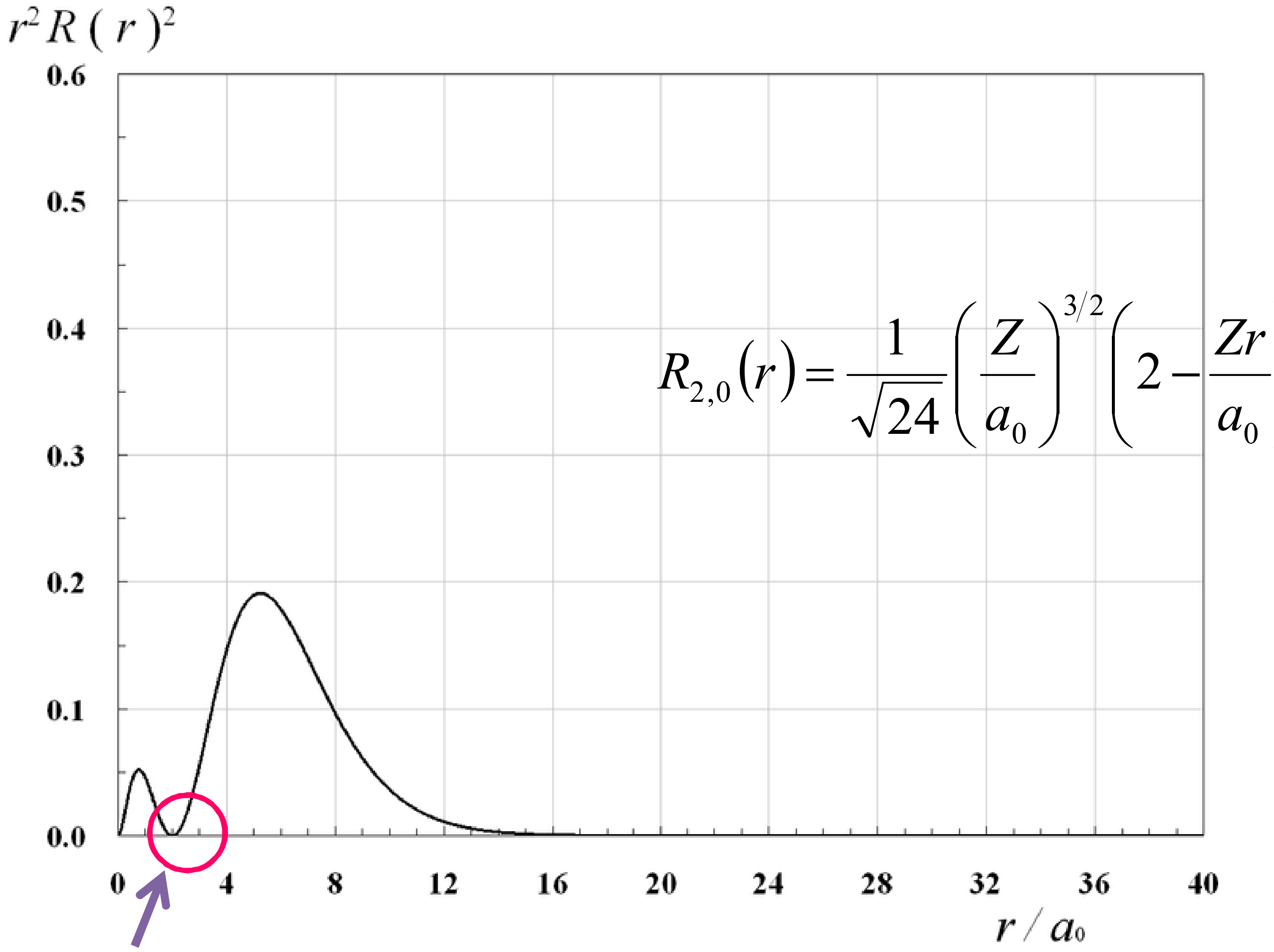
Radial distributed functions of 1s orbital



$$R_{0,0}(r) = 4\left(\frac{Z}{a_0}\right)^{3/2} \exp\left(-\frac{Zr}{a_0}\right)$$

Schrödinger equation of Hydrogen atom

Radial distributed functions of 2s orbital

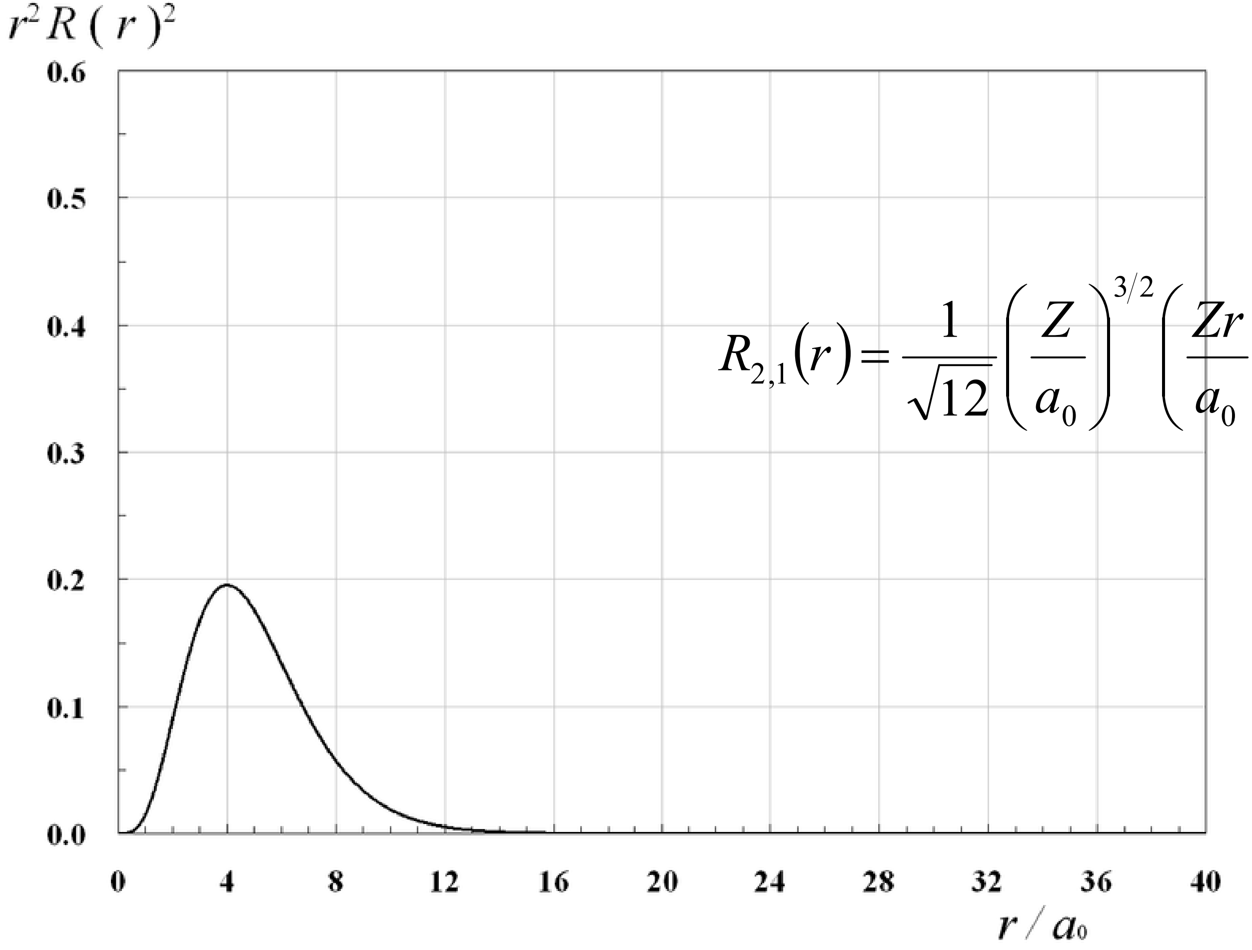


$$R_{2,0}(r)=\frac{1}{\sqrt{24}}\left(\frac{Z}{a_0}\right)^{3/2}\left(2-\frac{Zr}{a_0}\right)\exp\left(-\frac{Zr}{a_0}\right)$$

There is a node where electron density is zero.

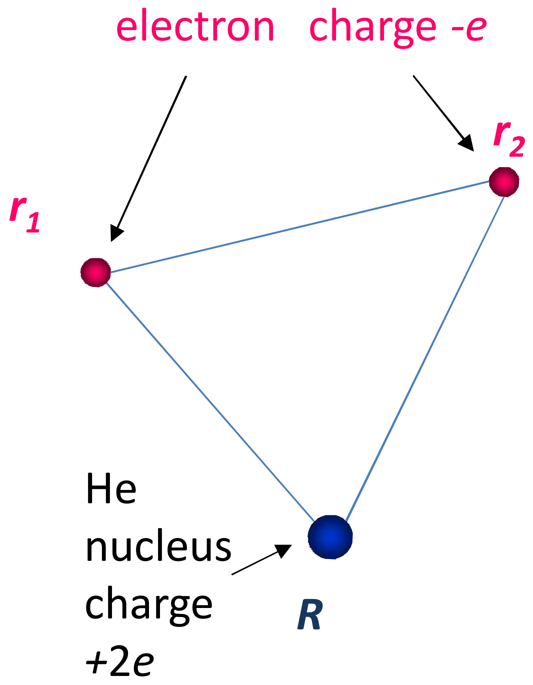
Schrödinger equation of Hydrogen atom

Radial distributed functions of 2p orbital



$$R_{2,1}(r) = \frac{1}{\sqrt{12}}\left(\frac{Z}{a_0}\right)^{3/2}\left(\frac{Zr}{a_0}\right)\exp\left(-\frac{Zr}{a_0}\right)$$

He atom



Hamiltonian

$$\left(-\frac{\hbar^2}{2M}\nabla^2-\frac{\hbar^2}{2m_e}\nabla_1^2-\frac{\hbar^2}{2m_e}\nabla_2^2\right)\psi(R,r_1,r_2)+$$

$$\left(-\frac{2e^2}{4\pi\varepsilon_0|R-r_1|}-\frac{2e^2}{4\pi\varepsilon_0|R-r_2|}+\frac{e^2}{4\pi\varepsilon_0|r_1-r_2|}\right)\psi(R,r_1,r_2)$$

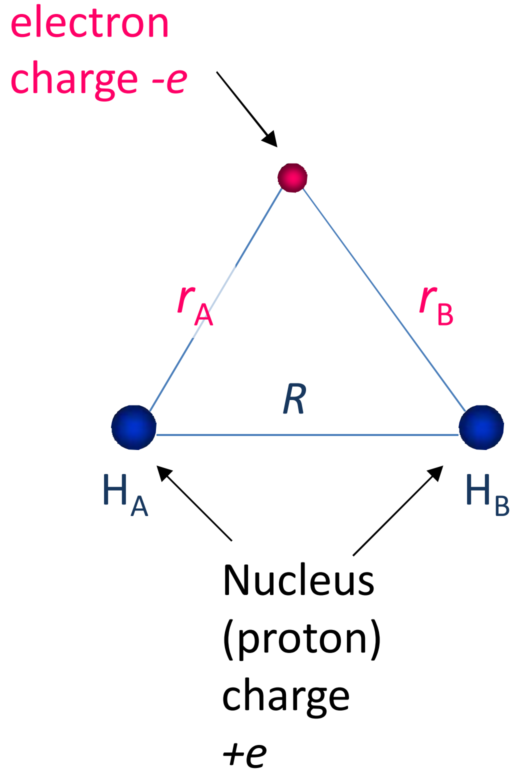
$$=E\psi(R,r_1,r_2)$$

If we ignore nucleus motion and take origin on the nucleus,

$$\left[-\frac{\hbar^2}{2m_e}\left(\nabla_1^2+\nabla_2^2\right)-\frac{2e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_1}+\frac{1}{r_2}\right)+\frac{e^2}{4\pi\varepsilon_0|r_1-r_2|}\right]\psi(r_1,r_2)=E\psi(r_1,r_2)$$

Still it requires some approximations
such as perturbation theory or variational theory.

H_2^+ molecule



Hamiltonian

$$\left(-\frac{\hbar^2}{2M}\nabla_A^2-\frac{\hbar^2}{2M}\nabla_B^2-\frac{\hbar^2}{2m_e}\nabla^2\right)\psi(R,r)$$

$$+\left(-\frac{e^2}{4\pi\varepsilon_0 r_A}-\frac{e^2}{4\pi\varepsilon_0 r_B}+\frac{e^2}{4\pi\varepsilon_0 R}\right)\psi(R,r)=E\psi(R,r)$$

If we ignore nucleus motion
and consider only electronic state
by fixing nuclear places...

Born-Oppenheimer approximation

$$\psi(R,r)\approx\psi_e(R,r)\psi_n(R)$$

$$\left(-\frac{\hbar^2}{2m_e}\nabla^2-\frac{e^2}{4\pi\varepsilon_0 r_A}-\frac{e^2}{4\pi\varepsilon_0 r_B}+\frac{e^2}{4\pi\varepsilon_0 R}\right)\psi_e(R,r)=E_e(R)\psi_e(R,r)$$

H_2^+ molecule

$$\left(-\frac{\hbar^2}{2m_e}\nabla^2-\frac{e^2}{4\pi\varepsilon_0 r_A}-\frac{e^2}{4\pi\varepsilon_0 r_B}+\frac{e^2}{4\pi\varepsilon_0 R}\right)\psi_e(R,r)=E_e(R)\psi_e(R,r)$$

Introduce atomic unit

mass $1\,a.u.=m_e$

charge $1\,a.u.=e$

length $1\,a.u.=a_0=\dfrac{4\pi\varepsilon_0\hbar^2}{m_e e^2}$

Energy $1\,a.u.=E_{hartree}=\dfrac{e^2}{4\pi\varepsilon_0 a_0}$

$$\left(-\frac{1}{2}\nabla^2-\frac{1}{r_A}-\frac{1}{r_B}+\frac{1}{R}\right)\psi_e(R,r)=E_e(R)\psi_e(R,r)$$

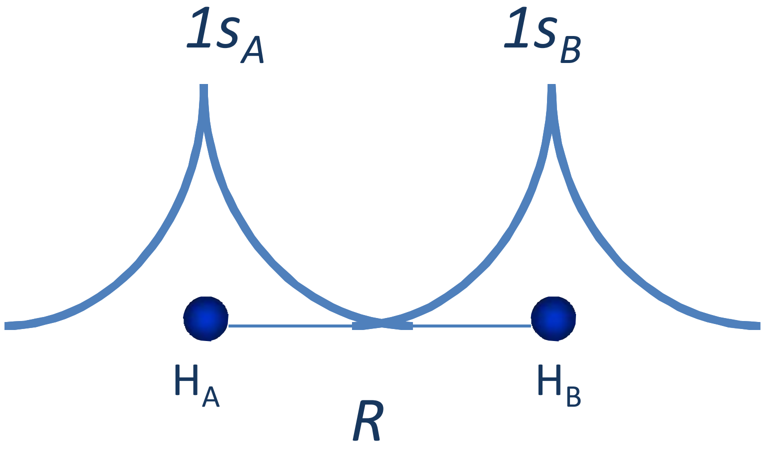
Simplified!

H_2^+ molecule

$$\left(-\frac{1}{2}\nabla^2-\frac{1}{r_A}-\frac{1}{r_B}+\frac{1}{R}\right)\psi_e(R,r)=E(R)\psi_e(R,r)$$

Let's consider the wave function is represented as a linear combination of 1s orbitals of nucleus H_A and H_B.

$$\psi_e(R,r)=c_A\phi_{1s_A}(R,r)+c_B\phi_{1s_B}(R,r)$$



$$\phi_{1s_A}(R,r)=\frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\exp\left(-\frac{Z|\mathbf{r}-\mathbf{R_A}|}{a_0}\right)$$

$$\phi_{1s_B}(R,r)=\frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\exp\left(-\frac{Z|\mathbf{r}-\mathbf{R}_B|}{a_0}\right)$$

Linear Combination of Atomic Orbital (LCAO)

H_2^+ molecule

$$\left(-\frac{1}{2}\nabla^2-\frac{1}{r_A}-\frac{1}{r_B}+\frac{1}{R}\right)\psi_e(R,r)=E(R)\psi_e(R,r)$$

$$\hat{H}\psi=E\psi \qquad E=\frac{\int d\mathbf{r}\,\psi^*\hat{H}\psi}{\int d\mathbf{r}\,\psi^*\psi}=\frac{\langle\psi|\hat{H}|\psi\rangle}{\langle\psi|\psi\rangle}$$

$$H_{AB}=H_{BA}=\langle\phi_{1s_A}|\hat{H}|\phi_{1s_B}\rangle=\langle\phi_{1s_B}|\hat{H}|\phi_{1s_A}\rangle$$

$$H_{AA}=H_{BB}=\langle\phi_{1s_A}|\hat{H}|\phi_{1s_A}\rangle=\langle\phi_{1s_B}|\hat{H}|\phi_{1s_B}\rangle$$

$$S_{AB}=S_{BA}=\langle\phi_{1s_A}|\phi_{1s_B}\rangle=\langle\phi_{1s_B}|\phi_{1s_A}\rangle=S$$

$$S_{AA}=S_{BB}=\langle\phi_{1s_A}|\phi_{1s_A}\rangle=\langle\phi_{1s_B}|\phi_{1s_B}\rangle=1$$

E is expressed as follows.

$$E=\frac{c_A^2H_{AA}+c_B^2H_{BB}+2c_Ac_BH_{AB}}{c_A^2+c_B^2+2c_Ac_BS}$$

H_2^+ molecule

Atomic orbital (AO) integral of H_2^+

$$H_{AA}=\left\langle \phi_{1s_A}\left|-\frac{1}{2}\nabla^2-\frac{1}{r_A}-\frac{1}{r_B}+\frac{1}{R}\right|\phi_{1s_A}\right\rangle=\left\langle \phi_{1s_A}\left|-\frac{1}{2}\nabla^2-\frac{1}{r_A}\right|\phi_{1s_A}\right\rangle+\left\langle \phi_{1s_A}\left|-\frac{1}{r_B}+\frac{1}{R}\right|\phi_{1s_A}\right\rangle$$

$$=E_{1S}+J$$

$$H_{AB}=\left\langle \phi_{1s_A}\left|-\frac{1}{2}\nabla^2-\frac{1}{r_A}-\frac{1}{r_B}+\frac{1}{R}\right|\phi_{1s_B}\right\rangle=\left\langle \phi_{1s_A}\left|-\frac{1}{2}\nabla^2-\frac{1}{r_B}\right|\phi_{1s_B}\right\rangle+\left\langle \phi_{1s_A}\left|-\frac{1}{r_A}+\frac{1}{R}\right|\phi_{1s_A}\right\rangle$$

$$=E_{1S}\left\langle \phi_{1s_A}\middle|\phi_{1s_B}\right\rangle+K=E_{1S}S+K$$

We can fortunately calculate these integrals analytically as functions of R.

$$S=\left\langle \phi_{1s_A}\middle|\phi_{1s_B}\right\rangle=\exp(-R)\left(1+R+\frac{R^2}{3}\right)$$

Overlap integral

$$J=\left\langle \phi_{1s_A}\left|-\frac{1}{r_B}+\frac{1}{R}\right|\phi_{1s_A}\right\rangle$$

$$=-\int\frac{d\mathbf{r}1s_A^*1s_A}{r_B}+\frac{1}{R}=\exp(-2R)\left(1+\frac{1}{R}\right)$$

Coulomb integral

$$K=\left\langle \phi_{1s_A}\left|-\frac{1}{r_A}+\frac{1}{R}\right|\phi_{1s_B}\right\rangle$$

$$=-\int\frac{d\mathbf{r}1s_A^*1s_B}{r_A}+\frac{S}{R}=\frac{S}{R}-\exp(-R)(1+R$$

Exchange integral

H_2^+ molecule

$$E\left(c_A^2+c_B^2+2c_Ac_BS\right)=c_A^2H_{AA}+c_B^2H_{BB}+2c_Ac_BH_{AB}$$

Differentiate the above equation with c_A or c_B

and insert $\dfrac{\partial E}{\partial c_A}=0$ or $\dfrac{\partial E}{\partial c_B}=0$.

Variational theory

$$\frac{\partial E}{\partial c_A}\left(c_A^2+c_B^2+2c_Ac_BS\right)+E\left(2c_A+2c_BS\right)=2c_AH_{AA}+2c_BH_{AB}$$

$$E\left(2c_A+2c_BS\right)=2c_AH_{AA}+2c_BH_{AB}$$

$$\boxed{\left(H_{AA}-E\right)c_A+\left(H_{AB}-ES\right)c_B=0}$$

$$\frac{\partial E}{\partial c_B}\left(c_A^2+c_B^2+2c_Ac_BS\right)+E\left(2c_B+2c_AS\right)=2c_BH_{BB}+2c_AH_{AB}$$

$$E\left(2c_B+2c_AS\right)=2c_BH_{BB}+2c_AH_{AB}$$

$$\boxed{\left(H_{AB}-ES\right)c_A+\left(H_{BB}-E\right)c_B=0}$$

H_2^+ molecule

$$(H_{AA}-E)c_A+(H_{AB}-ES)c_B=0$$

$$(H_{AB}-ES)c_A+(H_{BB}-E)c_B=0$$

To have non trivial solution of c_A and c_B

$$\begin{vmatrix} H_{AB}-ES & H_{BB}-E \\ H_{BB}-E & H_{AB}-ES \end{vmatrix}=0$$

Secular equation

must be hold.

$$(H_{AB}-ES)^2-(H_{AA}-E)^2=0$$

$$H_{AB}-ES=\pm(H_{AA}-E)$$

$$E_+=\frac{H_{AA}+H_{AB}}{1+S}\ ,\ E_-=\frac{H_{AA}-H_{AB}}{1-S}$$

H_2^+ molecule

When $\boxed{E_+ = \frac{H_{AA} + H_{AB}}{1+S}}$

$$\left(H_{AA} - \frac{H_{AA} + H_{AB}}{1+S}\right)c_A + \left(H_{AB} - \frac{H_{AA} + H_{AB}}{1+S}S\right)c_B = 0$$

$$\left(H_{AA}(1+S) - H_{AA} - H_{AB}\right)c_A + \left(H_{AB}(1+S) - (H_{AA} + H_{AB})S\right)c_B = 0$$

$$\left(H_{AA}S - H_{AB}\right)c_A + \left(H_{AB} - H_{AA}S\right)c_B = 0$$

$$\boxed{c_A = c_B}$$

When $\boxed{E_- = \frac{H_{AA} - H_{AB}}{1-S}}$

$$\left(H_{AA} - \frac{H_{AA} - H_{AB}}{1-S}\right)c_A + \left(H_{AB} - \frac{H_{AA} - H_{AB}}{1-S}S\right)c_B = 0$$

$$\left(H_{AA}(1-S) - H_{AA} + H_{AB}\right)c_A + \left(H_{AB}(1-S) - (H_{AA} - H_{AB})S\right)c_B = 0$$

$$\left(-H_{AA}S + H_{AB}\right)c_A + \left(H_{AB} - H_{AA}S\right)c_B = 0$$

$$\boxed{c_A = -c_B}$$

H_2^+ molecule

From the normalization condition of $\psi = c_A \phi_A + c_B \phi_B$,

$$\langle \psi | \psi \rangle = c_A{}^2 \langle \phi_A | \phi_A \rangle + c_B{}^2 \langle \phi_B | \phi_B \rangle + 2 c_A c_B \langle \phi_A | \phi_B \rangle$$

$$= c_A{}^2 + c_B{}^2 + 2 c_A c_B S = 1$$ should be satisfied.

