Energy-Resolved Wannier States with Assigned Local Symmetry

Wei Ku (顧 威)
Brookhaven National Lab
SUNY Stony Brook University

supported by DOE Grant No. DE-FG03-01ER45876

Generalized Wannier function

$$|\mathbf{R}n\rangle \equiv |\bar{\mathbf{k}}n\rangle e^{-i\bar{\mathbf{k}}\cdot\mathbf{R}}/\sqrt{\#}$$

$$|\mathbf{k}n\rangle = |\phi_{\mathbf{k}\bar{m}}\rangle\langle\phi_{\mathbf{k}\bar{m}}|\mathbf{k}n\rangle$$

$$\langle\phi_{\mathbf{k}m}|\mathbf{k}n\rangle = \langle\phi_{\mathbf{k}m}|g_{\bar{n}'}\rangle M_{\bar{n}'n}$$

$$M^{-2}_{n'n} \equiv \langle g_{n'}|\phi_{\mathbf{k}\bar{m}}\rangle\langle\phi_{\mathbf{k}\bar{m}}|g_n\rangle$$

DFT

$$h^{DFT} \rightarrow \left\{\varepsilon_{\mathbf{k}\,j}, |\phi_{\mathbf{k}\,j}\rangle\right\}$$

Initial construction

- multiple energy windows
- point group symmetries
- multiple projections
- biased subspace selection

Refinement :

- gauge transformation
- constrained MaxLoc

Nicola Marzari and David Vanderbilt, *Phys. Rev. B* **56**, 12847 (1997).
Ivo Souza, Nicola Marzari, and David Vanderbilt, *Phys. Rev. B* **65**, 035109 (2002)
Wei Ku, H. Rosner, W. E. Pickett, and R. T. Scalettar, *Phys. Rev. Lett.* **89**, 167204 (2002)

Multi-Energy-Resolved Construction with Symmetry

DFT

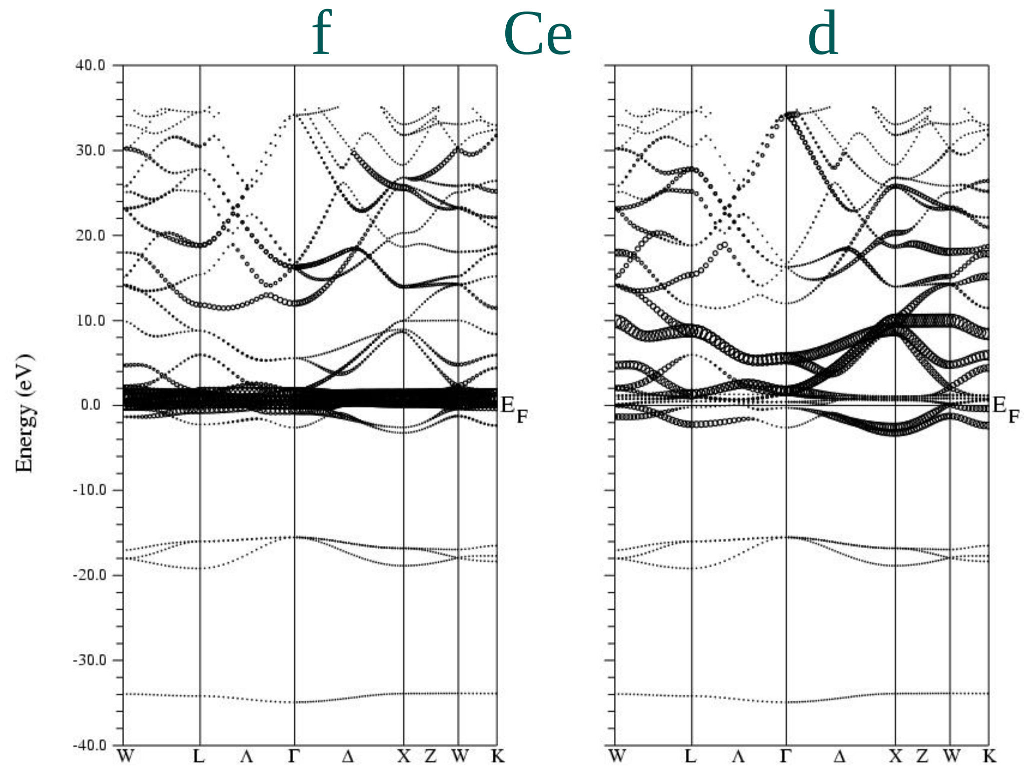
$$h^{DFT} \rightarrow \left\{ \varepsilon_{\mathbf{k}\,j}, \left| \phi_{\mathbf{k}\,j} \right\rangle \right\}$$

Initial construction

- multiple energy windows
- point group symmetries
- multiple projections
- biased subspace selection

Refinement :

- gauge transformation
- constrained MaxLoc



$$\left| \mathbf{R} n \right\rangle \equiv \left| \bar{\mathbf{k}} n \right\rangle e^{-i\bar{\mathbf{k}}\cdot\mathbf{R}} / \sqrt{\#}$$

$$\left| \mathbf{k} n \right\rangle = \left| \phi_{\mathbf{k}\bar{m}} \right\rangle \left\langle \phi_{\mathbf{k}\bar{m}} \middle| \mathbf{k} n \right\rangle$$

$$\left\langle \phi_{\mathbf{k}m} \middle| \mathbf{k} n \right\rangle = \left\langle \phi_{\mathbf{k}m} \middle| g_{\bar{n}'} \right\rangle M_{\bar{n}'n}$$

$$M^{-2}_{n'n} \equiv \left\langle g_{n'} \middle| \phi_{\mathbf{k}\bar{m}} \right\rangle \left\langle \phi_{\mathbf{k}\bar{m}} \middle| g_n \right\rangle$$

Wei Ku, H. Rosner, W. E. Pickett, and R. T. Scalettar, Phys. Rev. Lett. **89**, 167204 (2002)

Desired Properties of Wannier States

Simplest physical picture

→ essential Hilbert space including as much physics/chemistry as possible

→ more control on the construction, instead of unique MaxLoc. choice

- Locality

  → ideal / natural in strongly correlated systems

- Energy resolution [1]

  → minimal, simplest basis for low energy physics

  → non-perturbative inclusion of hybridization

  → narrow energy spectrum, good for RG and MBPT, and analyzing experiments

- Point symmetries [2]

  → simpler analysis & increased sparseness in “couplings”

- Orthonormality [1]

  → well-defined basis for the 2nd quantization

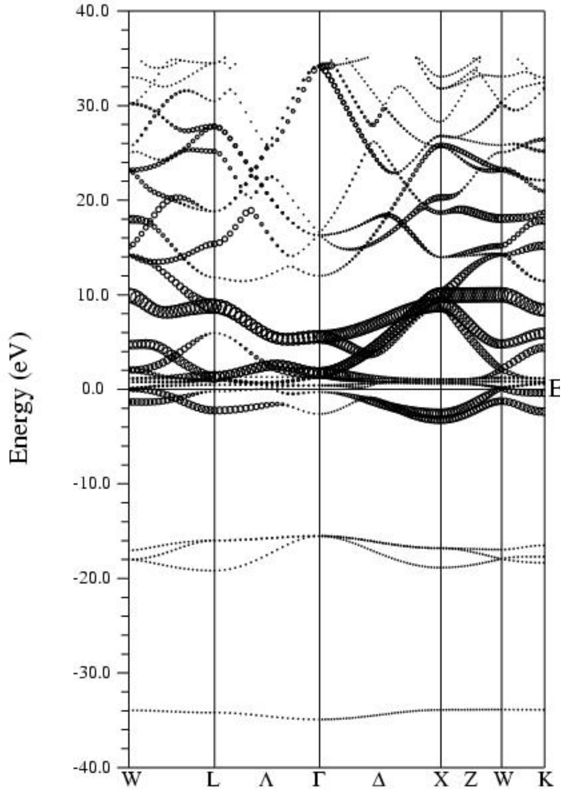
- Flexible choice of Hilbert space [1,2,3]
- Simple, efficient procedure of construction (avoid $\left\langle \phi_{\mathbf{k}\,j} \middle| e^{-i\mathbf{q}\mathbf{x}} \middle| \phi_{\mathbf{k}+\mathbf{q}\,j'} \right\rangle$ or iterations) [2]
- General procedure independent of underlying representation [3]

1. in contrast with atomic representation
2. in contrast with MaxLoc construction
3. in contrast with “down-folding” of NMTO

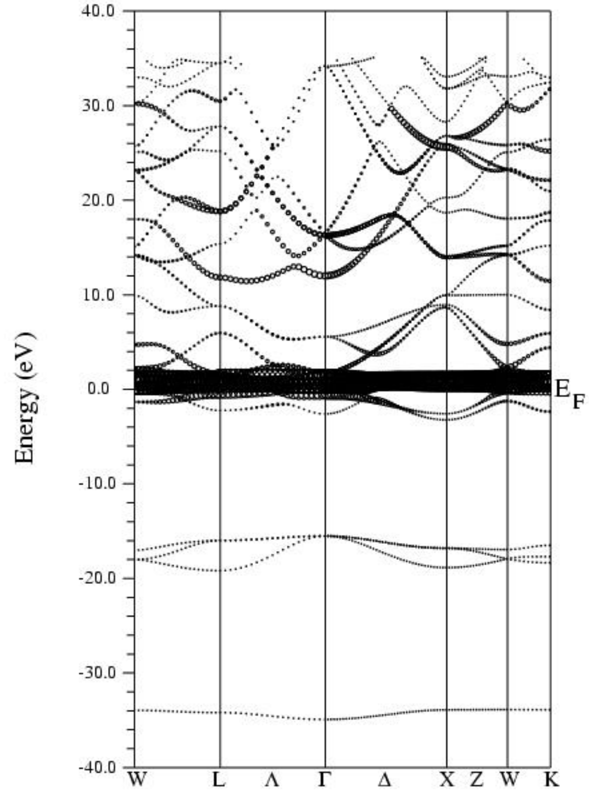
Definition of (Generalized) Wannier States

$$|Rn\rangle \equiv |\bar{k}n\rangle e^{-i\bar{k}\cdot R}/\sqrt{\#}$$

$$|kn\rangle = |\phi_{k\bar{m}}\rangle\langle\phi_{k\bar{m}}|kn\rangle$$



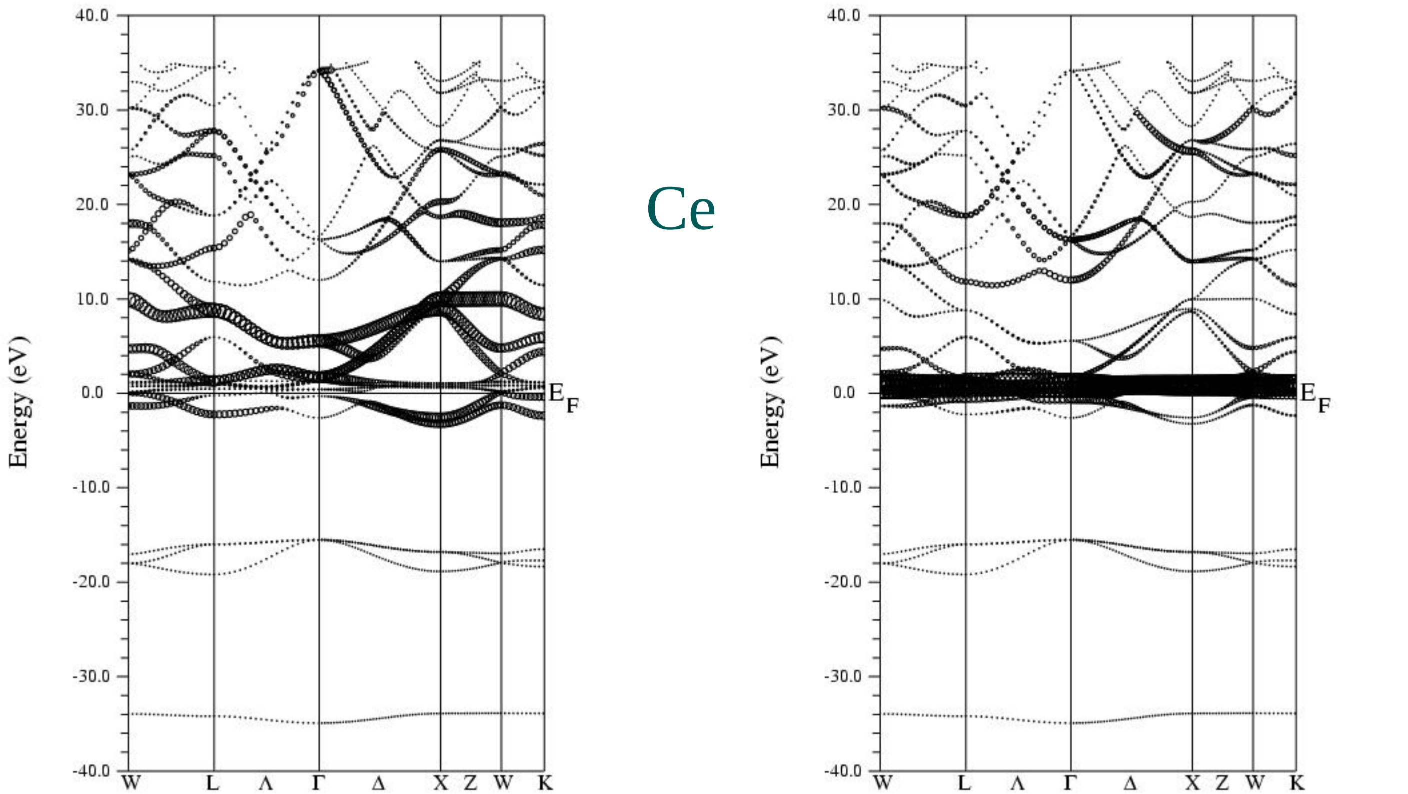
d



f

Our Strategy:

- Information from Bloch states and their eigenvalues
- Multiple-energy windows
- Maximized contribution in specified local symmetry
- Specified bias for better control



d

Ce

f

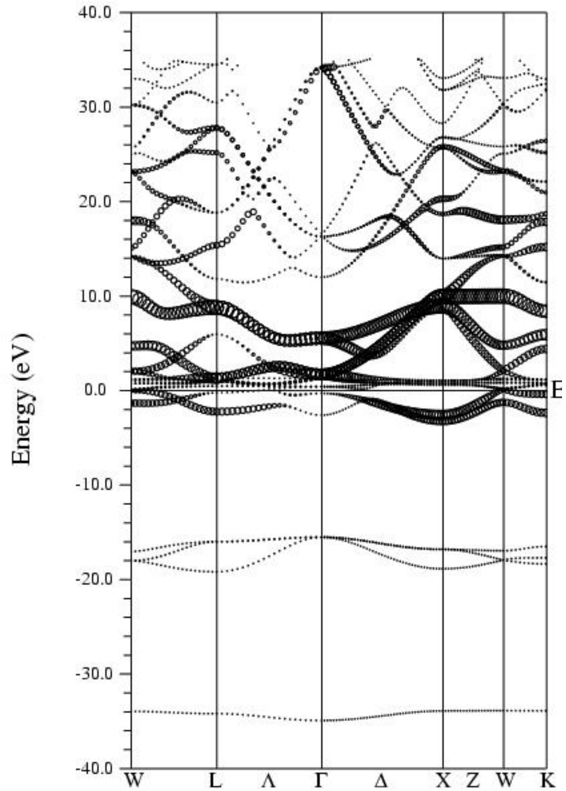
Definition of (Generalized) Wannier States

$$\left|Rn\right\rangle \equiv \left|\bar{k}n\right\rangle e^{-i\bar{k}\cdot R}/\sqrt{\#}$$

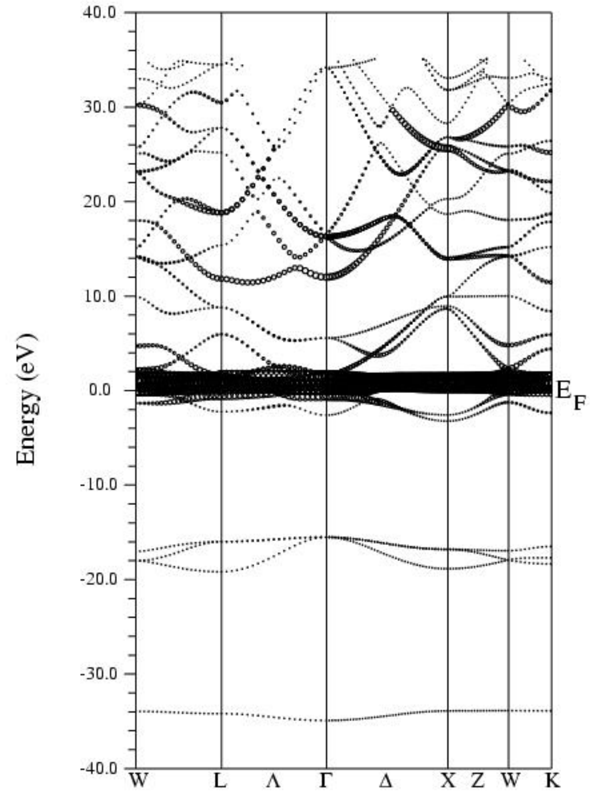
$$\left|kn\right\rangle = \left|\phi_{k\bar{m}}\right\rangle\left\langle\phi_{k\bar{m}}\middle|kn\right\rangle$$

$$\left\langle\phi_{km}\middle|kn\right\rangle = \left\langle\phi_{km}\middle|g_{\bar{n}'}\right\rangle M_{\bar{n}'n}$$

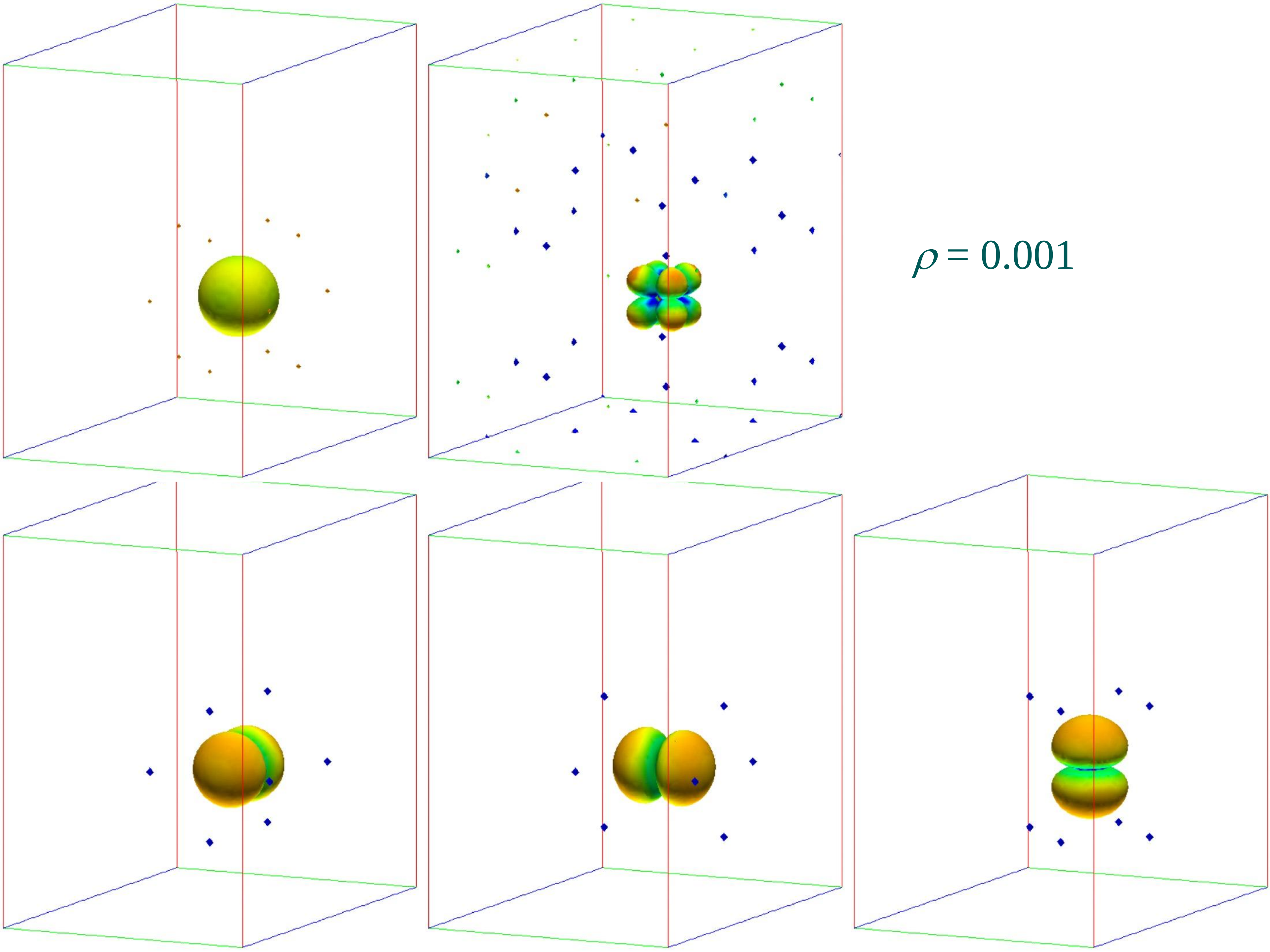
$$M^{-2}_{n'n} \equiv \left\langle g_{n'}\middle|\phi_{k\bar{m}}\right\rangle\left\langle\phi_{k\bar{m}}\middle|g_{n}\right\rangle$$



