公募研究：ワニエ関数を軸とする準粒子自己無撞着法の新しい展開

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第一原理計算の基礎的な方法論
一体問題→低エネルギー励起、準粒子の寿命など
→不純物や分子、表面などへの応用

＊一体問題解法を整備する（オーダーNではない範囲）。局在基底と非局在基底。

＊「準粒子**self-consistent GW**法」の整備
（異方性、取り扱いやすさ、収束性、計算速度）。

＊ワニエ関数の構成。低エネルギー励起（フォノンやマグノンなど）。
それらによる自己エネルギーなど。

The PMT method: a new linearized method

PMT =A**P**W + **MT**O

Muffin-tin

Takao Kotani (tottori-u, Japan)

Outline

1. **Introduction**
   Motivation, linearized method, APW, MTO
2. **Formalism** A few key points
3. **Results**
   from H_2 through Kr_2 in PBE

ecalj google

Not organized well yet …
(MostofAll are still in Japanese…

Motivation:

Quasiparticle Self-consistent GW (QSGW) method

$\hat{H} = \hat{H}_0 + (\hat{H} - \hat{H}_0)$と分ける方法

をFP-LMTOをもとに開発してきた。

→方法論的には成功した。現状では
数値的に問題点は色々ある。
Empty spheres,
Not systematic convergence,
計算のパラメータ設定が面倒。

→ **Look for a better linearized method.**

Look for a better linearized method!

Requirements:

＊速度、精度、ロバストネス:

Reliable in any atomic configurations.
Stable convergence (intrinsic stability).
Systematic convergence check.

＊更なる発展:

GW, Wannier functions, magnon, phonons…
excitations, their coupling, and total energy.

My conclusion:

To overcome shortcomings in FP-LAPW and FP-LMTO, we should use both of **APW and MTO together.**

The linearized method

- **Basis set**

→ eigenfunctions are given as:

$$\psi_p(\mathbf{r}) = \sum_j \alpha_p^j F_j(\mathbf{r}) \qquad \left\{F_j\right\}: \text{basis set}$$

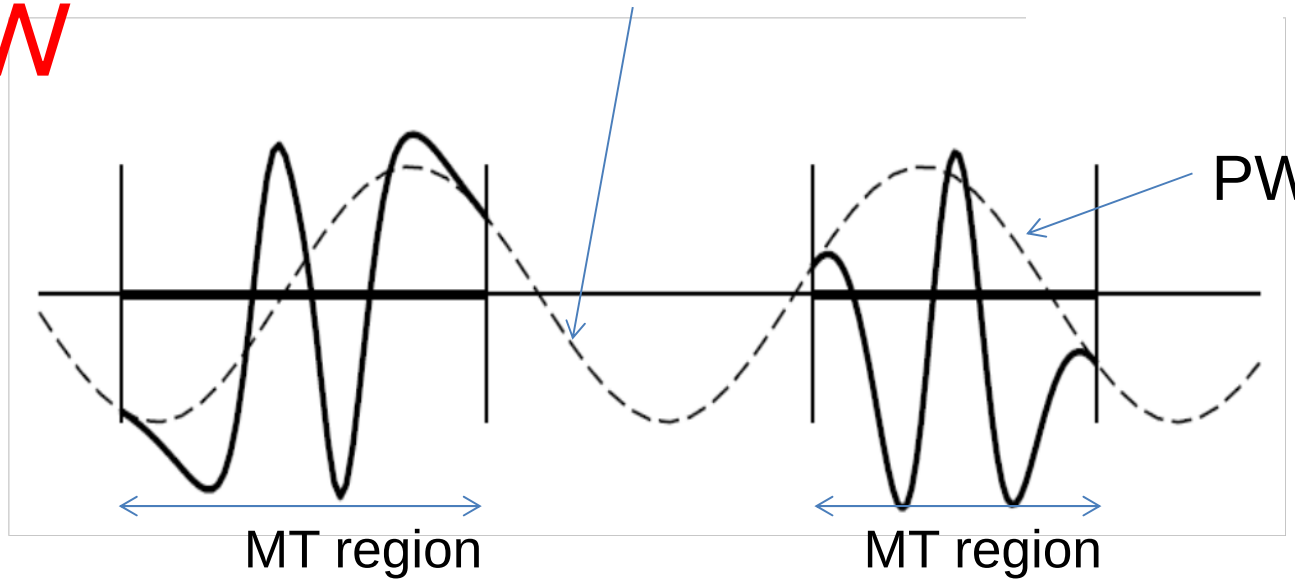
- **Total energy in DF** as a functional of $\left\{\psi_p\right\}$.

↓

Kohn-Sham equation

- For fixed $\left\{F_j\right\}$, minimization with respect to $\left\{\alpha_p^j\right\}$.
- For force, we take into account the changes of $\left\{F_j\right\}$; the Puley term.

APW



3-components

PW ＋ Atomic-like parts within MTs − Counter parts within MTs

0^{th} 1^{st} 2^{nd}

- Good for extended state such as Na(3s).
- Systematic
- Inefficient for Cu(3d), O(2p)