When $c_A = c_B$

$$c_A^2 + c_A^2 + 2c_A^2 S = 1$$

$$c_A = c_B = \frac{1}{\sqrt{2+2S}}$$

$$\psi_+ = \frac{1}{\sqrt{2+2S}}(\phi_A + \phi_B)$$

$$E_+ = \frac{H_{AA} + H_{AB}}{1+S}$$

When $c_A = -c_B$

$$c_A^2 + c_A^2 - 2c_A^2 S = 1$$

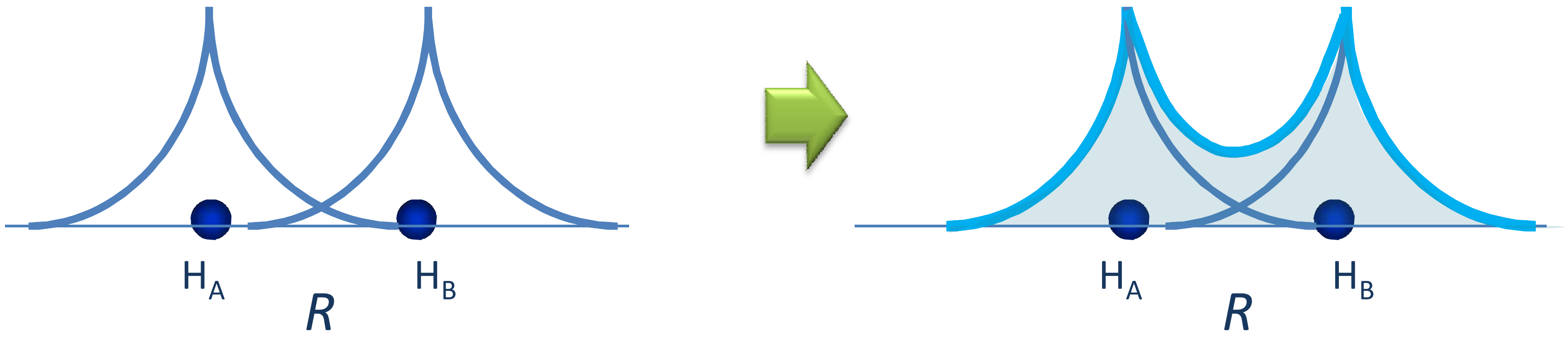
$$c_A = -c_B = \frac{1}{\sqrt{2-2S}}$$

$$\psi_- = \frac{1}{\sqrt{2-2S}}(\phi_A - \phi_B)$$

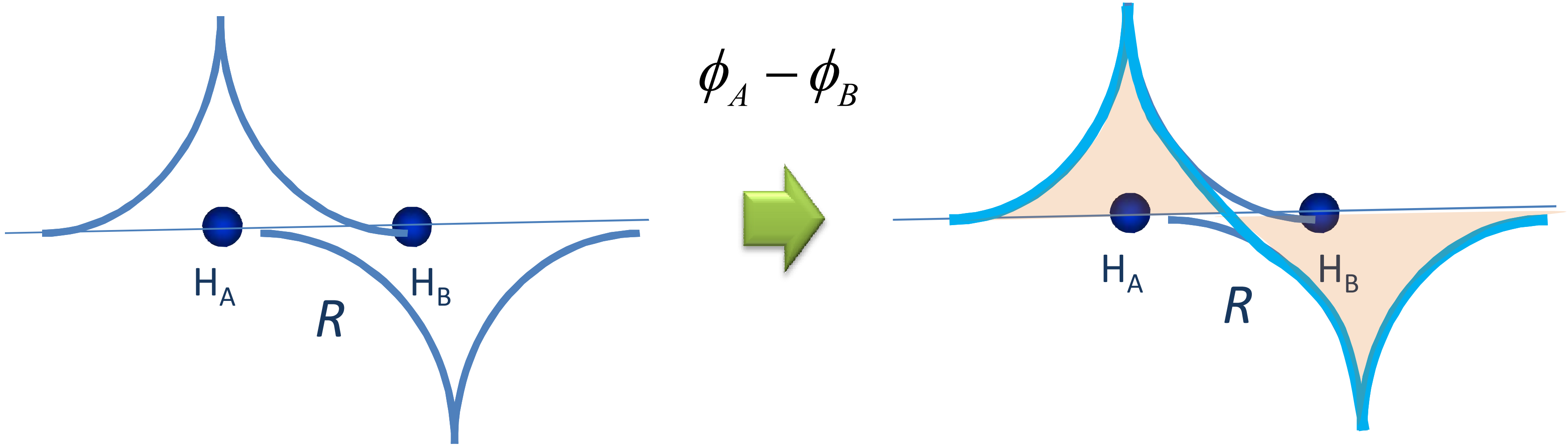
$$E_- = \frac{H_{AA} - H_{AB}}{1-S}$$

H_2^+ molecule

$$\phi_A + \phi_B$$



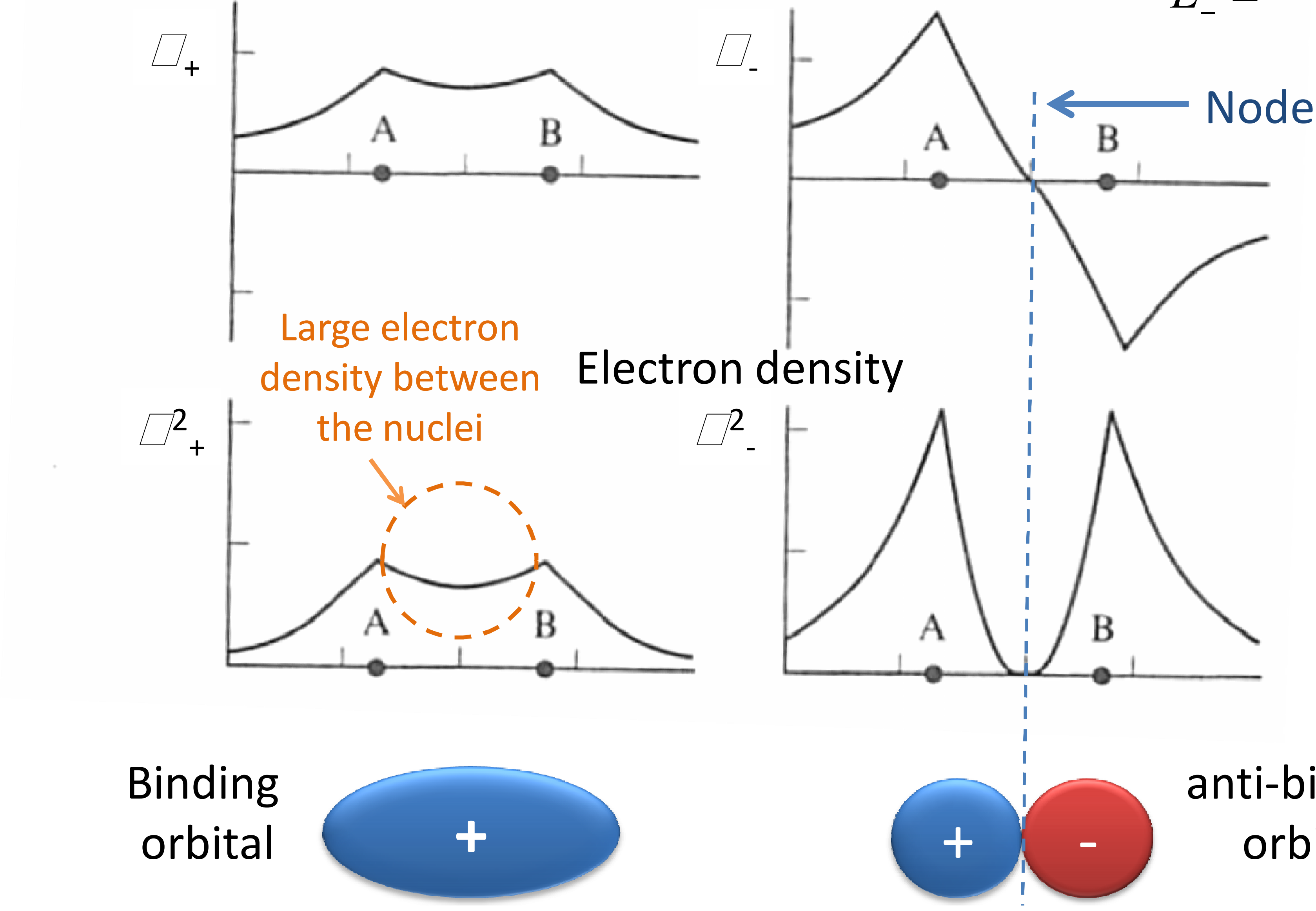
$$\phi_A - \phi_B$$



H_2^+ molecule

$$E_+ = \frac{H_{AA} + H_{AB}}{1+S}$$

$$E_- = \frac{H_{AA} - H_{AB}}{1-S}$$



Molecular orbital

Node

Large electron density between the nuclei

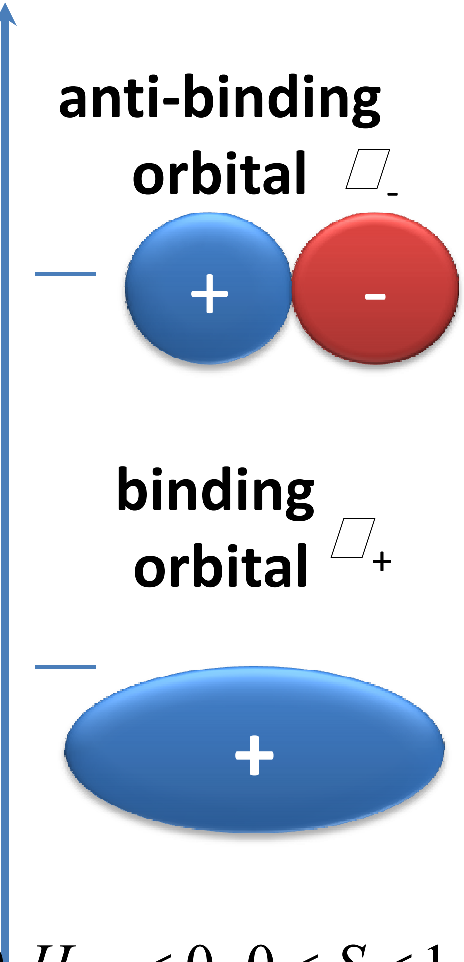
Electron density

Binding orbital

anti-binding orbital

H_2^+ molecule

Molecular orbital



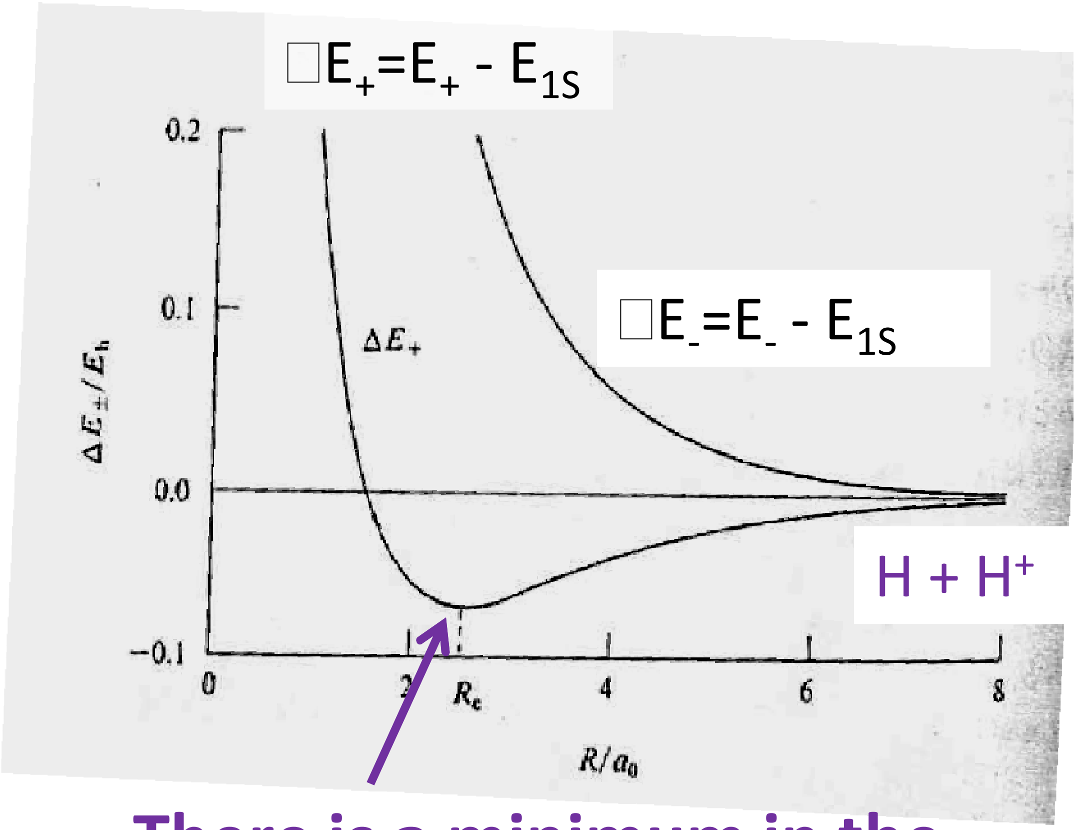
$$E_- = \frac{H_{AA} - H_{AB}}{1 - S}$$

anti-binding orbital $\square_-$

binding orbital $\square_+$

$$E_+ = \frac{H_{AA} + H_{AB}}{1 + S}$$

$$H_{AA} < 0, H_{AB} < 0,\ 0 < S < 1$$



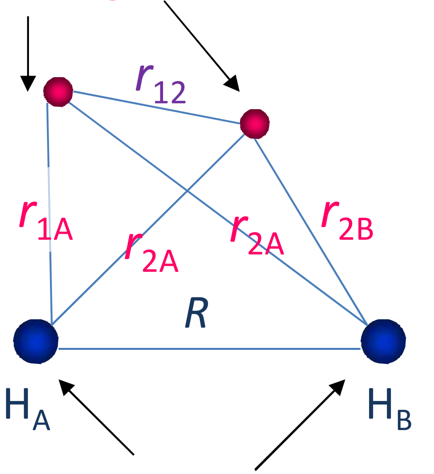
$\square E_+ = E_+ - E_{1S}$

$\square E_- = E_- - E_{1S}$

H + H^+

There is a minimum in the energy curve of E_+. (Binding)

H_2 molecule

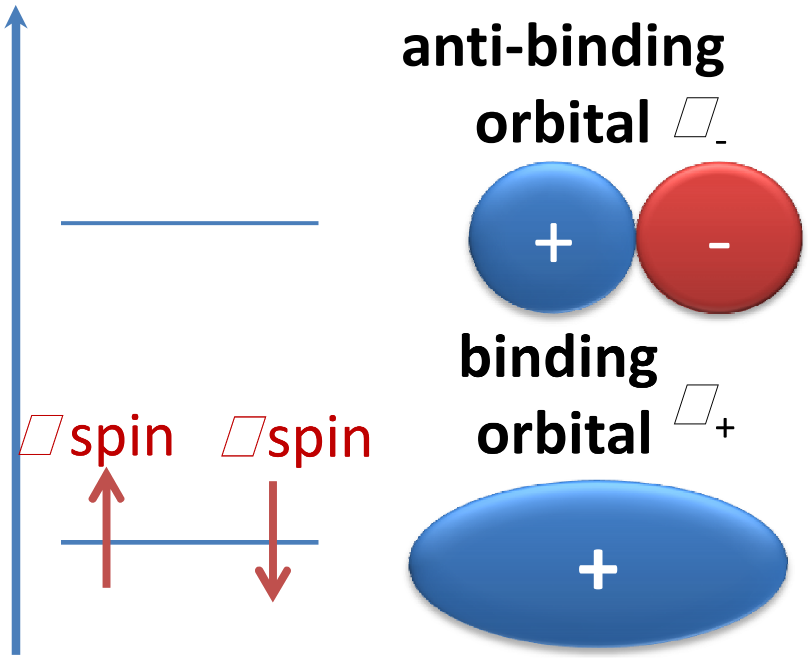


electrons
charge *-e*

Nucleus
(proton) charge *+e*

$$E_- = \frac{H_{AA} - H_{AB}}{1 - S}$$

$$E_+ = \frac{H_{AA} + H_{AB}}{1 + S}$$



anti-binding orbital □$_-$

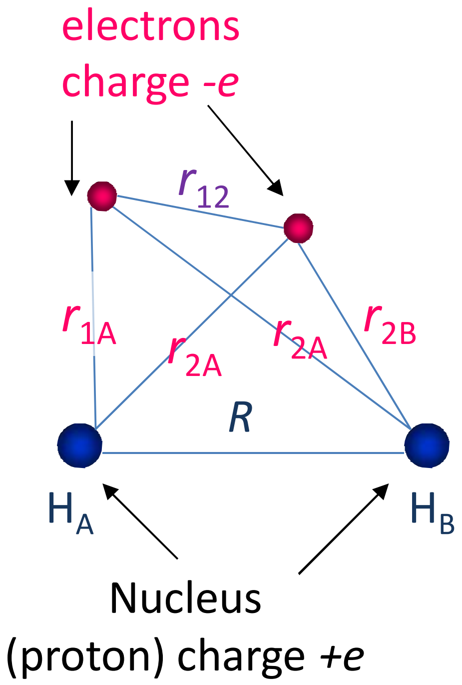
binding orbital □$_+$

Let's assume two electrons occupy in binding orbital of H_2^+.

To consider anti-symmetry of electronic wave function, $\Psi(1,2) = -\Psi(2,1)$
we introduce Slater determinant.

$$\Psi(1,2) = \boxed{\frac{1}{\sqrt{2!}} \begin{vmatrix} \psi_+(1)\alpha(1) & \psi_+(1)\beta(1) \\ \psi_+(2)\alpha(2) & \psi_+(2)\beta(2) \end{vmatrix}} = \frac{1}{\sqrt{2!}} \psi_+(1)\psi_+(2)\{\alpha(1)\beta(2) - \beta(1)\alpha(2)\}$$

H_2 molecule


electrons charge -*e*

Nucleus (proton) charge +*e*

Hamiltonian

$$\left(-\frac{1}{2}\nabla_1^2-\frac{1}{2}\nabla_2^2-\frac{1}{r_{1A}}-\frac{1}{r_{1B}}-\frac{1}{r_{2A}}-\frac{1}{r_{2B}}\right)\psi_e(R,r_1,r_2)$$

$$\left(\frac{1}{r_{12}}\right)\psi_e(R,r_1,r_2)+\left(\frac{1}{R}\right)\psi_e(R,r_1,r_2)$$

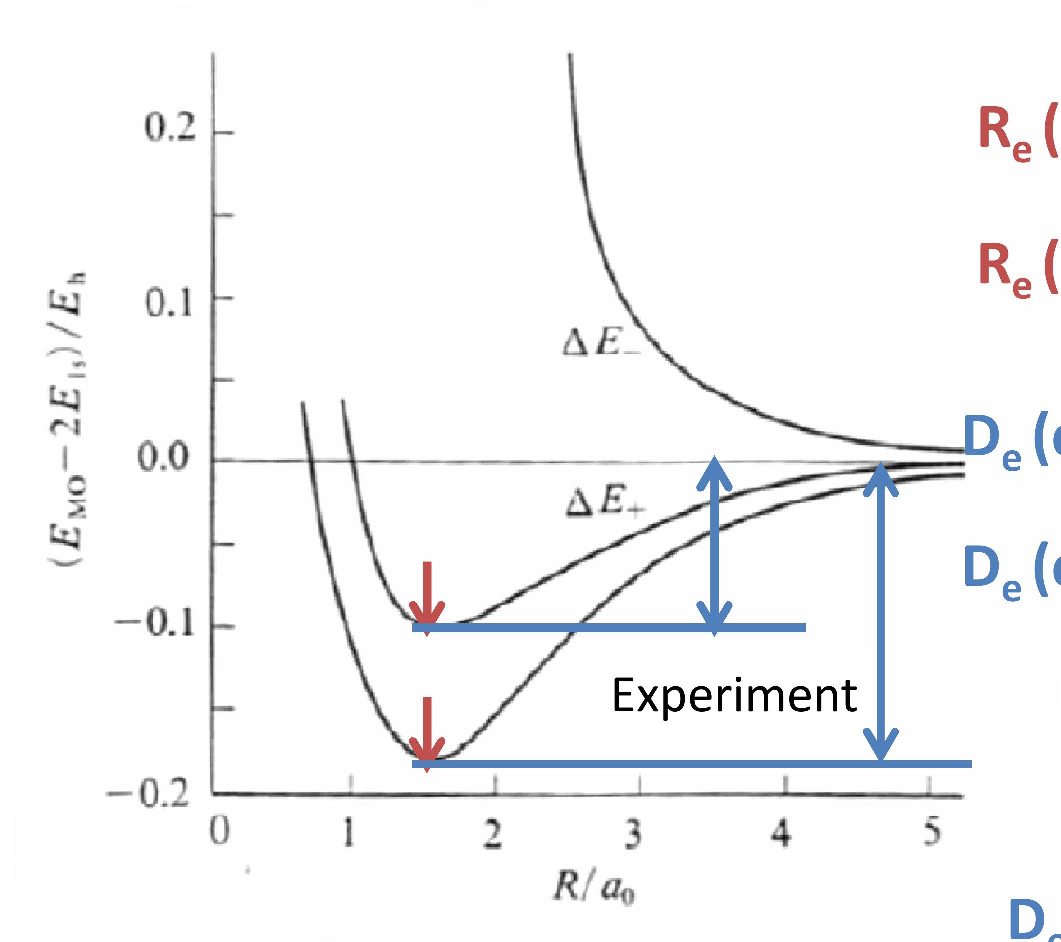
$$=\hat{H}\psi_e(R,r_1,r_2)=E(R)\psi_e(R,r_1,r_2)$$

$$E(R)=\langle\psi_e(R,r_1,r_2)|\hat{H}|\psi_e(R,r_1,r_2)\rangle$$

$$\approx\int d\mathbf{r}_1 d\mathbf{r}_2\psi_+(r_1)\hat{H}\psi_+(r_2)\int \underbrace{d\omega_1 d\omega_2\frac{1}{\sqrt{2!}}\{\alpha(1)\beta(2)-\beta(1)\alpha(2)\}^2}_{\searrow 1}$$

$$=\int d\mathbf{r}_1 d\mathbf{r}_2\psi_+(r_1)\hat{H}\psi_+(r_2)$$

H_2 molecule



R_e (calculated) = 0.85 Å

R_e (experiment) = 0.741 Å

D_e (calculated) = 260 kJ/mol

D_e (experiment) = 457 kJ/mol

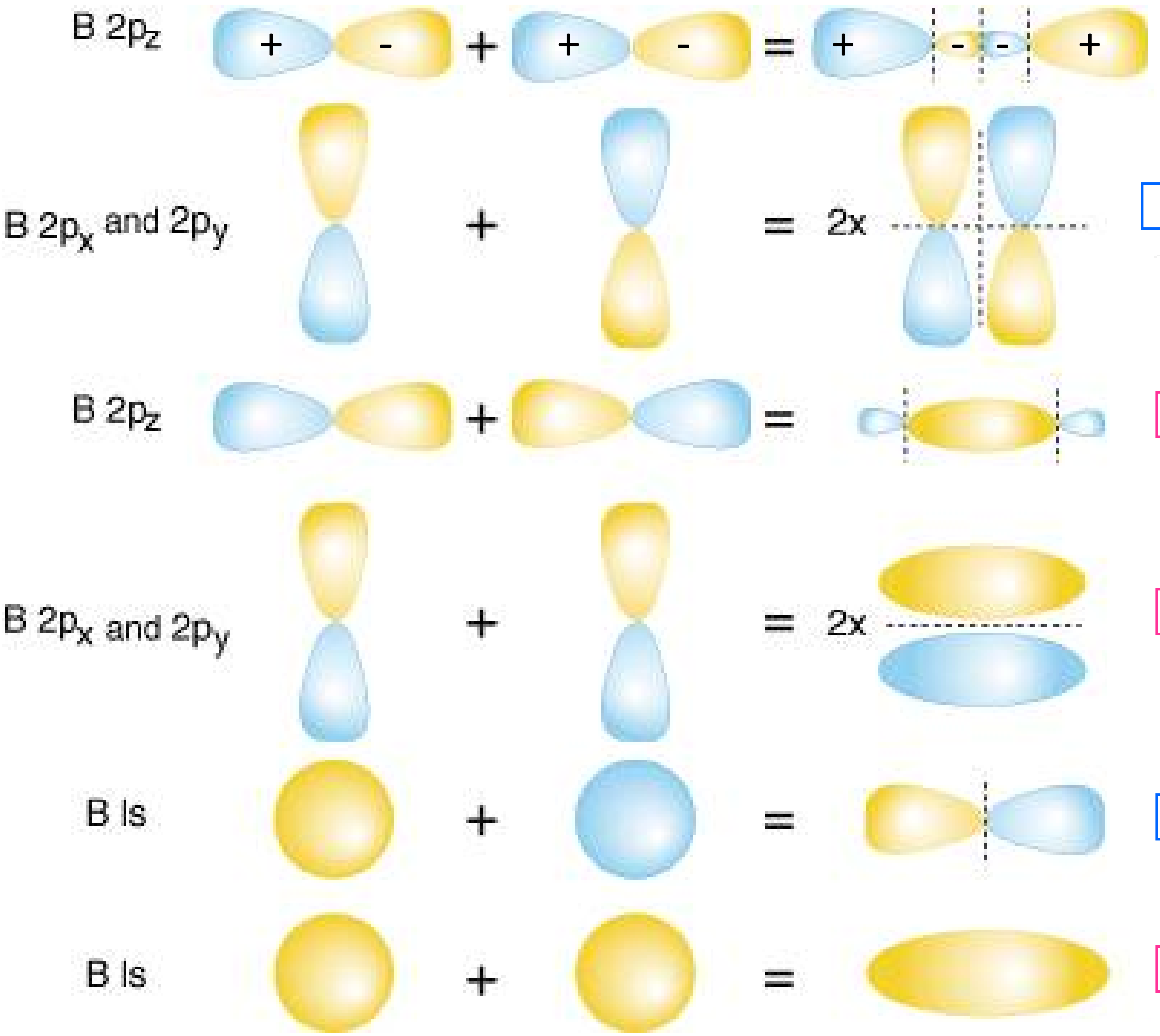
R_e (HF limit) = 0.741 Å

D_e (HF limit) = 351 kJ/mol

These values are improved when we consider molecular orbital optimized for H_2 by the Hartree-Fock method.

Diatomic molecular orbital

s and p orbital interaction



Anti-binding □$_{2pz}$□

Anti-binding □□

Binding □$_{2pz}$

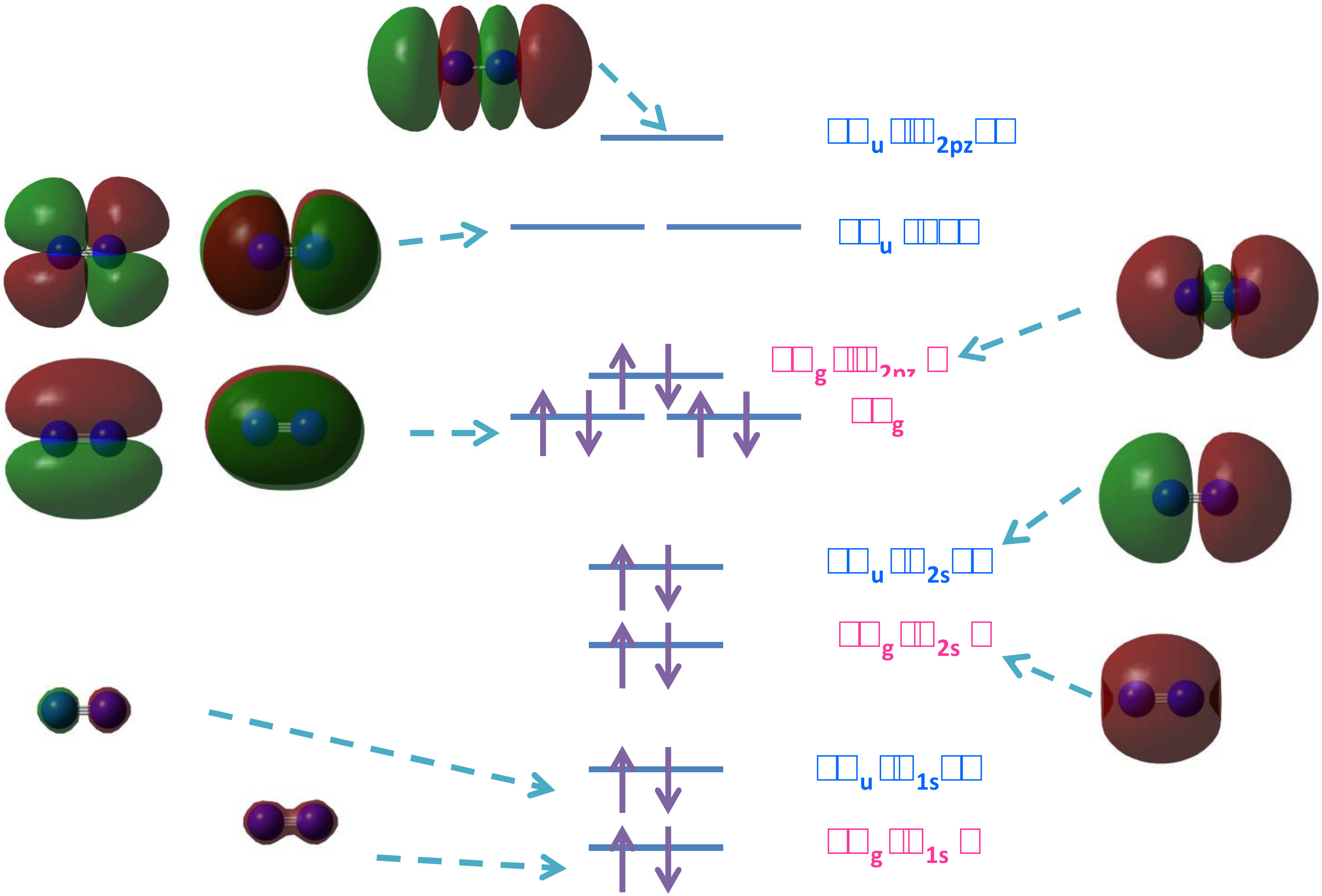
doubly degenerated

Binding □

Anti-binding □$_{s}$□

Binding □$_{s}$

Homo-nucleus diatomic molecular orbital



□□$_u$ □□□$_{2pz}$□□

□□$_u$ □□□□

□□$_g$ □□□$_{2pz}$ □

□□$_g$

□□$_u$ □□$_{2s}$□□

□□$_g$ □□$_{2s}$ □

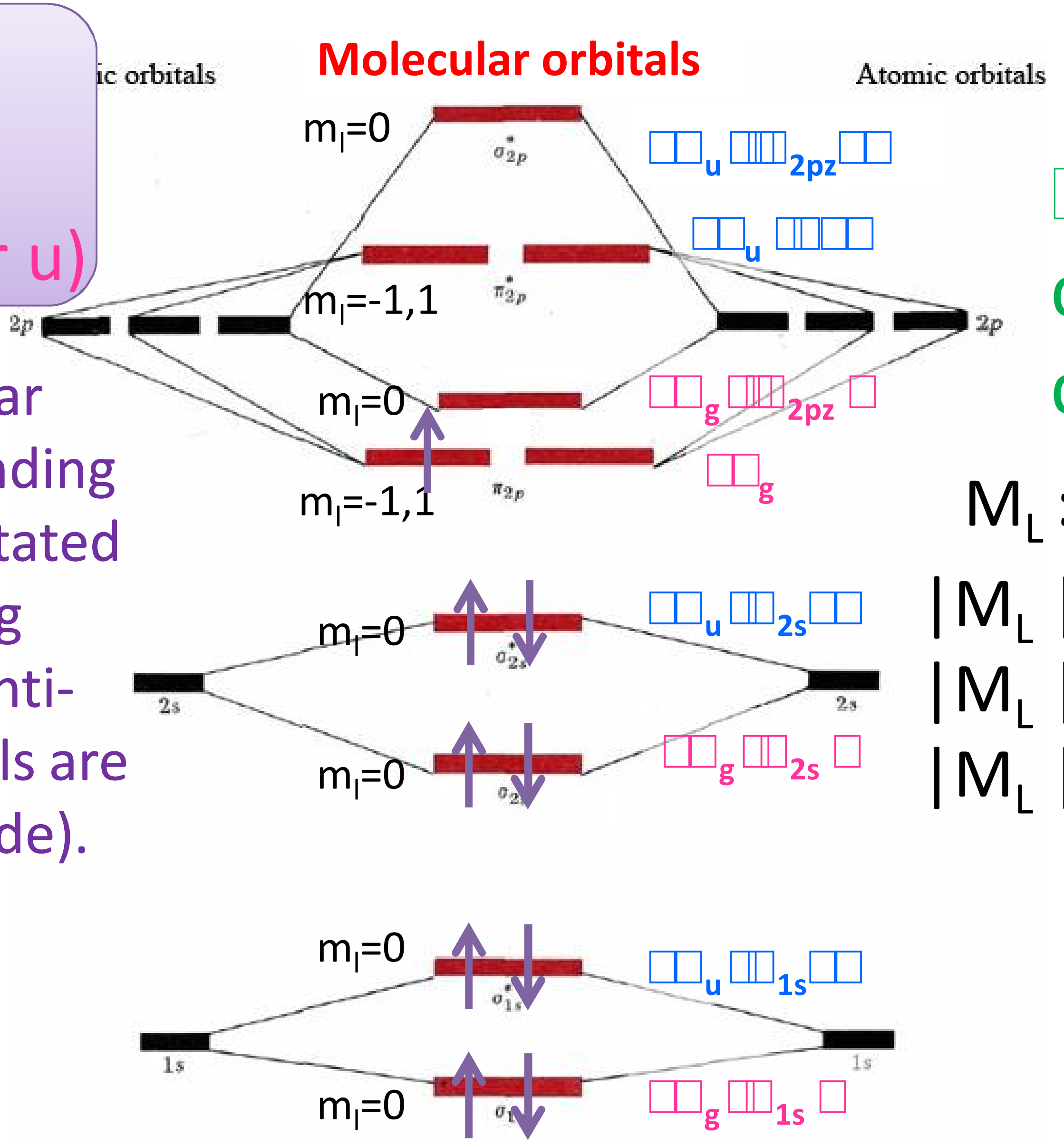
□□$_u$ □□$_{1s}$□□

□□$_g$ □□$_{1s}$ □

Diatomic molecular orbital

Terms

$^{2S+1}□_{(g\ or\ u)}$



In homo-nuclear molecules, bonding orbitals are notated with subscript g (gerade) and anti-bonding orbitals are with u (ungerade).

g × g=g
u × g=u
u × u=g

□ □is determined from M_l.