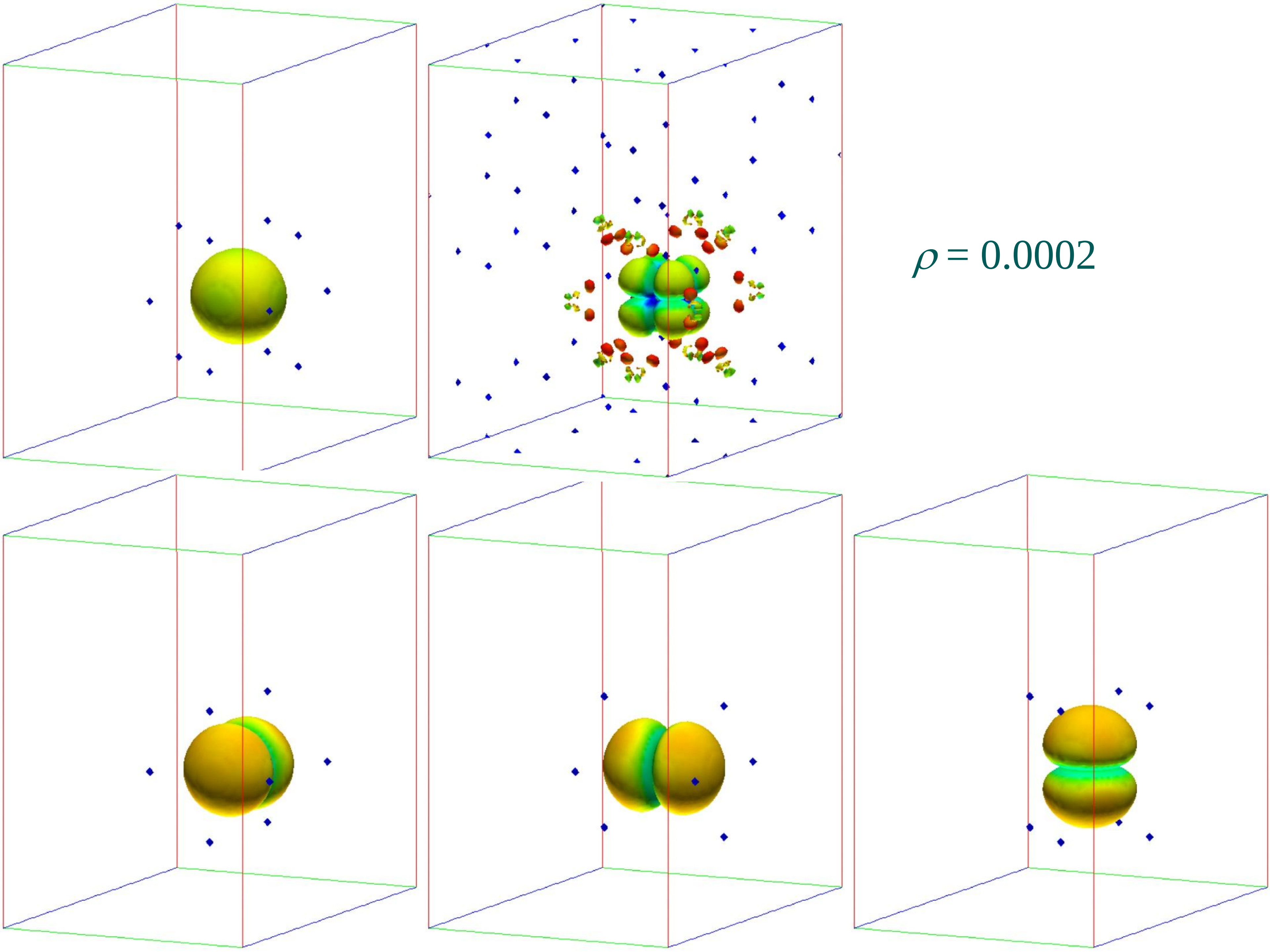
d

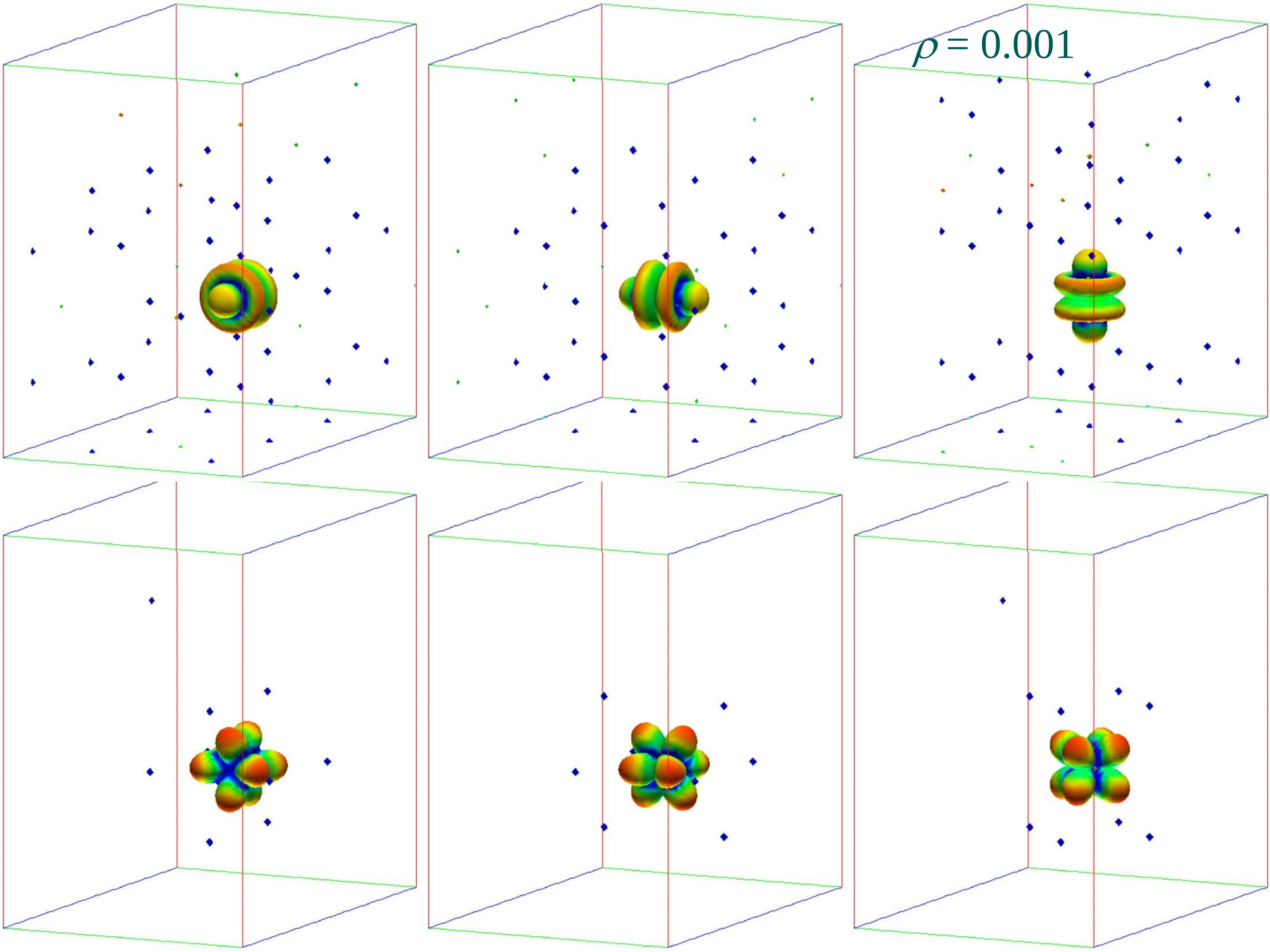


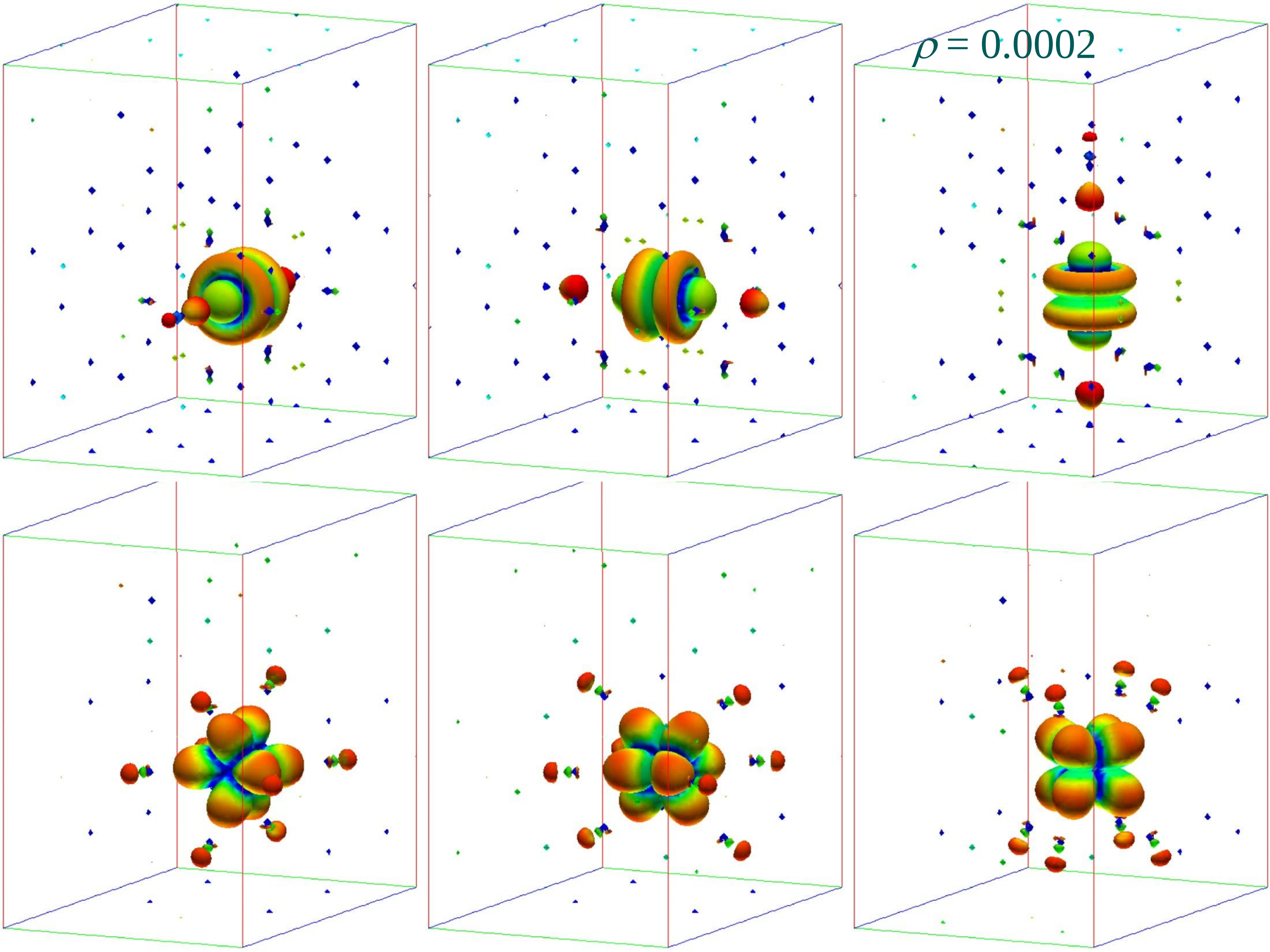
f

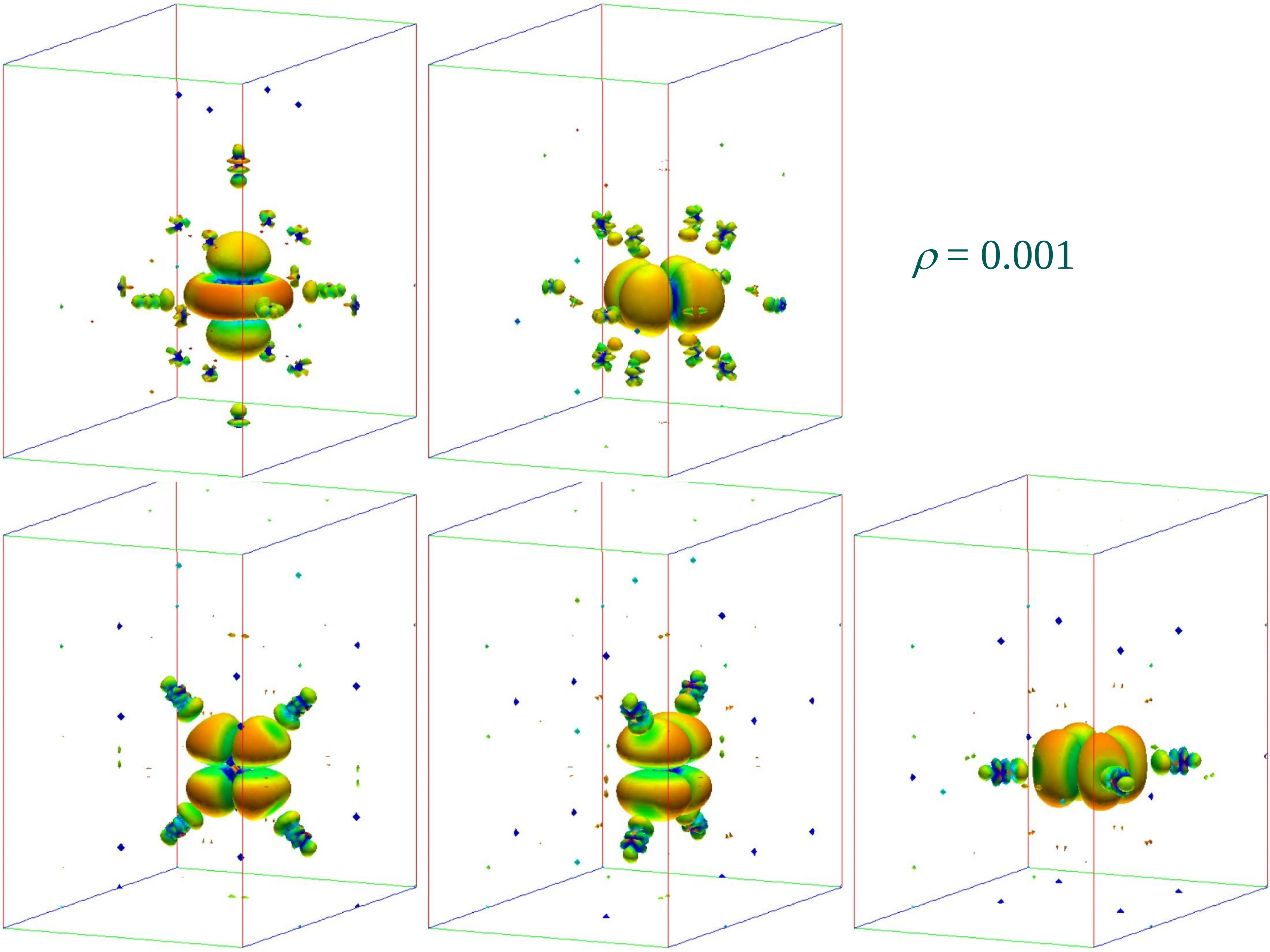


$\rho = 0.001$

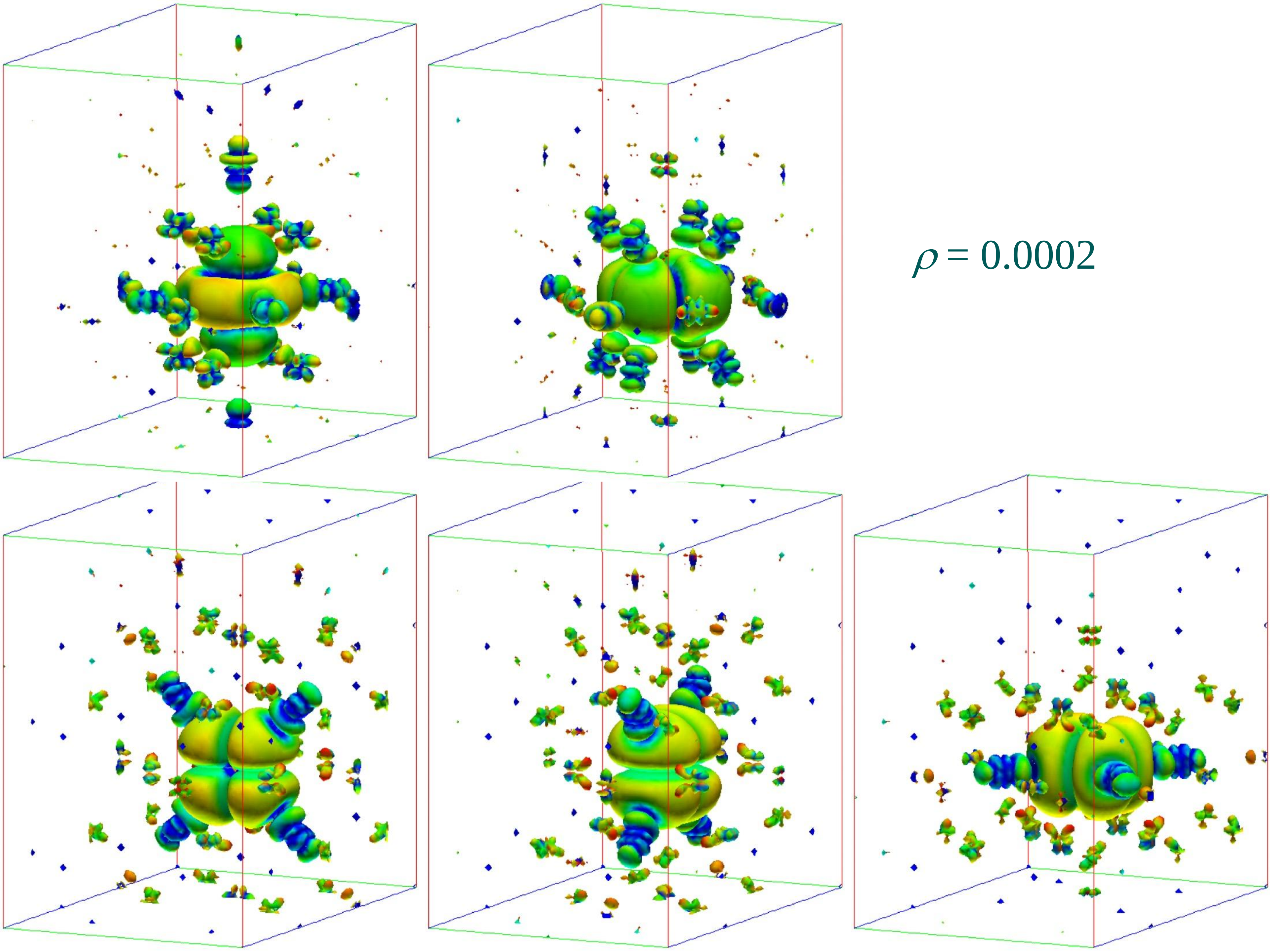

$\rho = 0.0002$

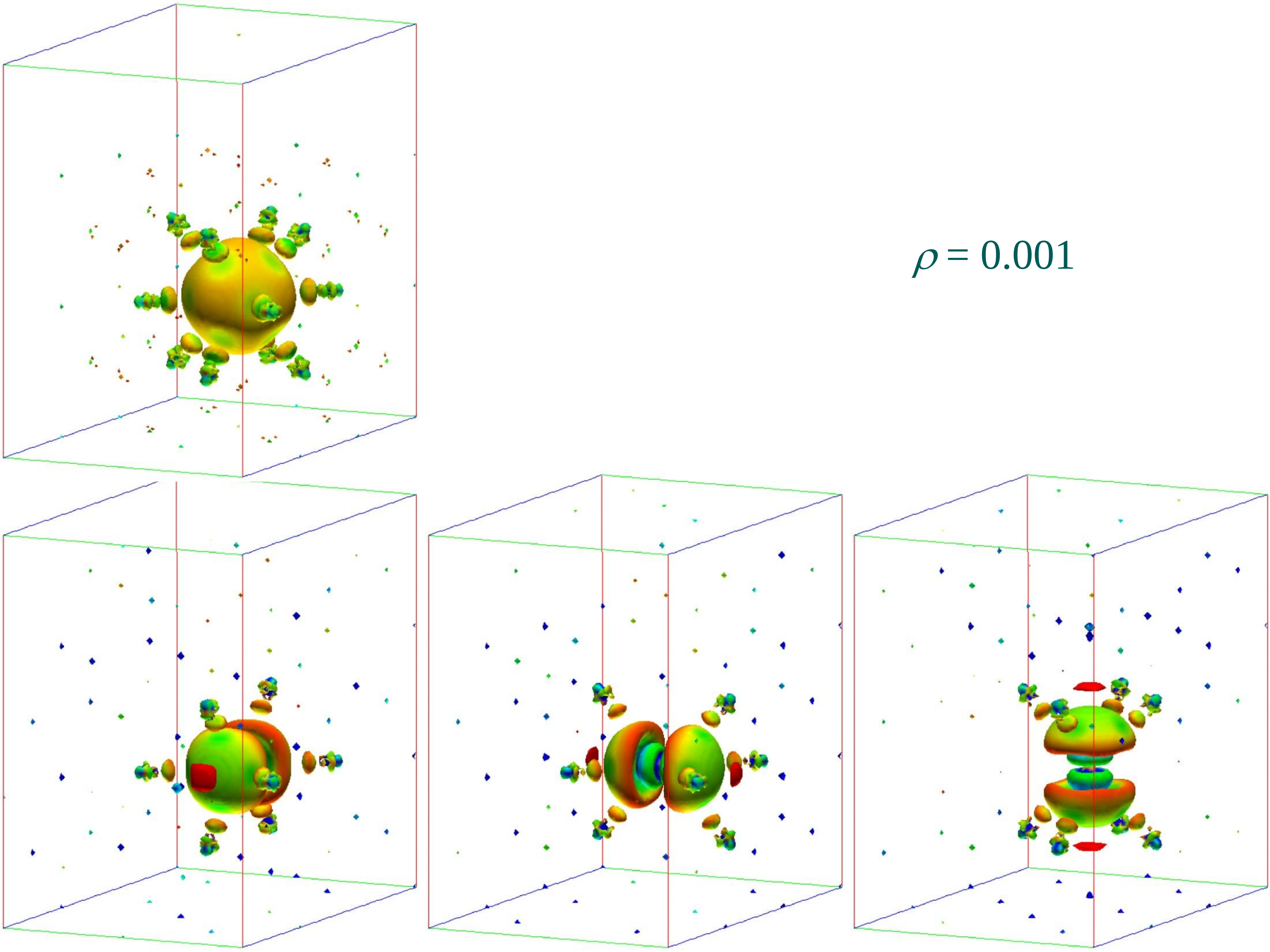

$\rho = 0.001$


$\rho = 0.0002$

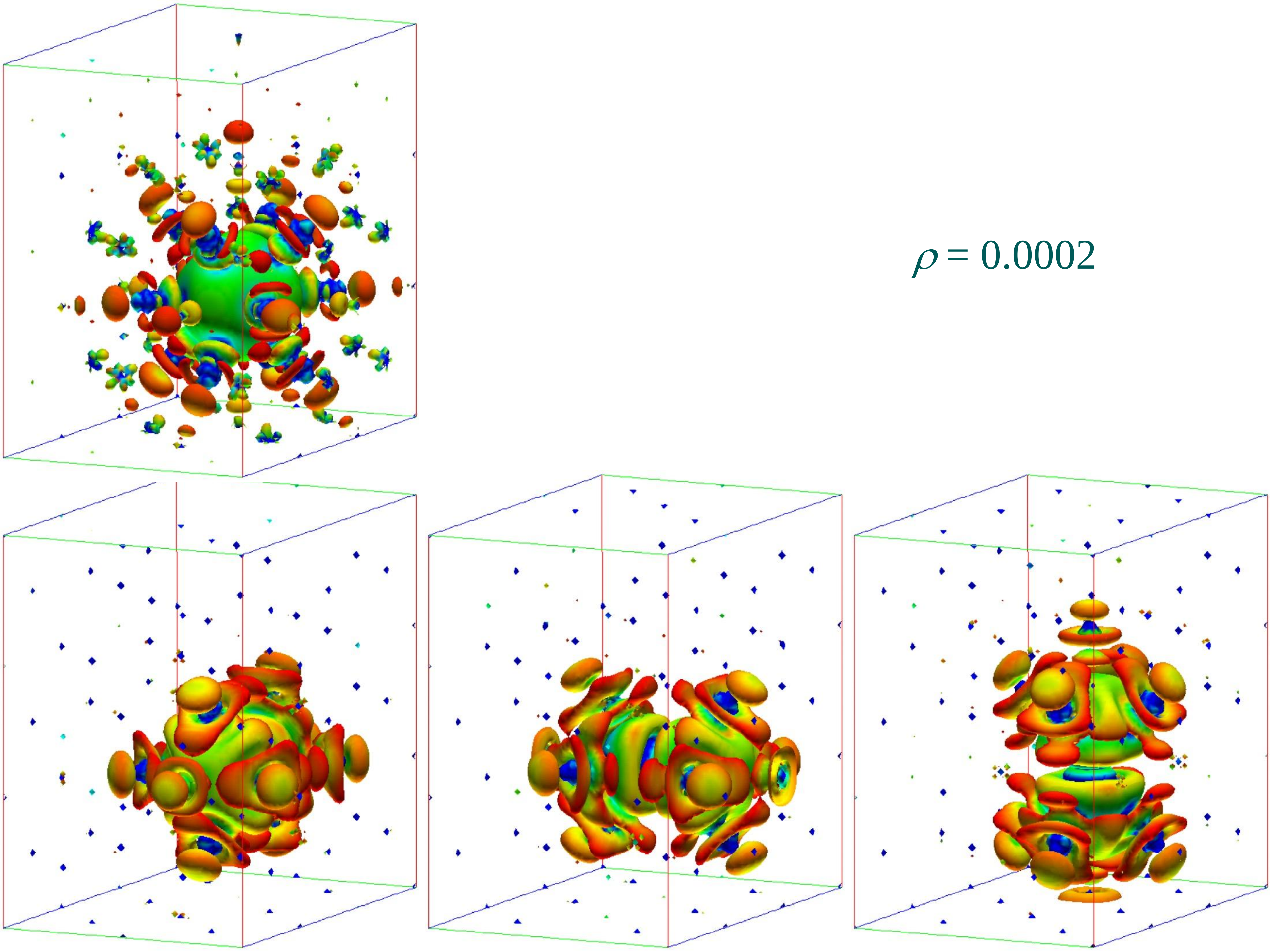


$\rho = 0.001$


$\rho = 0.0002$



$\rho = 0.001$


$\rho = 0.0002$

Tight-Binding Parameters

< R j' | h^{DFT} | 0 j > of γ-Ce (eV)

occupation #	2	2	2	2	0.159	0.148	0.148	0.148	0.039	0.039	0.039	0.540	0.540	0.565	0.565	0.565	0.344	
(0 0 0)	s	p x	p y	p z	f xyz	f x(5x2-3r2)	f y(5y2-3r2)	f z(5z2-3r2)	f x(y2-z2)	f y(z2-x2)	f z(x2-y2)	d 3z2-r2	d x2-y2	d yz	d zx	d xy	s	(0 0 0)
s	-34.216																	s
p x		-17.143																p x
p y			-17.143															p y
p z				-17.143														p z
f xyz					0.885													f xyz
f x(5x2-3r2)						0.795												f x(5x2-3r2)
f y(5y2-3r2)							0.795											f y(5y2-3r2)
f z(5z2-3r2)								0.795										f z(5z2-3r2)
f x(y2-z2)									0.619									f x(y2-z2)
f y(z2-x2)										0.619								f y(z2-x2)
f z(x2-y2)											0.619							f z(x2-y2)
d 3z2-r2												3.570						d 3z2-r2
d x2-y2													3.570					d x2-y2
d yz														3.592				d yz
d zx															3.592			d zx
d xy																3.592		d xy
