Molecular orbital based calculations for the search of the electron EDM using the Coupled-Cluster method in the Dirac-Coulomb Approximation

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What is observed about e-EDM in molecules?

Interaction energy of Electron EDM with internal electric field of molecule

Collaboration of three different fields!

Particle Physics
Prediction of d_e CP violation?

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

Molecular (or atomic) Optical experiments
Observation of the total interaction

Relativistic quantum chemistry
Calculation of effective electric field, $\mathbf{E}_{\text{eff}}$

1. Operator form; E_{eff}
2. Qualitative consideration of internal E (E_{int})
3. Effective one-body operator: p^2
4. Singly occupied molecular orbital analysis at Hartree-Fock

Our method

5. Beyond HF; CC method
6. Results in YbF

Form of E_{eff}

- E_{eff} appears only in relativistic frame work.

Multi-electronic Dirac-Coulomb Hamiltonian

$$\hat{H}_{DC} = \sum_i^{N_{elec}} \left[c\alpha p_i + \beta mc^2 - \sum_A^{N_{nuc}} \frac{Z_A}{|\mathbf{r}_i - \mathbf{R}_A|} \right] + \sum_{i<j}^{N_{elec}} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \qquad \Psi_{DC} = \begin{pmatrix} \psi_\alpha^L \\ \psi_\beta^L \\ \psi_\alpha^S \\ \psi_\beta^S \end{pmatrix}$$

Kinetic and relativistic correction

Nuclear attraction

Electron repulsion

Eigenfunction of Dirac-Coulomb Hamiltonian, four component!

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

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.
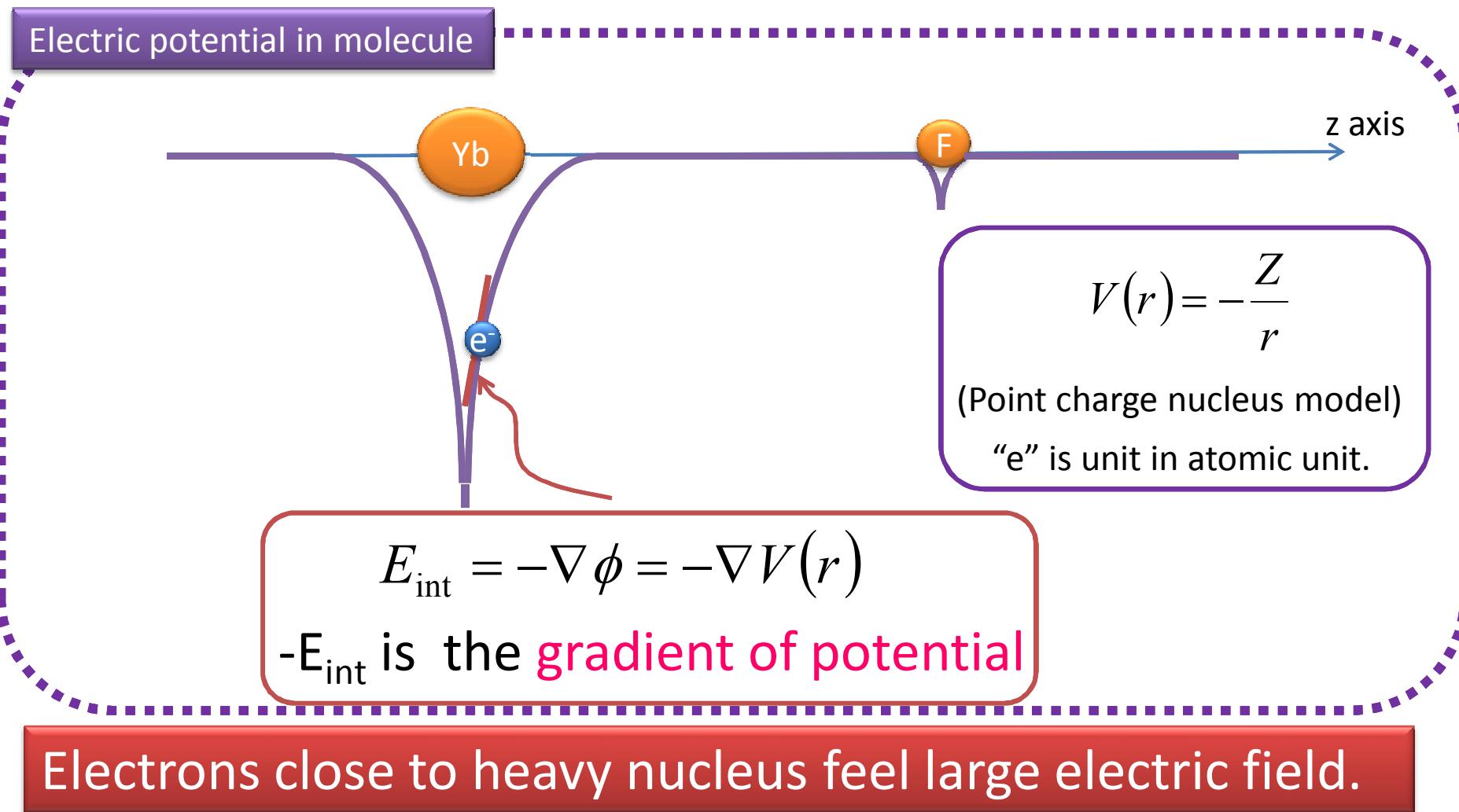
Electric potential in molecule

z axis

Yb

F

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

(Point charge nucleus model)

"e" is unit in atomic unit.

e⁻

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

-E_{int} is the gradient of potential

Electrons close to heavy nucleus feel large electric field.