M_L :sum of m_l

$|M_L|$ =0, ➔ □
$|M_L|$ =1, ➔ □
$|M_L|$ =2, ➔ □

……

□

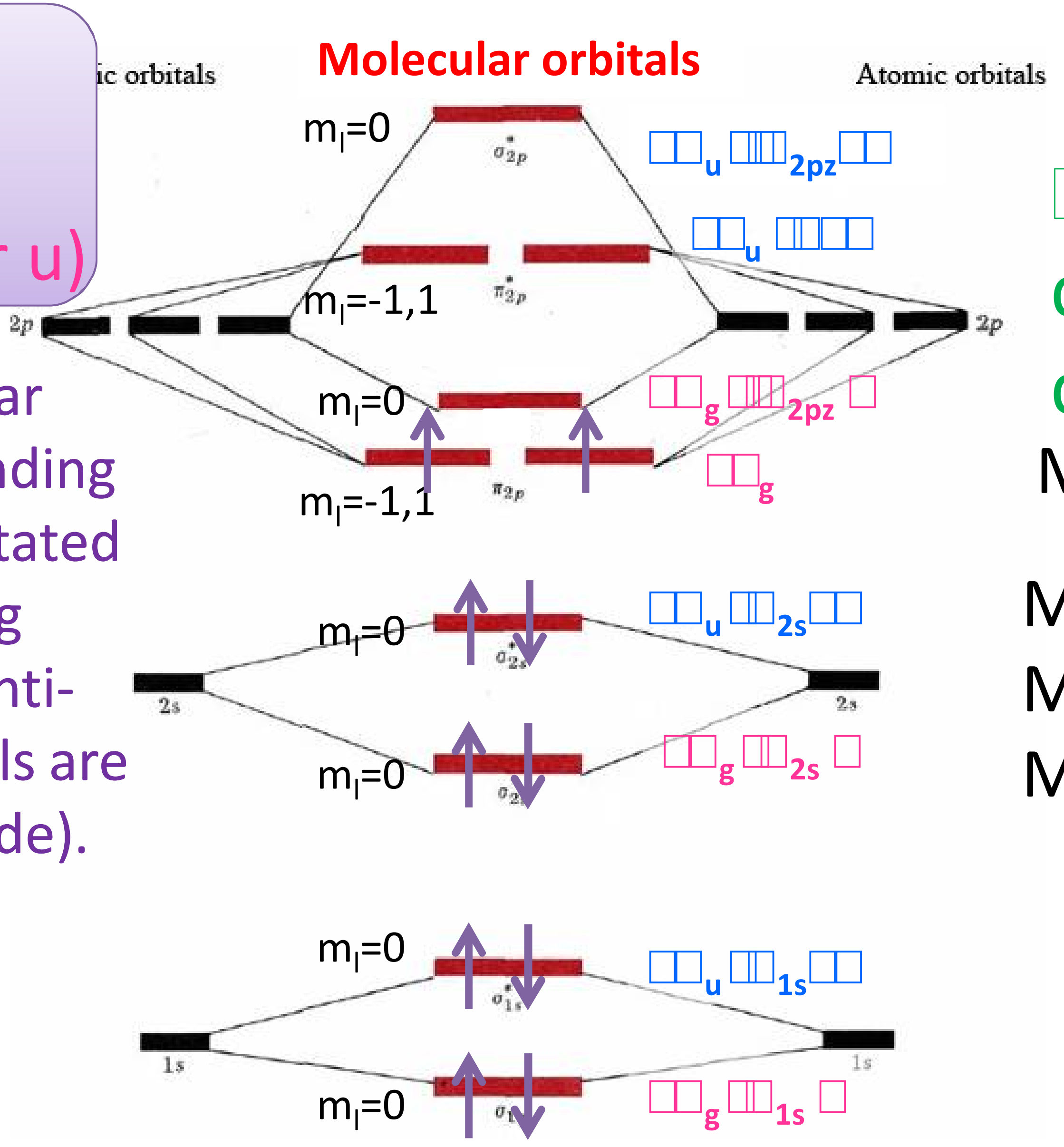
$^2□_g$

Diatomic molecular orbital

Terms

$^{2S+1}\square_{(g \text{ or } u)}$

In homo-nuclear molecules, bonding orbitals are notated with subscript g (gerade) and anti-bonding orbitals are with u (ungerade).



□ □is determined from M_l.

M_L :sum of m_l

$M_L=0$, ➔ □
$M_L=1$, ➔ □
$M_L=2$, ➔ □

……

□

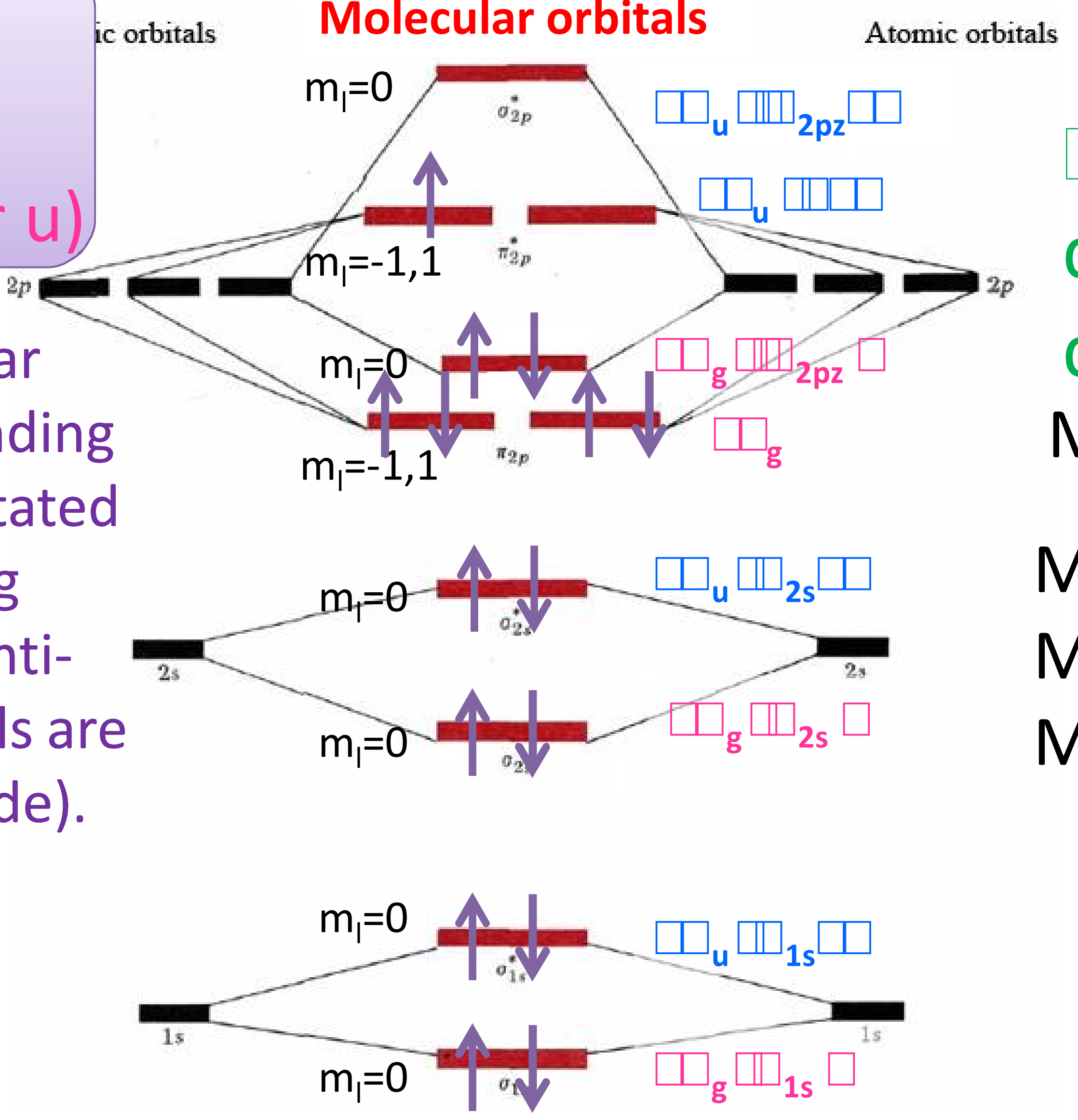
$^{3}\square_{g}$

g × g=g
u × g=u
u × u=g

Diatomic molecular orbital

Terms

$^{2S+1}□_{(g\ or\ u)}$



In homo-nuclear molecules, bonding orbitals are notated with subscript g (gerade) and anti-bonding orbitals are with u (ungerade).

g × g=g
u × g=u
u × u=g

□ □is determined from M_l.

M_L :sum of m_l

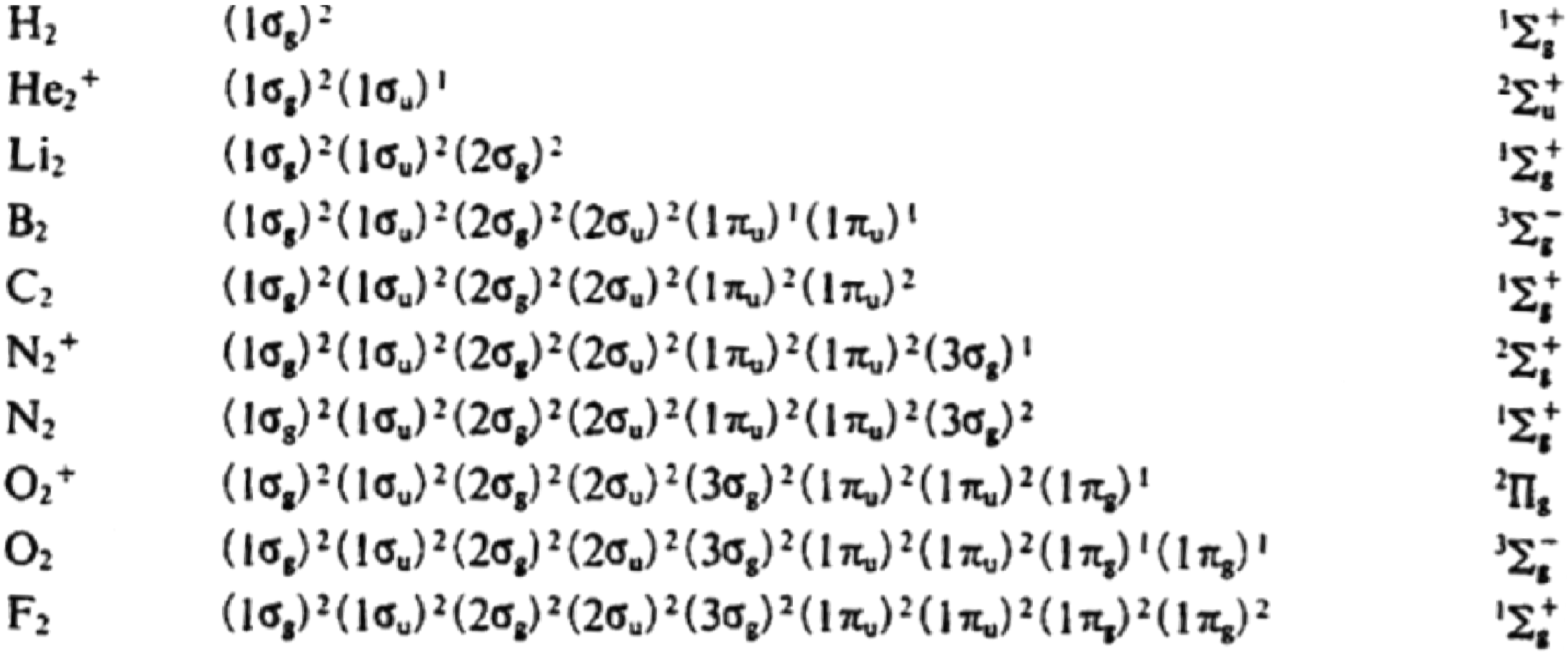
$M_L=0$, → □
$M_L=1$, → □
$M_L=2$, → □
……

□

$^2□_u$

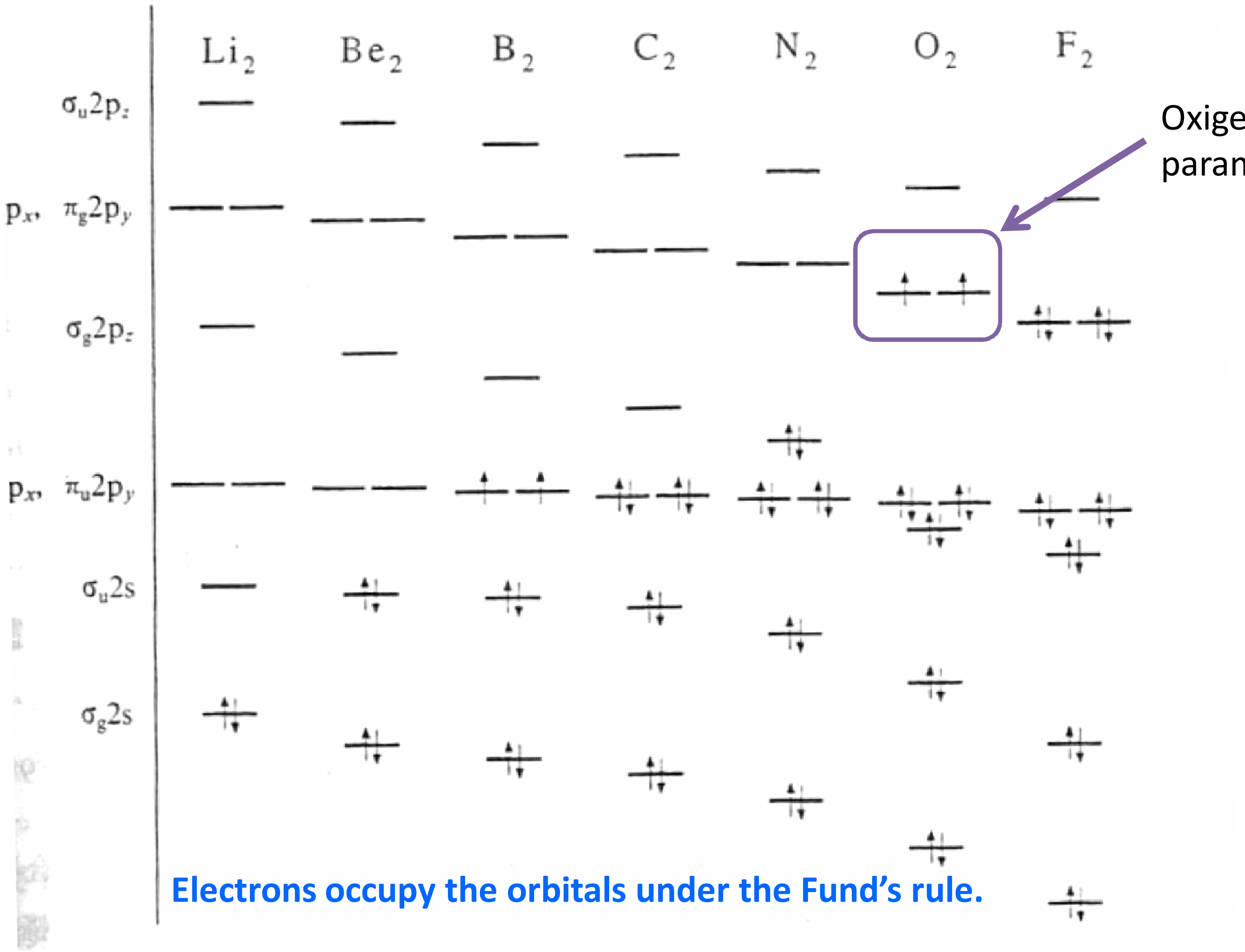
Diatomic molecular orbital

Configurations and terms



H_2	$(1\sigma_g)^2$	$^1\Sigma_g^+$
He_2^+	$(1\sigma_g)^2(1\sigma_u)^1$	$^2\Sigma_u^+$
Li_2	$(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2$	$^1\Sigma_g^+$
B_2	$(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^1(1\pi_u)^1$	$^3\Sigma_g^-$
C_2	$(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^2(1\pi_u)^2$	$^1\Sigma_g^+$
N_2^+	$(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^2(1\pi_u)^2(3\sigma_g)^1$	$^2\Sigma_g^+$
N_2	$(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^2(1\pi_u)^2(3\sigma_g)^2$	$^1\Sigma_g^+$
O_2^+	$(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)^2(1\pi_u)^2(1\pi_u)^2(1\pi_g)^1$	$^2\Pi_g$
O_2	$(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)^2(1\pi_u)^2(1\pi_u)^2(1\pi_g)^1(1\pi_g)^1$	$^3\Sigma_g^-$
F_2	$(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)^2(1\pi_u)^2(1\pi_u)^2(1\pi_g)^2(1\pi_g)^2$	$^1\Sigma_g^+$

Homo-diatomic molecular orbital



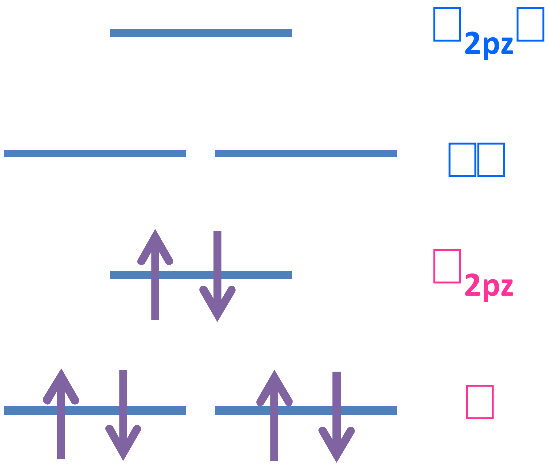
Oxigen is paramagnetic!

Electrons occupy the orbitals under the Fund’s rule.

Homo-diatomic molecular orbital

When bonds are strong?

(Bond order) =
[(number of elec. in bonding orbital)
- (number of elec. in anti-bonding orbital)]/2



Example of N_2

(bond order)=(6-0)/2=3

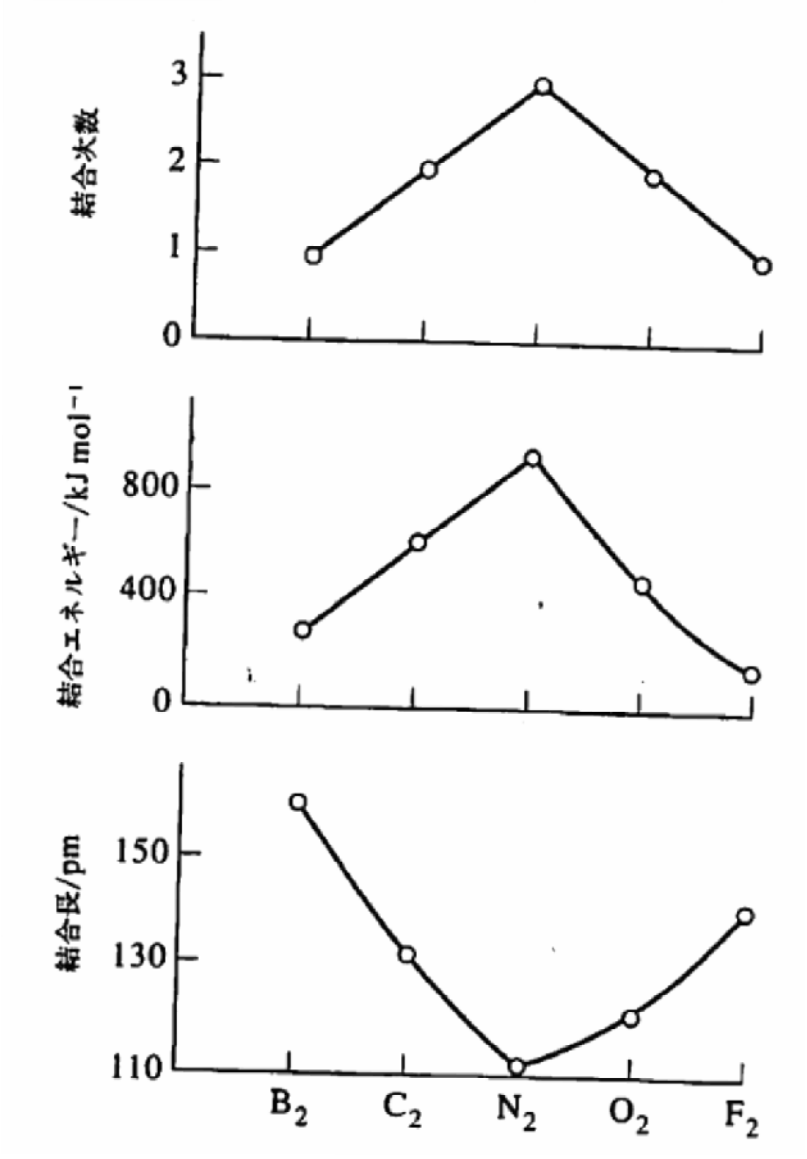
$N \equiv N$

Homo-diatomic molecular orbital

Bond order

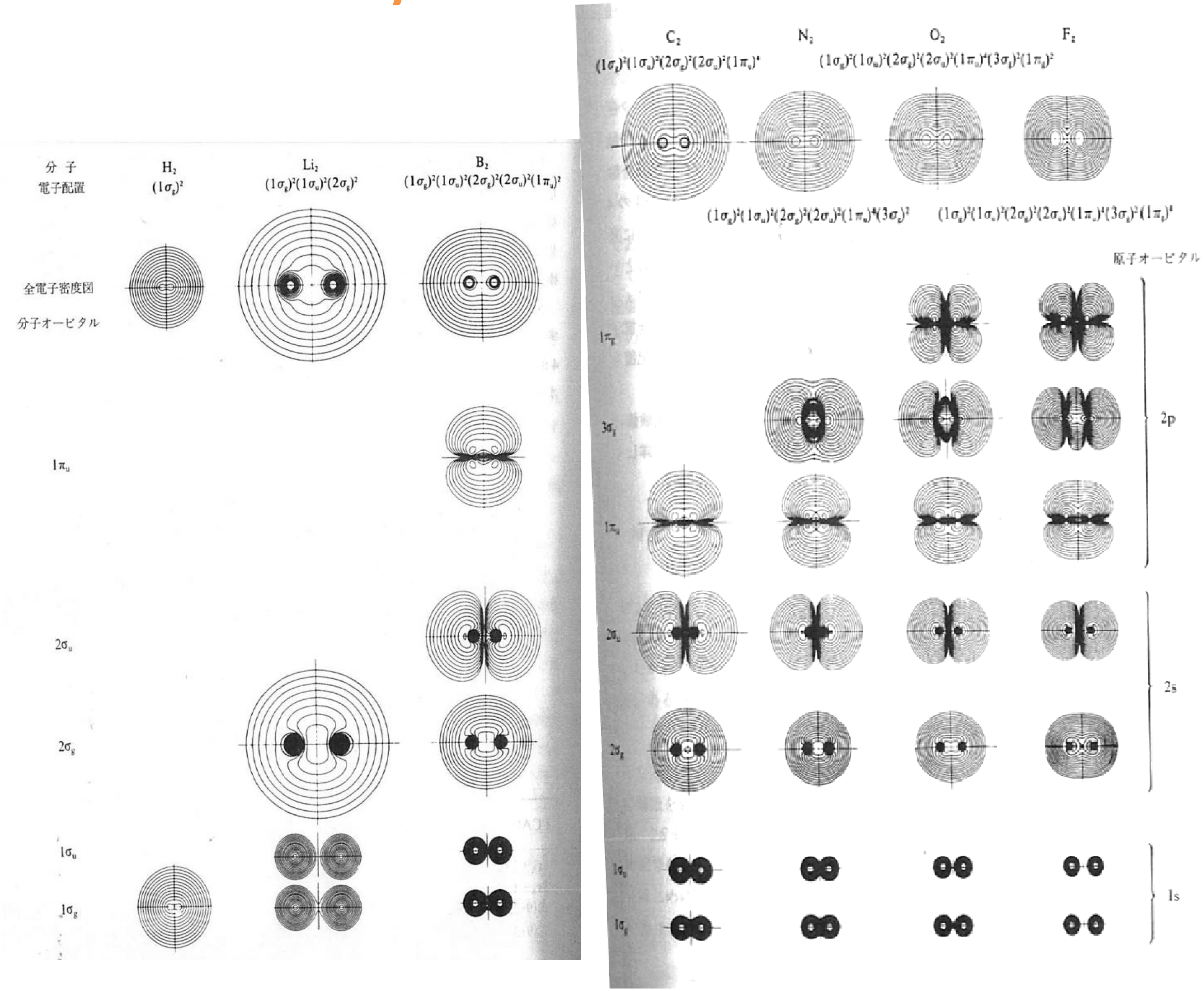
Bond energy
(kJ/mol)

Bond length
(pm)



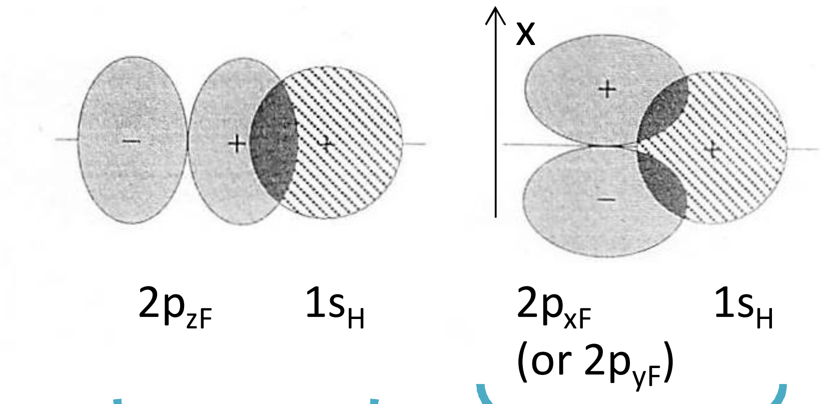
Homo-diatomic molecular orbital

Electron density of molecular orbitals



Hetero-diatomic molecular orbital

$$\left(\begin{array}{l}\langle s|\hat{H}_{atom}|p_1\rangle = 0,\\ \langle s|\hat{H}_{atom}|p_{-1}\rangle = 0,\\ \langle s|\hat{H}_{atom}|p_0\rangle = 0\end{array}\right)$$



They can interact!
They create
□ and □□ orbitals.

They cannot interact!