s																	9.614	s
(0 1 1) / 2	s	p x	p y	p z	f xyz	f x(5x2-3r2)	f y(5y2-3r2)	f z(5z2-3r2)	f x(y2-z2)	f y(z2-x2)	f z(x2-y2)	d 3z2-r2	d x2-y2	d yz	d zx	d xy	s	(0 1 1) / 2
s	-0.064																	s
p x		-0.047																p x
p y			0.215	0.273														p y
p z			0.273	0.215														p z
f xyz					-0.023	0.038									-0.029	-0.029		f xyz
f x(5x2-3r2)					0.038	-0.081									0.020	0.020		f x(5x2-3r2)
f y(5y2-3r2)							-0.044	0.030		0.018	0.029	0.022	0.009	-0.016			-0.004	f y(5y2-3r2)
f z(5z2-3r2)							0.030	-0.044		-0.029	-0.018	-0.018	-0.015	-0.016			-0.004	f z(5z2-3r2)
f x(y2-z2)									0.036						0.004	-0.004		f x(y2-z2)
f y(z2-x2)							0.018	-0.029		0.036	-0.047	-0.002	-0.004	0.011			-0.004	f y(z2-x2)
f z(x2-y2)							0.029	-0.018		-0.047	0.036	-0.005		-0.011			0.004	f z(x2-y2)
d 3z2-r2							-0.022	0.018		0.002	0.005	0.578	0.607	-0.428			0.116	d 3z2-r2
d x2-y2							-0.009	0.015		0.004		0.607	-0.124	0.742			-0.200	d x2-y2
d yz							0.016	0.016		-0.011	0.011	-0.428	0.742	-1.247			0.369	d yz
d zx					0.029	-0.020			-0.004						0.348	0.632		d zx
d xy					0.029	-0.020			0.004						0.632	0.348		d xy
s							0.004	0.004		0.004	-0.004	0.116	-0.200	0.369			-1.197	s
	s	p x	p y	p z	f xyz	f x(5x2-3r2)	f y(5y2-3r2)	f z(5z2-3r2)	f x(y2-z2)	f y(z2-x2)	f z(x2-y2)	d 3z2-r2	d x2-y2	d yz	d zx	d xy	s	

sparser than atomic tight-binding parameters !