Parity symmetric orbital cannot have E_{eff}

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

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

Electron density

Atom without external field
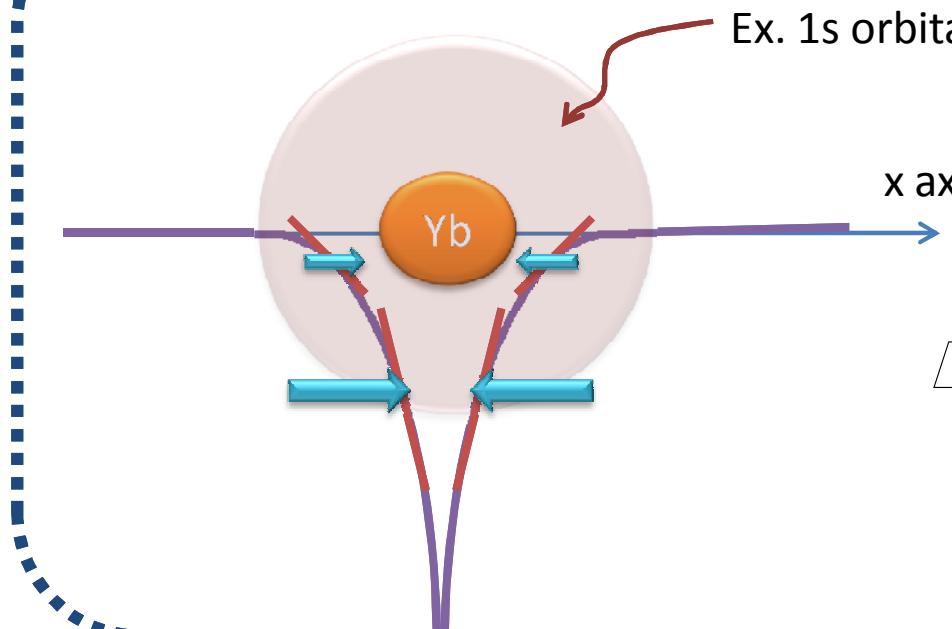
Ex. 1s orbital

x axis

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

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

➡ E_{eff} is zero.

Parity symmetric orbital cannot have E_{eff}

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

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

Electron density

Homo diatomic molecule
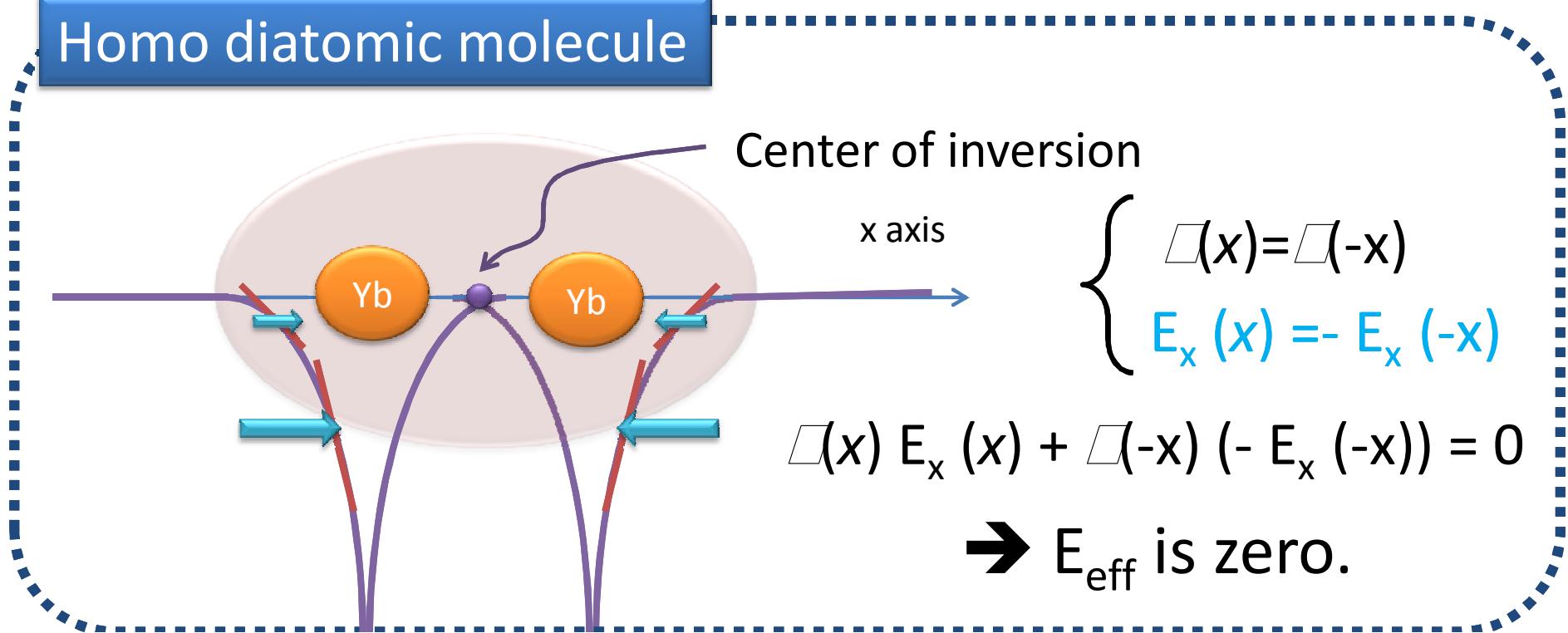
Center of inversion