Linearized APW

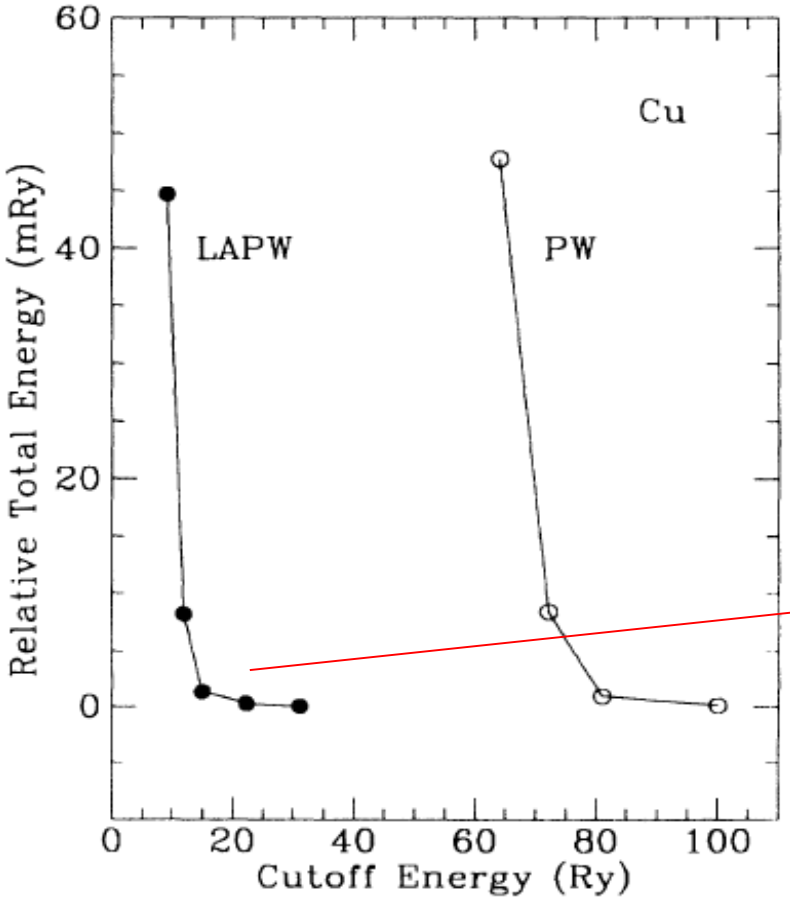


FIG. 1. Relative total energy of fcc Cu plotted against plane-wave cutoff energy.

fcc Cu

plane wave is not so efficient for *3d*

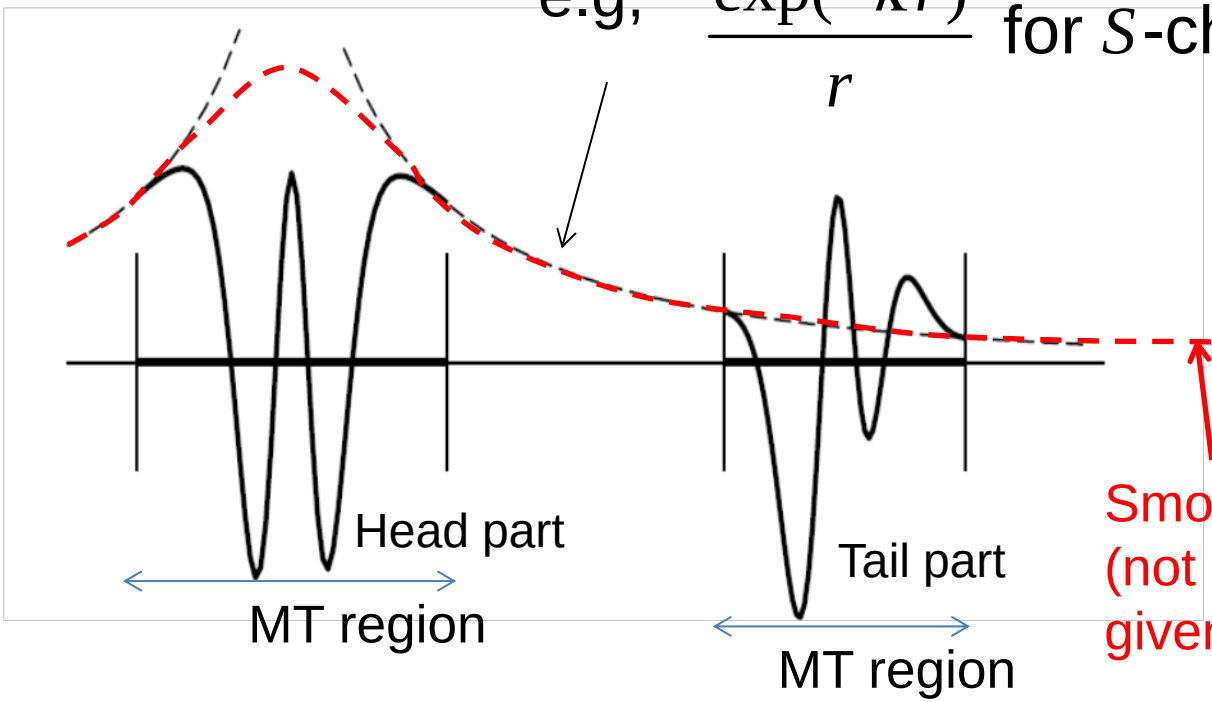
15Ry or more for ~1mRy convergence

D.Singh et al PRB49,17424

MTO

"Atom-centered Hankel function" $\times Y_{lm}$,

e.g, $\frac{\exp(-\kappa r)}{r}$ for S-channel



3-components

Hankel ＋ Atomic-like parts within MT − Counter parts of Hankel within MT

0^{th} 1^{st} 2^{nd}

- Good for localized orbitals such as Cu(3d), O(2p)
- Not so good for extended states.
- Not systematic

PMT =APW + MTO

This is physically reasonable. Complementary.

T.K and M.van Schilfgaarde
arXiv:0808.1604
Phys. Rev. B 81, 125117 (2010)

→Highly accurate for solids.
No empty sphere.
Small number of APWs.
(Parameters of MTO controlled by hand).

--- Recent development ---

T.K and Hiori Kino

- Formulation based on a general theory of augmentation.
- Results for dimers from H_2 through Kr_2 in PBE.
  Simple setting of MTOs with APWs (Energy cutoff 2~4Ry) .

2.Formalism

A general formalism of augmentation wave.

Key points:

- 3-component Hilbert space
- Augmentation for product of envelope functions.

A basis function

MT centers at $\mathbf{R}_a$. Radis R_a.

- Spin index is not shown explicitly.

a basis $F_j(\mathbf{r})$ consists of 3-kinds of components

$$F_{0j}(\mathbf{r}), \qquad \left\{F_{1j,a}(\mathbf{r})\right\} \qquad \left\{F_{2j,a}(\mathbf{r})\right\}$$

Envelope function
PW or
Hankel(Bloch sum)

Atomic-like parts
for $|\mathbf{r}| < R_a$

Counter parts
for $|\mathbf{r}| < R_a$

Cutoff: $l \le l_{\max} \sim 4$, Radial-part : ~5th-order Laguere polynomials

Augmentation procedure depend on Envelop functions

Conventional representation of augmented wave (Soler-Williams type)

$$F_j(\mathbf{r}) = F_{0j}(\mathbf{r}) + \sum_a F_{1j,a}(\mathbf{r}-\mathbf{R}_a) - \sum_a F_{2j,a}(\mathbf{r}-\mathbf{R}_a)$$

Conventional Soler-Williams formalism

$$F_j(\mathbf{r}) = F_{0\,j}(\mathbf{r}) + \sum_a F_{1\,j,a}(\mathbf{r}-\mathbf{R}_a) - \sum_a F_{2\,j,a}(\mathbf{r}-\mathbf{R}_a)$$

- Eigenfunctions $\psi_p = \sum_j \alpha_p^j F_j$
- Product

$$F_i^*(\mathbf{r})F_j(\mathbf{r}) = \left(F_{0i}^*(\mathbf{r}) + \sum_a F_{1i,a}^*(\mathbf{r}-\mathbf{R}_a) - \sum_a F_{2i,a}^*(\mathbf{r}-\mathbf{R}_a) \right)$$

$$\times \left(F_{0j}(\mathbf{r}) + \sum_a F_{1j,a}(\mathbf{r}-\mathbf{R}_a) - \sum_a F_{2j,a}(\mathbf{r}-\mathbf{R}_a) \right)$$

contains cross terms.→ Approximaiton: we neglect these terms

→DF total energy, Kohn-Sham equation.