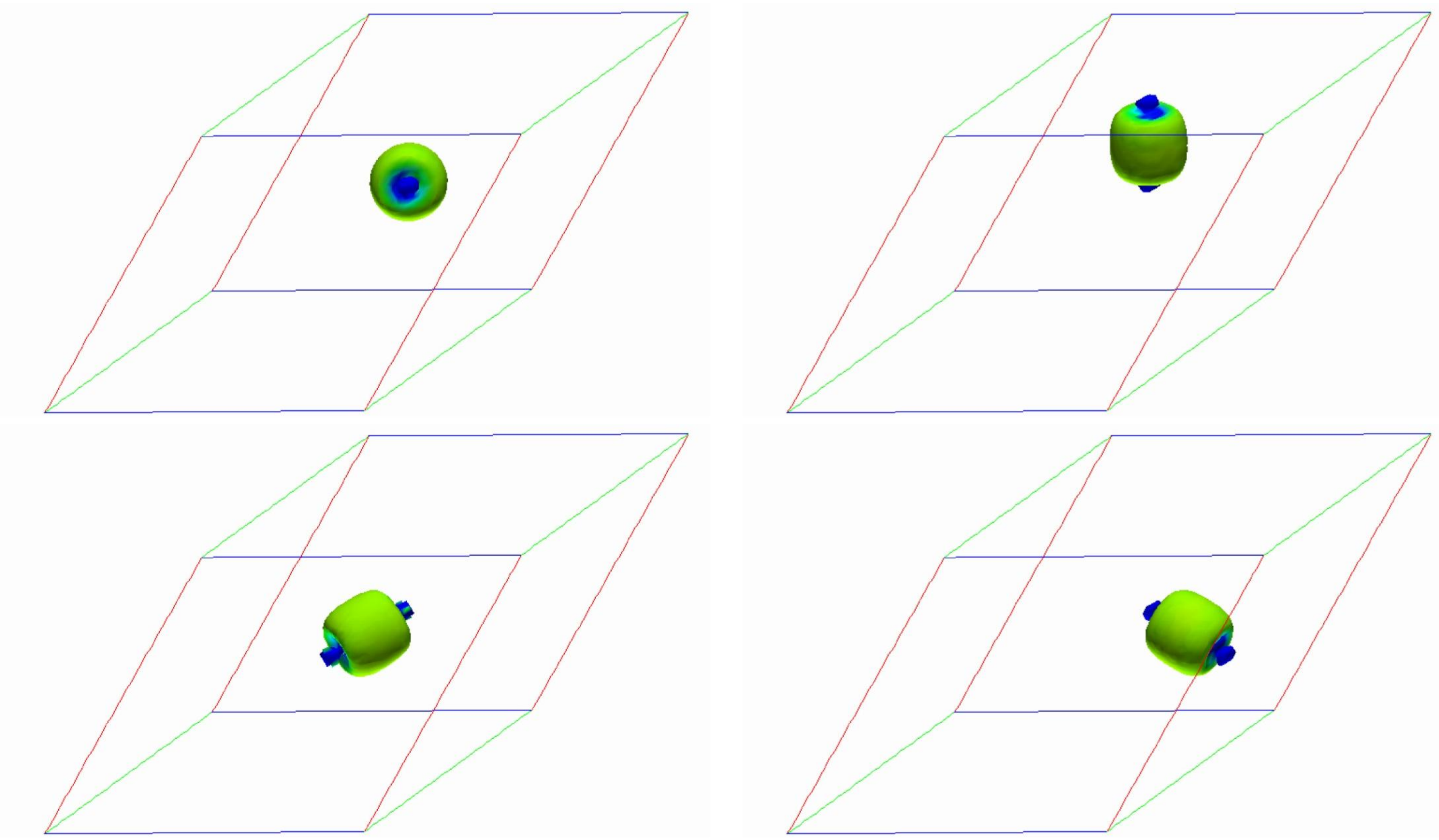
Tight-Binding Parameters

(1 0 0)	s	p x	p y	p z	f xyz	f x(5x2-3r2)	f y(5y2-3r2)	f z(5z2-3r2)	f x(y2-z2)	f y(z2-x2)	f z(x2-y2)	d 3z2-r2	d x2-y2	d yz	d zx	d xy	s	(1 0 0)
s																		s
p x		0.003																p x
p y			0.001															p y
p z				0.001														p z
f xyz					0.031									-0.015				f xyz
f x(5x2-3r2)						-0.023						-0.010	0.017				-0.003	f x(5x2-3r2)
f y(5y2-3r2)							-0.004			-0.009						0.009		f y(5y2-3r2)
f z(5z2-3r2)								-0.004			0.009				0.009			f z(5z2-3r2)
f x(y2-z2)									-0.002			-0.002	-0.001					f x(y2-z2)
f y(z2-x2)							-0.009			0.011						-0.007		f y(z2-x2)
f z(x2-y2)								0.009			0.011				0.007			f z(x2-y2)
d 3z2-r2						0.010			0.002			-0.115	0.019				-0.228	d 3z2-r2
d x2-y2						-0.017			0.001			0.019	-0.137				0.395	d x2-y2
d yz					0.015									0.145				d yz
d zx								-0.009			-0.007				0.013			d zx
d xy							-0.009			0.007						0.013		d xy
s						0.003						-0.228	0.395				-0.244	s

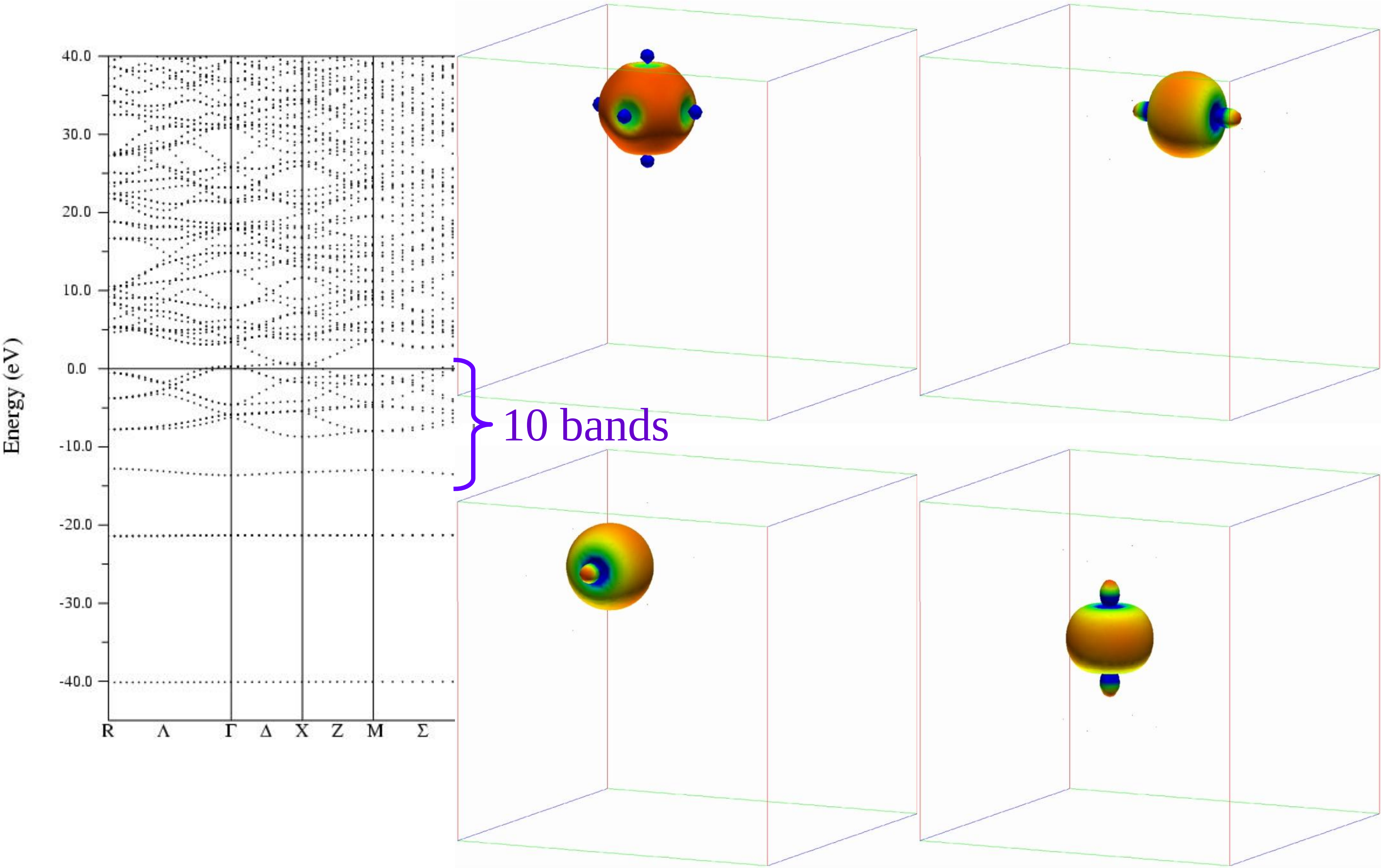
(2 1 1) / 2	s	p x	p y	p z	f xyz	f x(5x2-3r2)	f y(5y2-3r2)	f z(5z2-3r2)	f x(y2-z2)	f y(z2-x2)	f z(x2-y2)	d 3z2-r2	d x2-y2	d yz	d zx	d xy	s	(2 1 1) / 2
s	0.001																	s
p x		0.001																p x
p y			-0.003	0.004														p y
p z			0.004	-0.003														p z
f xyz					-0.024	0.001	-0.005	-0.005		0.001	-0.001	0.001	-0.001	-0.011	0.001	0.001	-0.006	f xyz
f x(5x2-3r2)					0.001	0.012	0.015	0.015		0.006	-0.006	-0.002	0.004	0.004	-0.001	-0.001	-0.001	f x(5x2-3r2)
f y(5y2-3r2)					-0.005	0.015	0.003	-0.011	0.013	-0.005	-0.001	-0.011		0.004	-0.002	-0.002	0.001	f y(5y2-3r2)
f z(5z2-3r2)					-0.005	0.015	-0.011	0.003	-0.013	0.001	0.005	0.006	0.009	0.004	-0.002	-0.002	0.001	f z(5z2-3r2)
f x(y2-z2)							0.013	-0.013	-0.020	-0.001	-0.001	0.002	0.001		0.010	-0.010		f x(y2-z2)
f y(z2-x2)					0.001	0.006	-0.005	0.001	-0.001	0.004	0.002		0.001	0.005	0.001	0.003	0.003	f y(z2-x2)
f z(x2-y2)					-0.001	-0.006	-0.001	0.005	-0.001	0.002	0.004	0.001	-0.001	-0.005	-0.003	-0.001	-0.003	f z(x2-y2)
d 3z2-r2					-0.001	0.002	0.011	-0.006	-0.002		-0.001	-0.038	0.014	-0.041	-0.023	-0.010	-0.033	d 3z2-r2
d x2-y2					0.001	-0.004		-0.009	-0.001	-0.001	0.001	0.014	-0.054	0.071	0.025	0.033	0.058	d x2-y2
d yz					0.011	-0.004	-0.004	-0.004		-0.005	0.005	-0.041	0.071	0.026	-0.032	-0.032	0.134	d yz
d zx					-0.001	0.001	0.002	0.002	-0.010	-0.001	0.003	-0.023	0.025	-0.032	-0.053	0.001	0.028	d zx
d xy					-0.001	0.001	0.002	0.002	0.010	-0.003	0.001	-0.010	0.033	-0.032	0.001	-0.053	0.028	d xy
s					0.006	0.001	-0.001	-0.001		-0.003	0.003	-0.033	0.058	0.134	0.028	0.028	0.087	s
	s	p x	p y	p z	f xyz	f x(5x2-3r2)	f y(5y2-3r2)	f z(5z2-3r2)	f x(y2-z2)	f y(z2-x2)	f z(x2-y2)	d 3z2-r2	d x2-y2	d yz	d zx	d xy	s	

no fitting!