x axis

Yb   Yb

$\square(x) = \square(-x)$

$E_x(x) = - E_x(-x)$

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

$\rightarrow E_{eff}$ is zero.

Parity symmetric orbital cannot have E_{eff}

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

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

Electron density

Hetero diatomic molecule
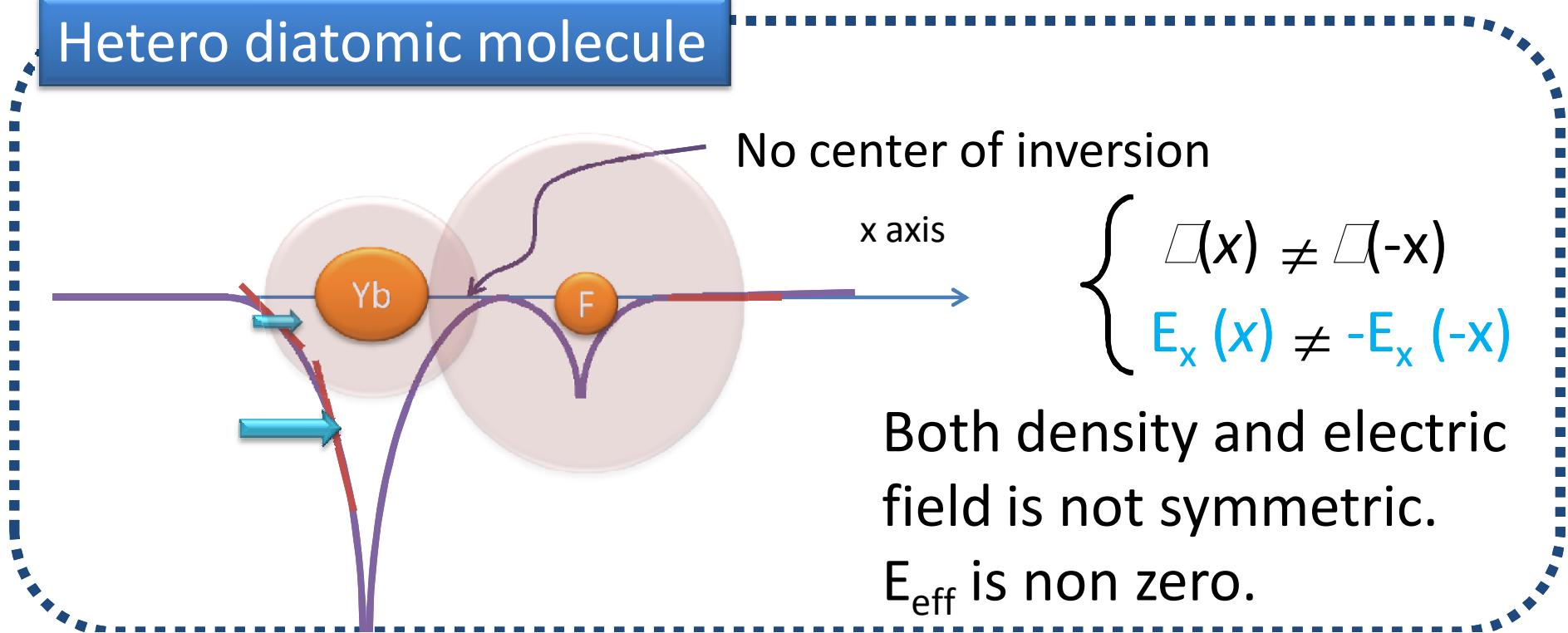
No center of inversion