A problematic logic…

It is better to say no cross terms by definition.

How to formulate?(next page)

we start over from the definition of the Hilbert space.

3-component Hilbert space

A basis itself is a set of functions :

$$F_j = \left\{ F_{0\,j}(\mathbf{r}),\ \left\{ F_{1\,j,a}(\mathbf{r}) \right\},\ \left\{ F_{2\,j,a}(\mathbf{r}) \right\} \right\}$$

$\{...\}$ means a set.

The set of F_j, $\left\{ F_j \right\}$ is a Hilbert space
(as a direct sum of linear spaces).

→ 3-component Hilbert space

We define a quantum mechanical system in this space. Then we apply DFT.

In the 3-component Hilbert space

$$F_j = \left\{ F_{0\,j}(\mathbf{r}),\ \left\{ F_{1\,j,a}(\mathbf{r}) \right\},\ \left\{ F_{2\,j,a}(\mathbf{r}) \right\} \right\},$$

- Eigenfunction: $\psi_p = \sum_j \alpha_p^j F_j$
- Definition of product for bilinear quantities:

$$F_i^*(\mathbf{r}) F_j(\mathbf{r}') = \left\{ F_{0i}^*(\mathbf{r}) F_{0\,j}(\mathbf{r}'),\ \left\{ F_{1i,a}^*(\mathbf{r}) F_{1\,j,a}(\mathbf{r}') \right\},\ \left\{ F_{2i,a}^*(\mathbf{r}) F_{2\,j,a}(\mathbf{r}') \right\} \right\}$$

$$\psi_{p'}^*(\mathbf{r}) \psi_p(\mathbf{r}') = \sum_{i,j} \alpha_{p'}^{i*} \alpha_p^j\ F_i^*(\mathbf{r}) F_j(\mathbf{r}')$$

Product is defined→ How to connect to real world?

Mapping from the 3-component Hilbert space to real world:

$$F_i^*(\mathbf{r})F_j(\mathbf{r}') = \left\{ F_{0i}^*(\mathbf{r})F_{0j}(\mathbf{r}'),\ \left\{F_{1i,a}^*(\mathbf{r})F_{1j,a}(\mathbf{r}')\right\},\ \left\{F_{2i,a}^*(\mathbf{r})F_{2j,a}(\mathbf{r}')\right\} \right\}$$

$\mathcal{R}$-mapping, $\mathcal{R}[\ldots]$

$$\mathcal{R}\left[F_i^*(\mathbf{r})F_j(\mathbf{r}')\right] = F_{0i}^*(\mathbf{r})F_{0j}(\mathbf{r}') + \sum_a F_{1i,a}^*(\mathbf{r}-\mathbf{R}_a)F_{1j,a}(\mathbf{r}'-\mathbf{R}_a) - \sum_a F_{2i,a}^*(\mathbf{r}-\mathbf{R}_a)F_{2j,a}(\mathbf{r}'-\mathbf{R}_a)$$

Meaningful when $\mathbf{r} \approx \mathbf{r}'$:
(1)Both are in the same MT;(2)Both are in interstitial region.

augmentation for the product of Envelope functions

(the essence of Soler-Williams formulation)

c.f.

$$\mathcal{R}\left[F_i^*(\mathbf{r})\right]\mathcal{R}\left[F_j(\mathbf{r}')\right]$$

$\mathcal{R}$-mapping is not to basis functions, but to the products.

"density-matrix-like product"

$$\psi_p = \sum_j \alpha_p^j F_j \qquad \rho_{ij} = \sum_P^{\text{OCCUPIED}} \alpha_p^{i*} \alpha_p^j$$

$$\sum_{i,j} \rho_{ij} F_i^*(\mathbf{r}) F_j(\mathbf{r}') = \left\{ \begin{array}{l} \sum_{i,j} \rho_{ij} F_{0i}^*(\mathbf{r}) F_{0j}(\mathbf{r}'), \\ \sum_{i,j} \rho_{ij} F_{1i}^*(\mathbf{r}) F_{1j}(\mathbf{r}'),\ \sum_{i,j} \rho_{ij} F_{2i}^*(\mathbf{r}) F_{2j}(\mathbf{r}') \end{array} \right\}$$

3-component

↓ $\mathcal{R}$-mapping

$$\mathcal{R}\left[\sum_{i,j} \rho_{ij} F_i^*(\mathbf{r}) F_j(\mathbf{r}') \right] = \sum_{i,j} \rho_{ij} F_{0i}^*(\mathbf{r}) F_{0j}(\mathbf{r}')$$

$$+\sum_{i,j} \rho_{ij} F_{1i}^*(\mathbf{r}-\mathbf{R}) F_{1j}(\mathbf{r}'-\mathbf{R}) - \sum_{i,j} \rho_{ij} F_{2i}^*(\mathbf{r}-\mathbf{R}) F_{2j}(\mathbf{r}'-\mathbf{R})$$

→ density, kinetic energy density, and so on in the Hilbert space.

(Another approximation to the Hartree term (Weinert method)

→ as a functional of the 3-component density $n(\mathbf{r}) = \sum_{i,j} \rho_{ij} F_i^*(\mathbf{r}) F_j(\mathbf{r})$

Finally, we can give total energy in DFT as a functional of $\psi_p = \sum_j \alpha_p^j F_j$

Minimization of the total energy gives the Kohn-Sham equation.

Our formalism results in the equivalent equations with previous articles, but :

- Consistency is transparent.
- Definition of diatomic quantities in the cutoff model is clear.
- Convenient to derive atomic forces (clear about surface term).