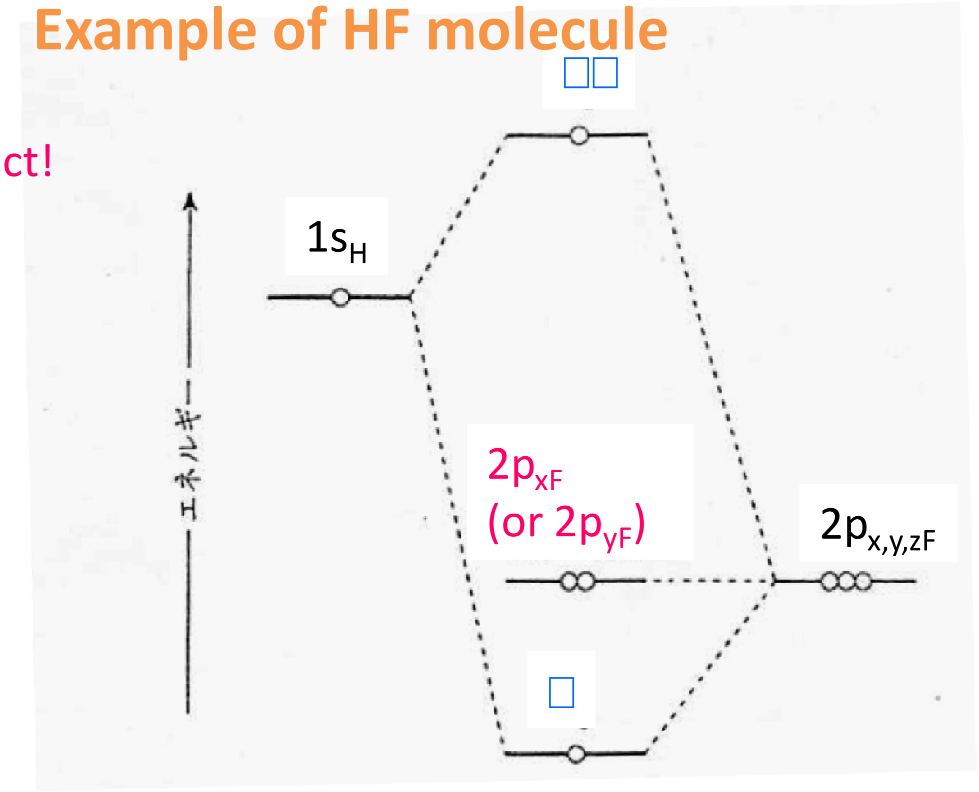
$$\langle s_A|\hat{H}_{mol}|p_{zA}\rangle = \langle s_A|\hat{H}_{mol}|p_{0A}\rangle \neq 0$$

$$\langle s_A|\hat{H}_{mol}|p_{zB}\rangle = \langle s_A|\hat{H}_{mol}|p_{0B}\rangle \neq 0$$

$$\langle s_A|\hat{H}_{mol}|p_{xA}\rangle = 0, \langle s_A|\hat{H}_{mol}|p_{yA}\rangle = 0$$

$$\langle s_A|\hat{H}_{mol}|p_{xB}\rangle = 0, \langle s_A|\hat{H}_{mol}|p_{yB}\rangle = 0$$

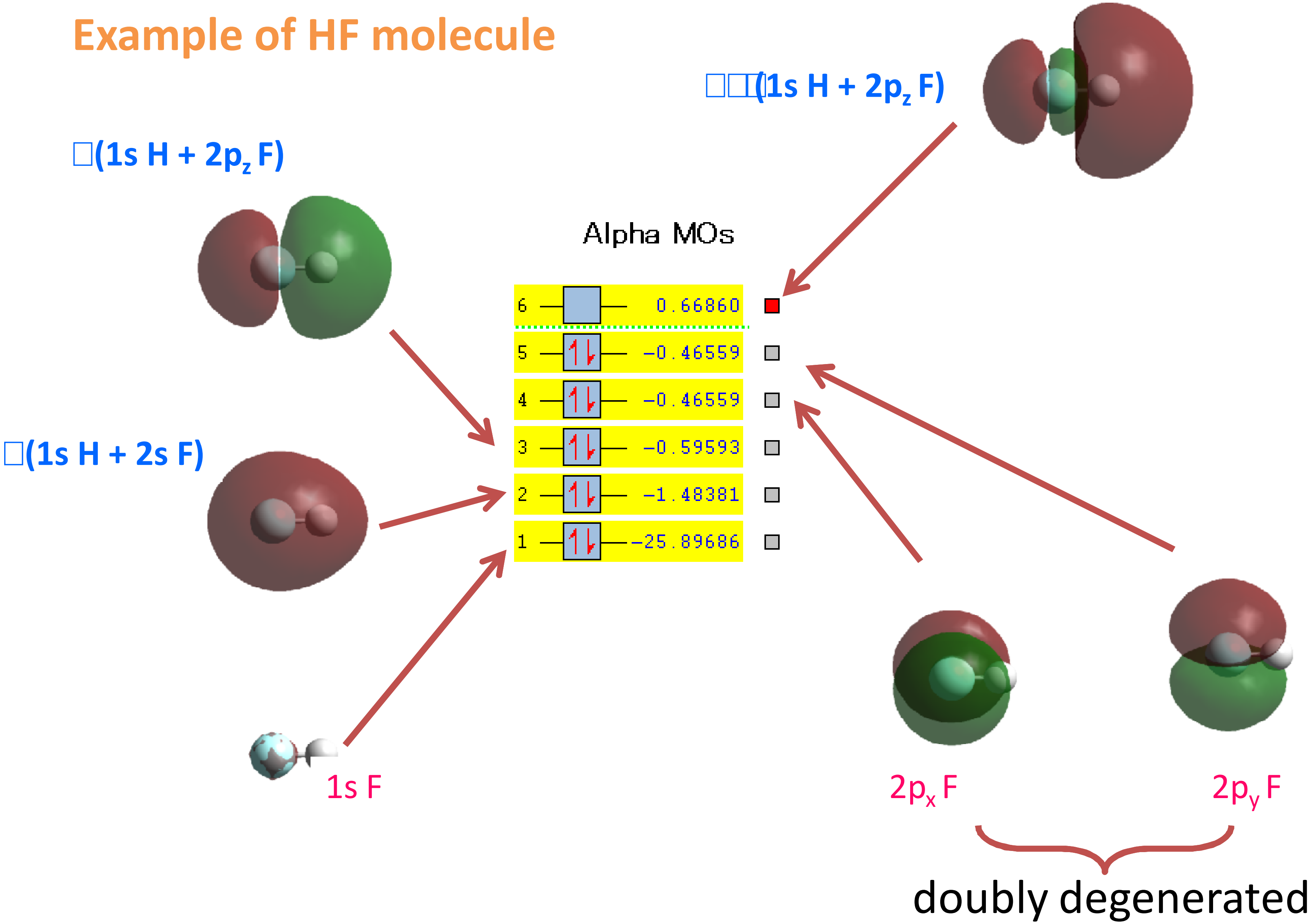
Example of HF molecule



Only p_z orbital can interact with s orbital of other atom.
p_x and p_y remain as lone pairs.

Hetero-diatomic molecular orbital

Example of HF molecule



□□□(1s H + $2p_z$ F)

□(1s H + $2p_z$ F)

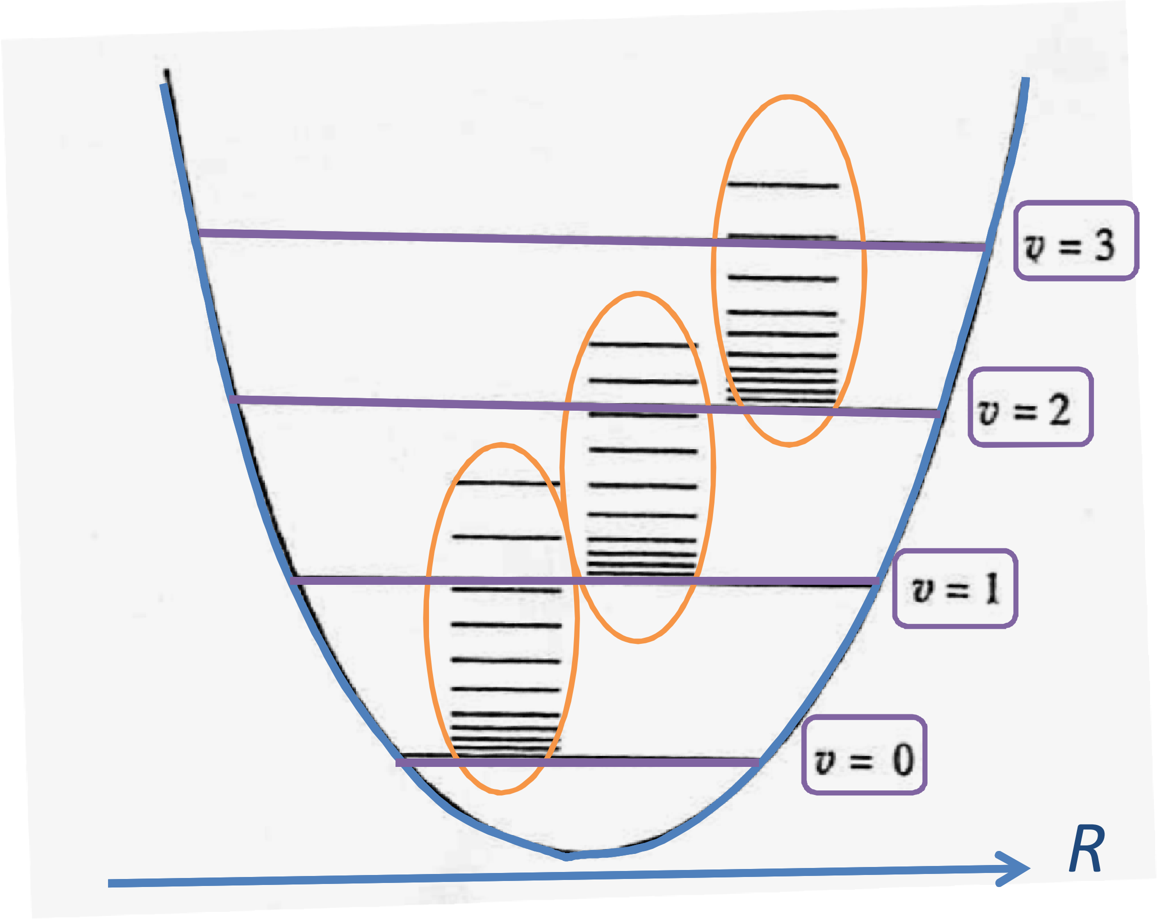
□(1s H + 2s F)

Alpha MOs

6		0.66860
5	↑↓	−0.46559
4	↑↓	−0.46559
3	↑↓	−0.59593
2	↑↓	−1.48381
1	↑↓	−25.89686

doubly degenerated

Vibration and Rotation



After obtaining electronic energy (E(R)), we can calculate vibrational and rotational levels.

Rigid Rotator model

$$\text{Total Molecular energy} = \underline{E(R)} + \underline{E_{vib}} + \underline{E_{rot}}$$

Electronic energy

Nuclear Schrödinger equation

General Hamiltonian for molecule

$$\widehat{H}\psi_e = E\psi_e$$

$$\left(\sum_{i=1}^{N_e}\left(-\frac{1}{2}\nabla_i^2 - \sum_{A=1}^{N_n}\frac{1}{r_{iA}}\right) + \sum_{i,j(i\neq j)}^{N_e}\frac{1}{r_{ij}} + \sum_{A,B(A\neq B)}^{N_n}\frac{1}{R_{AB}}\right)\psi_e = E\psi_e$$

$$\sum_{i=1}^{N_e}\left(-\frac{1}{2}\nabla_i^2 - \sum_{A=1}^{N_n}\frac{1}{r_{iA}}\right) \equiv \sum_{i=1}^{N_e}\hat{h}_i$$

One-electron operator

$$\sum_{i>j}^{N_e}\frac{1}{r_{ij}} \equiv \sum_{i=1}^{N_e}\hat{g}_{ij}$$

Two-electron operator

$$\sum_{A>B}^{N_n}\frac{1}{R_{AB}} \equiv V(R)$$

Nuclear potential (Constant)

Slater determinant for molecule

Slater determinant

$$\psi = \frac{1}{\sqrt{N!}}\det\begin{vmatrix} \varphi_1(\tau_1) & \varphi_2(\tau_1) & \dots & \varphi_{N_e}(\tau_1) \\ \varphi_1(\tau_2) & \varphi_2(\tau_2) & \dots & \varphi_{N_e}(\tau_2) \\ \dots & \dots & \dots & \dots \\ \varphi_1(\tau_{N_e}) & \varphi_2(\tau_{N_e}) & \dots & \varphi_{N_e}(\tau_{N_e}) \end{vmatrix}$$

One-electron spin-orbital

$$\varphi_i(\tau) = \sum_{p=1}^{N_{AO}} c_{ip}\phi_p(\tau)$$

Energy (i.e. Expectation value of single Slater determinant)

$$E = \langle \psi | \hat{H} | \psi \rangle = \sum_{i=1}^{N_e} \langle \varphi_i | \widehat{h} | \varphi_i \rangle$$

$$+ \sum_{i>j}^{N_e} \left(\left\langle \varphi_i(\tau_1)\varphi_j(\tau_2) \right| \frac{1}{r_{12}} \left| \varphi_i(\tau_1)\varphi_j(\tau_2) \right\rangle - \left\langle \varphi_i(\tau_1)\varphi_j(\tau_2) \right| \frac{1}{r_{12}} \left| \varphi_j(\tau_1)\varphi_i(\tau_2) \right\rangle \right)$$

$$+ V(R) = \sum_{i=1}^{N_e} \langle \varphi_i | \widehat{h} | \varphi_i \rangle + \sum_{i>j}^{N_e} \left(\langle ij | ij \rangle - \langle ij | ji \rangle \right) + V(R)$$

Fock operator

E should be minimized for all φ_i
under the orthonomal conditions of $\langle \varphi_i | \varphi_j \rangle = \delta_{ij}$.
Let’s consider a Lagrangian as follows.

$$L = E - \sum_{i,j}^{n} \lambda_{ji} \left(\langle \varphi_i | \varphi_j \rangle - \delta_{ij} \right)$$

Impose the first order variation of Lagrangian to be zero.

……(After some algebra)……

One electron wave functions should be the eigen functions of the Fock operator. $\hat{f}(\tau)\varphi_i(\tau) = \varepsilon_i \varphi_i(\tau)$

$$\hat{f}(\tau_1) = \hat{h}(\tau_1) + \hat{v}_{HF}(\tau_1)$$

$$\hat{v}_{HF}(\tau_1)\varphi_i(\tau_1) = \sum_{j \neq i}^{N_e} \left[\left(\int d\tau_2 \varphi_j^*(\tau_2) \frac{1}{r_{12}} \varphi_j(\tau_2) \right) \varphi_i(\tau_1) - \left(\int d\tau_2 \varphi_j^*(\tau_2) \frac{1}{r_{12}} \varphi_i(\tau_2) \right) \varphi_j(\tau_1) \right]$$

$$= \hat{J}\varphi_i(\tau_1) - \hat{K}\varphi_i(\tau_1)$$

Hartree-Fock-Roothaan equation

$$\hat{f}(\tau)\varphi_i(\tau)=\varepsilon_i\varphi_i(\tau)$$

$$\varphi_i(\tau)=\sum_{p=1}^{N_{AO}} c_{ip}\phi_p(\tau)$$

Expand by AO (basis set)
C is molecular orbital coefficient

$$\hat{f}(\tau)\sum_{p=1}^{N_{AO}} c_{ip}\phi_p(\tau)=\varepsilon_i\sum_{p=1}^{N_{AO}} c_{ip}\phi_p(\tau)$$

Multiply
$\phi_q^*(\tau)$
and integrate

$$\sum_{p=1}^{N_{AO}} c_{ip}\left\langle \phi_q \middle| \hat{f} \middle| \phi_p \right\rangle=\varepsilon_i\sum_{p=1}^{N_{AO}} c_{ip}\left\langle \phi_q \middle| \phi_p \right\rangle$$

$$\sum_{p=1}^{N_{AO}} F_{qp}c_{pi}=\varepsilon_i\sum_{p=1}^{N_{AO}} S_{qp}c_{pi}$$

$$\mathbf{FC}=\mathbf{SC\varepsilon}$$

Hartree-Fock Roothaan equation

Hartree-Fock-Roothaan equation

F matrix actually depends on molecular orbital information due to the two-electron operators.

$$F_{pq} = h_{pq} + \sum_{r,s}^{N} D_{rs}\left[2\left(pq|rs\right) - \left(ps|rq\right)\right] \qquad D_{pq} = \sum_{i}^{N_{elec}} C_{pi}^{*} C_{qi}$$

Density matrix

$$\mathbf{F}\left(\mathbf{C}\right)\mathbf{C} = \mathbf{SC}\boldsymbol{\varepsilon}$$ Non linear equation!

We need to solve it iteratively.

$$\mathbf{F}\left(\mathbf{C}_n\right)\mathbf{C}_{n+1} = \mathbf{SC}_{n+1}\boldsymbol{\varepsilon}$$

$$\left|\mathbf{C}_{n+1} - \mathbf{C}_n\right| < threshold$$ → Converged!

Hartree-Fock-Roothaan equation

$$\boxed{F_{pq} = h_{pq} + \sum_{r,s}^{N} D_{rs}\left[2\left(pq|rs\right) - \left(ps|rq\right)\right]}$$

Nuclear attraction

kinetic

$$\hat{h}_{pq=}\left\langle \phi_p \left\| \left(-\frac{1}{2}\nabla^2 - \sum_{A=1}^{N_n} \frac{1}{r_A} \right) \right\| \phi_q \right\rangle = \int d\tau_1 d\tau_2 \left[\phi_p^*(\tau_1) \left(-\frac{1}{2}\nabla^2 - \sum_{A=1}^{N_n} \frac{1}{r_A} \right) \phi_q(\tau_1) \right]$$

$$\left(pq|rs\right) = \int\int d\tau_1 d\tau_2 \left(\phi_p^*(\tau_1)\phi_r^*(\tau_2) \frac{1}{r_{12}} \phi_q(\tau_1)\phi_s(\tau_2) \right)$$

Two-electron repulsion

$$\hat{S}_{pq=}\left\langle \phi_p | \phi_q \right\rangle = \int d\tau_1 d\tau_2 \left[\phi_p^*(\tau_1)\phi_q(\tau_1) \right]$$

Overlap

To solve Hartree-Fock-Roothaan equation, we need to calculate these integrals with the atomic basis set orbital. We need efficient functions for basis sets.

Basis set functions

In poly-atomic systems, polar coordinate is no more useful because we have various centers in a molecule.

Slater orbital (1s)

$$\exp\left(-\zeta r\right)$$

$$=\exp\left(-\zeta\sqrt{\left(x-X_A\right)^2+\left(y-Y_A\right)^2+\left(z-Z_A\right)^2}\right)$$

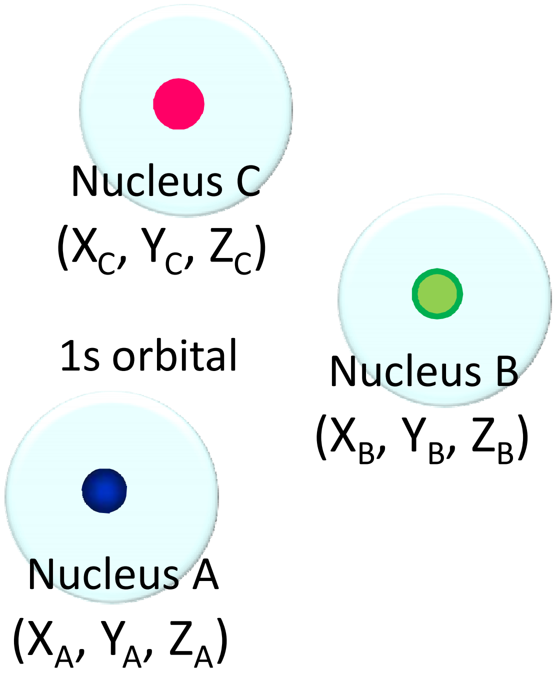
Gaussian orbital (1s)

$$\exp\left(-\alpha r^2\right)$$

$$=\exp\left(-\alpha\left(\left(x-X_A\right)^2+\left(y-Y_A\right)^2+\left(z-Z_A\right)\right)\right)$$

$$=\exp\left(-\alpha\left(\left(x-X_A\right)^2+\left(y-Y_A\right)^2+\left(z-Z_A\right)\right)\right)$$

$$=\exp\left(-\alpha\left(x-X_A\right)^2\right)\exp\left(-\alpha\left(y-Y_A\right)^2\right)\exp\left(-\alpha\left(z-Z_A\right)^2\right)$$



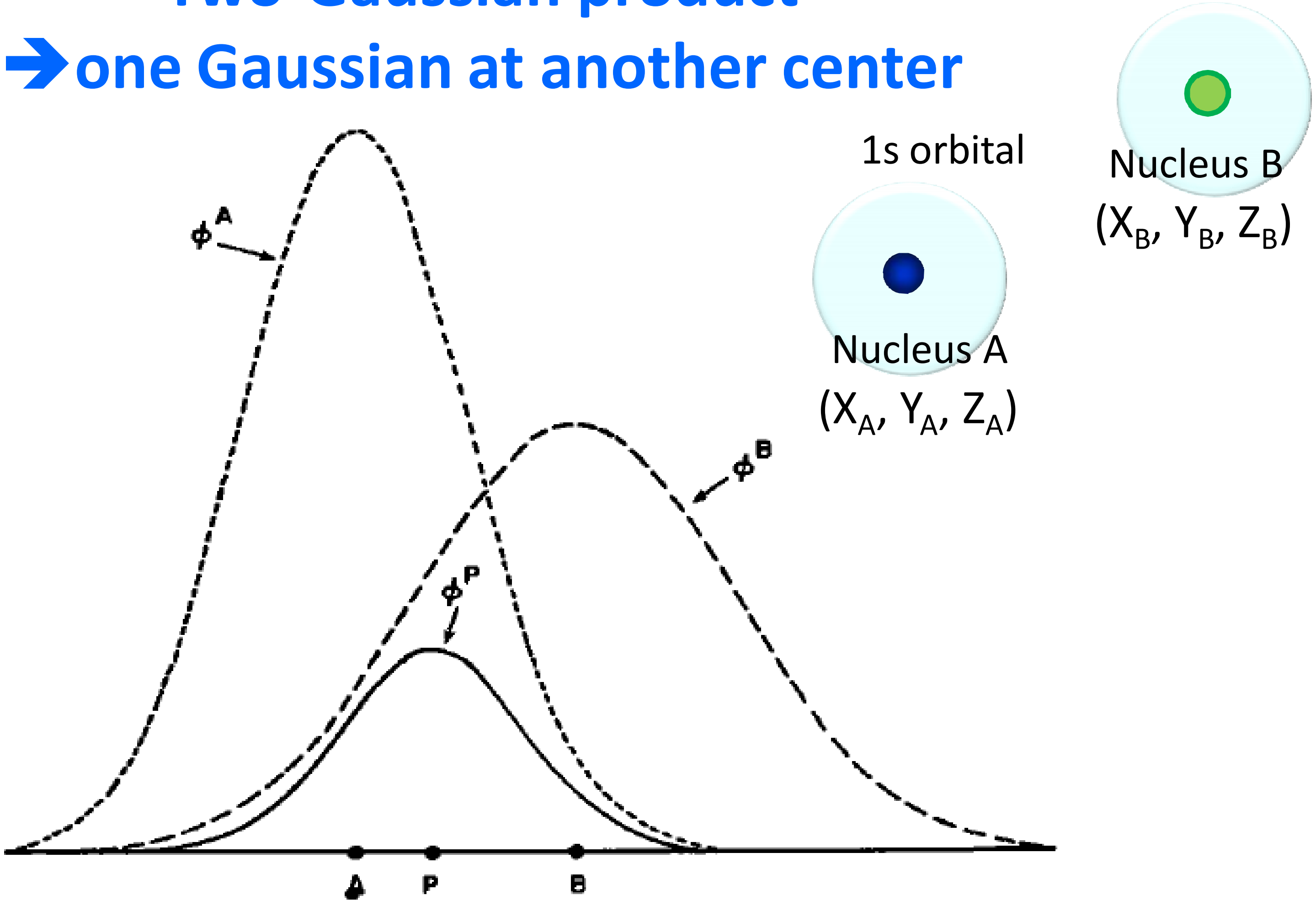
We can separate x, y, z variable easily.

Basis set functions

Gaussian product rules

Two-Gaussian product

➔one Gaussian at another center



1s orbital

Nucleus A

(X_A, Y_A, Z_A)

Nucleus B

(X_B, Y_B, Z_B)

Figure 3.1 The product of two 1*s* Gaussians is a third 1*s* Gaussian.

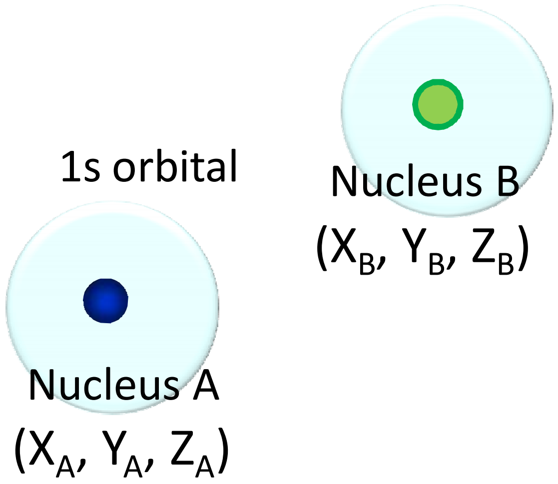
Basis set functions

Ex. Overlap of two centers

$$\int dxdydz \exp\left(-\alpha_A r_A{}^2\right)\exp\left(-\alpha_B r_B{}^2\right)$$

$$= \int dxdydz \exp\left(-\alpha_A r_A{}^2 - \alpha_B r_B{}^2\right)$$

$$\left.\begin{aligned} &= A_{Px} \int dx \exp\left(-\alpha_P (x - X_P)^2\right) \\ &\times A_{Py} \int dy \exp\left(-\alpha_P (y - Y_P)^2\right) \\ &\times A_{Pz} \int dz A_P \exp\left(-\alpha_P (z - Z_P)^2\right) \end{aligned}\right\}$$



Easy to calculate!

Basis set functions

If we consider Cartesian functions, it's written by very simple polynomials of x, y, and z for higher angular parts.