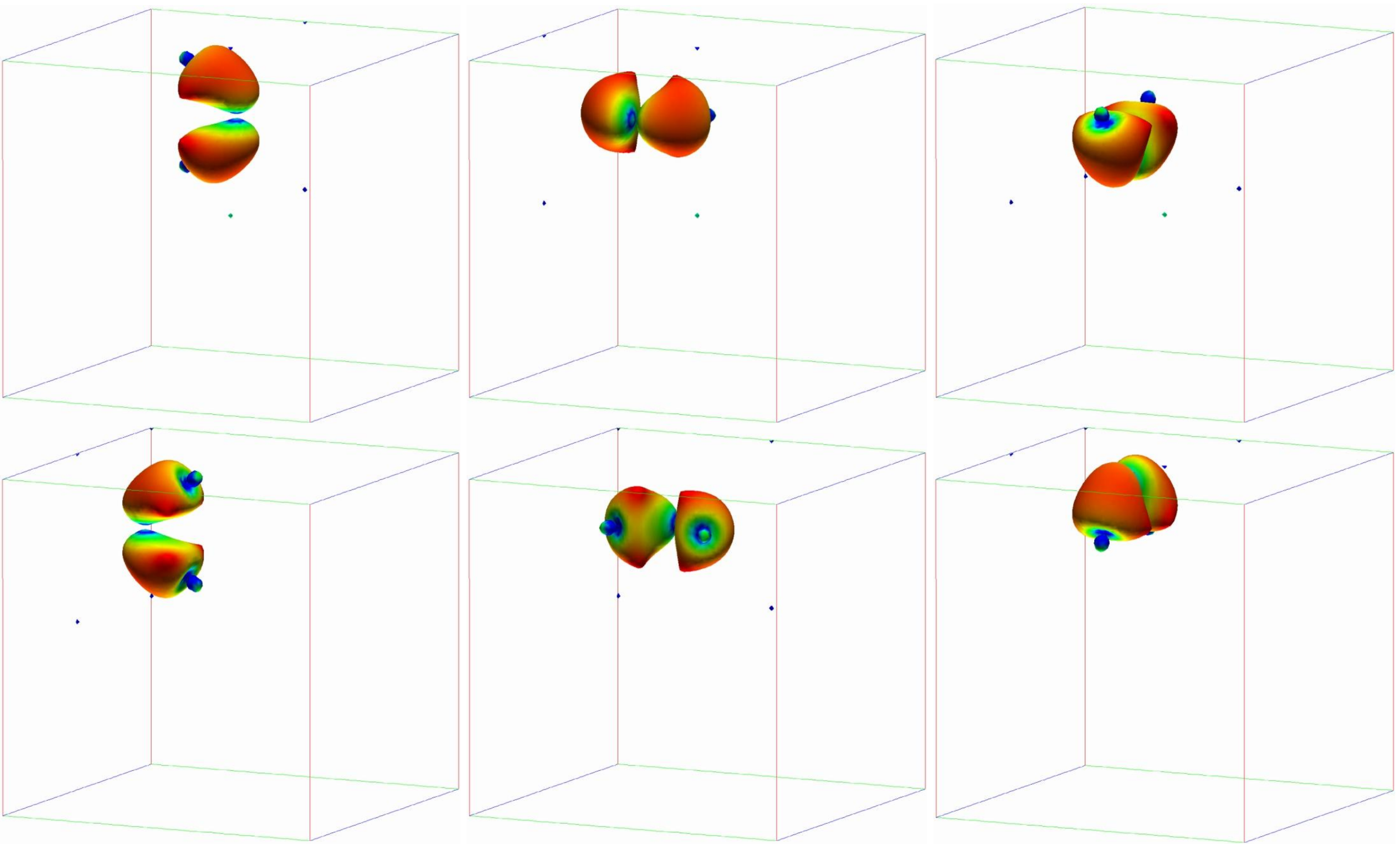
Bond-Centered WS – Si



Bond-centered Wannier orbitlas in CaB6

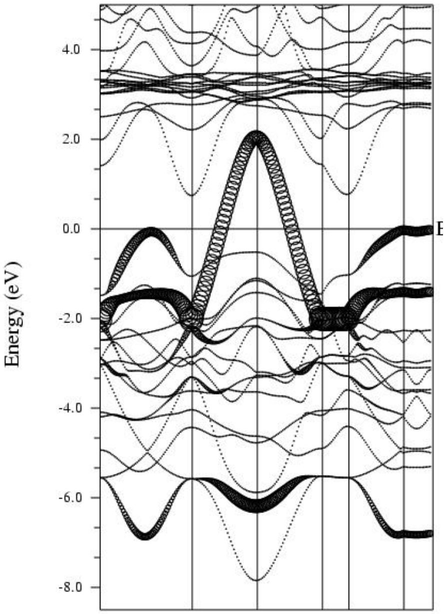


Non-Trivial Symmetry – CaB6

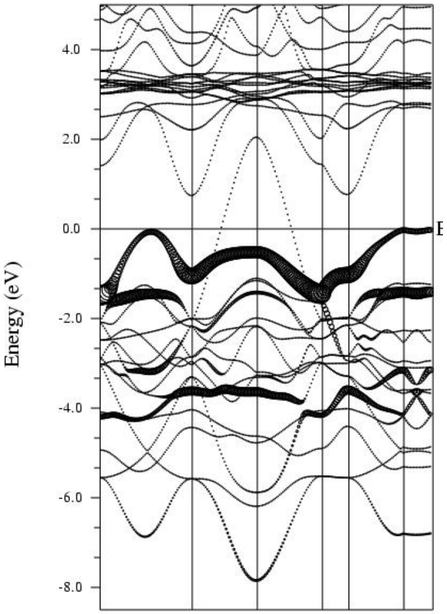


Bias for More Control – La_2CuO_4

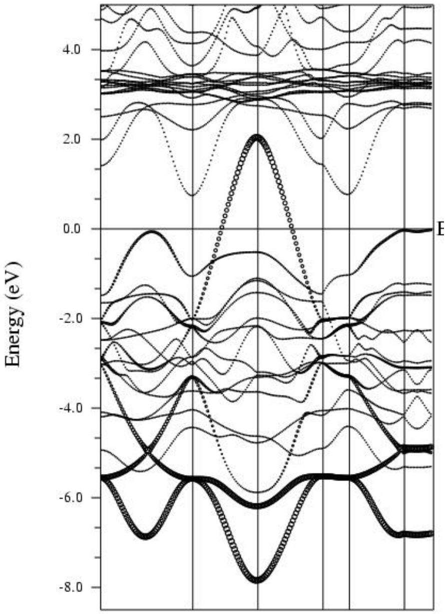
Cu – d x2-y2



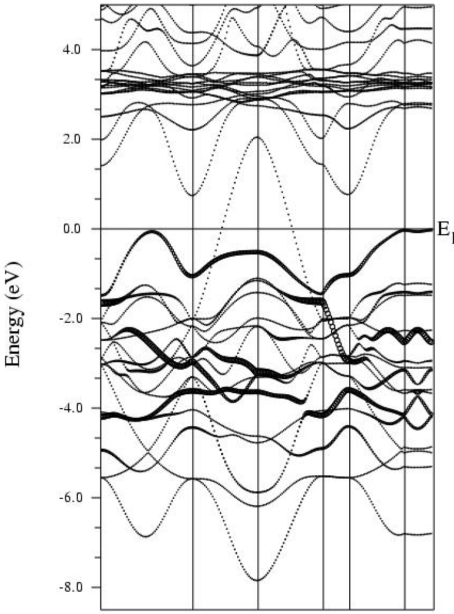
Cu – d z2



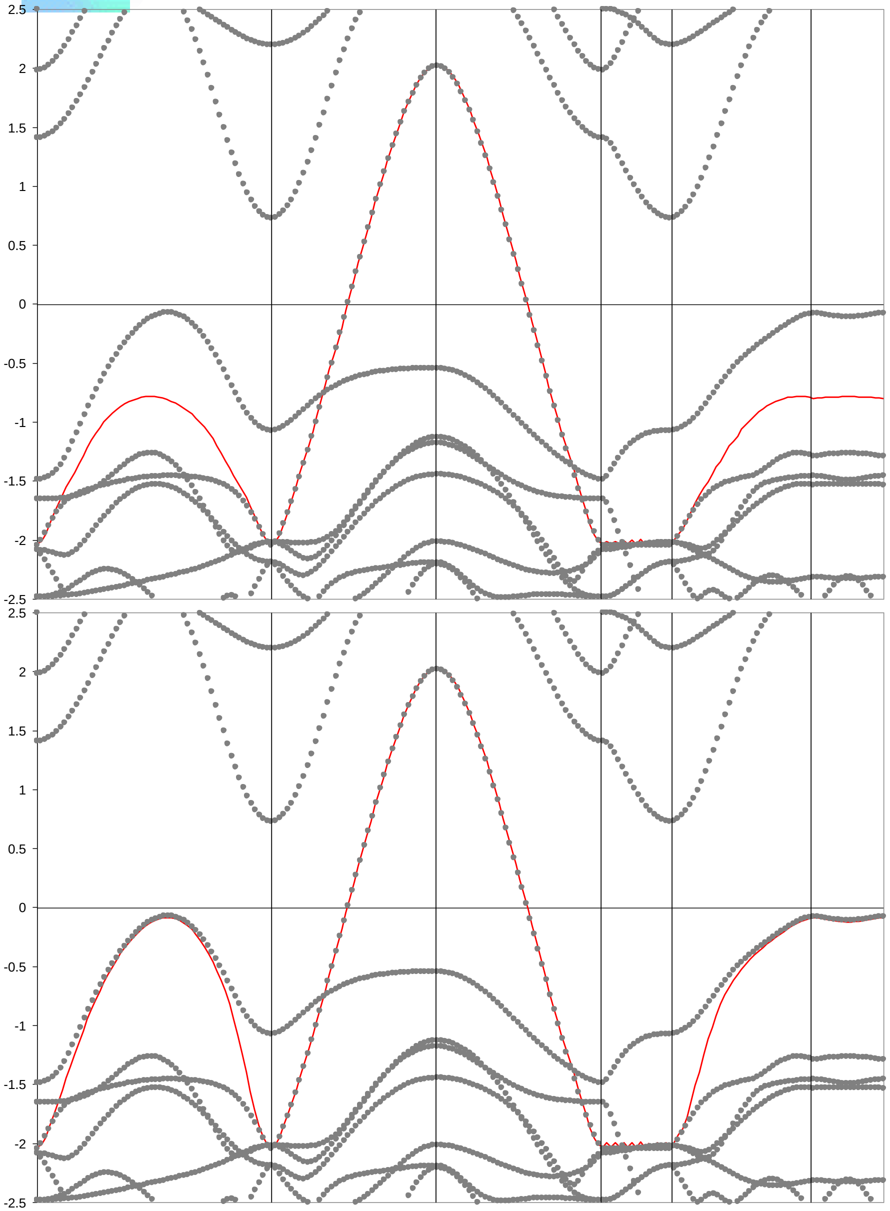
O1 – p y

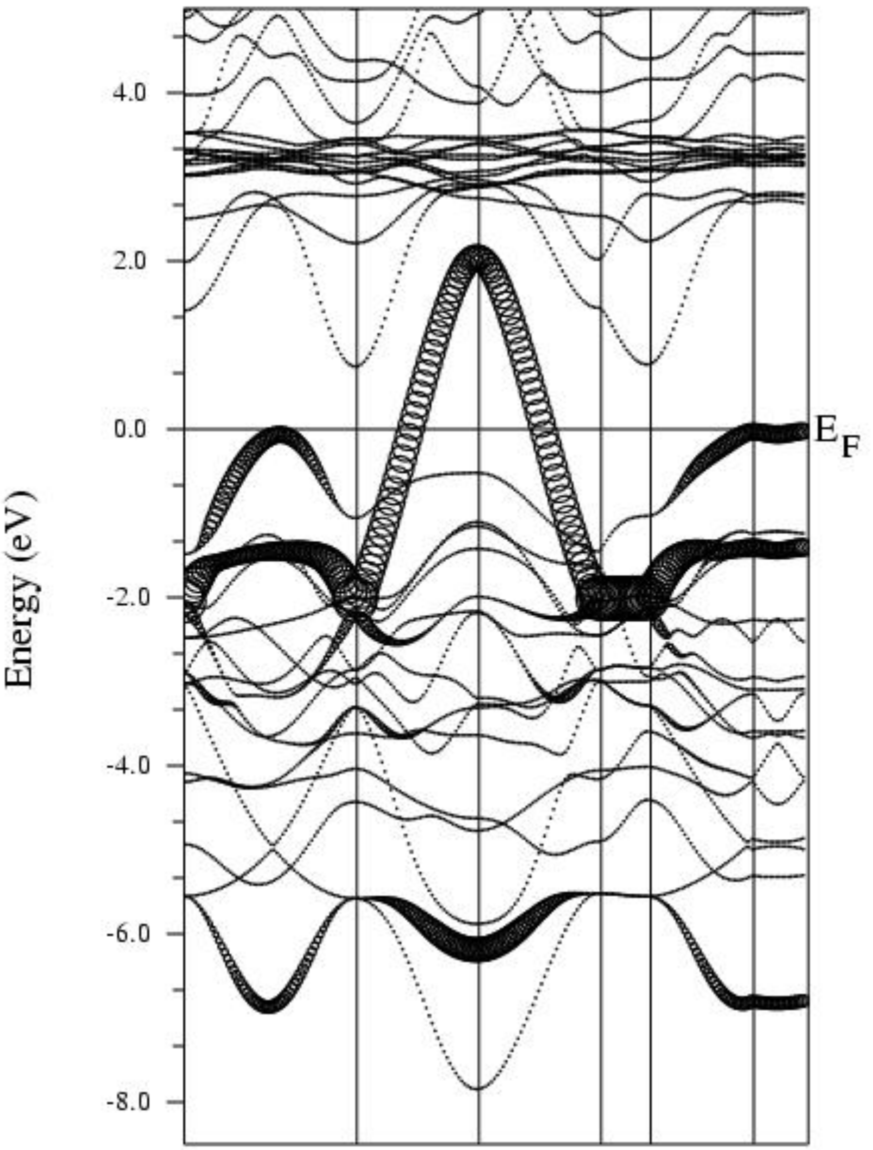


O2 – p z

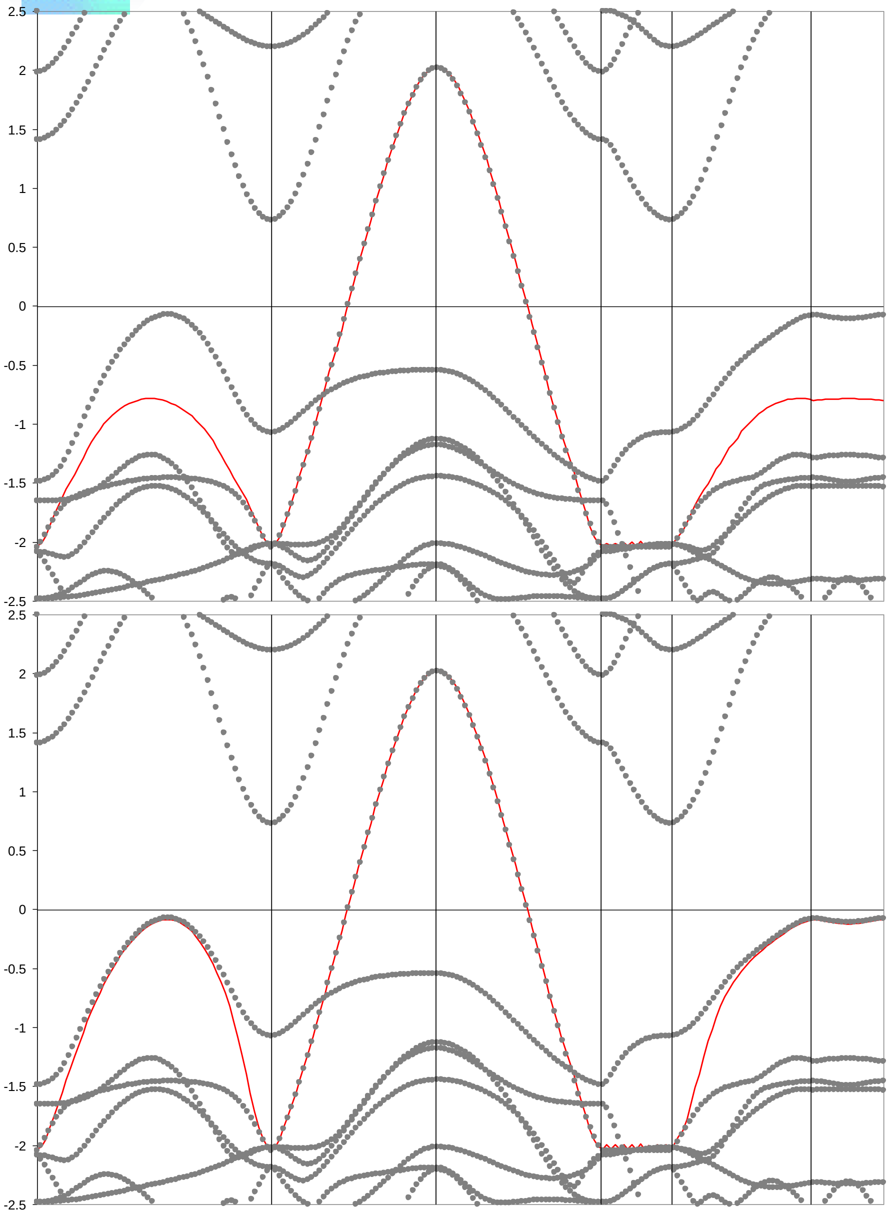


Bias for More Control