Hilbert space in the Real-world

A basis function

$$F_i(\mathbf{r}) = F_{0i}(\mathbf{r}) + F_{1i}(\mathbf{r}-\mathbf{R}) - F_{2i}(\mathbf{r}-\mathbf{R})$$

↓

product $F_i^*(\mathbf{r})F_j(\mathbf{r}')$

↓

Bilinear quantities:
norm, density, and so on.
Coulomb interaction also.

↓ No cutoff limit

Exact Solution

3-component Hilbert space (artificial)

A basis function

$$F_i(\mathbf{r}) = \{F_{0i}(\mathbf{r}),\ F_{1i}(\mathbf{r}),\ F_{2i}(\mathbf{r})\}$$

↓

Define product $F_i^*(\mathbf{r})F_j(\mathbf{r}')$

By definition, No cross terms

↓

Define bilinear quantities, Coulomb interaction and so on.

↓ No cutoff limit

Exact Solution

Both should be the same

Basis is in real world→Approximation

Numerically solvable model.
Well-defined for finite cutoff.

c.f. PAW treated the Hilbert space of "pseudo wave functions".
($F_{0i}(\mathbf{r})$ determins $F_{1i}(\mathbf{r})$ and $F_{2i}(\mathbf{r})$ uniquely.)

- Prepare 3-comonents Hilbert space
- Define products and so on in the space
- For given $\psi_p = \sum_j \alpha_p^j F_j$,
  we can evaluate (or define) bilinear quantities as a functional in the space through $\mathcal{R}$-mapping.

Problems:

Positive definiteness of overlap matrix

Null vector problems

Orthogonality to core (since we use frozen core approximation).

RESULTS

- PBE, Colinear Spin, Scalar Relativistic DFT
- Large supercell 13.5 Å × 15 Å × 16.5 Å .
- APW and Atom-centered localized basis (MTO and lo)
- Ferro-magnetic. Only inversion symmetry. Γ point only.

MTO set (part)

Mg		2s2p(lo)	$3s3p3d4f$
Al		2s2p(lo)	$3s3p3d4f$
Si			$3s3p3d4f$
P			$3s3p3d4f$
S			$3s3p3d4f$
Cl			$3s3p3d4f$
Ar		3s3p(lo)	$4s4p3d4f$
K		3s3p(lo)	$4s4p3d4f$
Ca		3s3p(lo)	$4s4p3d4f$
Sc		3s3p(lo)	$4s4p3d4f$
Ti		3s3p(lo)	$4s4p3d4f$

× 2

Number of local basis (1+3+5+7) × 2+ (1+3)=36

Atom-independent setteing of MTO parameters

(not shown here)

Atom in supercell

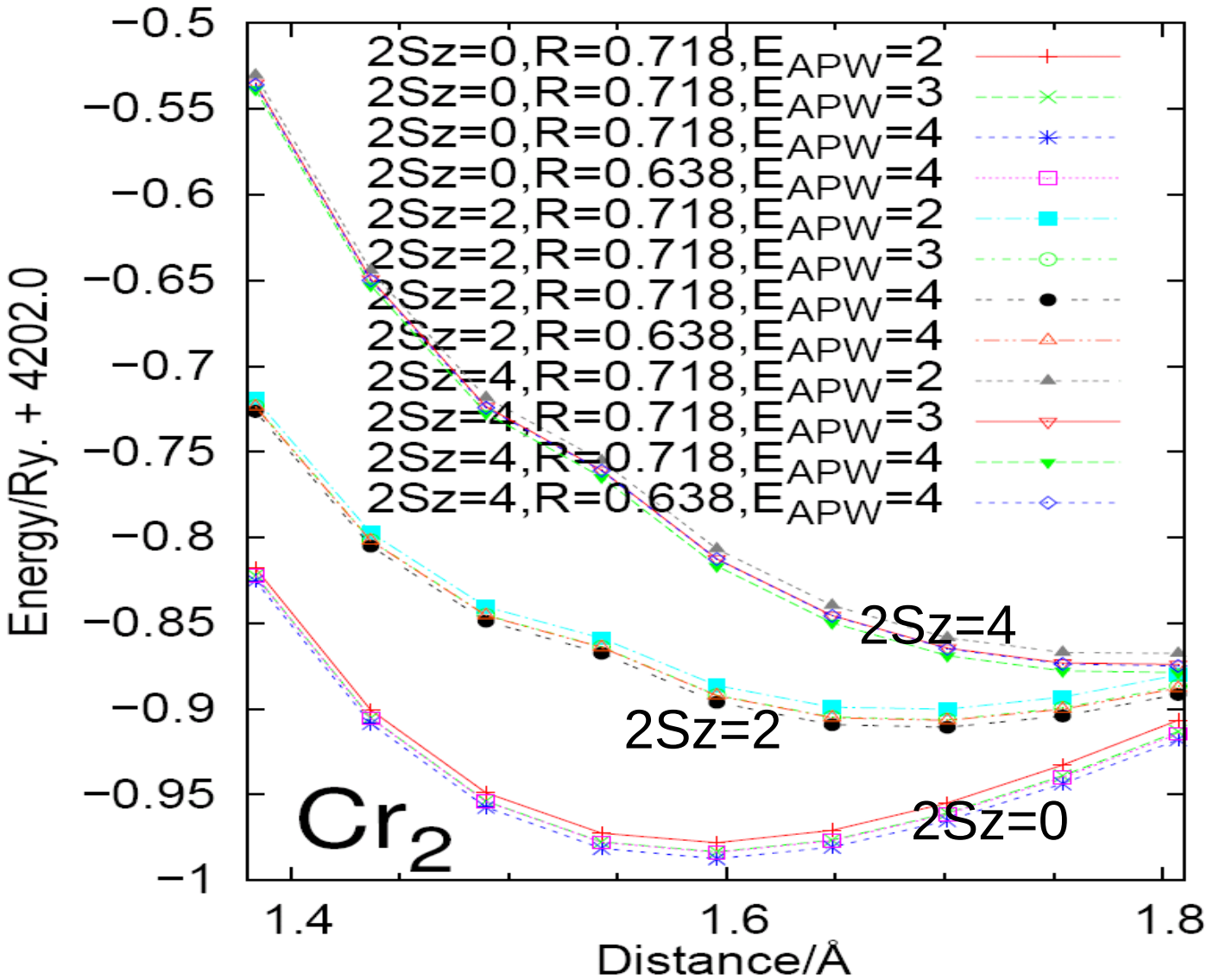
	$E_{\mathrm{MAX}}^{\mathrm{APW}}$=2	$E_{\mathrm{MAX}}^{\mathrm{APW}}$=3	$E_{\mathrm{MAX}}^{\mathrm{APW}}$=4	(Ry)
O, $2S_z$=2	E_e/Ry= -150.0 + ΔE_e/Ry			
R=0.427Å	-0.10930,	-0.12201,	-0.12852	
R=0.488Å	-0.12950,	-0.13640,	-0.13949	
R=0.549Å	-0.13609,	-0.13983,	-0.14139	
R=0.610Å	-0.13913,	-0.14098,	-0.14172	
Cr, $2S_z$=6	E_e/Ry= -2101.0 + ΔE_e/Ry			
R=0.638Å	-0.42852,	-0.43596,	-0.44023	
R=0.718Å	-0.43316,	-0.43807,	-0.44141	
R=0.797Å	-0.43110,	-0.43763,	-0.44198	