Ex. Form of d orbital basis except exponential part

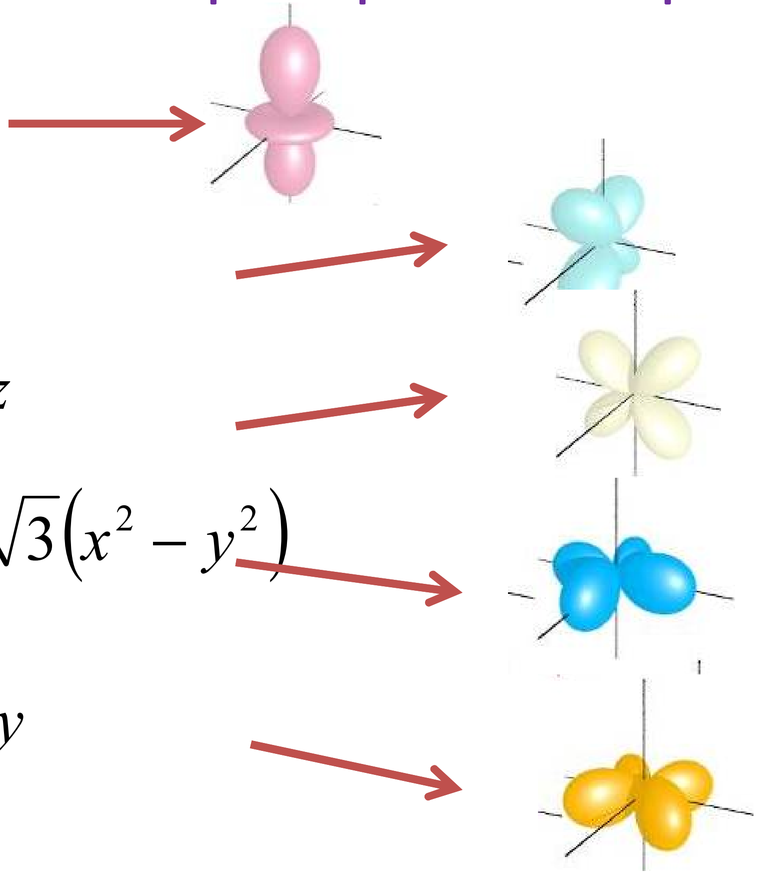
$$d_{z^2} \equiv r^2 Y_2^0 = \frac{1}{2}\left(3z^2 - r^2\right)$$

$$d_{xz} \equiv r^2\left(Y_2^1 + Y_2^{-1}\right) = \sqrt{3}xz$$

$$d_{yz} \equiv \frac{1}{\sqrt{2i}} r^2\left(Y_2^1 - Y_2^{-1}\right) = \sqrt{3}yz$$

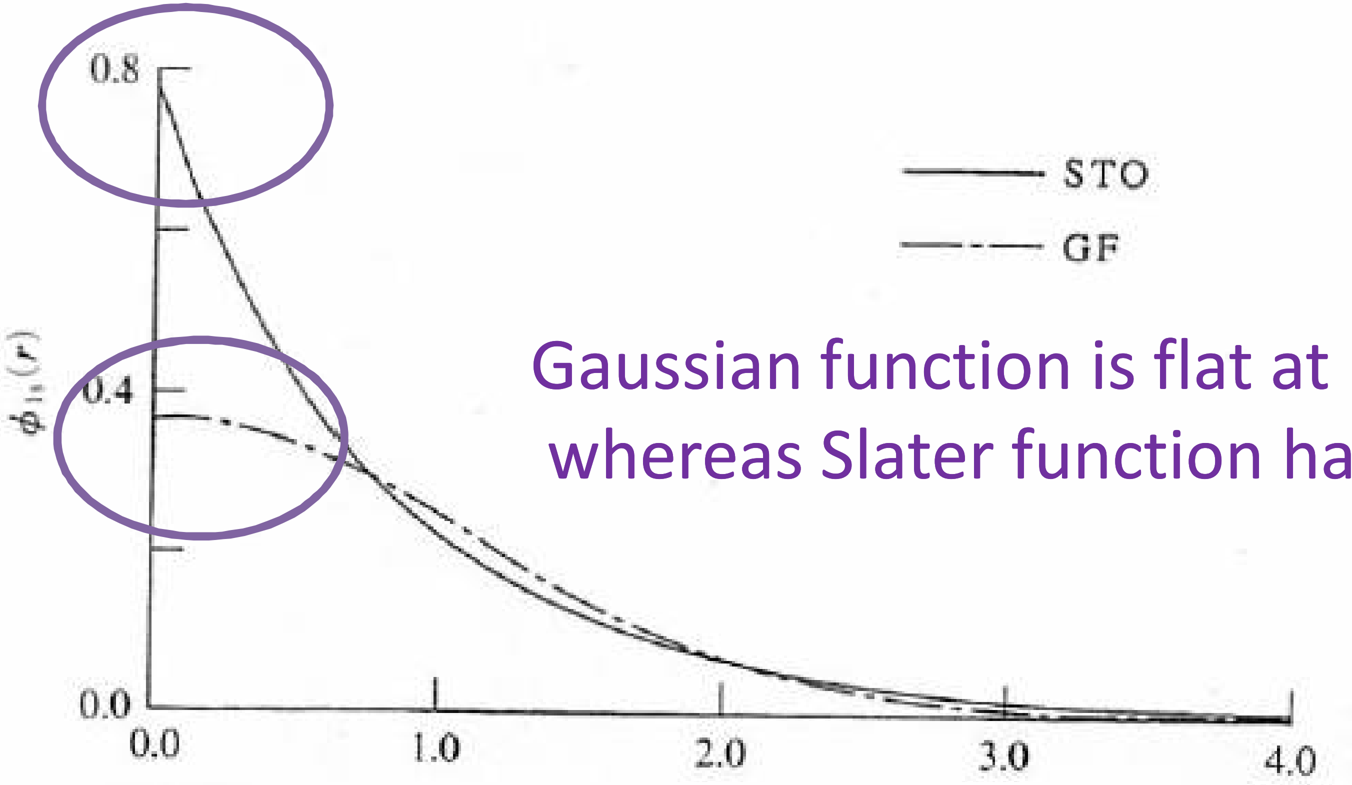
$$d_{x^2-y^2} \equiv \frac{1}{\sqrt{2}} r^2\left(Y_2^2 + Y_2^{-2}\right) = \frac{1}{2}\sqrt{3}\left(x^2 - y^2\right)$$

$$d_{xy} \equiv \frac{1}{\sqrt{2i}} r^2\left(Y_2^2 - Y_2^{-2}\right) = \sqrt{3}xy$$



Basis set functions

Comparison between Gaussian and Slater functions



Gaussian function is flat at r=0 whereas Slater function has a cusp.

$$\phi_{1s}^{STO}(r,\zeta) = S_{100}(r,\zeta) = \left(\frac{\zeta^3}{\pi}\right)^{1/2} e^{-\zeta r}$$

□=1.24

$$\phi_{1s}^{GF}(r,\alpha) = G_{100}(r,\alpha) = \left(\frac{2\alpha}{\pi}\right)^{3/4} e^{-\alpha r^2}$$

□=1.24

Basis set functions

STO-3G

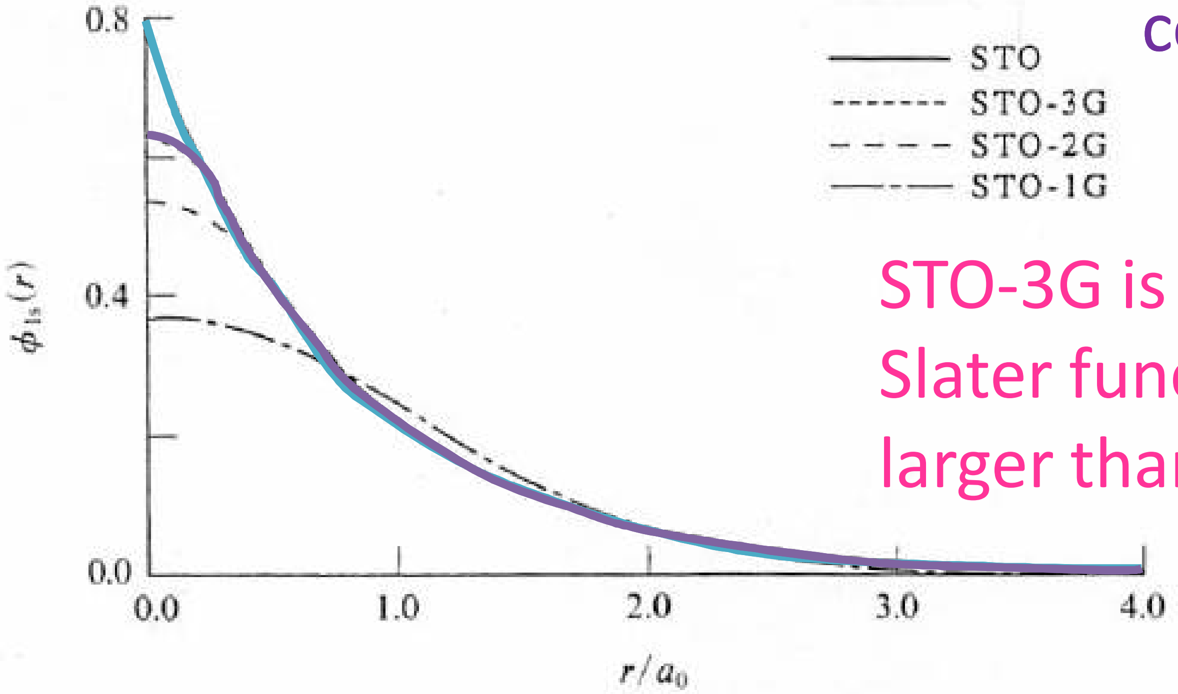
Slater functions are fitted by the linear combination of three Gaussian functions.

$$\phi_{1s}^{STO}(r) = \sum_{i=1}^{3} d_{1si}\,\phi_{1s}^{GF}(r, \alpha_{1si})$$

α Exponential coefficients
d contraction coefficients

$$= 0.4446\,\phi_{1s}^{GF}(r, 0.1688) + 0.5353\,\phi_{1s}^{GF}(r, 0.6239) + 0.1543\,\phi_{1s}^{GF}(r, 3.425)$$

contraction basis set



STO-3G is close to the Slater function when *r* is larger than a_0.

Basis set functions

In the sense of linear combination of atomic orbital (LCAO), we usually use contracted-Gaussian basis functions. Contraction coefficients are normally determined from atomic calculations.

To describe molecular bonds well;

1. we decontract or split basis sets for valence orbitals. (Ex"valence double-zeta")

2. We sometimes add diffuse functions, with small exponent coefficients.

3. We sometimes add polarization functions, higher angular momentum functions.

Basis set functions

contraction coefficients

exponential coefficients

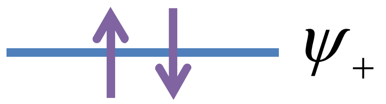
quadruple zeta

Dyall-QZ-c basis

S	1s	2s	3s	4s	5s	6s
6.5973426E+07	9 9782180E-05	-3.7200758E-05	1.7519609E-05	8.5062625E-06	3.2603668E-06	-8.3449817E-07
1.7573042E+07	2 3885301E-04	-8.9322205E-05	4.2086226E-05	2.0436349E-05	7.8332122E-06	-2.0049375E-06
6.0368629E+06	4 8228463E-04	-1.8095458E-04	8.5305558E-05	4.1427940E-05	1.5879797E-05	-4.0644893E-06
2.3148616E+06	8 8873685E-04	-3.3516266E-04	1.5812708E-04	7.6807417E-05	2.9441998E-05	-7.5358548E-06
9.7498001E+05	1 6115692E-03	-6.1126323E-04	2.8865029E-04	1.4023603E-04	5.3759158E-05	-1.3759946E-05
4.3572342E+05	2 8710341E-03	-1.0971913E-03	5.1870929E-04	2.5207492E-04	9.6635219E-05	-2.4734770E-05
2.0470199E+05	5 1348039E-03	-1.9786885E-03	9.3667476E-04	4.5532856E-04	1.7457384E-04	-4.4683531E-05
9.9654250E+04	9 2072616E-03	-3.5840701E-03	1.6992363E-03	8.2632136E-04	3.1681877E-04	-8.1094980E-05
4.9983316E+04	1 6583606E-02	-6.5322387E-03	3.1029055E-03	1.5095694E-03	5.7888801E-04	-1.4817268E-04
2.5663485E+04	2 9818647E-02	-1.1931486E-02	5.6815266E-03	2.7657042E-03	1.0606081E-03	-2.7149014E-04
1.3440699E+04	5 2950673E-02	-2.1662469E-02	1.0353665E-02	5.0443789E-03	1.9350958E-03	-4.9532159E-04
7.1598929E+03	9 0977035E-02	-3.8543746E-02	1.8528281E-02	9.0395936E-03	3.4681500E-03	-8.8782782E-04
3.8753556E+03	1 4628804E-01	-6.5598978E-02	3.1847069E-02	1.5573611E-02	5.9794889E-03	-1.5306719E-03
2.1307057E+03	2 0889813E-01	-1.0286939E-01	5.0763430E-02	2.4921791E-02	9.5740825E-03	-2.4513911E-03
1.1898903E+03	2 4396201E-01	-1.3823205E-01	7.0048345E-02	3.4607750E-02	1.3320170E-02	-3.4104986E-03
6.7429769E+02	2 0474701E-01	-1.3342031E-01	6.9688307E-02	3.4691717E-02	1.3362843E-02	-3.4233136E-03
3.8724214E+02	1 0102651E-01	-2.4179884E-02	8.1792671E-03	3.5358781E-03	1.3346475E-03	-3.3860593E-04
2.2481397E+02	2 1298438E-02	2.1261417E-01	-1.5951971E-01	-8.6463521E-02	-3.4004530E-02	8.7246883E-03
1.3362161E+02	1 3981505E-03	4.1121363E-01	-3.7713017E-01	-2.1585010E-01	-8.5749185E-02	2.2051823E-02
8.1281158E+01	4 1116786E-05	3.5057833E-01	-4.0182068E-01	-2.4250758E-01	-9.7776272E-02	2.5149688E-02
5.0939803E+01	3 8127887E-05	1.4856492E-01	-1.0447585E-01	-6.8770856E-02	-2.8918209E-02	7.5361505E-03
3.2280526E+01	-1 0441931E-04	2.9528209E-02	4.0069785E-01	3.6353582E-01	1.6166297E-01	-4.2214557E-02
2.0394685E+01	3 6942048E-05	1.8089816E-03	6.1447118E-01	7.4823240E-01	3.5515598E-01	-9.3081510E-02
1.2503244E+01	-3 2526750E-05	3.5775229E-04	3.2470347E-01	3.7866373E-01	1.6908482E-01	-4.4203642E-02
7.2874456E+00	2 4471759E-05	-3.1026960E-04	5.4055539E-02	-4.6352619E-01	-2.8413146E-01	7.6523038E-02
4.3210001E+00	-1 1535675E-05	3.3408769E-05	2.2180494E-03	-7.3973061E-01	-5.9688417E-01	1.6916103E-01
2.5234051E+00	3 3346020E-06	-7.0668008E-05	1.2025946E-03	-3.2042059E-01	-3.8288855E-01	1.1465921E-01
1.4175240E+00	-4 8775188E-06	3.8350509E-05	-2.7428342E-04	-3.8335074E-02	2.2717730E-01	-7.9496271E-02
7.9157400E-01	2.7643534E-06	-1.7666327E-05	9.1058439E-05	-1.4535011E-03	6.2283403E-01	-2.2484198E-01
4.4198499E-01	-1.7465836E-06	1.3620169E-05	-9.8219827E-05	-7.9721646E-04	4.5570588E-01	-2.7116462E-01
2.4345371E-01	8.5919476E-07	-6.0619634E-06	3.2241392E-05	-6.7667385E-05	1.0609629E-01	-1.5553717E-01
1.1878413E-01	-4.2231693E-07	3.0886469E-06	-1.6573828E-05	3.8028070E-05	5.1623573E-03	1.8463795E-01
6.1739139E-02	2.3280153E-07	-1.6835017E-06	1.4079000E-05	2.1992554E-04	3.9420751E-03	5.2053680E-01
3.1922684E-02	-9.6968198E-08	7.1602848E-07	-3.7927686E-07	1.6873698E-04	3.2883261E-03	4.4423560E-01
1.6420495E-02	2.3449273E-08	-1.6889708E-07	1.6939352E-06	3.5436438E-05	6.4944623E-04	8.6473321E-02

Beyond the HF method

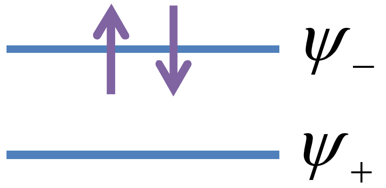
There is no reason that the Single determinant can really describe the true wave function.



$$\Psi(1,2)=\frac{1}{\sqrt{2!}}\begin{vmatrix}\psi_+(1)\alpha(1) & \psi_+(1)\beta(1)\\ \psi_+(2)\alpha(2) & \psi_+(2)\beta(2)\end{vmatrix}$$

$$=\frac{1}{\sqrt{2!}}\psi_+(1)\psi_+(2)\{\alpha(1)\beta(2)-\beta(1)\alpha(2)\}$$

These are different functions!



$$\Psi'(1,2)=\frac{1}{\sqrt{2!}}\begin{vmatrix}\psi_-(1)\alpha(1) & \psi_-(1)\beta(1)\\ \psi_-(2)\alpha(2) & \psi_-(2)\beta(2)\end{vmatrix}$$

$$=\frac{1}{\sqrt{2!}}\psi_-(1)\psi_-(2)\{\alpha(1)\beta(2)-\beta(1)\alpha(2)\}$$

Mixing the various determinants (configurations) improve the solution. (Configuration interaction)

Beyond the HF method

If we consider the wave function as the linear combination of full configurations (Full-CI) with infinite number of orthogonal 1-electron orbital basis, it should be "Exact".
(Of course, impossible. Number of basis sets is finite!)
We need approximation methods.

Major approximation methods
(post-HF or electron correlation method)

- Perturbation theory; MP2, MP4, …
- (Truncated) configuration interaction theory; SDCI,SDTQCI,…,RASCI
- Coupled Cluster theory; CCSD, CCSDT, …

↓ More accurate

Multi reference electron correlation methods will be discussed in Dr. Geetha's talk.

Single and Doubles CI method

Exact within the used basis sets!

$$\left|\Psi_{Full-CI}\right\rangle = \left(t_0 + \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \cdots\right)\left|\Psi_{HF}\right\rangle$$

$\hat{T}_N$: N-electron excitation operator

Creation and Annihilation operator (delete i and create a orbital)

$$\hat{T}_1 = \sum_{a \in vir, i \in occ} t_1(a,i) \left| \begin{matrix} a \\ i \end{matrix} \right\rangle = \sum_{a \in vir, i \in occ} t_1(a,i) \boxed{a_a^{+} a_i} \left| HF \right\rangle$$

<u>t_1, t_2, … coefficients are the parameters to be obtained</u>.

$$\left|\Psi_{SDCI}\right\rangle = \left(t_0 + \hat{T}_1 + \hat{T}_2\right)\left|\Psi_{HF}\right\rangle$$

$$E_{SDCI} = \left\langle \Psi_{SDCI} \middle| \hat{H} \middle| \Psi_{SDCI} \right\rangle$$

<u>t_0, t_1, t_2 coefficients are optimized as the energy is to be minimum.</u>
<u>(Please read Szabo's book! for more details.)</u>

Ex. Two electron excitation operator

$$\hat{T}_2 = \sum_{\substack{a>b\in vir \\ i>j\in occ}} \left| \begin{matrix} ab \\ ij \end{matrix} \right\rangle = \sum_{\substack{a>b\in vir \\ i>j\in occ}} t_2(a,b,i,j)\, a_b^+ a_j a_a^+ a_i \left| HF \right\rangle$$

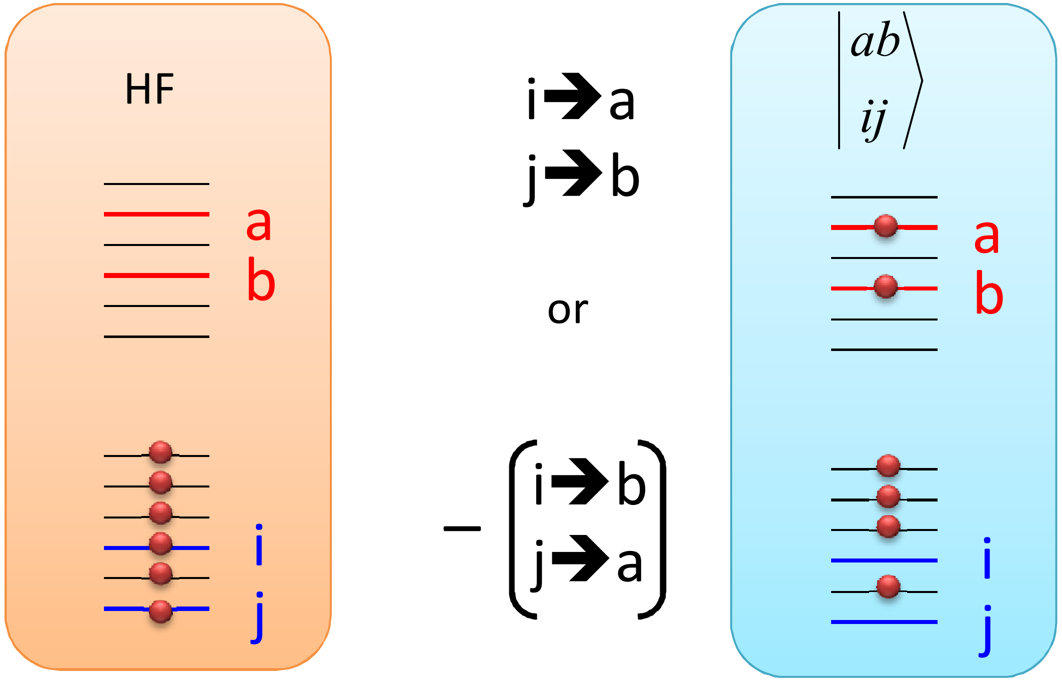
$(a > b,\ i > j)$

a, b,c: virtual orbital

i,j,k: occupied orbital

p: general orbital

$$\left(a_b^+ a_j a_a^+ a_i \left| HF \right\rangle = a_a^+ a_i\, a_b^+ a_j \left| HF \right\rangle = -a_a^+ a_j a_b^+ a_i \left| HF \right\rangle = -a_b^+ a_i\, a_a^+ a_j \left| HF \right\rangle \right)$$



i → a
j → b

or

$-\begin{pmatrix} i \rightarrow b \\ j \rightarrow a \end{pmatrix}$

Coupled Cluster method

One of the most accurate methods to take into account electron correlation within single reference theory

$$\hat{H}_{HF}\left|\Phi_{HF}\right\rangle = E_{HF}\left|\Phi_{HF}\right\rangle \quad \Rightarrow \quad \hat{H}\left|\Psi_{exact}\right\rangle = E\left|\Psi_{exact}\right\rangle$$

$$\left|\Psi_{exact}\right\rangle \equiv \exp\left(\hat{T}\right)\left|\Phi_{HF}\right\rangle = \left(1+\hat{T}+\frac{\left(\hat{T}\right)^2}{2}+\cdots\right)\left|\Phi_{HF}\right\rangle$$

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 \ldots$$

$\hat{T}_N$: N-electron excitation operator

$$\left(\hat{T}_1 = \sum_{a\in vir,\, i\in occ} t_1(a,i)\left|\begin{matrix} a \\ i \end{matrix}\right\rangle = \sum_{a\in vir,\, i\in occ} t_1(a,i)\, a_a^{+} a_i \left|HF\right\rangle\right)$$

t_1, t_2, … coefficients are the parameters to be obtained.

$$\hat{H}_N = \hat{H} - E_{HF}$$

$$\hat{H}_N \exp\left(\hat{T}\right)\left|\Phi_{HF}\right\rangle = \Delta E \exp\left(\hat{T}\right)\left|\Phi_{HF}\right\rangle$$

$$\exp\left(-\hat{T}\right)\hat{H}_N \exp\left(\hat{T}\right)\left|\Phi_{HF}\right\rangle = \Delta E\left|\Phi_{HF}\right\rangle$$

ΔE

Electron correlation energy

Coupled Cluster method

$$\exp(-T)\hat{H}_N\exp(T)$$

$$=\hat{H}_N+\left[\hat{H}_N,T\right]+\frac{1}{2!}\left[\left[\hat{H}_N,T\right],T\right]+\ldots+\frac{1}{4!}\left[\left[\left[\left[\hat{H}_N,T\right],T\right],T\right],T\right]$$

$$=\left(\hat{H}_N\exp(T)\right)_C$$

The above exponential expansion is terminate after four commutations because H_N is at most two-electron operator. $\left(\hat{H}_N\exp(T)\right)_C$ means collect only connected terms which provide non-zero values.

Coupled Cluster singles and doubles (CCSD) equations

$$\begin{cases}\left\langle\Phi_{HF}\middle|\left(\hat{H}_N\exp(T)\right)_C\middle|\Phi_{HF}\right\rangle=\Delta E & \hat{T}=\hat{T}_1+\hat{T}_2\\ \left\langle\Phi_i^a\middle|\left(\hat{H}_N\exp(T)\right)_C\middle|\Phi_{HF}\right\rangle=0\ \ldots(1) & \left|\Phi_i^a\right\rangle \text{ One-electron excited determinant}\\ \left\langle\Phi_{ij}^{ab}\middle|\left(\hat{H}_N\exp(T)\right)_C\middle|\Phi_{HF}\right\rangle=0\ \ldots(2) & \left|\Phi_{ij}^{ab}\right\rangle \text{ Two-electron excited determinant}\end{cases}$$

CCSD amplitude equations

$$\Delta E = E_{CCSD} = \sum_{I,A} F_A^I T_I^A + \sum_{I<J,A<B} V_{AB}^{IJ} \tau_{IJ}^{AB}$$

$$F_I^A - 2\sum_{K,C} F_C^K T_K^A T_I^C + \sum_C H_C^A T_I^C - \sum_K H_I^K T_K^A + \sum_{K,C} H_C^K \left(T_{IK}^{AC} + T_K^A T_I^C \right)$$
$$+ \sum_{K,C} V_{IC}^{AK} T_K^C + \sum_{K,C<D} V_{CD}^{AK} \tau_{IK}^{CD} - \sum_{K<L,C} V_{IC}^{KL} \tau_{KL}^{AC} = 0 \qquad \text{... (1)}$$

$$V_{IJ}^{AB} + P_{AB}\left(\sum_C G_C^A T_{IJ}^{CB} - \sum_K V_{IJ}^{AB} T_K^B \right) - P_{IJ}\left(\sum_K G_I^K T_{KJ}^{AB} - \sum_C V_{IC}^{AB} T_J^C \right)$$
$$+ \sum_{K<L} A_{IJ}^{KL} \tau_{KL}^{AB} + \sum_{C<D} B_{CD}^{AB} \tau_{IJ}^{CD} + P_{IJ} P_{AB} \left(\sum_{K,C} H_{IC}^{AK} T_{JK}^{BC} - \sum_{K,C} V_{IC}^{AK} T_J^C T_K^B \right) = 0 \qquad \text{... (2)}$$

Non linear equations of T_1 and T_2,
iteratively to be solved.

Term notation of DIRAC08 RELCCSD
from L. Vischer's JCP paper

Problem in coupled cluster method for expectation value

For expectation value, CC method do not terminate in expansion. (Note that not inverse but dagger in bra part.)

$$\left\langle \widehat{O}_N \right\rangle = \frac{\left\langle HF \right| \left(1 + \hat{T}^{+} + \frac{\left(\hat{T}^{+}\right)^2}{2} + \cdots \right) \hat{O}_N \left(1 + \hat{T} + \frac{\hat{T}^2}{2} + \cdots \right) \left| HF \right\rangle}{\left\langle HF \right| \left(1 + \hat{T}^{+} + \frac{\left(\hat{T}^{+}\right)^2}{2} + \cdots \right) \left(1 + \hat{T} + \frac{\hat{T}^2}{2} + \cdots \right) \left| HF \right\rangle}$$

We need to use more complicated method to get expectation value.

We can calculate expectation value by solving Lambda equation, but it requires another effort. (Both programming and computational time)

Relativistic Quantum Chemistry

Non-relativistic quantum mechanics

Time dependent Schrodinger equation for free particle

$$\hat{H}\psi = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial^2 x}+\frac{\partial^2}{\partial^2 y}+\frac{\partial^2}{\partial^2 z}\right)\psi = i\hbar\frac{\partial}{\partial t}\psi = E\psi$$

$$\psi = \psi(x, y, z, t)$$

First-differential equation with respect to time but Second-differential equation with respect to space.

$$x' = \frac{x - Vt}{\sqrt{1-\beta^2}}, y' = y, z' = z, t' = \frac{t - Vx/c^2}{\sqrt{1-\beta^2}}$$

The Schrodinger equation is
Lorenz variant and no-relativity!

Dirac equation

First differential of space

First-differential of time

$$(c\boldsymbol{\alpha} \bullet \mathbf{p} + \beta mc^2)\psi = i\hbar \frac{\partial}{\partial t}\psi = E\psi$$

$$\boldsymbol{\alpha} \cdot \mathbf{p} = \begin{pmatrix} \mathbf{0} & \boldsymbol{\sigma} \cdot \mathbf{p}_\lambda \\ \boldsymbol{\sigma} \cdot \mathbf{p}_\lambda & \mathbf{0} \end{pmatrix} \qquad \boldsymbol{\beta} = \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{pmatrix}$$

$$\boldsymbol{\sigma} \cdot \mathbf{p}_\lambda = -i \begin{pmatrix} \dfrac{\partial}{\partial z_\lambda} & \left(\dfrac{\partial}{\partial x_\lambda} - i \dfrac{\partial}{\partial y_\lambda} \right) \\ \left(\dfrac{\partial}{\partial x_\lambda} + i \dfrac{\partial}{\partial y_\lambda} \right) & -\dfrac{\partial}{\partial z_\lambda} \end{pmatrix} \qquad \mathbf{1} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

$$\Psi = \begin{pmatrix} \psi_\alpha^L \\ \psi_\beta^L \\ \psi_\alpha^S \\ \psi_\beta^S \end{pmatrix}$$

Dirac equation is Lorenz invariant and correspond to Schrodinger equation when *v/c* goes to 0 (non-relativistic limit).