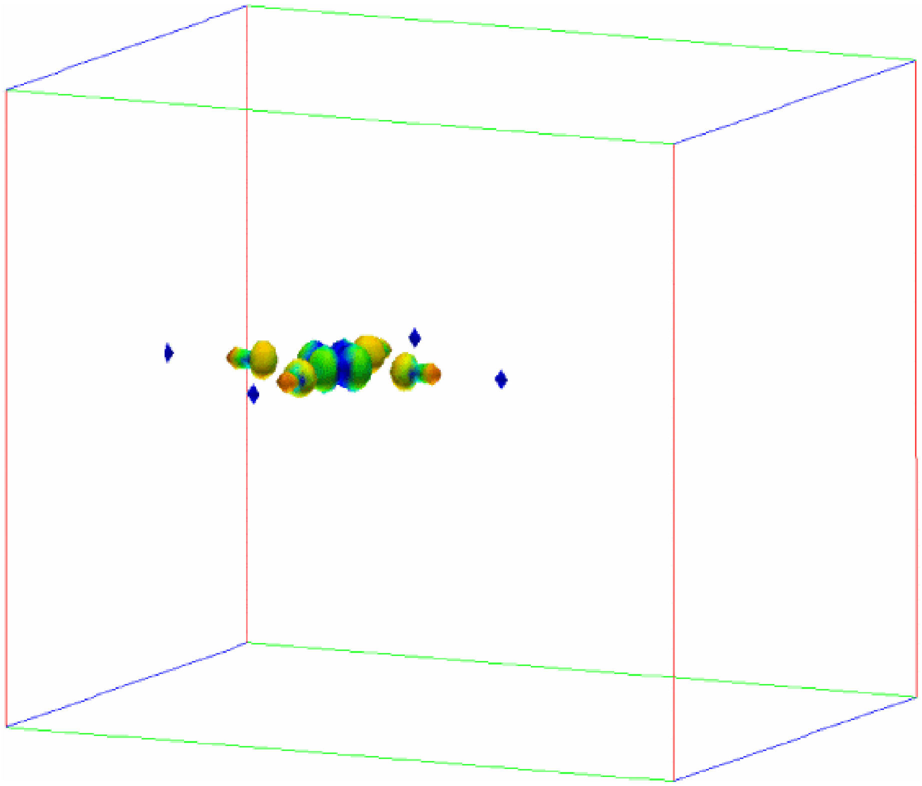


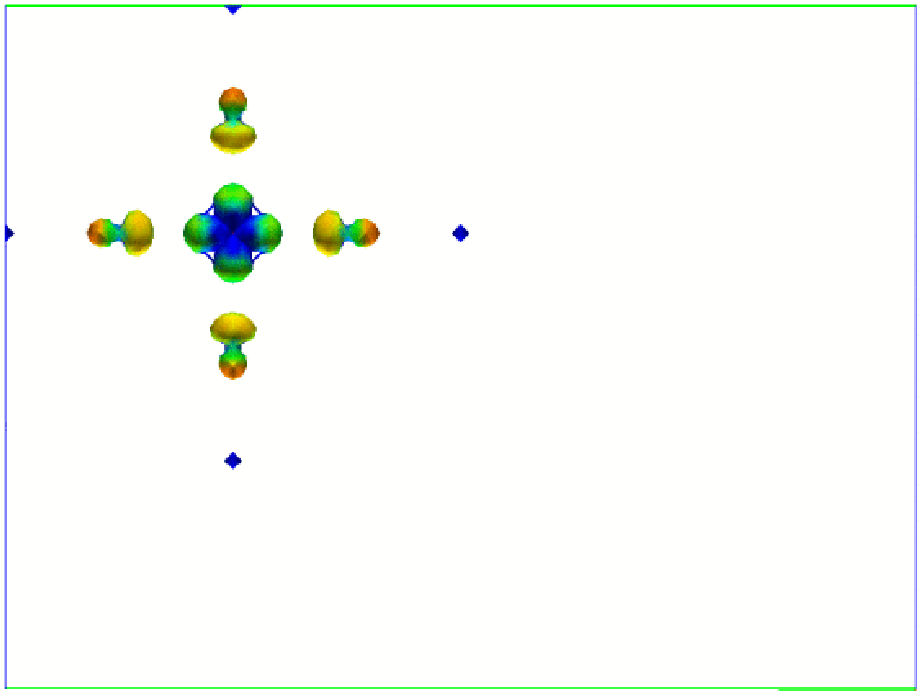
Bias for More Control



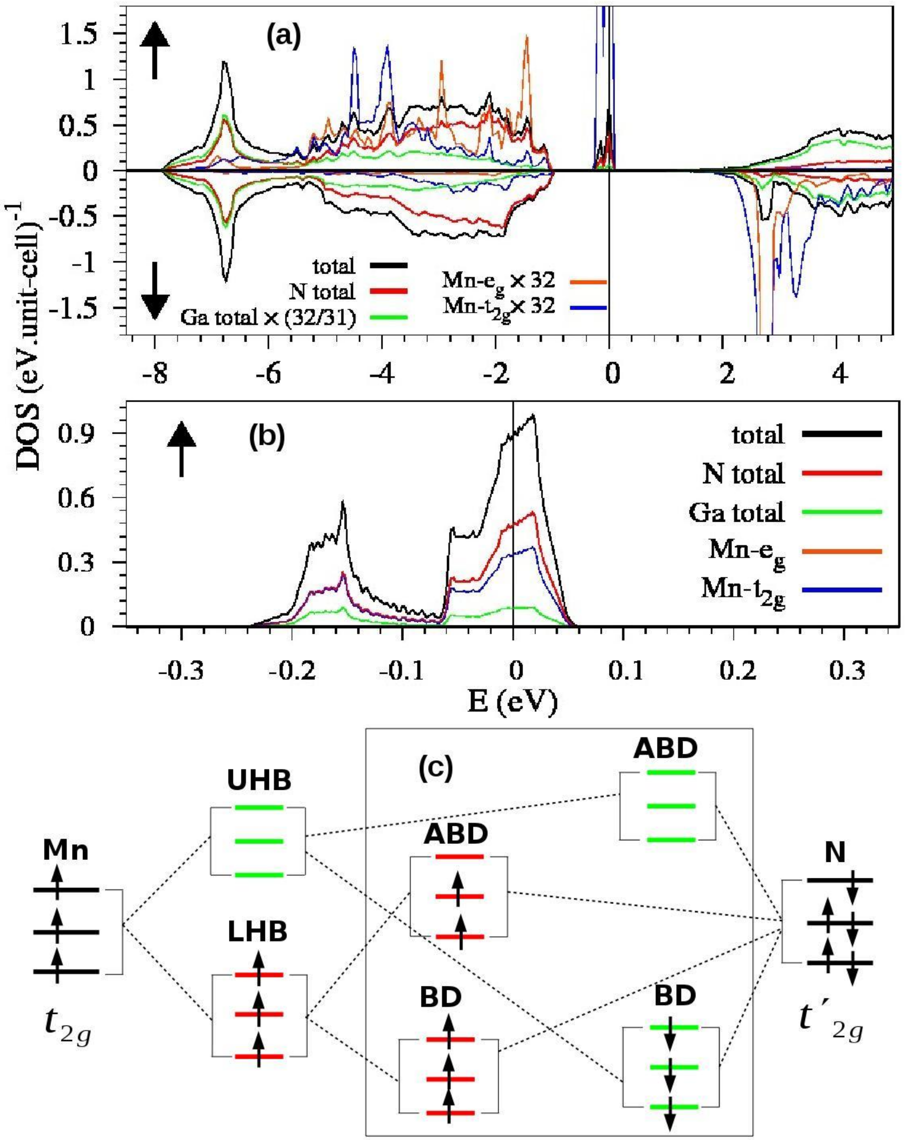
(alpha')	(meV)	(meV)
0 0 0	-85.3	94.5
0 1 0	-471.6	-430.0
-1 0 0	-471.6	-430.0
1 1 0	107.9	33.6
1 -1 0	107.9	33.6
0.5 0.5 0.5	2.9	-10.1
-0.5 -0.5 0.5	2.9	-10.1
0 2 0	-72.7	-30.8
-2 0 0	-72.7	-30.8
1 2 0	-0.7	-27.6
2 -1 0	-0.7	-27.6
0.5 1.5 0.5	-1.1	0.1
-1.5 -0.5 0.5	-1.1	0.1
1.5 1.5 0.5	-0.7	8.9
1.5 -1.5 0.5	-0.7	8.9
2 2 0	8.5	-1.0
2 -2 0	8.5	-1.0
0 3 0	-19.2	4.3
-3 0 0	-19.2	4.3