x axis

Yb   F

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

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

Parity symmetric orbital cannot have E_{eff}

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

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

Electron density

Hetero but almost similar diatomic molecule
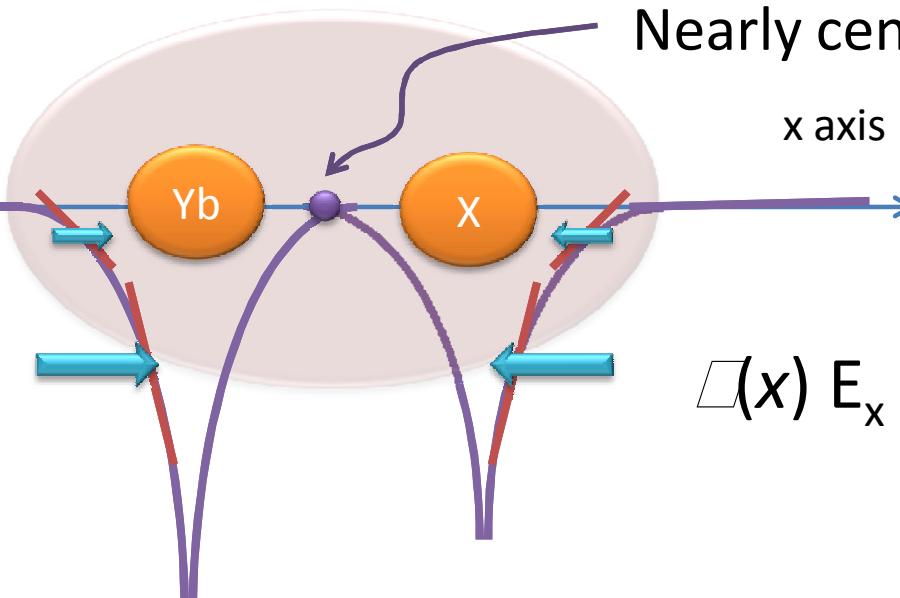
Nearly center of inversion

x axis

Yb   X

$\square(x) \approx \square(-x)$

$E_x(x) \approx - E_x(-x)$

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

➔ E_{eff} is small.

Effective Hamiltonian of E_{eff}

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

$$= \left[-\frac{d_e}{e} \beta \sigma \cdot \nabla, \hat{H}_{DC} \right] + 2i \frac{d_e}{e} c \beta \gamma_5 p^2 \quad \boxed{\text{By B. P. Das}}$$

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

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

One-electron molecular orbital

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

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

Integrals are cancelled in between Kramers-paired orbitals and singly occupied orbital determines the nature of E_{eff} at the HF level.

Large and small component
of atomic orbital (basis sets)

$$s_{1/2}^{-1/2} \begin{pmatrix} 0 \\ -s_0 \\ 2\zeta(p_{+1}-ip_{-1}) \\ -2\zeta p_0 \end{pmatrix}$$

Large component

Small component

$$s_{1/2}^{1/2} \begin{pmatrix} s_0 \\ 0 \\ -2\zeta p_0 \\ -2\zeta(p_{+1}+ip_{-1}) \end{pmatrix}$$

$$p_{1/2}^{-1/2} \begin{pmatrix} -(p_{+1}-ip_{-1}) \\ p_0 \\ 0 \\ -(3s_0-2\zeta r^2 s_0) \end{pmatrix}$$

$$p_{1/2}^{1/2} \begin{pmatrix} p_0 \\ p_{+1}+ip_{-1} \\ 3s_0-2\zeta r^2 s_0 \\ 0 \end{pmatrix}$$

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

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

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

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

Yanai et al.
JCP, 114, 6526, 2001.

Small component is very very small in light element system.
It becomes 0 in non-relativistic limit.

Differentiation and angular moment

$$\phi^S = \frac{c}{2mc^2 - V + \varepsilon}(\boldsymbol{\sigma} \cdot \mathbf{p})\phi^L \approx \frac{(\boldsymbol{\sigma} \cdot \mathbf{p})}{2mc}\phi^L$$

Kinetic balance condition

$$\phi^L = \frac{c}{-V + \varepsilon}(\boldsymbol{\sigma} \cdot \mathbf{p})\phi^S$$

$$\left\langle \varphi^L \left| p^2 \right| \varphi^S \right\rangle = \left\langle \varphi^L \left| (\boldsymbol{\sigma} \cdot \mathbf{p})(\boldsymbol{\sigma} \cdot \mathbf{p}) \right| \varphi^S \right\rangle = \frac{-V + \varepsilon}{c} \left\langle \varphi^L \left| (\boldsymbol{\sigma} \cdot \mathbf{p}) \right| \varphi^L \right\rangle$$

Differentiation of *s* spherical harmonics function

➔ *p* spherical harmonics function

Differentiation of *p* spherical harmonics function

➔ *s and d* spherical harmonics function

…

Differentiation makes *l* number lower and higher by one. See Yanai's paper.

When is the matrix element large?

$$\langle s|(\boldsymbol{\sigma}\cdot\mathbf{p})|p\rangle, \langle p|(\boldsymbol{\sigma}\cdot\mathbf{p})|s\rangle, \langle p|(\boldsymbol{\sigma}\cdot\mathbf{p})|d\rangle, \ \langle d|(\boldsymbol{\sigma}\cdot\mathbf{p})|p\rangle, \langle d|(\boldsymbol{\sigma}\cdot\mathbf{p})|f\rangle$$

are non zero.

Angular moment of bra and ket should differ by one
to give nonzero matrix element.