Relativistic quantum mechanics!

Dirac equation

First differential of space

First-differential of time

$$(c\boldsymbol{\alpha}\bullet\overset{\downarrow}{\mathbf{p}}+\beta mc^2)\psi = i\hbar\frac{\partial}{\partial t}\psi = E\psi$$

$$\boldsymbol{\alpha}\cdot\mathbf{p}=\begin{pmatrix}\mathbf{0} & \boldsymbol{\sigma}\cdot\mathbf{p}_{\boldsymbol{\lambda}}\\ \boldsymbol{\sigma}\cdot\mathbf{p}_{\boldsymbol{\lambda}} & \mathbf{0}\end{pmatrix}\qquad \boldsymbol{\beta}=\begin{pmatrix}\mathbf{1} & \mathbf{0}\\ \mathbf{0} & -\mathbf{1}\end{pmatrix}$$

$$\boldsymbol{\sigma}\cdot\mathbf{p}_{\lambda}=-i\begin{pmatrix}\dfrac{\partial}{\partial z_\lambda} & \left(\dfrac{\partial}{\partial x_\lambda}-i\dfrac{\partial}{\partial y_\lambda}\right)\\ \left(\dfrac{\partial}{\partial x_\lambda}+i\dfrac{\partial}{\partial y_\lambda}\right) & -\dfrac{\partial}{\partial z_\lambda}\end{pmatrix}\qquad \mathbf{1}=\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix}$$

$$\Psi=\begin{pmatrix}\psi_\alpha^L\\ \psi_\beta^L\\ \psi_\alpha^S\\ \psi_\beta^S\end{pmatrix}$$

Complicated features

1. **Four-dimensional matrix operator**
2. **Four-dimensional component in solution**
3. **Negative energy states continue to minus infinity…**

⇒indicating the existence of anti-particle of electron. (positron)

Merits of Dirac equation

- We can solve Dirac equation analytically for Hydrogen atom.

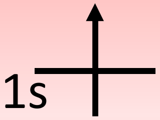
- What’s the mean of four component?

Information of positronic states

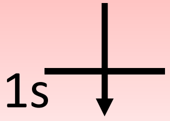
Information of spin

$\boxed{2 \times 2 = 4}$

$$\begin{pmatrix}\psi^{L}_{\alpha}\\ \psi^{L}_{\beta}\\ \psi^{S}_{\alpha}\\ \psi^{S}_{\beta}\end{pmatrix}=\begin{pmatrix}\text{Large component for electron; up spin}\\ \text{Large component for electron; down spin}\\ \text{Small component for electron; up spin}\\ \text{Small component for electron; down spin}\end{pmatrix}$$



$\begin{pmatrix}1s\\ 0\end{pmatrix}$



$\begin{pmatrix}0\\ 1s\end{pmatrix}$

Example of two-component structure by introducing spin

Solution of Dirac equation of H atom

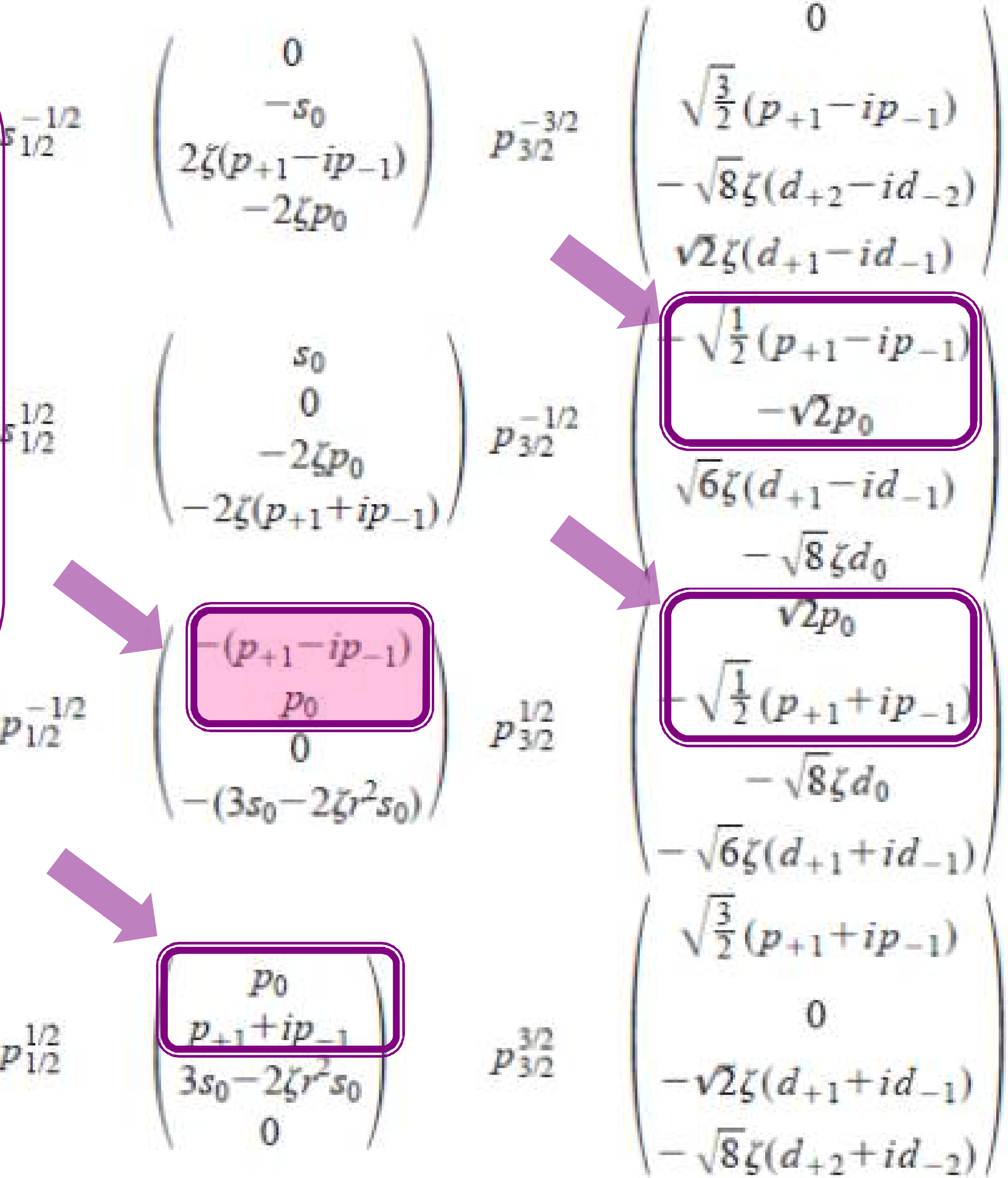
For Ex. $p_{1/2}^{-1/2}$

Up spin component $-(p_{+1}-ip_{-1})$

Down spin component p_0

Up spin and down spin are mixed in one-electron orbital.

Relativistic effect related with spin: Spin-orbit interaction



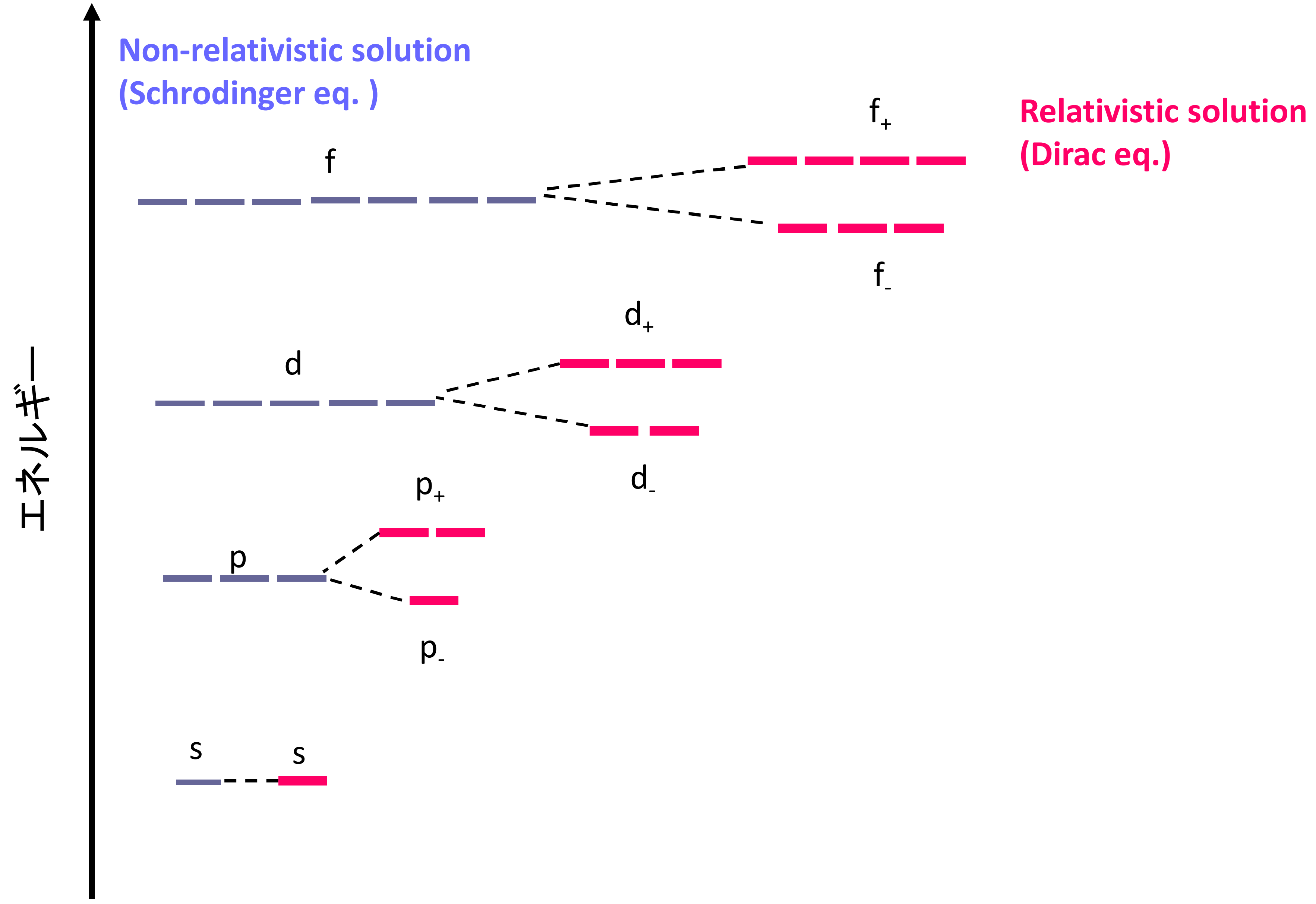
$$s_{1/2}^{-1/2}\begin{pmatrix}0\\-s_0\\2\zeta(p_{+1}-ip_{-1})\\-2\zeta p_0\end{pmatrix}\qquad p_{3/2}^{-3/2}\begin{pmatrix}0\\\sqrt{\frac{3}{2}}(p_{+1}-ip_{-1})\\-\sqrt{8}\zeta(d_{+2}-id_{-2})\\\sqrt{2}\zeta(d_{+1}-id_{-1})\end{pmatrix}$$

$$s_{1/2}^{1/2}\begin{pmatrix}s_0\\0\\-2\zeta p_0\\-2\zeta(p_{+1}+ip_{-1})\end{pmatrix}\qquad p_{3/2}^{-1/2}\begin{pmatrix}-\sqrt{\frac{1}{2}}(p_{+1}-ip_{-1})\\-\sqrt{2}p_0\\\sqrt{6}\zeta(d_{+1}-id_{-1})\\-\sqrt{8}\zeta d_0\end{pmatrix}$$

$$p_{1/2}^{-1/2}\begin{pmatrix}-(p_{+1}-ip_{-1})\\p_0\\0\\-(3s_0-2\zeta r^2 s_0)\end{pmatrix}\qquad p_{3/2}^{1/2}\begin{pmatrix}\sqrt{2}p_0\\-\sqrt{\frac{1}{2}}(p_{+1}+ip_{-1})\\-\sqrt{8}\zeta d_0\\-\sqrt{6}\zeta(d_{+1}+id_{-1})\end{pmatrix}$$

$$p_{1/2}^{1/2}\begin{pmatrix}p_0\\p_{+1}+ip_{-1}\\3s_0-2\zeta r^2 s_0\\0\end{pmatrix}\qquad p_{3/2}^{3/2}\begin{pmatrix}\sqrt{\frac{3}{2}}(p_{+1}+ip_{-1})\\0\\-\sqrt{2}\zeta(d_{+1}+id_{-1})\\-\sqrt{8}\zeta(d_{+2}+id_{-2})\end{pmatrix}$$

Spin-orbit interaction



EDM in molecule

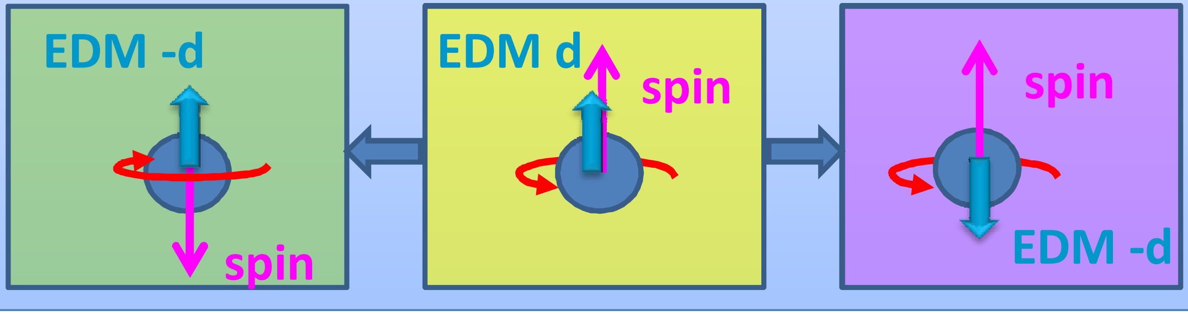
1. EDM of elementary particle and CP violation
2. What is measured as the prove of EDM in atoms or molecules
3. How to measure it
4. Why theoretical work is important
5. Formula of theoretical work
6.

EDM and P/T violation

If non-zero EDM exists in an elementary particle,
there must be P and T symmetry violation!
（Purcell, Ramsey, 1950)

Time reversal
(t → -t)

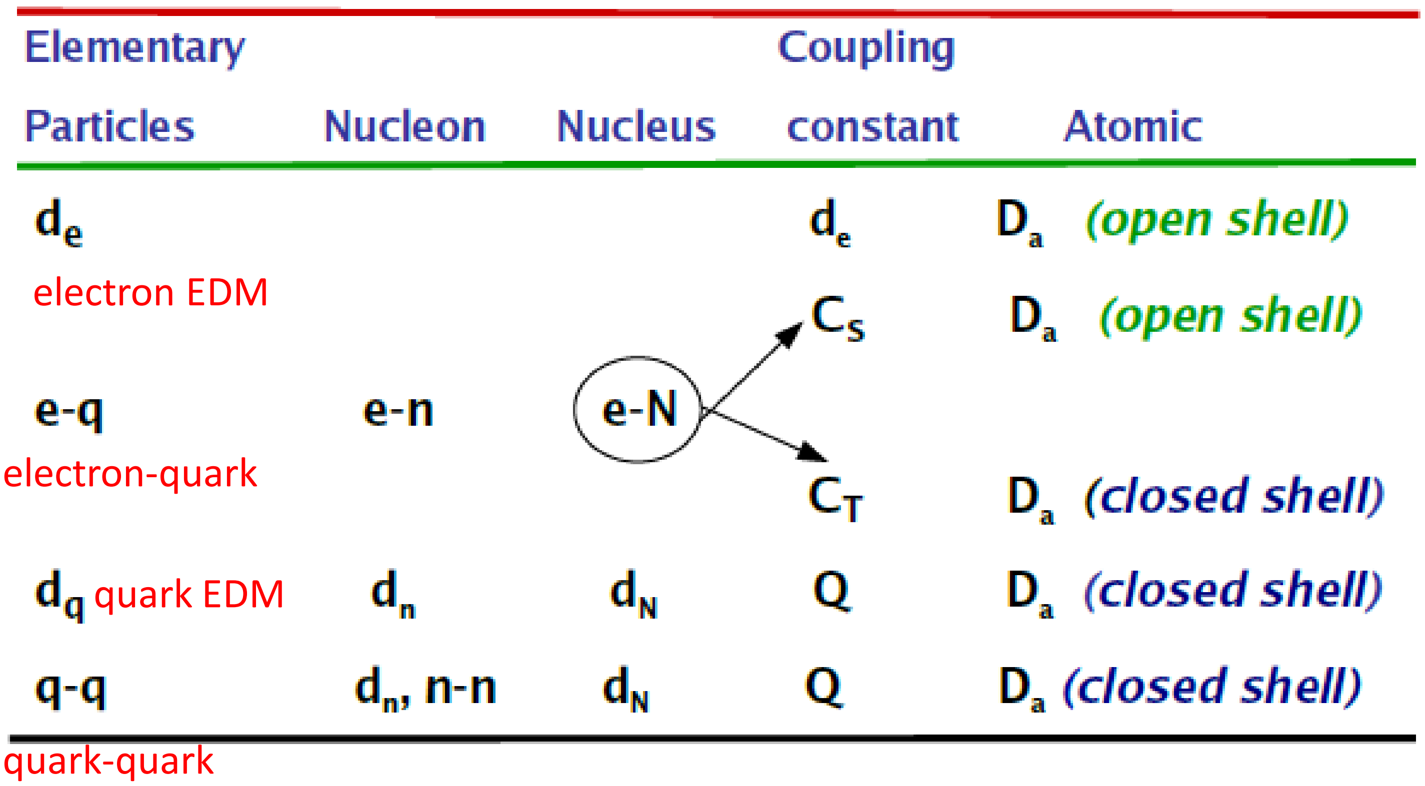
Parity reversal
(r → -r)



T-symmetry breaking→CP symmetry breaking via CPT theorem

EDM measurement may improve Kobayashi-Masukawa theorem and
explain the disappearance of anti-particles in the present universe .

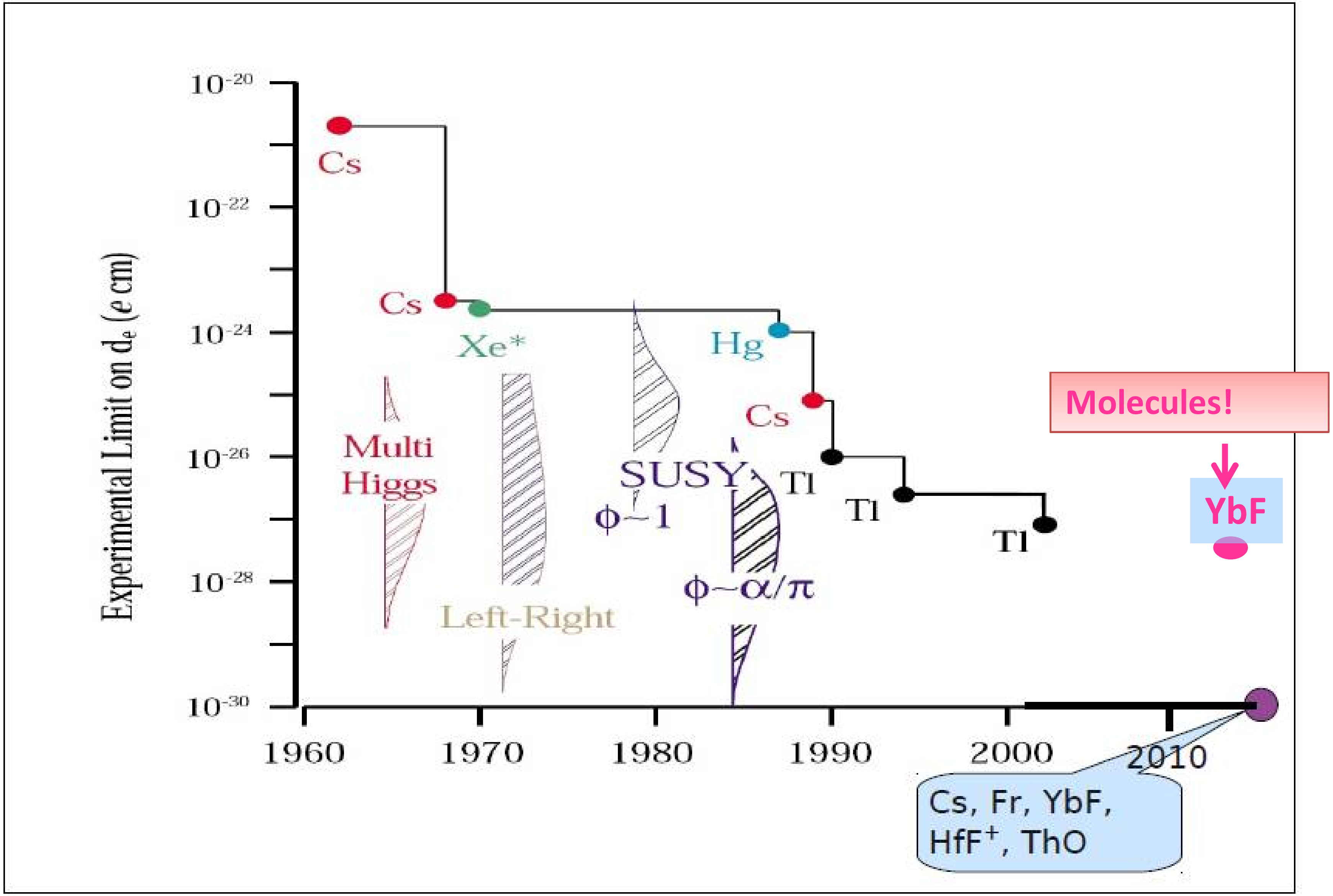
Source of EDM in atoms or molecules



Elementary Particles	Nucleon	Nucleus	Coupling constant	Atomic
d_e electron EDM			d_e	D_a *(open shell)*
			C_S	D_a *(open shell)*
e-q electron-quark	e-n	e-N		
			C_T	D_a *(closed shell)*
d_q quark EDM	d_n	d_N	Q	D_a *(closed shell)*
q-q quark-quark	d_n, n-n	d_N	Q	D_a *(closed shell)*

There may be various source for EDM in atoms or molecules. Here we only consider open shell systems and assume that molecular EDM comes from only electron EDM to obtain upper limit of d_e.

History of e-EDM



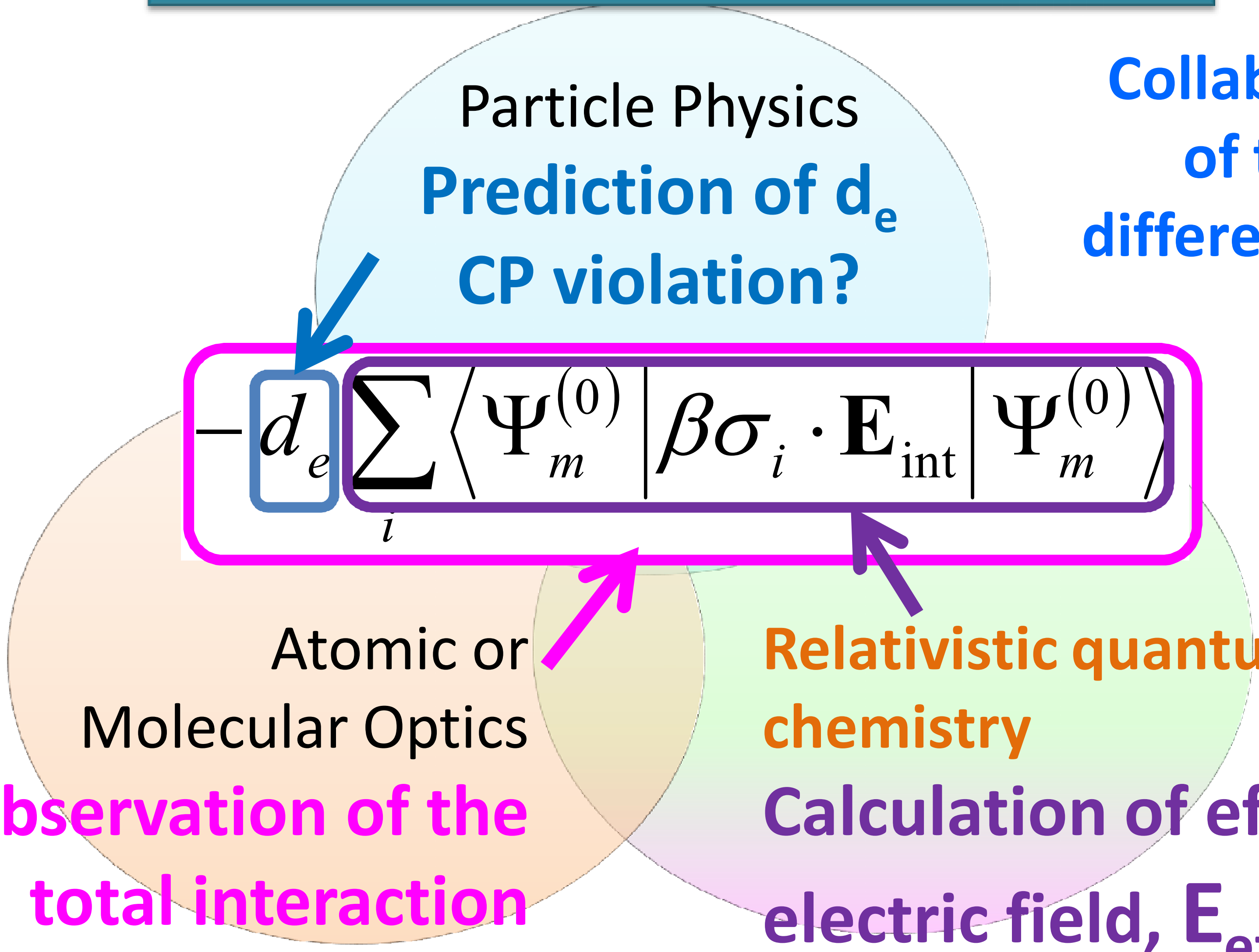
Molecules!

YbF

Cs, Fr, YbF, HfF^+, ThO

What is observed and calculated for e-EDM?

Interaction energy of Electron EDM with internal electric field of molecule



Collaboration of three different fields!