N_{APW} =1081, 1973, 3025

N_{BASIS}=1081+36, 1973+36, 3025+36

Diatomic molecules

(From H_2 through Kr_2)



(E_{APW} means E_{MAX}^{APW})

	E_{APW}=2	E_{APW}=3	E_{APW}=4
N_{APW}	1081	1973	3025
N_{BASIS}	1081+36x2	1973+36x2	3025+36x2

Cr_2 at equilibrium atomic distance

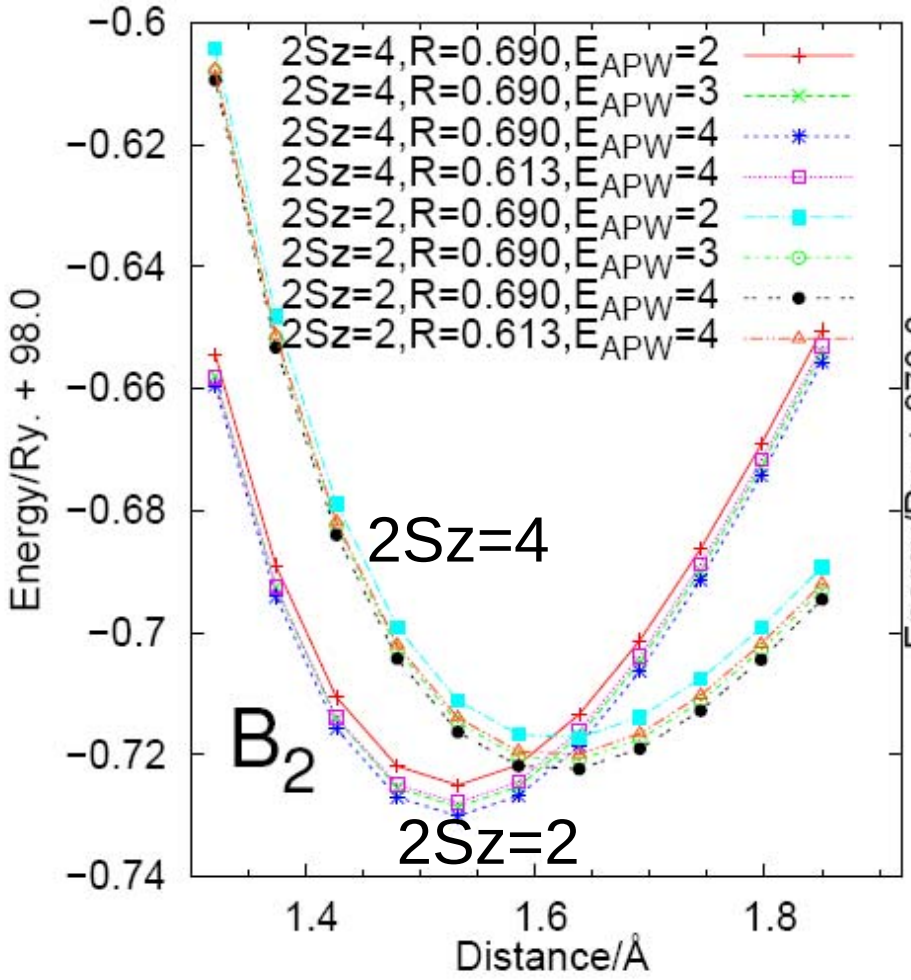
Vibrational frequency

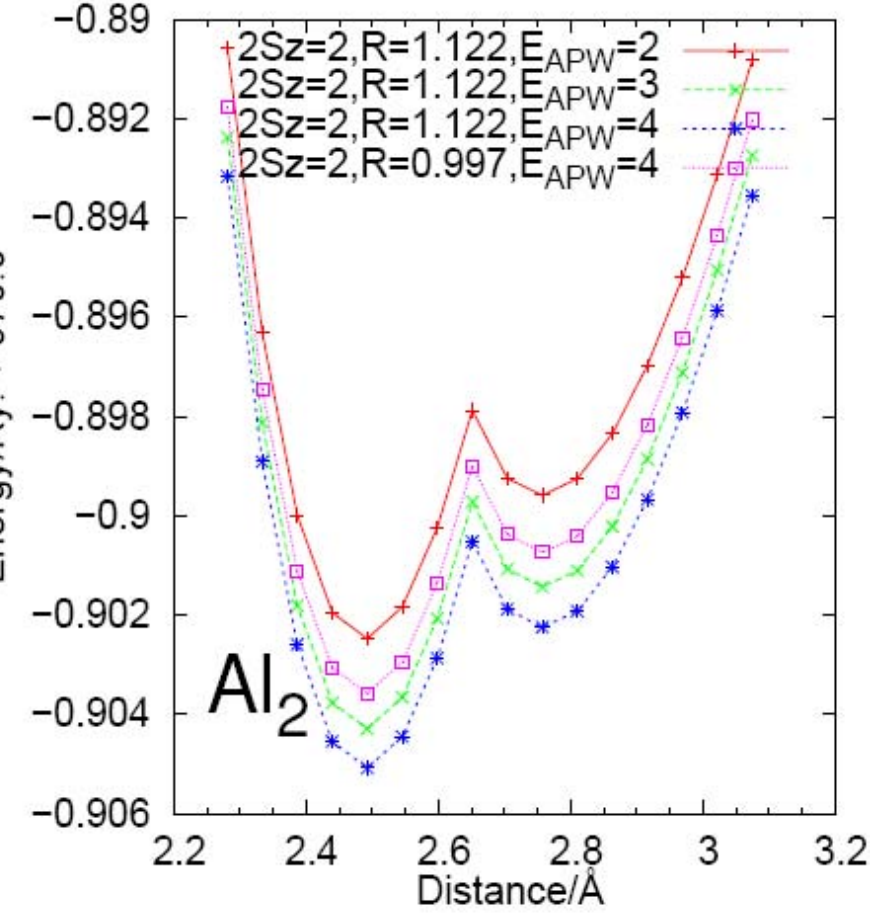
Equilibrium Atomic distance

$E_{\mathrm{MAX}}^{\mathrm{APW}}$ /Ry (N_{APW})	r_e/Å	E_e/Ry	D_e/(Kcal/mol)	ω_e/(cm^{-1})
2 (1081)	1.589	-4202.97816	35.0868	819.273
3 (1973)	1.590	-4202.98356	33.7052	816.532
4 (3025)	1.591	-4202.98747	32.8334	813.296
5 (4245)	1.591	-4202.99086	32.2915	811.480
6 (5573)	1.592	-4202.99388	31.9939	808.289
7 (7025)	1.593	-4202.99664	31.8474	806.676
8 (8611)	1.593	-4202.99917	31.8164	806.530

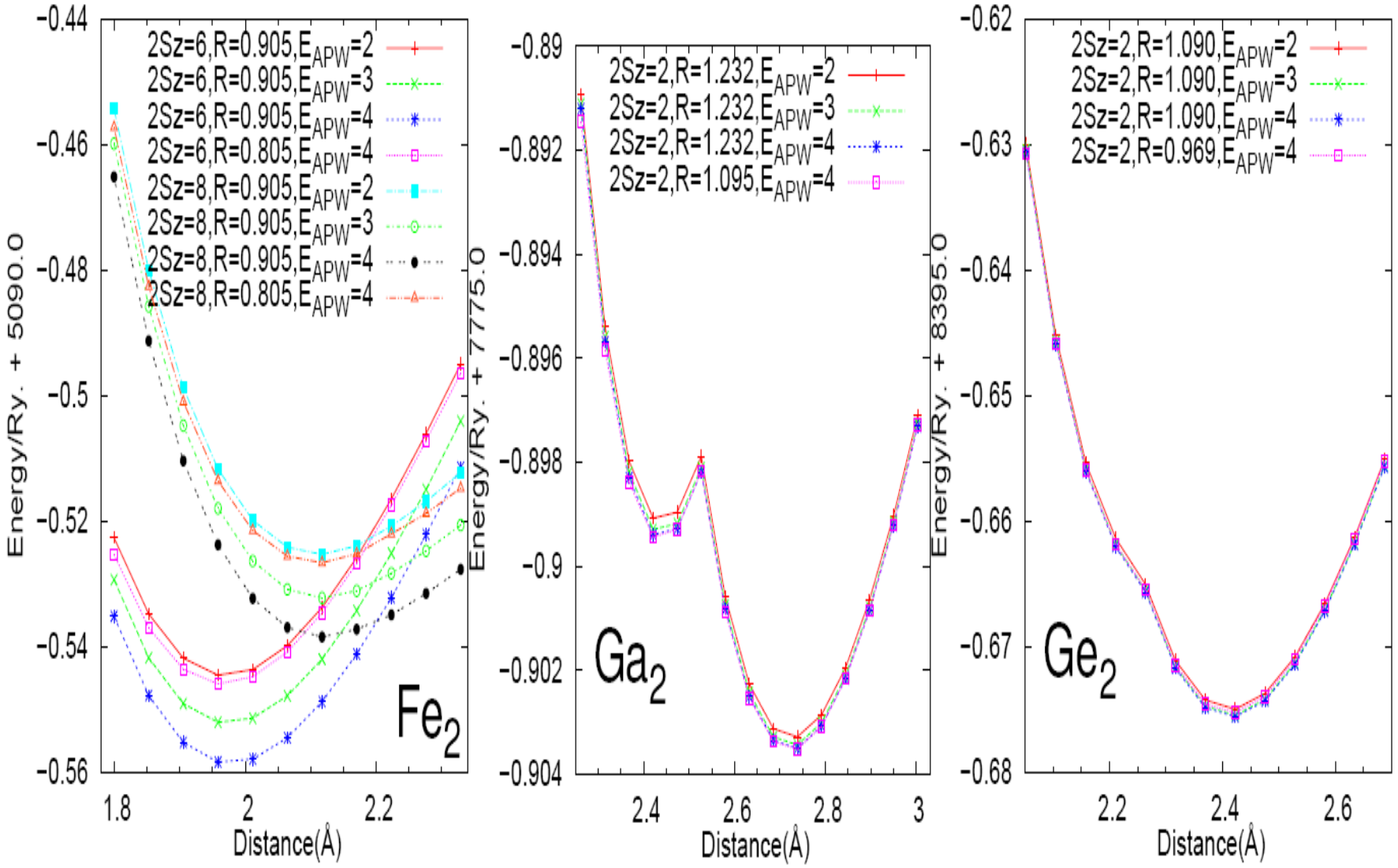
Atomization energy

$1\mathrm{eV}=1/13.605\ \mathrm{Ry}=23.06\mathrm{Kcal/mol}.$