Mixing of (*s* and *p*), (*p* and *d*), or (*d* and *f*) in molecular orbital
is important for large value of E_{eff} .

This agrees with the concept of parity mixing in atomic EDM.

The *s* and *p* combination especially provide largest value
because they are close to nucleus and relativistic effect is
large. (Small component is large)

Let's examine some molecules with 6s and 6p valence.

Analysis of SOMO in YbF

16.7 GV/cm

atom	basis type	J	mj	MO coeff.	weight
1Yb	4S	1/2	1/2	0.055	0.00
1Yb	**6S**	**1/2**	**1/2**	**1.371**	**0.76**
1Yb	5S	1/2	1/2	-0.206	0.02
1Yb	8S	1/2	1/2	-0.252	0.03
1Yb	**4P**	**1/2**	**1/2**	**0.050**	**0.00**
1Yb	5P	1/2	1/2	0.038	0.00
1Yb	6P	1/2	1/2	-0.031	0.00
1Yb	4P	3/2	1/2	-0.071	0.00
1Yb	5P	3/2	1/2	0.049	0.00
1Yb	4D	3/2	1/2	0.032	0.00
1Yb	4D	5/2	1/2	0.045	0.00
2F	2S	1/2	1/2	-0.064	0.00
2F	**3S**	**1/2**	**1/2**	**0.627**	**0.16**
2F	4S	1/2	1/2	0.115	0.01
2F	1P	1/2	1/2	0.047	0.00
2F	2P	1/2	1/2	0.120	0.01
2F	3P	1/2	1/2	0.058	0.00
2F	1P	3/2	1/2	0.062	0.00
2F	2P	3/2	1/2	0.171	0.01
2F	3P	3/2	1/2	0.090	0.00

80% contribution of Yb
20% contribution of F

Mixing of s and p?
➔ so so
Heavy element ?
Z=70 ➔ so so

Analysis of SOMO in HgF

Preliminary calculation
with Fægri's basis

79.3 GV/cm

atom	basis type	J	mj	MO coeff.	weight
1Hg	5S	1/2	1/2	0.077	0.00
1Hg	**6S**	**1/2**	**1/2**	**0.679**	**0.28**
1Hg	7S	1/2	1/2	-0.042	0.00
1Hg	**8S**	**1/2**	**1/2**	**-0.617**	**0.23**
1Hg	4P	1/2	1/2	-0.043	0.00
1Hg	**6P**	**1/2**	**1/2**	**-0.091**	**0.01**
1Hg	**5P**	**3/2**	**1/2**	**0.124**	**0.01**
1Hg	5P	1/2	1/2	0.077	0.00
1Hg	3P	3/2	1/2	-0.041	0.00
1Hg	6P	3/2	1/2	-0.071	0.00
1Hg	3D	3/2	1/2	-0.127	0.01
1Hg	3D	5/2	1/2	-0.205	0.03
2F	2S	1/2	1/2	-0.115	0.01
2F	4S	1/2	1/2	-0.165	0.02
2F	2P	1/2	1/2	0.201	0.02
2F	1P	3/2	1/2	0.362	0.08
2F	3P	3/2	1/2	-0.049	0.00
2F	**3S**	**1/2**	**1/2**	**0.551**	**0.19**
2F	1P	1/2	1/2	0.271	0.05
2F	3P	1/2	1/2	-0.035	0.00

60% contribution of Hg
40% contribution of F

Mixing of s and p?
➔Very good!

Heavy element ?
Z=80➔ yes

Analysis of SOMO in HgH

Preliminary calculation with Fægri's basis

80.1 GV/cm

atom	basis type	J	mj	MO coeff.	weight
1Hg	3S	1/2	1/2	-0.033	0.00
1Hg	5S	1/2	1/2	-0.303	0.04
1Hg	7S	1/2	1/2	0.280	0.04
1Hg	4S	1/2	1/2	0.099	0.00
1Hg	**6S**	**1/2**	**1/2**	**1.136**	**0.59**
1Hg	8S	1/2	1/2	-0.157	0.01
1Hg	**4P**	**1/2**	**1/2**	**-0.101**	0.00
1Hg	**4P**	**3/2**	**1/2**	**-0.133**	**0.01**
1Hg	5P	3/2	1/2	0.061	0.00
1Hg	5P	1/2	1/2	0.057	0.00
1Hg	6P	1/2	1/2	-0.091	0.00
1Hg	6P	3/2	1/2	-0.055	0.00
1Hg	3D	3/2	1/2	-0.140	0.01
1Hg	3D	5/2	1/2	-0.207	0.02
1Hg	5D	3/2	1/2	-0.099	0.00
1Hg	5D	5/2	1/2	-0.122	0.01
2H	**1S**	**1/2**	**1/2**	**0.625**	**0.18**
2H	2S	1/2	1/2	0.196	0.02
2H	3S	1/2	1/2	0.356	0.06
2H	2P	1/2	1/2	0.065	0.00

70% contribution of Hg
30% contribution of F

Mixing of s and p?
➔ good!