Particle Physics

Prediction of d_e

CP violation?

$$\boxed{-\boxed{d_e}\boxed{\sum_i \left\langle \Psi_m^{(0)} \middle| \beta\sigma_i \cdot \mathbf{E}_{\mathrm{int}} \middle| \Psi_m^{(0)} \right\rangle}}$$

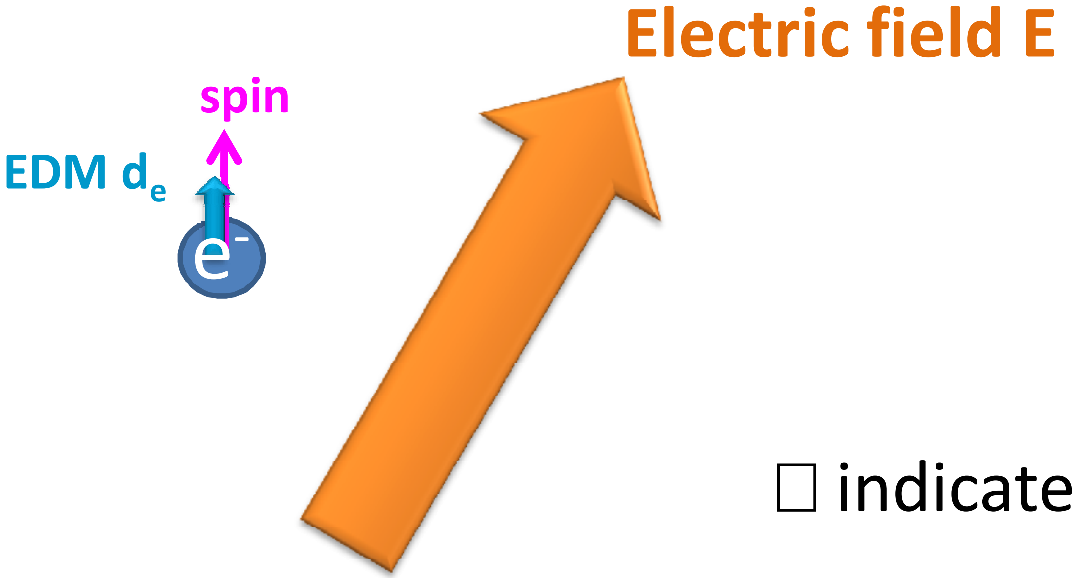
Atomic or Molecular Optics

Observation of the total interaction

Relativistic quantum chemistry

Calculation of effective electric field, E_{eff}

Electron EDM interacts with Electric field



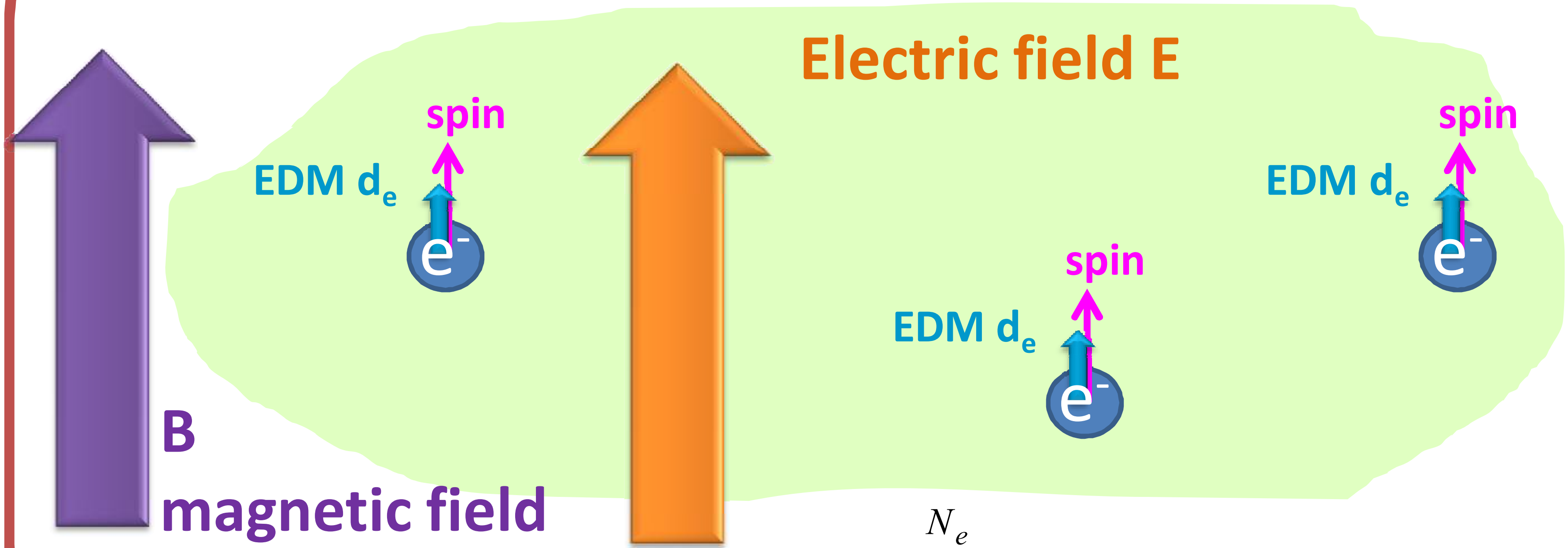
□ indicates spin direction.

Interaction energy = $-d_e \boldsymbol{\sigma} \cdot \mathbf{E}$

If Electric field is large, interaction energy is large and easy to be measured.

Electron EDM interacts with Electric field

In atoms or molecules there are a number of electrons.

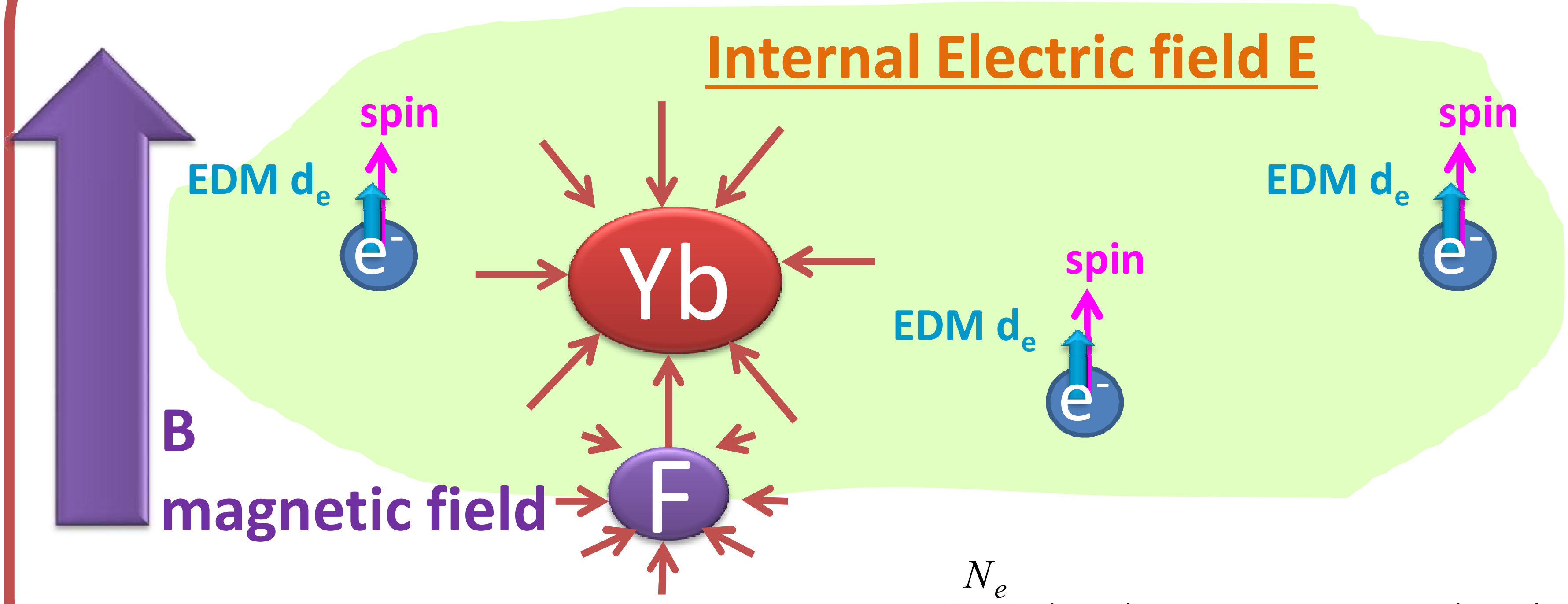


Interaction energy = $-d_e \sum_{i=1}^{N_e} \langle \varphi_i | \beta \boldsymbol{\sigma}_i \cdot \mathbf{E}_i | \varphi_i \rangle$

If we apply **external magnetic field**, electron spin and e-EDM becomes parallel to B. If we apply external electric field parallel or antiparallel to B, then the interaction becomes maximum.

Electron EDM interacts with Electric field

In polar molecules, **internal electric field is already there.**



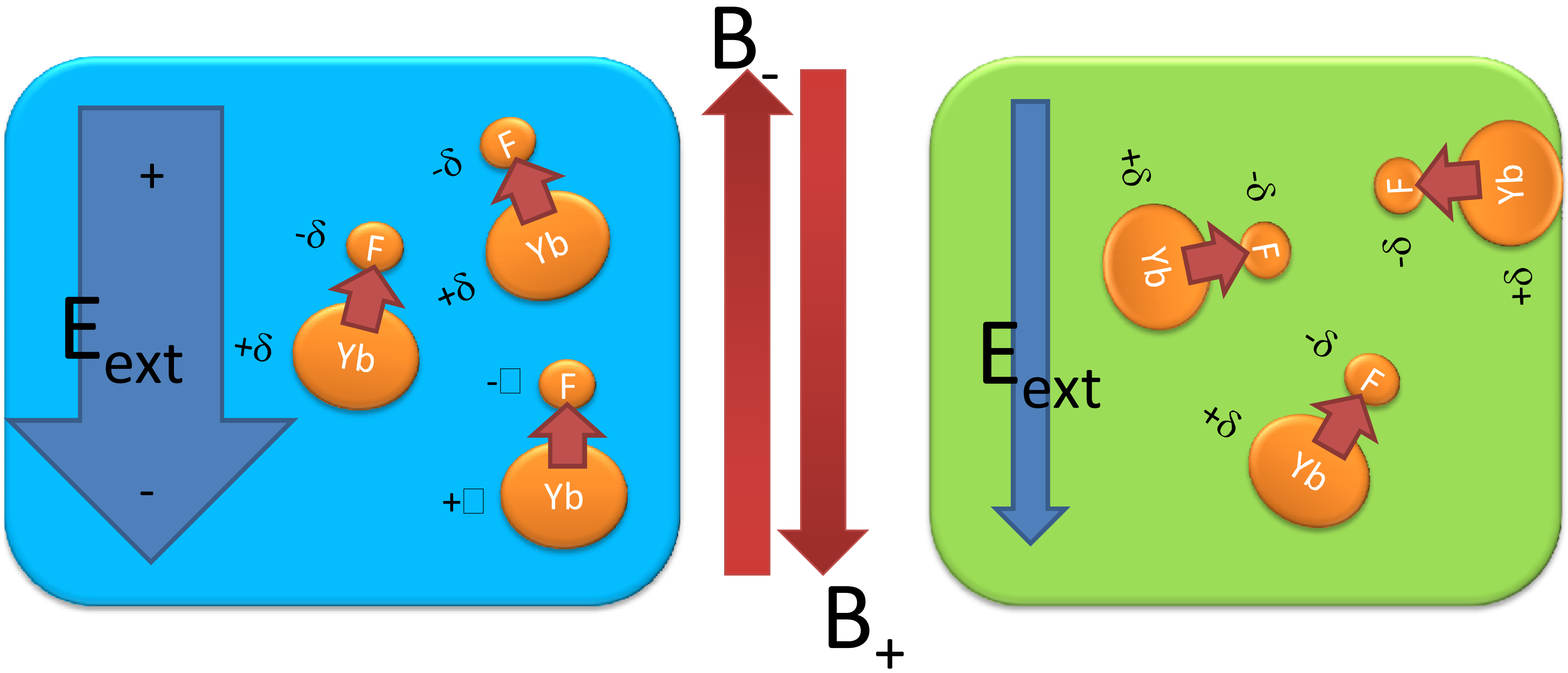
Effective electric field

$$E_{eff} \equiv \sum_{i=1}^{N_e} \left\langle \Psi \middle| \beta \boldsymbol{\sigma}_i \cdot \mathbf{E}_i^{\text{internal}} \middle| \Psi \right\rangle$$

We need to know effective electric field from quantum chemistry calculations to elucidate d_e itself from experiments.

External and internal electric field

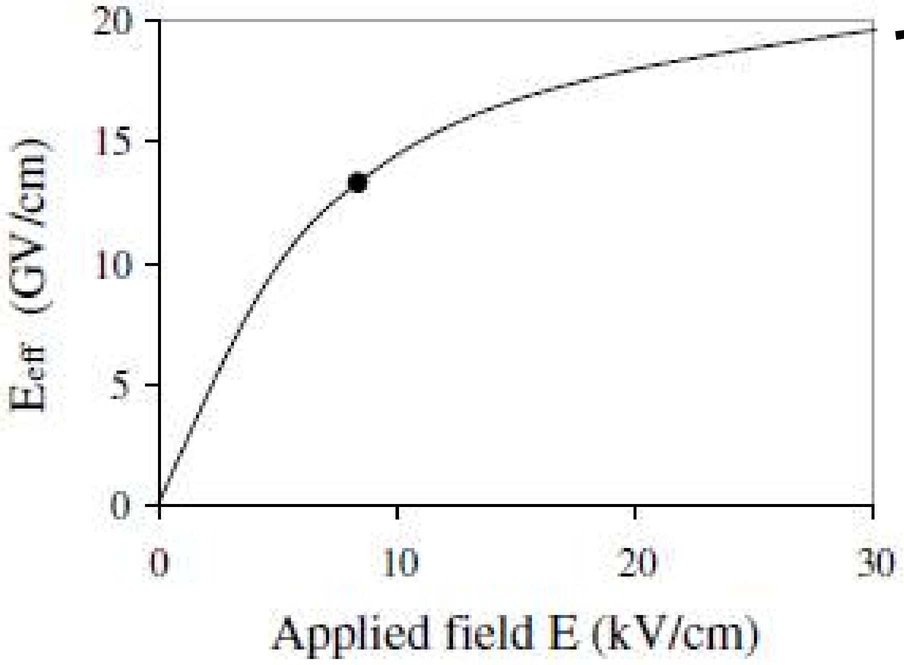
External electric field is necessary to align polar molecules. The largest internal electric fields may be along with the molecular axis. Furthermore, we apply a magnetic field with parallel or anti-parallel to the electric field, such that the interaction between e-EDM and E_{int} becomes large.



YbF experiment in 2002

Effective electric field

Theoretical estimation:
26GV/cm in YbF



Effective electric field will be the internal electric field in limit. The internal electric field can be obtained by ab initio calculations.

FIG. 1. Effective electric field interacting with the electron edm in YbF versus applied electric field. The dot shows the field at which we operate.

The form of the curve $\langle \sigma \cdot \lambda s \rangle$polarization of rigid rotator.
λ is the direction of molecule axis.

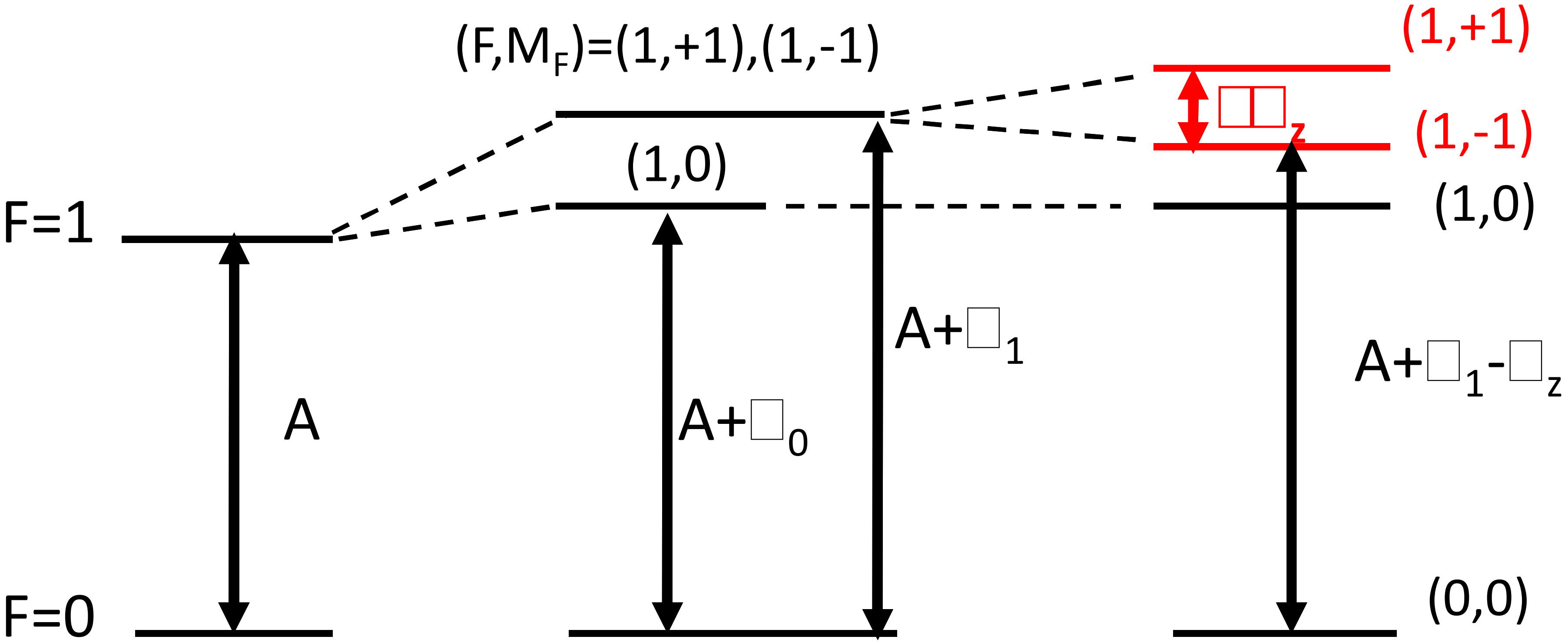
YbF experiment in 2002

Consider YbF electronic ground state ^{2}□

v(vibrational)=0, N(rotational)=0

J=1/2 (electron spin), I=1/2(nuclear spin)

=> F(total spin) =0 or 1

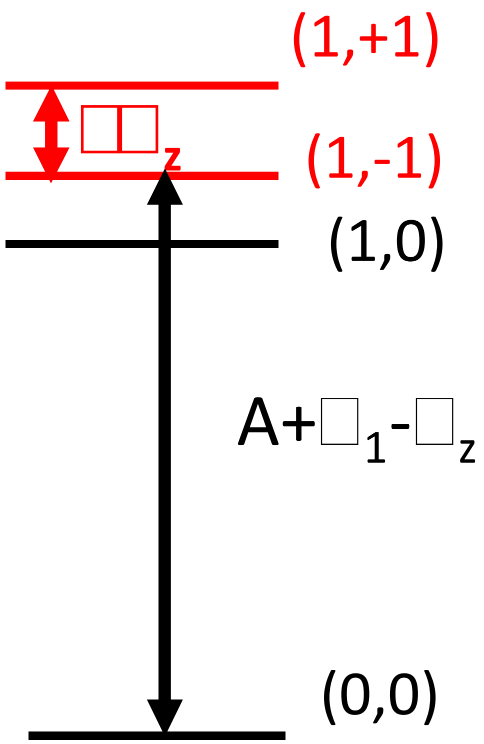


Without external field

With E (Stark shift)

With E and B
(Stark & Zeeman shift)

YbF experiment in 2002

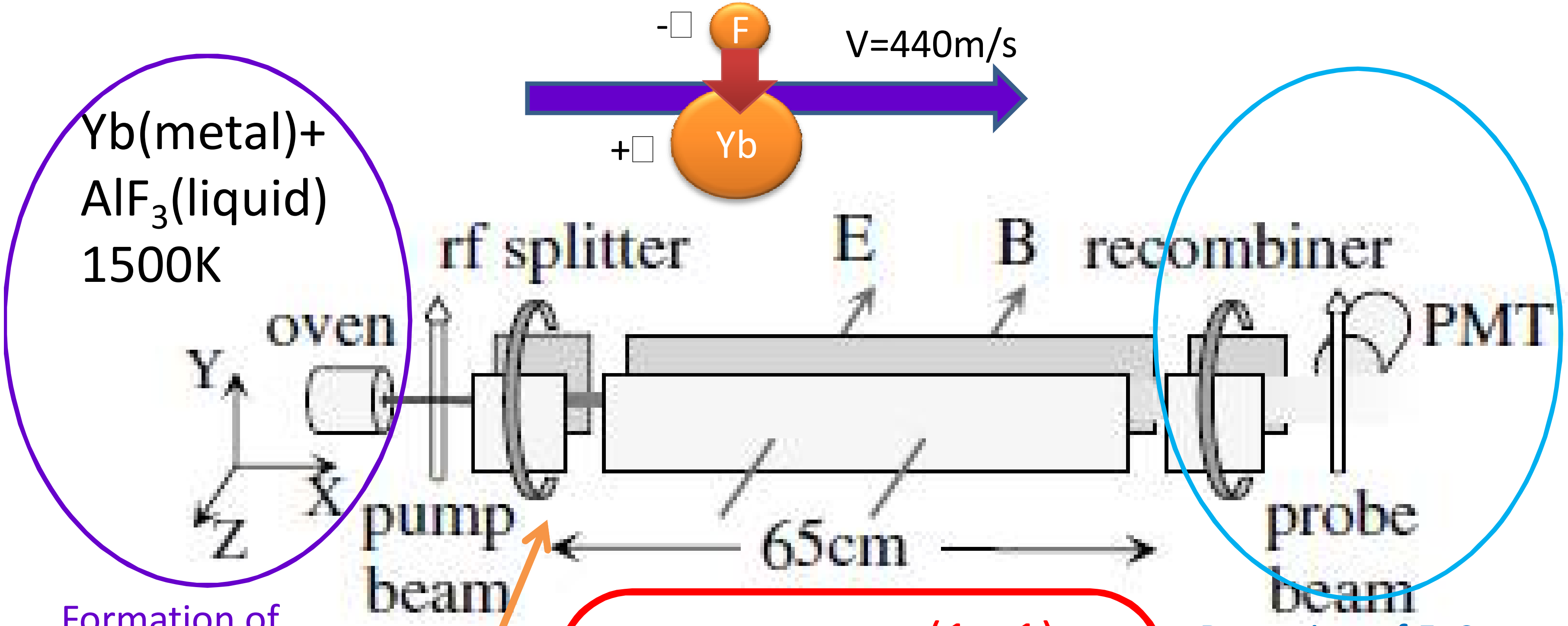


With E and B
(Stark & Zeeman shift)

$$2\Delta_z = 2\left(\pm d_e \mathbf{E}_{eff} \mp \mu_B B\right)T/\hbar$$

Interaction of electron EDM and effective electric field is spin-dependent and can appear with Zeeman shift.
If we apply **E** and **B** in same direction and opposite direction, the two types of energy shift of $2□_z$ is differently observed.

Equipment



Yb(metal)+
AlF_3(liquid)
1500K

Formation of YbF molecule

Detection of F=0 state (Fluorescence)

$\propto \cos^2 \Delta_z$

(1,+1)

□□$_z$

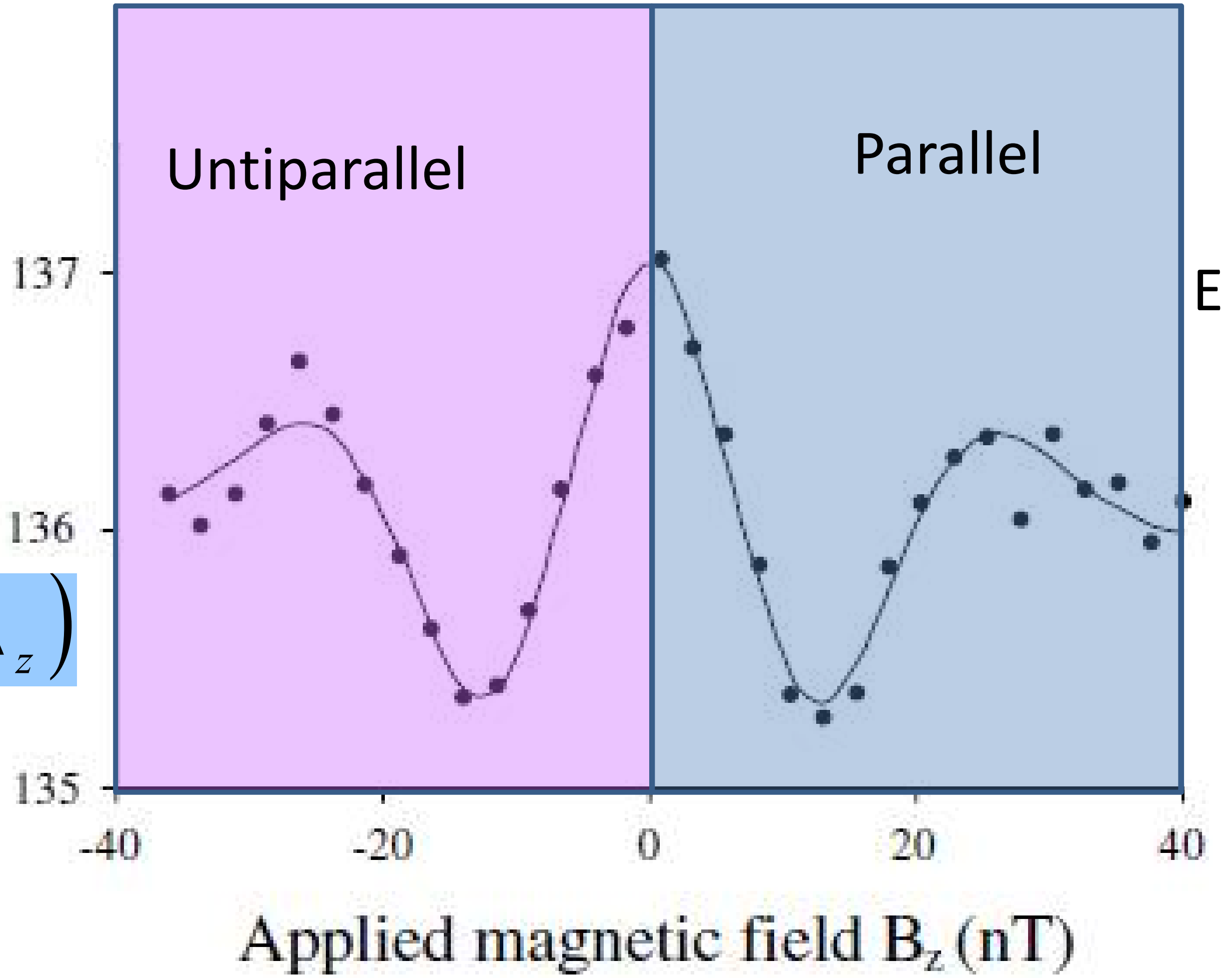
(1,-1)

Coherent superposition

$$\frac{1}{\sqrt{2}}\left|1,+1\right\rangle + \frac{1}{\sqrt{2}}\left|1,-1\right\rangle$$

Collect F=0 state by some lasers

Result



E_{ext}=8.3kV/cm

$\left(\propto \cos^2 \Delta_z\right)$

FIG. 4. Interference fringe in the $F = 0$ state population versus magnetic field. Each point represents 12 s of integration time. The curve is a velocity-averaged calculation whose only free parameters are the normalization, a field offset, and a sloping background.

The upper limit of d_e

J. J. Hudson, B. E. Sauer, M. R. Tarbutt, and E.A. Hinds, PRL, 89,023003,2002

$$d_e = \left(-0.2 \pm 3.2_{stat}\right) \times 10^{-26}\, ecm$$

The latest report about YbF molecule

“Improved measurement of the shape of the electron”
J. J. Hudson, D. M. Kara, I. J. Smallman, B. E. Sauer, M. R. Tarbutt & E. A. Hinds, NATURE , 494 , VOL 473 ,2011

$$d_e = \left(-2.4 \pm 5.2_{stat} \pm 1.5_{syst}\right) \times 10^{-28}\, ecm$$

Form of E_{eff}

- We cannot measure E_{eff} but can calculate it.
- E_{eff} appears only in relativistic frame work.