N_{basis}=1081+36×2, 1973+36×2, 3025+36×2



N_{basis}=1081+36×2, 1973+36×2, 3025+36×2

Comparison with Gaussian

		r_e (Å)	D_e(Kcal/mol)	ω_e (cm^{-1})
$H_2, 2S_z=0$	PMT	0.749	104.678	4317.959
	PMT(NR)	0.750	104.764	4311.202
	GTO	0.752	104.552	4311.816
$O_2, 2S_z=2$	PMT	1.218	143.741	1564.787
	PMT(NR)	1.218	144.984	1568.867
	GTO	1.220	~~139.815~~	1554.249
	VASP		143.3	
$Cr_2, 2S_z=0$	PMT	1.591	32.833	813.296
	PMT(NR)	1.589	30.191	818.483
	GTO	1.595	26.192	808.148
$Fe_2, 2S_z=6$	PMT	1.977	57.596	397.673
	PMT(NR)	1.991	58.770	386.597
	GTO	2.012	56.902	397.228
$Cu_2, 2S_z=0$	PMT	2.218	51.169	269.326
	PMT(NR)	2.251	48.503	254.321
	GTO	2.251	48.645	255.768

NR : non relativistic GTO : 6-311+G(d,p)

Sumary

- Formalism based on “3-component Hilbert space”.
  Theoretical consistency is transparent for cutoffed model.
  Atomic force is derived systematically (not shown).