Heavy element ?
Z=80 ➔ yes

Analysis of SOMO in PbF

-40.5 GV/cm

atom	basis type	J	mj	MO coeff.	weight
1Pb	**6S**	**1/2**	**1/2**	**0.057**	0.00
1Pb	**5P**	**1/2**	**1/2**	**0.922**	**0.82**
1Pb	4P	3/2	1/2	-0.077	0.01
1Pb	6P	3/2	1/2	-0.143	0.02
1Pb	3D	3/2	1/2	-0.040	0.00
1Pb	8S	1/2	1/2	-0.036	0.00
1Pb	7P	1/2	1/2	0.029	0.00
1Pb	5P	3/2	1/2	-0.284	0.08
1Pb	7P	3/2	1/2	-0.064	0.00
1Pb	5D	3/2	1/2	0.038	0.00
2F	2S	1/2	1/2	-0.050	0.00
2F	3S	1/2	1/2	0.055	0.00
2F	4S	1/2	1/2	-0.037	0.00
2F	2P	1/2	1/2	-0.084	0.01
2F	2P	3/2	1/2	0.100	0.01
2F	1P	1/2	1/2	-0.082	0.01
2F	**1P**	**3/2**	**1/2**	**0.199**	**0.04**
2F	3P	3/2	1/2	-0.033	0.00

90% contribution of Pb
10% contribution of F

Mixing of s and p?
➔ Less

Heavy element ?
Z=82 ➔ yes

"Major p and minor s" is weaker than "major s and minor p" mixing?

Analysis of SOMO in BiO

6.9 GV/cm

atom	basis type	J	mj	MO coeff.	weight
1Bi	8S	1/2	1/2	-0.073	0.01
1Bi	6P	1/2	1/2	0.042	0.00
1Bi	5P	3/2	1/2	-0.258	0.06
1Bi	7P	3/2	1/2	0.039	0.00
1Bi	5P	1/2	1/2	0.214	0.04
1Bi	7P	1/2	1/2	0.109	0.01
1Bi	6P	3/2	1/2	0.027	0.00
1Bi	5D	3/2	1/2	0.029	0.00
1Bi	3D	3/2	1/2	-0.086	0.01
1Bi	3D	5/2	1/2	0.029	0.00
2O	**1P**	**1/2**	**1/2**	**-0.653**	**0.41**
2O	**1P**	**3/2**	**1/2**	**0.686**	**0.45**
2O	2D	5/2	1/2	0.026	0.00
2O	3S	1/2	1/2	0.030	0.00
2O	2P	1/2	1/2	-0.046	0.00
2O	2P	3/2	1/2	0.079	0.01

10% contribution of Bi
90% contribution of O

Mixing of s and p?
➔Less

Heavy element ?
Z=83➔ yes, very much

Analysis of SOMO in BiO

6.9 GV/cm

atom	basis type	J	mj	MO coeff.	weight
1Bi	8S	1/2	1/2	-0.073	0.01
1Bi	6P	1/2	1/2	0.042	0.00
1Bi	5P	3/2	1/2	-0.258	0.06
1Bi	7P	3/2	1/2	0.039	0.00
1Bi	5P	1/2	1/2	0.214	0.04
1Bi	7P	1/2	1/2	0.109	0.01
1Bi	6P	3/2	1/2	0.027	0.00
1Bi	5D	3/2	1/2	0.029	0.00
1Bi	3D	3/2	1/2	-0.086	0.01
1Bi	3D	5/2	1/2	0.029	0.00
2O	1P	1/2	1/2	-0.653	0.41
2O	1P	3/2	1/2	0.686	0.45
2O	2D	5/2	1/2	0.026	0.00
2O	3S	1/2	1/2	0.030	0.00
2O	2P	1/2	1/2	-0.046	0.00
2O	2P	3/2	1/2	0.079	0.01

10% contribution of Bi
90% contribution of O

Mixing of s and p?
➜ Less

Heavy element ?
Z=83 ➜ yes, very much

E_{eff} at HF level is very small but it improves to be **-32 GV/cm** after the calculation of electron correlation (CCSD).

Summary for large E_{eff}

1. Parity violated molecule with heavy and light atoms.

2. Singly occupied molecular orbital (SOMO) should consists of atomic orbital of heavy element.

3. SOMO should contains both s and p orbital.

   If SOMO is in □ orbital (p_x, p_y), it is not good since s can only mix with p_z (□) orbital.

   However, it can have large E_{eff} after spin-orbit coupling.

4. Hartree-Fock may not be good approximation sometimes. Electron correlation change the world.

Beyond the HF method

There is no reason that the single Slater determinant can really describe the exact wave function.

H$_2$ molecule (HF state)

ψ_- ——————

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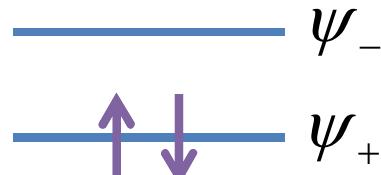
$$\Psi(1,2) = \frac{1}{\sqrt{2!}} \begin{vmatrix} \psi_+(1)\alpha(1) & \psi_+(1)\beta(1) \\ \psi_+(2)\alpha(2) & \psi_+(2)\beta(2) \end{vmatrix}$$

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

These are different (orthogonal) functions!