Multi-electronic Dirac-Coulomb Hamiltonian

$$\hat{H}_{DC} = \sum_{i}^{N_{elec}} \left[c\alpha p_i + \beta mc^2 - \sum_{A}^{N_{nuc}} \frac{Z_A}{\left|\mathbf{r}_i - \mathbf{R}_A\right|} \right] + \sum_{i<j}^{N_{elec}} \frac{1}{\left|\mathbf{r}_i - \mathbf{r}_j\right|}$$

$$\Psi_{DC} = \begin{pmatrix} \psi_{\alpha}^{L} \\ \psi_{\beta}^{L} \\ \psi_{\alpha}^{S} \\ \psi_{\beta}^{S} \end{pmatrix}$$

Kinetic and relativistic correction

Nuclear attraction

Electron repulsion

Eigenfunction of Dirac-Coulomb Hamiltonian, four component!

$$E_{eff} \equiv \sum_{i}^{N_{elec}} \left\langle \Psi_{DC} \middle| \beta \sigma_i \cdot \mathbf{E}_{\mathrm{int}} \middle| \Psi_{DC} \right\rangle$$

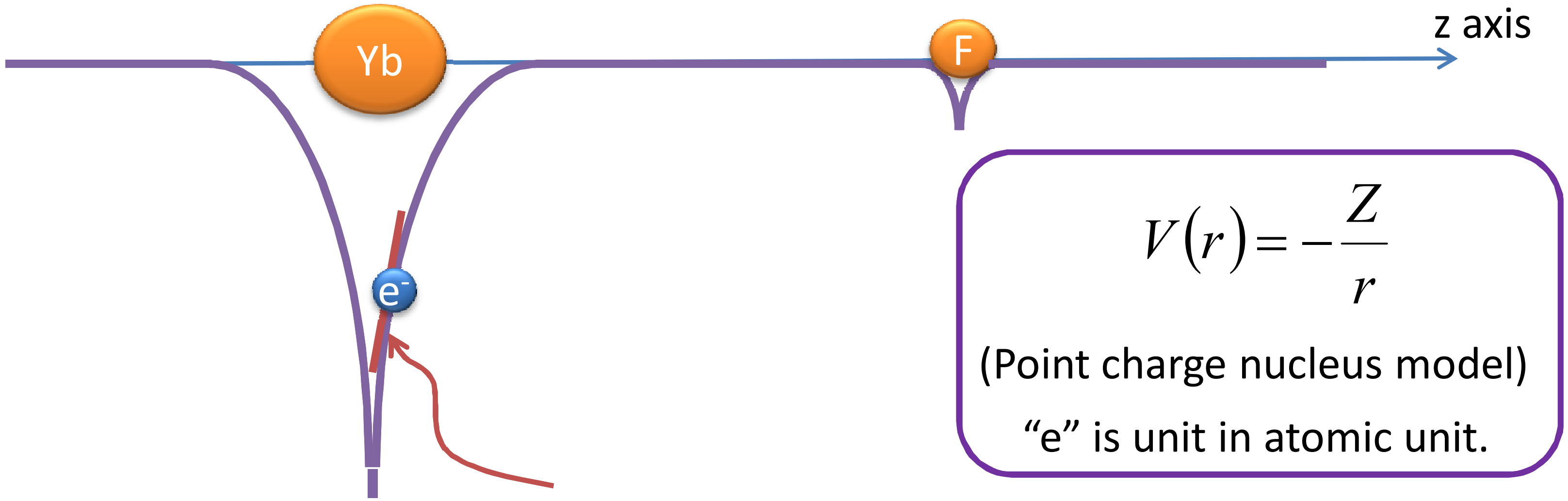
Expectation value of internal-electric-field projected into spin axis multiplied by beta matrix, coming from relativistic correction.

$$\beta = \begin{pmatrix} 1_{2\times2} & 0_{2\times2} \\ 0_{2\times2} & -1_{2\times2} \end{pmatrix}$$

Internal electric field E_{int}

Mostly, it comes from nuclear attraction potentials.

Electric potential in molecule



$$V(r) = -\frac{Z}{r}$$

(Point charge nucleus model)

"e" is unit in atomic unit.

$$E_{\text{int}} = -\nabla\phi = -\nabla V(r)$$

$-E_{\text{int}}$ is the tangent of potential.

Electrons close to heavy nucleus feel large electric field.

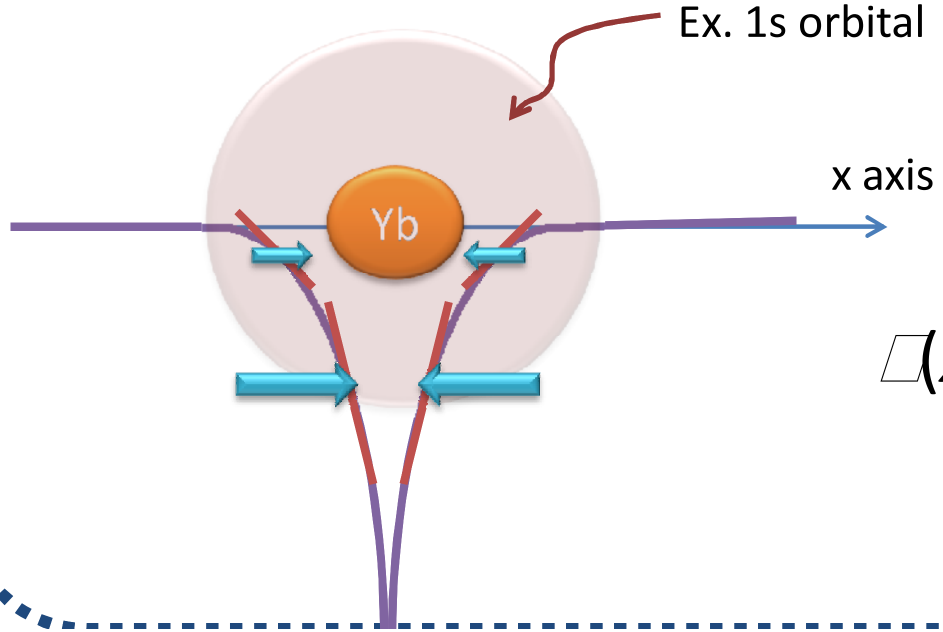
Parity symmetric orbital cannot have E_{eff}

$$E_{eff} = \sum_{i}^{N_{elec}} \int_{0}^{\infty} \Psi^{*}{}_{DC}\left(r_1, r_2, \ldots, r_{N_{elec}}\right) \beta \sigma_i \cdot \mathbf{E}_{\text{int}} \Psi^{*}{}_{DC}\left(r_1, r_2, \ldots, r_{N_{elec}}\right) dr_1 dr_2 \ldots dr_{N_{elec}}$$

$$= \sum_{i}^{N_{elec}} \int_{0}^{\infty} \rho_{DC}\left(r_1, r_2, \ldots, r_{N_{elec}}\right) \beta \sigma_i \mathbf{E}_{\text{int}} dr_1 dr_2 \ldots dr_{N_{elec}}$$

Electron density

Atom without external field



$$\begin{cases} \square(x)=\square(-x) \\ E_x(x) =- E_x(-x) \end{cases}$$

$$\square(x)\, E_x(x) + \square(-x)\,(- E_x(-x)) = 0$$

➔ E_{eff} is zero.

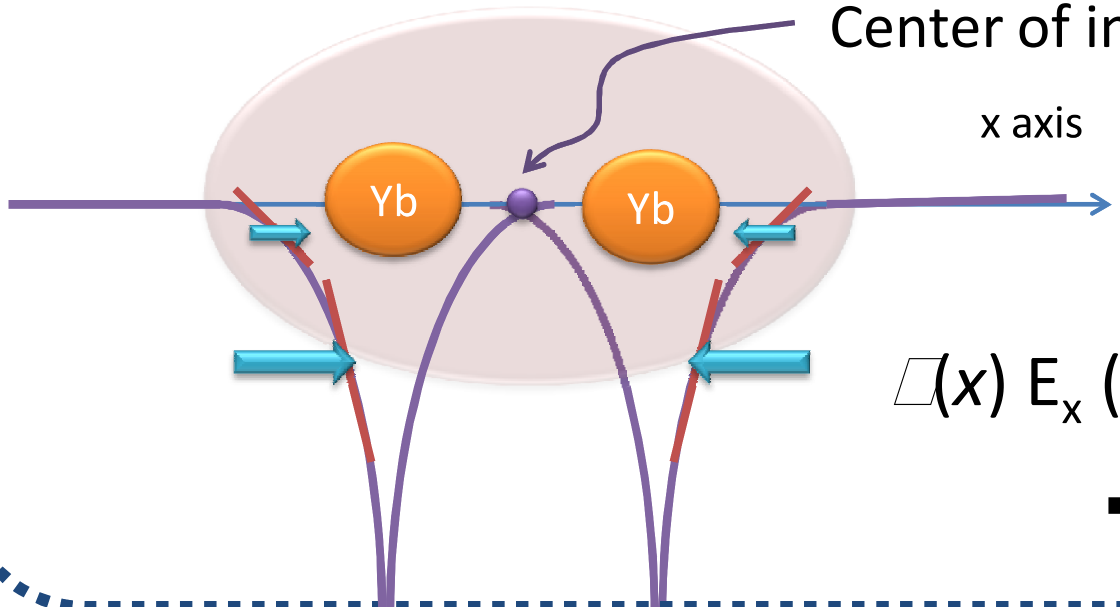
Parity symmetric orbital cannot have E_{eff}

$$E_{eff} = \sum_i^{N_{elec}} \int_0^{\infty} \Psi^{*}{}_{DC}\left(r_1, r_2, \ldots, r_{N_{elec}}\right) \beta\sigma_i \cdot \mathbf{E}_{\text{int}} \Psi^{*}{}_{DC}\left(r_1, r_2, \ldots, r_{N_{elec}}\right) dr_1 dr_2 \ldots dr_{N_{elec}}$$

$$= \sum_i^{N_{elec}} \int_0^{\infty} \rho_{DC}\left(r_1, r_2, \ldots, r_{N_{elec}}\right) \beta\sigma_i \mathbf{E}_{\text{int}} dr_1 dr_2 \ldots dr_{N_{elec}}$$

Electron density

Homo diatomic molecule



$$\begin{cases} \square(x) = \square(-x) \\ E_x(x) = -E_x(-x) \end{cases}$$

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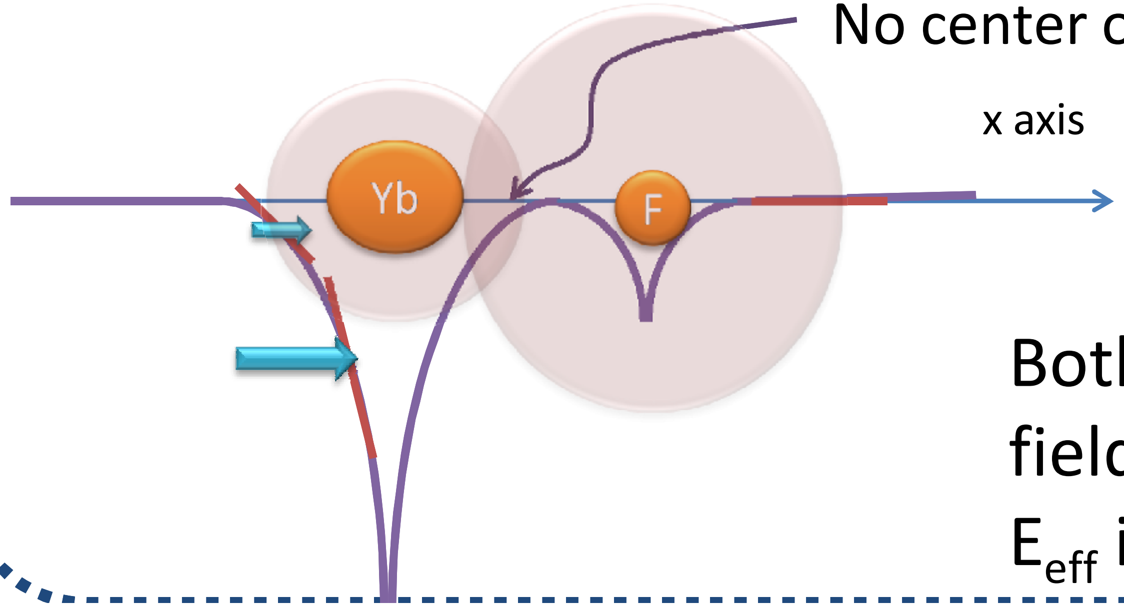
Parity symmetric orbital cannot have E_{eff}

$$E_{eff} = \sum_{i}^{N_{elec}} \int_{0}^{\infty} \Psi^{*}{}_{DC}\left(r_1, r_2, \ldots, r_{N_{elec}}\right) \beta \sigma_i \cdot \mathbf{E}_{\text{int}} \Psi^{*}{}_{DC}\left(r_1, r_2, \ldots, r_{N_{elec}}\right) dr_1 dr_2 \ldots dr_{N_{elec}}$$

$$= \sum_{i}^{N_{elec}} \int_{0}^{\infty} \rho_{DC}\left(r_1, r_2, \ldots, r_{N_{elec}}\right) \beta \sigma_i \, \mathbf{E}_{\text{int}} \, dr_1 dr_2 \ldots dr_{N_{elec}}$$

Electron density

Hetero diatomic molecule



No center of inversion

$$\begin{cases} \square(x) \neq \square(-x) \\ E_x(x) \neq -E_x(-x) \end{cases}$$

Both density and electric field is not symmetric. E_{eff} is non zero.

Effective Hamiltonian of E_{eff}

$$\hat{H}_{EDM} = -d_e \beta\sigma\cdot E_{\text{int}}$$

$$= \left[-\frac{d_e}{e}\beta\sigma\cdot\nabla, \hat{H}_{DC}\right] + 2i\frac{d_e}{e}c\beta\gamma_5 p^2$$

By B. P. Das

$$\frac{1}{d_e}\left\langle\Psi_{DC}\left|\hat{H}_{EDM}\right|\Psi_{DC}\right\rangle = \boxed{2i\frac{c}{e}\sum_i^{N_{elec}}\left\langle\Psi_{DC}\left|\beta\gamma_5 p^2\right|\Psi_{DC}\right\rangle}$$

$$2ic\left\langle\underline{\varphi_i^{4cmp}}\left|\beta\gamma_5 p^2\right|\varphi_i^{4cmp}\right\rangle = -4c\,\mathrm{Re}\left\langle\varphi_i^L\left|p^2\right|\varphi_i^S\right\rangle$$

One-electron molecular orbital

$$E_{eff}\,\big|_{DCROHF} = -4c\sum_i^{N_{elec}}\mathrm{Re}\left\langle\varphi_i^L\left|p^2\right|\varphi_i^S\right\rangle$$

$$= -4c\,\mathrm{Re}\left\langle\underline{\varphi_{SOMO}^L\left|p^2\right|\varphi_{SOMO}^S}\right\rangle$$

Kramers-paired orbitals are cancelled in each other due to the spin projection of the electric field.

Singly occupied orbital determines the nature of E_{eff} at the HF level.

Comparison of the previous works inYbF

Method	Ref	E_{eff} GV/cm
Quasi-relativistic		
Semi-empirical	Kozlov, 1997	26.1
GRECP-RASSCF	Titov et al. 1997	18.8
GRECP-RASSCF-EO	Mosyagin et al. 1998	24.9
GRECP-MRCI-SOCO	Meyer et al. 2006	43.0
4-component Dirac		
DHF+CP	Quiney et al. 1998	24.8
UDF (unpaired electron)	Parpia, 1998	19.9
UDF (all electrons)	Parpia, 1998	24.9
DF	Nayak et al. 2006	19.9
RASCI	Nayak et al. 2006	22.5
MBPT(2)	Nayak et al. 2007	21.6
DHF (Faegri's contracted basis)	**This work**	**16.7**
DHF (uncontracted s basis)	**This work**	**17.0**

Results at the Dirac-Coulomb-ROHF level

Faegri's 4cmp-basis set (valence triple zeta)

		Eeff (GV/cm)	PDM (Debye)
YbF	abe	16.7	4.20
	Meyer	24.7	3.55
BaF	abe	5.8	4.21
	Meyer	7.4	3.51
HgF	abe	79.3	4.98
	Meyer	99	4.14
PbF	abe	-40.5	4.42
	Meyer	-29	3.38

		Eeff (GV/cm)	PDM (Debye)
$YbSr^+$	abe	3.1	6.56
	Meyer	-11.3	5.1
$YbBa^+$	abe	0.7	4.50
	Meyer	1.2	5.1
YbRb	abe	0.3	0.61
	Meyer	-0.7	0.21
YbCs	abe	0.2	0.77
	Meyer	0.54	0.24

Meyer et al: GRECP + MRCI + SOCI, Electric field of two nuclei and a lot of approximations… (50 % error contains)

We need to beyond the Hartree-Fock level to get more reliable results. → Coupled Cluster method

Coupled Cluster method

One of the most accurate methods to take into account electron correlation within single reference theory

$$\hat{H}_{HF}\left|\Phi_{HF}\right\rangle = E_{HF}\left|\Phi_{HF}\right\rangle \quad \Rightarrow \quad \hat{H}\left|\Psi_{exact}\right\rangle = E\left|\Psi_{exact}\right\rangle$$

$$\left|\Psi_{exact}\right\rangle \equiv \exp\left(\hat{T}\right)\left|\Phi_{HF}\right\rangle = \left(1+\hat{T}+\frac{\left(\hat{T}\right)^2}{2}+\cdots\right)\left|\Phi_{HF}\right\rangle$$

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 \ldots$$

$\hat{T}_N$: N-electron excitation operator

$$\left(\hat{T}_1 = \sum_{a\in vir,\, i\in occ} t_1(a,i)\left|\begin{matrix}a\\ i\end{matrix}\right\rangle = \sum_{a\in vir,\, i\in occ} t_1(a,i)\, a_a^{+} a_i \left|HF\right\rangle\right)$$

t_1, t_2, … coefficients are the parameters to be obtained.

$$\hat{H}_N = \hat{H} - E_{HF}$$

$$\hat{H}_N \exp\left(\hat{T}\right)\left|\Phi_{HF}\right\rangle = \Delta E \exp\left(\hat{T}\right)\left|\Phi_{HF}\right\rangle$$

$$\exp\left(-\hat{T}\right)\hat{H}_N \exp\left(\hat{T}\right)\left|\Phi_{HF}\right\rangle = \Delta E\left|\Phi_{HF}\right\rangle$$

ΔE

Electron correlation energy

Coupled Cluster method

$$\begin{aligned} &\exp(-T)\hat{H}_N\exp(T) \\ &= \hat{H}_N + \left[\hat{H}_N, T\right] + \frac{1}{2!}\left[\left[\hat{H}_N, T\right], T\right] + \ldots + \frac{1}{4!}\left[\left[\left[\left[\hat{H}_N, T\right], T\right], T\right], T\right] \\ &= \left(\hat{H}_N \exp(T)\right)_C \end{aligned}$$

The above exponential expansion is terminate after four commutations because H_N is at most two-electron operator. $\left(\hat{H}_N \exp(T)\right)_C$ means collect only connected terms which provide non-zero values.

Coupled Cluster singles and doubles (CCSD) equations

$$\left\{\begin{array}{l} \left\langle \Phi_{HF} \middle| \left(\hat{H}_N \exp(T)\right)_C \middle| \Phi_{HF} \right\rangle = \Delta E \\ \left\langle \Phi_i^a \middle| \left(\hat{H}_N \exp(T)\right)_C \middle| \Phi_{HF} \right\rangle = 0 \quad \text{... (1)} \\ \left\langle \Phi_{ij}^{ab} \middle| \left(\hat{H}_N \exp(T)\right)_C \middle| \Phi_{HF} \right\rangle = 0 \quad \text{... (2)} \end{array}\right.$$

$\hat{T} = \hat{T}_1 + \hat{T}_2$

$\left|\Phi_i^a\right\rangle$ One-electron excited determinant

$\left|\Phi_{ij}^{ab}\right\rangle$ Two-electron excited determinant

CCSD amplitude equations

$$\Delta E = E_{CCSD} = \sum_{I,A} F_A^I T_I^A + \sum_{I<J,A<B} V_{AB}^{IJ} \tau_{IJ}^{AB}$$

$$F_I^A - 2\sum_{K,C} F_C^K T_K^A T_I^C + \sum_{C} H_C^A T_I^C - \sum_{K} H_I^K T_K^A + \sum_{K,C} H_C^K \left(T_{IK}^{AC} + T_K^A T_I^C \right)$$
$$+ \sum_{K,C} V_{IC}^{AK} T_K^C + \sum_{K,C<D} V_{CD}^{AK} \tau_{IK}^{CD} - \sum_{K<L,C} V_{IC}^{KL} \tau_{KL}^{AC} = 0 \qquad \ldots (1)$$

$$V_{IJ}^{AB} + P_{AB} \left(\sum_{C} G_C^A T_{IJ}^{CB} - \sum_{K} V_{IJ}^{AB} T_K^B \right) - P_{IJ} \left(\sum_{K} G_I^K T_{KJ}^{AB} - \sum_{C} V_{IC}^{AB} T_J^C \right)$$
$$+ \sum_{K<L} A_{IJ}^{KL} \tau_{KL}^{AB} + \sum_{C<D} B_{CD}^{AB} \tau_{IJ}^{CD} + P_{IJ} P_{AB} \left(\sum_{K,C} H_{IC}^{AK} T_{JK}^{BC} - \sum_{K,C} V_{IC}^{AK} T_J^C T_K^B \right) = 0 \qquad \ldots (2)$$

Non linear equations of T_1 and T_2,
iteratively to be solved.

Term notation of DIRAC08 RELCCSD
from L. Vischer's JCP paper

Problem in coupled cluster method for expectation value

For expectation value, CC method do not terminate in expansion. (Note that not inverse but dagger in bra part.)

$$\left\langle \widehat{O}_N \right\rangle = \frac{\left\langle HF \right| \left(1 + \hat{T}^{+} + \frac{\left(\hat{T}^{+}\right)^2}{2} + \cdots \right) \hat{O}_N \left(1 + \hat{T} + \frac{\hat{T}^2}{2} + \cdots \right) \left| HF \right\rangle}{\left\langle HF \right| \left(1 + \hat{T}^{+} + \frac{\left(\hat{T}^{+}\right)^2}{2} + \cdots \right) \left(1 + \hat{T} + \frac{\hat{T}^2}{2} + \cdots \right) \left| HF \right\rangle}$$

We need to use more complicated method to get expectation value.

We can calculate expectation value by solving Lambda equation, but it requires another effort. (Both programming and computational time)

Our approximation for expectation value

Expand the exponential operator in the Taylor series and truncate them only to the linear term for CCSD.

$\hat{O}_N = \hat{O} - \langle O \rangle_{HF}$ Normal order operator

$$\langle \hat{O}_N \rangle = \frac{\left\langle HF \left| \left(1 + \hat{T}^+ + \frac{\left(\hat{T}^+\right)^2}{2} + \cdots \right) \hat{O}_N \left(1 + \hat{T} + \frac{\hat{T}^2}{2} + \cdots \right) \right| HF \right\rangle}{\left\langle HF \left| \left(1 + \hat{T}^+ + \frac{\left(\hat{T}^+\right)^2}{2} + \cdots \right) \left(1 + \hat{T} + \frac{\hat{T}^2}{2} + \cdots \right) \right| HF \right\rangle}$$

$$= \left\langle HF \left| \left(1 + \hat{T}^+ + \frac{\left(\hat{T}^+\right)^2}{2} + \cdots \right) \hat{O}_N \left(1 + \hat{T} + \frac{\hat{T}^2}{2} + \cdots \right) \right| HF \right\rangle_C$$

$$\boxed{\approx \left\langle HF \left| \left(1 + \hat{T}_1^+ + \hat{T}_2^+ \right) \hat{O}_N \left(1 + \hat{T}_1^+ + \hat{T}_2^+ \right) \right| HF \right\rangle_C}$$

We can easily calculate this value using t1 and t2 amplitudes obtained from CCSD.

Our contracted basis sets

- We usually use contracted basis sets for molecules in non-relativistic case. (6-31G, cc-pvnZ, ANO, etc)

- In the 4-component Dirac case, contracted basis sets sometimes cause problems so called “variational collapse” (converge to extremely low energy or not converge due to the contamination of negative energy levels).

- However, if we use the two-component spinor basis scheme used in UTChem, we can avoid the problem and keep the concept of LCAO.

- Contracted basis set is more compact and faster in calculation than the primitive basis sets. Primitive basis set cannot be considered as full space in CCSD calculation.

Contracted basis set functions

contraction coefficients

exponential coefficients

Dyall-QZ-c basis

S	1s	2s	3s	4s	5s	6s
6.5973426E+07	9.9782180E-05	-3.7200758E-05	1.7519609E-05	8.5062625E-06	3.2603668E-06	-8.3449817E-07
1.7573042E+07	2.3885301E-04	-8.9322205E-05	4.2086226E-05	2.0436349E-05	7.8332122E-06	-2.0049375E-06
6.0368629E+06	4.8228463E-04	-1.8095458E-04	8.5305558E-05	4.1427940E-05	1.5879797E-05	-4.0644893E-06
2.3148616E+06	8.8873685E-04	-3.3516266E-04	1.5812708E-04	7.6807417E-05	2.9441998E-05	-7.5358548E-06
9.7498001E+05	1.6115692E-03	-6.1126323E-04	2.8865029E-04	1.4023603E-04	5.3759158E-05	-1.3759946E-05
4.3572342E+05	2.8710341E-03	-1.0971913E-03	5.1870929E-04	2.5207492E-04	9.6635219E-05	-2.4734770E-05
2.0470199E+05	5.1348039E-03	-1.9786885E-03	9.3667476E-04	4.5532856E-04	1.7457384E-04	-4.4683531E-05
9.9654250E+04	9.2072616E-03	-3.5840701E-03	1.6992363E-03	8.2632136E-04	3.1681877E-04	-8.1094980E-05
4.9983316E+04	1.6583606E-02	-6.5322387E-03	3.1029055E-03	1.5095694E-03	5.7888801E-04	-1.4817268E-04
2.5663485E+04	2.9818647E-02	-1.1931486E-02	5.6815266E-03	2.7657042E-03	1.0606081E-03	-2.7149014E-04
1.3440699E+04	5.2950673E-02	-2.1662469E-02	1.0353665E-02	5.0443789E-03	1.9350958E-03	-4.9532159E-04
7.1598929E+03	9.0977035E-02	-3.8543746E-02	1.8528281E-02	9.0395936E-03	3.4681500E-03	-8.8782782E-04
3.8753556E+03	1.4628804E-01	-6.5598978E-02	3.1847069E-02	1.5573611E-02	5.9794889E-03	-1.5306719E-03
2.1307057E+03	2.0889813E-01	-1.0286939E-01	5.0763430E-02	2.4921791E-02	9.5740825E-03	-2.4513911E-03
1.1898903E+03	2.4396201E-01	-1.3823205E-01	7.0048345E-02	3.4607750E-02	1.3320170E-02	-3.4104986E-03
6.7429769E+02	2.0474701E-01	-1.3342031E-01	6.9688307E-02	3.4691717E-02	1.3362843E-02	-3.4233136E-03
3.8724214E+02	1.0102651E-01	-2.4179884E-02	8.1792671E-03	3.5358781E-03	1.3346475E-03	-3.3860593E-04
2.2481397E+02	2.1298438E-02	2.1261417E-01	-1.5951971E-01	-8.6463521E-02	-3.4004530E-02	8.7246883E-03
1.3362161E+02	1.3981505E-03	4.1121363E-01	-3.7713017E-01	-2.1585010E-01	-8.5749185E-02	2.2051823E-02
8.1281158E+01	4.1116786E-05	3.5057833E-01	-4.0182068E-01	-2.4250758E-01	-9.7776272E-02	2.5149688E-02
5.0939803E+01	3.8127887E-05	1.4856492E-01	-1.0447585E-01	-6.8770856E-02	-2.8918209E-02	7.5361505E-03
3.2280526E+01	-1.0441931E-04	2.9528209E-02	4.0069785E-01	3.6353582E-01	1.6166297E-01	-4.2214557E-02
2.0394685E+01	3.6942048E-05	1.8089816E-03	6.1447118E-01	7.4823240E-01	3.5515598E-01	-9.3081510E-02
1.2503244E+01	-3.2526750E-05	3.5775229E-04	3.2470347E-01	3.7866373E-01	1.6908482E-01	-4.4203642E-02
7.2874456E+00	2.4471759E-05	-3.1026960E-04	5.4055539E-02	-4.6352619E-01	-2.8413146E-01	7.6523038E-02
4.3210001E+00	-1.1535675E-05	3.3408769E-05	2.2180494E-03	-7.3973061E-01	-5.9688417E-01	1.6916103E-01
2.5234051E+00	8.3346020E-06	-7.0668008E-05	1.2025946E-03	-3.2042059E-01	-3.8288855E-01	1.1465921E-01
1.4175240E+00	-4.8775188E-06	3.8350509E-05	-2.7428342E-04	-3.8335074E-02	2.2717730E-01	-7.9496271E-02
7.9157400E-01	2.7643534E-06	-1.7666327E-05	9.1058439E-05	-1.4535011E-03	6.2283403E-01	-2.2484198E-01
4.4198499E-01	-1.7465836E-06	1.3620169E-05	-9.8219827E-05	-7.9721646E-04	4.5570588E-01	-2.7116462E-01
2.4345371E-01	8.5919476E-07	-6.0619634E-06	3.2241392E-05	-6.7667385E-05	1.0609629E-01	-1.5553717E-01
1.1878413E-01	-4.2231693E-07	3.0886469E-06	-1.6573828E-05	3.8028070E-05	5.1623573E-03	1.8463795E-01
6.1739139E-02	2.3280153E-07	-1.6835017E-06	1.4079000E-05	2.1992554E-04	3.9420751E-03	5.2053680E-01
3.1922684E-02	-9.6968198E-08	7.1602848E-07	-3.7927686E-07	1.6873698E-04	3.2883261E-03	4.4423560E-01
1.6420495E-02	2.3449273E-08	-1.6889708E-07	1.6939352E-06	3.5436438E-05	6.4944623E-04	8.6473321E-02

quadruple zeta