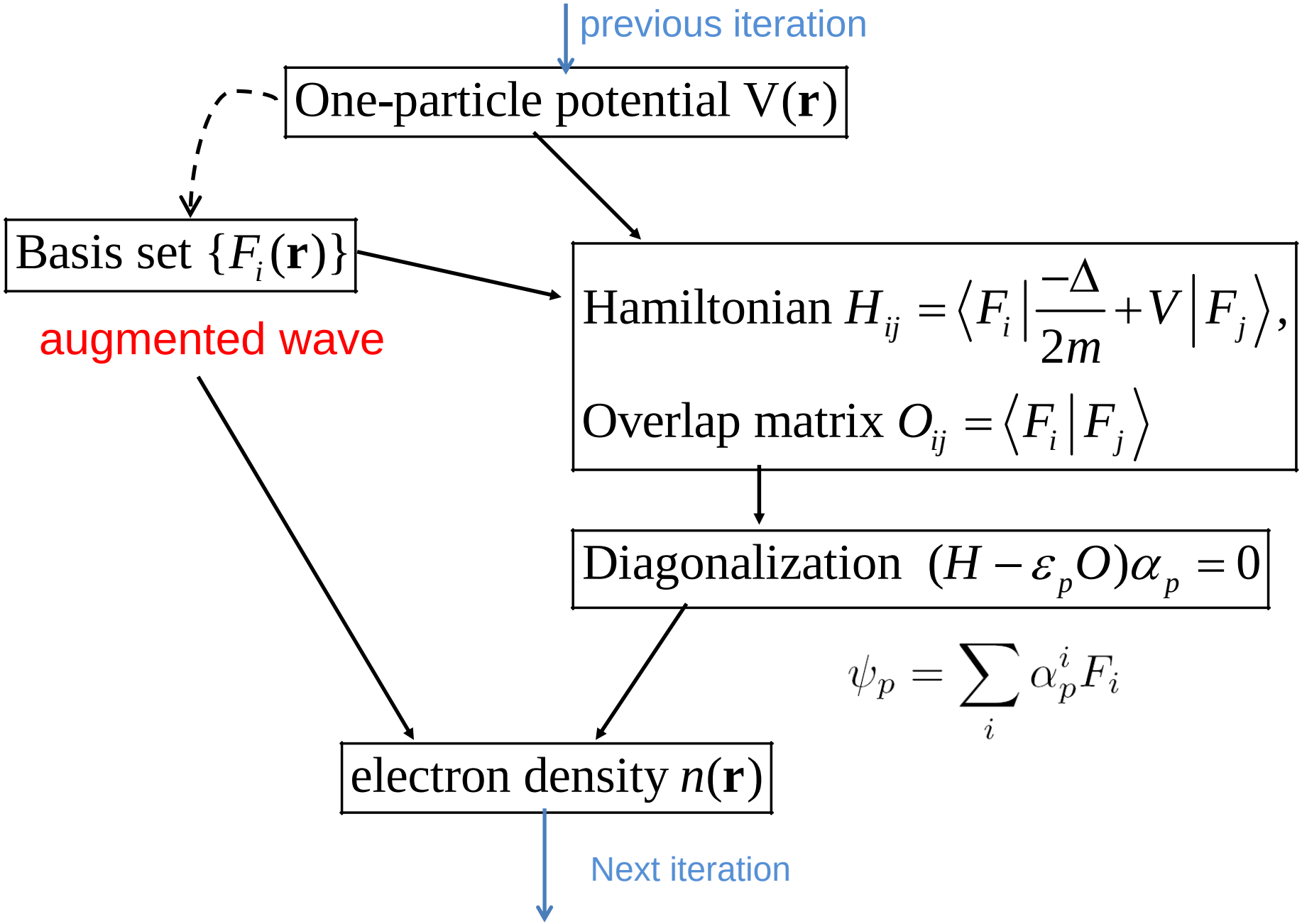
- With APW (cutoff energy is 2～4Ry), we can perform accurate calculations for homo nuclear diatomic molecules.

- Two kinds of augmented wave →very efficient calculations.
  For example, 300 atoms in 15 Å cell → roughly speaking,
  basis ~ 30 × 300 + 2000 (~ 10000 basis)

*Construction of the Wannier functions. (superposition of MTO).

* Better control for Positive definiteness of Norm.
  Null space problem:
  vectors with zero eigenvalues for Hamiltonian and Overlap matrix.