H$_2$ molecule

ψ_- ——↑↓——

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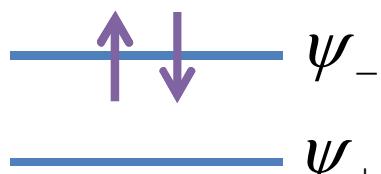
$$\Psi'(1,2) = \frac{1}{\sqrt{2!}} \begin{vmatrix} \psi_-(1)\alpha(1) & \psi_-(1)\beta(1) \\ \psi_-(2)\alpha(2) & \psi_-(2)\beta(2) \end{vmatrix}$$

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

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

Beyond the HF method

"Exact wave function"
can be a linear combination of full configurations (Full-CI)
created from infinite number of (orthogonal) 1-electron
orbital basis.

Of course, impossible and need approximations.

Step 1. Solve Hartree-Fock and determine orbital basis
Step 2. Electron correlation calculation
Perturbation theory; MP2, MP4, …
(Truncated) configuration interaction theory;
SDCI,SDTQCI,…,GASCI,RASCI
Coupled Cluster theory; CCSD, CCSD(T), …
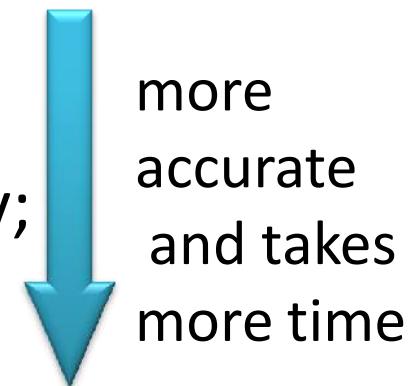
more
accurate
and takes
more time

Or start from multi-reference treatment …

CI method

Exact within the basis sets used!

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

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

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

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

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

For example of SDCI

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

t_0, t_1, t_2 coefficients are optimized as the energy is to be minimum.

Coupled Cluster method

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

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

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 \ldots \qquad \hat{T}_N \quad : \text{N-electron excitation operator}$$

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

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

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

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

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

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

$$\Delta E$$

Electron correlation energy
=Correction to the exact energy

Coupled Cluster method

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

$$= \hat{H}_N + \left[\hat{H}_N, T\right] + \frac{1}{2!}\left[\left[\hat{H}_N, T\right], T\right] + \frac{1}{3!}\left[\left[\left[\hat{H}_N, T\right], T\right], T\right] + \frac{1}{4!}\left[\left[\left[\left[\hat{H}_N, T\right], T\right], T\right], T\right]$$

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

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

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

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

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

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

Problem in CC method
for expectation value

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

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

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

We can explicitly 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 terms for CCSD.

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

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

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

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

Our contracted basis sets

- Chemists normally use contracted basis sets for molecules.
  (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).

- We can get rid of the problem if we use the two-component spinor basis scheme implemented **in UTChem software**.

- **Contracted basis sets** are more **compact and faster** in calculation than primitive basis sets.
  We don't need truncations of virtual spinors in CCSD unlikely to the primitive basis schemes.

Contracted basis set functions

Dyall-QZ basis S

$$\phi_i = \sum_{p=1}^{N} d_{p,i} \exp\left(-\alpha_p r^2\right)$$

Contracted basis sets 6 (+ 4) functions

Primitive basis sets 35 functions

S	1s	2s	3s	4s	5s	6s
6.5973426E+07	9.?782180E-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					1.5879797E-05	-4.0644893E-06
2.3148616E+06					2.9441998E-05	-7.5358548E-06
9.7498001E+05					5.3759158E-05	-1.3759946E-05
4.3572342E+05					9.6635219E-05	-2.4734770E-05
2.0470199E+05					1.7457384E-04	-4.4683531E-05
9.9654250E+04					3.1681877E-04	-8.1094980E-05
4.9983316E+04	1.658360?E-02	-6.?322387E-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						...32159E-04
7.1598929E+03						...82782E-04
3.8753556E+03						...06719E-03
2.1307057E+03						...13911E-03
1.1898903E+03						...04986E-03
6.7429769E+02						...33136E-03
3.8724214E+02		...0102651E-01	-2.4179884E-02	8.1792671E-03	3.5358781E-03	1.3346475E-03	-3.3860593E-04
2.2481397E+02		...1298438E-02	2.1261417E-01	-1.5951971E-01	-8.6463521E-02	-3.4004530E-02	8.7246883E-03
1.3362161E+02						...51823E-02
8.1281158E+01						...49688E-02
5.0939803E+01						...61505E-03
3.2280526E+01						...14557E-02
2.0394685E+01						...81510E-02
1.2503244E+01						...03642E-02
7.2874456E+00	2.44717?9E-05	3.1026960E-04	5.4055559E-02	4.6552619E-01	2.8413148E-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	-?.2231693E-07	3.0886469E-06	-1.6573828E-05	3.8028070E-05	5.1623573E-03	1.8463795E-01
6.1739139E-02	3.3280153E-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