Total energy minimization in the Linearized method

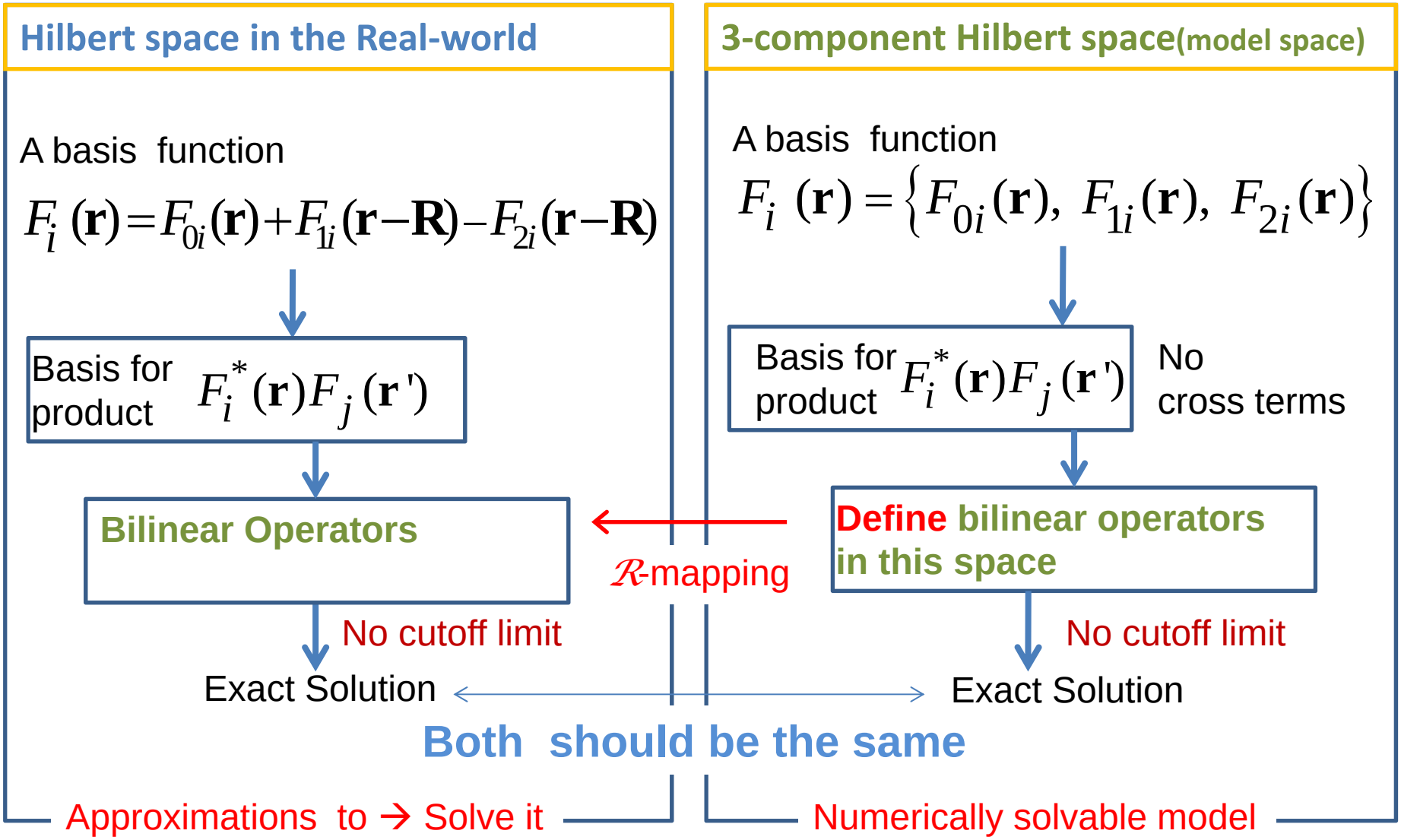


- inner product: $\left\langle F_i \middle| F_j \right\rangle =$

$$\int_{\text{Cell}} d^3 r F_{0i}^*(\mathbf{r}) F_{0j}(\mathbf{r}) + \int_{|\mathbf{r}|<R} d^3 r F_{1i}^*(\mathbf{r}) F_{1j}(\mathbf{r}) - \int_{|\mathbf{r}|<R} d^3 r F_{2i}^*(\mathbf{r}) F_{2j}(\mathbf{r})$$

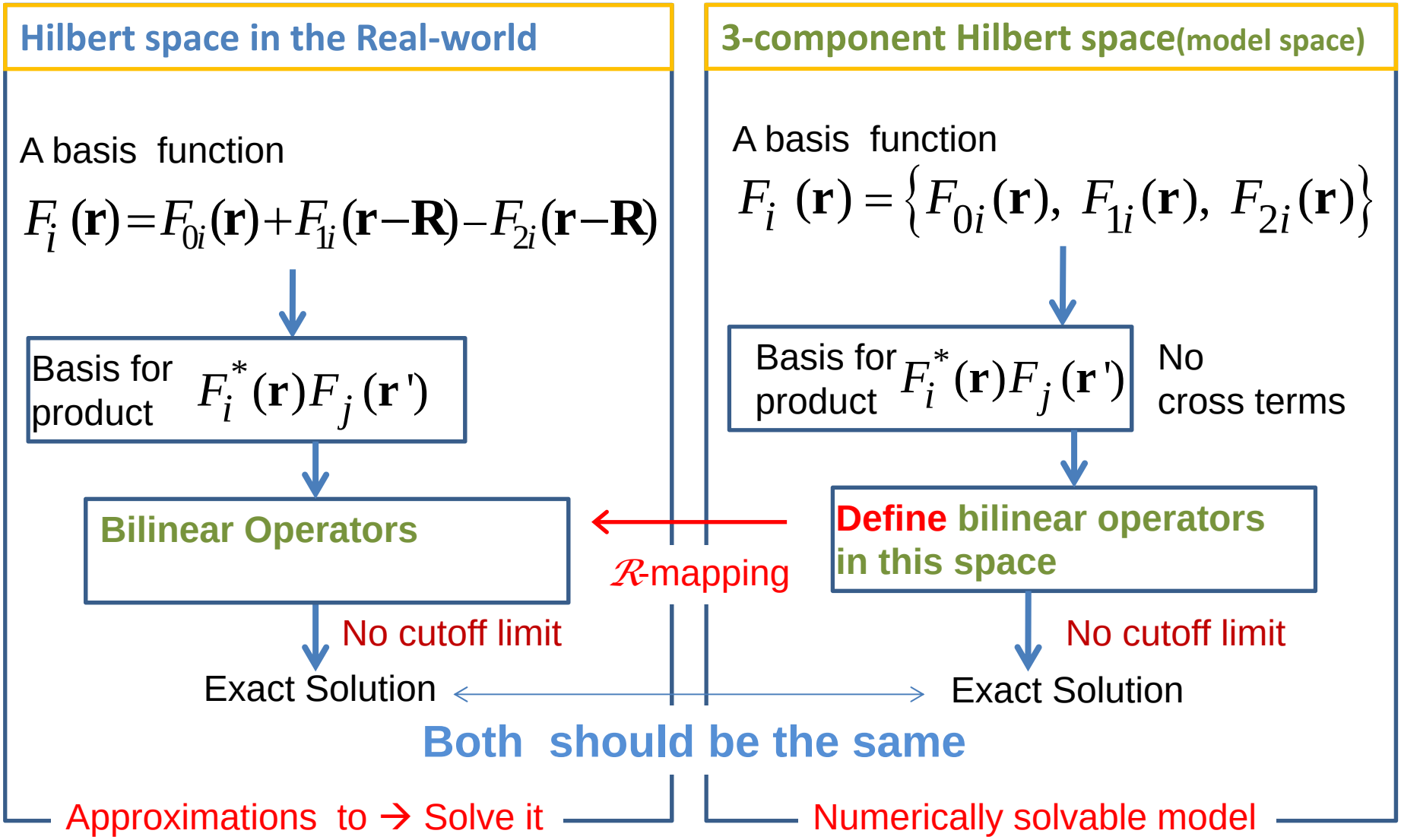
$$\int_{\text{Cell}} d^3 r F_{0i}^*(\mathbf{r}) F_{0j}(\mathbf{r}) - \int_{|\mathbf{r}|<R} d^3 r F_{2i}^*(\mathbf{r}) F_{2j}(\mathbf{r})$$

should be positive definite. Also for the Coulomb matrix.



1. Numerically solvable model → then apply DFT
2. The exact solution at the infinite cutoff limit.

c.f. PAW gives "quantum mechanism" in space of "pseudo wave functions".



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