Originality of our method

- All-electron four-component Dirac-Coulomb Hamiltonian (Accurate in relativity)

- The effective operator p^2 including E_{int} by both nuclei and electrons (Accurate)

- Two-component type contracted basis (Fast but need to check it working well)

- C_8 group symmetry (Fast and efficient)

- fully solved CCSD, but expectation values approximated to linear order

  (Fast but may less accurate)

Programs **DCHF in UTChem** + **CCSD in DIRAC10**

Comparison of the previous works in YbF

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 (Dyall's QZ primitive basis)	This work (2013)	18.2
DHF (Dyall's QZ contracted basis)	This work (2013)	18.1

Results with Dyall basis sets at DCHF

Basis set	Total number of basis spinors	Total Energy (a.u.)	Eeff (GV/cm)	Molecular dipole moment (D)
Yb(Dy-TZ-c) + F(Wa-QZ-c)	450	-14167.3216656327	17.9	3.21
Yb(Dy-TZ-p) + F(Wa-QZ-p)	846	-14167.3217911920	18.2	3.21
Yb(Dy-QZ-c) + F(Wa-QZ-c)	510	-14167.3230011980	18.1	3.21
Yb(Dy-QZ-p) + F(Wa-QZ-p)	888	-14167.3230627520	18.2	3.21
Exp.	-	-	-	3.91

The difference of primitive or contracted basis sets are only 10^{-4} a.u in total energy and 0.3 GV/cm in E_{eff}.
The number of primitive basis sets are 160% larger than contracted.

Results with Dyall basis sets at CCSD

Basis set	Correlation space (occ/vir spinors)	Total Energy (a.u.)	T1 diagnostic	Eeff (GV/cm) CCSD (HF)	Molecular DM (D)
Yb(Dy-TZ-c) + F(Wa-QZ-c)	41/371	-14169.3238622289	0.0778	19.1 (17.9)	3.44
Yb(Dy-TZ-p) + F(Wa-QZ-p)	41/511	-14169.5294823447	0.0824	18.8 (18.2)	3.35
Yb(Dy-QZ-c) + F(Wa-QZ-c)	41/431	-14169.4106511355	0.0687	20.1 (18.2)	3.43
Exp.	-	-	-	-	3.91

Dy:Dyall's four-component basis, Wa: Watanabe's four-component basis

Correlation effects increase the value of E_{eff} about 10%.
TZ basis series have slightly large T1 diagnostic value.

Results with Dyall basis sets at CCSD Correlation space dependence

Basis set	Correlation space (occ/vir spinors)	Total Energy (a.u.)	T1 diagnostic	Eeff (GV/cm)	Molecular DM (D)
Yb(Dy-QZ-c) + F(Wa-QZ-c)	31/431	-14168.8545733402	0.0421	22.2	3.64
Yb(Dy-QZ-c) + F(Wa-QZ-c)	41/431	-14169.4106511355	0.0687	20.1	3.43
Yb(Dy-QZ-c) + F(Wa-QZ-c)	49/431	-14169.6348960485	0.0577	20.5	3.46
Exp.	-	-	-	-	3.91

31-spinor correlation space
Yb: $(6s)^1$, $(4f)^{14}$, $(5p)^6$, $(5s)^2$ F: $(2p)^5$, $(2s)^2$

41-spinor correlation space
Yb: $(6s)^1$, $(4f)^{14}$, $(5p)^6$, $(5s)^2$, **$(4d)^{10}$** F: $(2p)^5$, $(2s)^2$

49-spinor correlation space
Yb: $(6s)^1$, $(4f)^{14}$, $(5p)^6$, $(5s)^2$, **$(4d)^{10}$, $(4p)^6$, $(4s)^2$** F: $(2p)^5$, $(2s)^2$

4d effect in E_{eff} is quite large!

Spectroscopic data

Basis set	Correlation space (occ/vir spinors)	R_e (Å)	$\square_e$ (cm^{-1})	
Yb(Dy-QZ-c) + F(Wa-QZ-c)	41/431	1.9919	466.0	Present work
Yb(Dy-QZ-c) + F(Wa-QZ-c)	31/431	2.0155	506.5	Present work
Yb(DY-QZ-p) +F(augccpvQZ-p)	31/593	2.0196	503.2	Gomes et al. TCA 2010
Exp.	-	2.0161	506.7	From Heltzberg's book

Dyall QZ contracted basis sets reproduces the value of R_e and $\square_e$ of Dyall's QZ primitive basis sets very well if we use same correlation space in occupied spinors.

Conclusion

- We have developed a new method and programs to calculate E_{eff} at the CCSD level.

- We have tested our method in YbF molecule using Dyall's contracted basis sets.

- Contracted basis sets are stable and reproduce the spectroscopic constants of primitive basis sets very well.

- E_{eff} of YbF is 20.5 GV/cm.

Programs **DCHF in UTChem** + **CCSD in DIRAC10** = works well!