Half-Filled Wannier States of Cu-O in La_2CuO_4

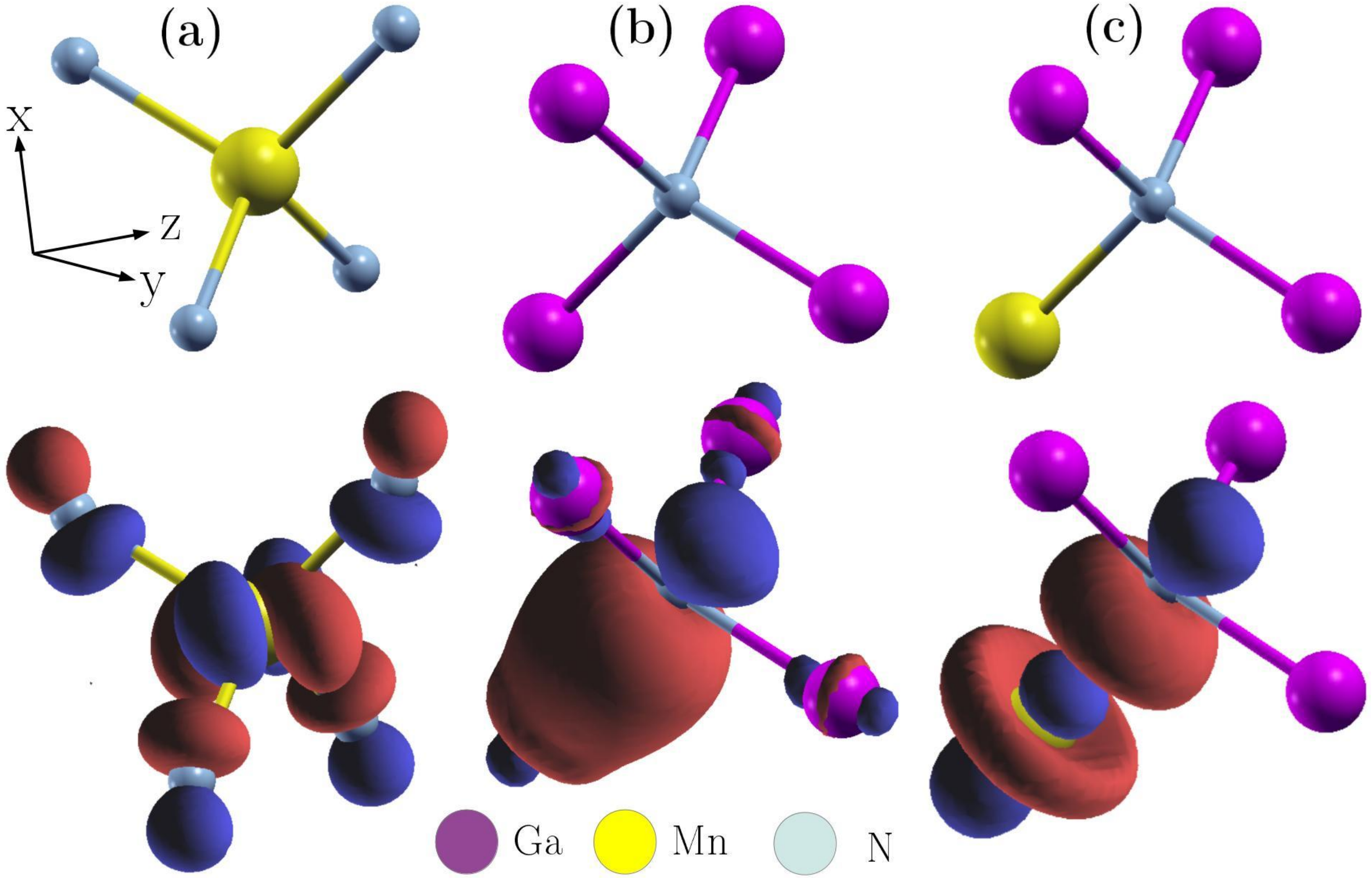




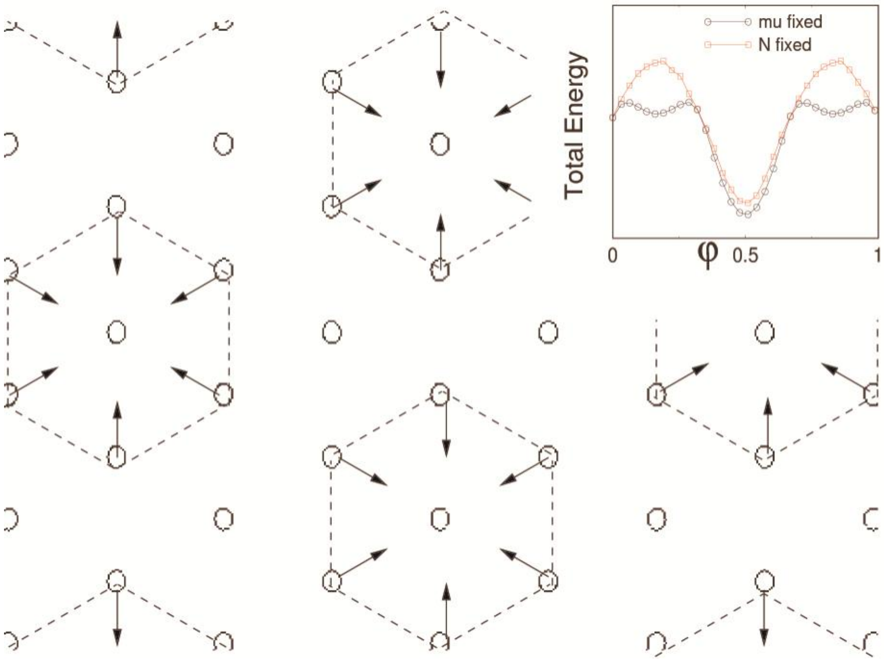
Systems with impurities: $Ga_{31}MnN_{32}$

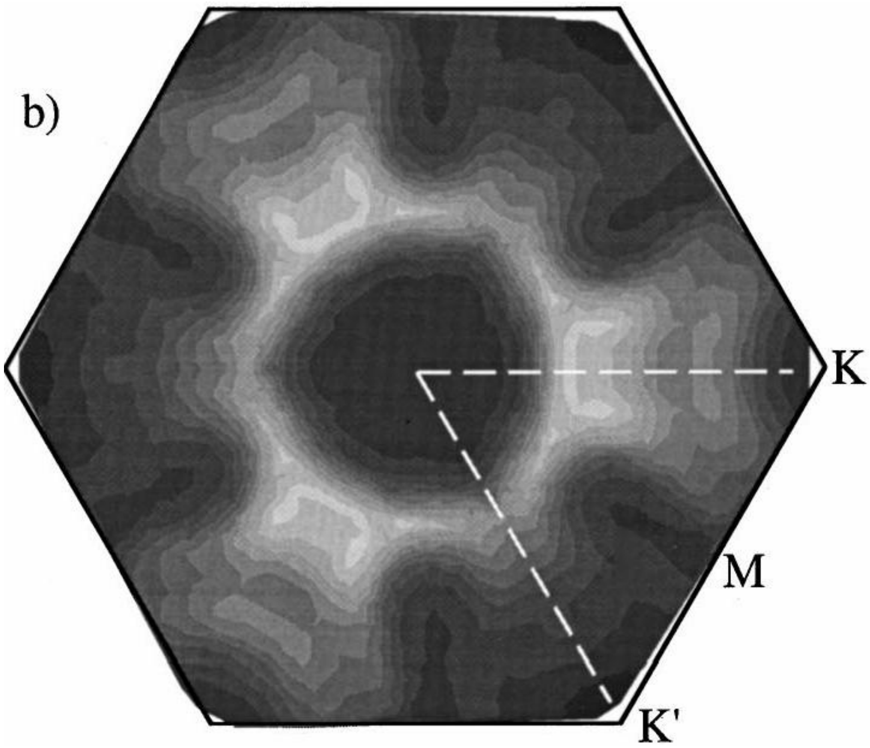


Two different representations: d_4 vs d_5



Gapless Charge-Density Wave in $TaSe_2$

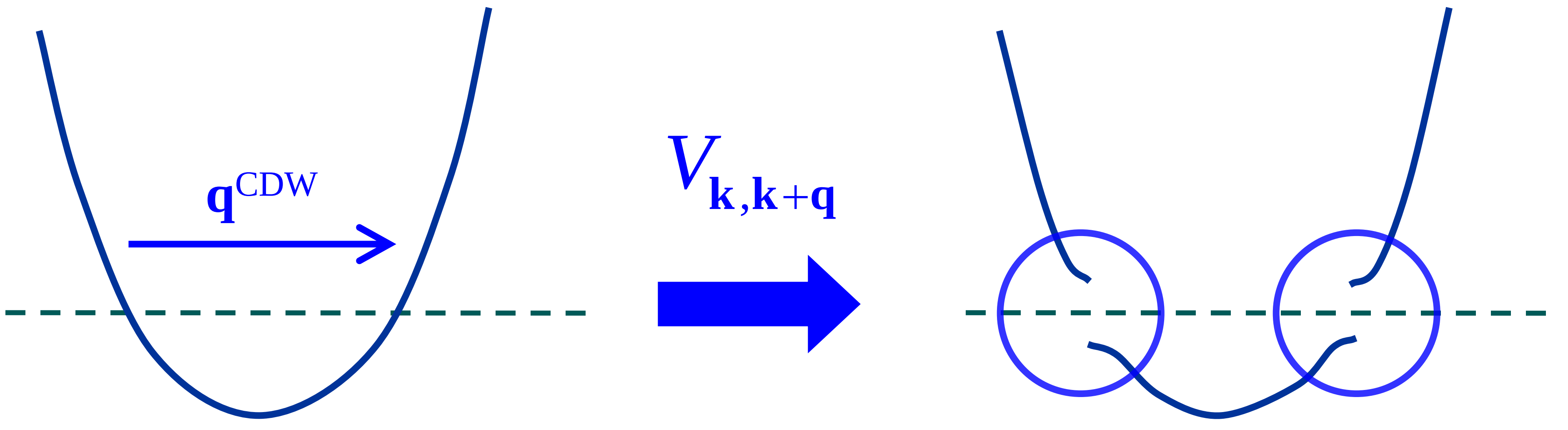




- commensurate CDW
- gapless excitations throughout the whole Fermi surface in CDW phase ?
- Fermi surface Nesting vector too large for q^{CDW} ?

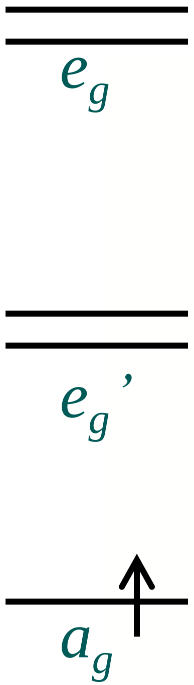
R. Liu, et. al. Phys. Rev. B, 5212 (2000)

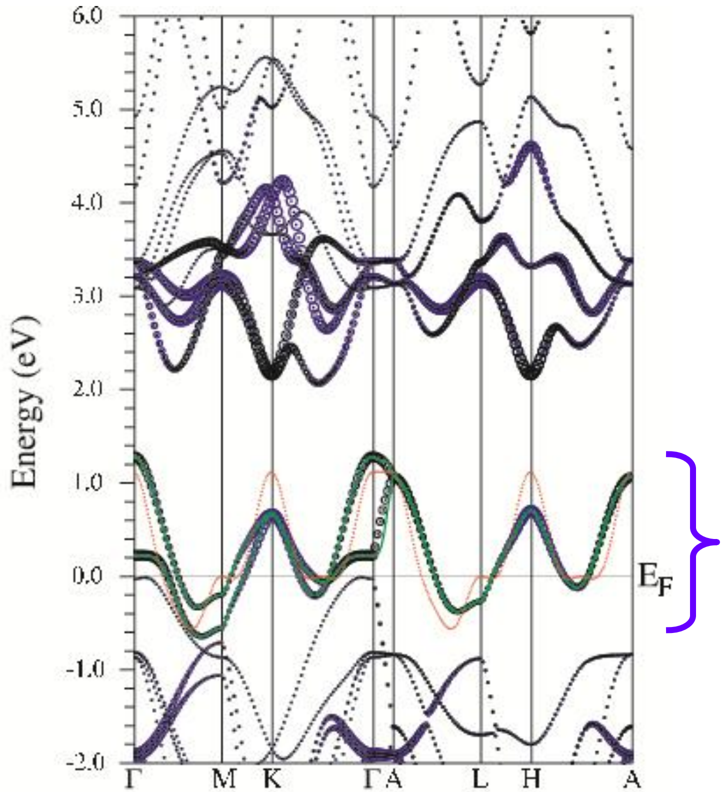
Conventional gapped CDW picture

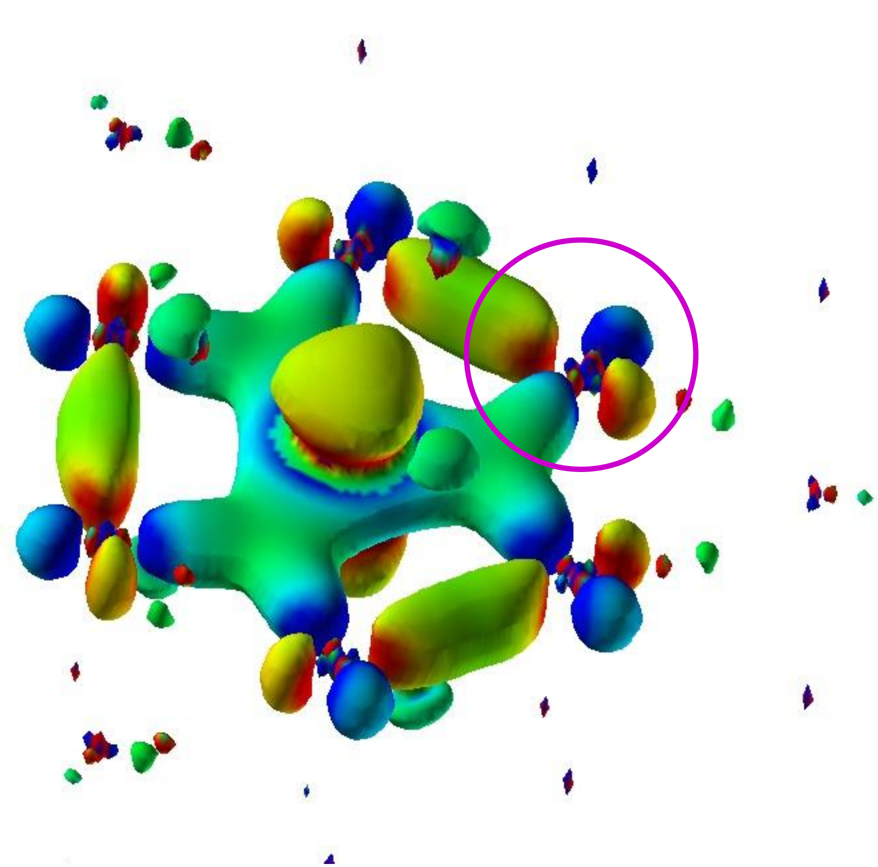


- Fermi surface instability
  - → divergent $\chi\left(\mathbf{q}^{\mathrm{CDW}},\omega\to 0\right)$
  - → nesting preferred
- gap → energy gain

Local Picture: Low-Energy Wannier Function







- $3z^2 - r^2$ (a_g) symmetry near EF, noticeable hybridization with e_g'
- WS in one site contains complete information of the full k-space
- center: a_g symmetry; tail: e_g' symmetry

Surprising Hopping Path

$$t^{DFT}_{Rn,R'n'} = \left\langle Rn \middle| h^{DFT} \middle| R'n' \right\rangle$$

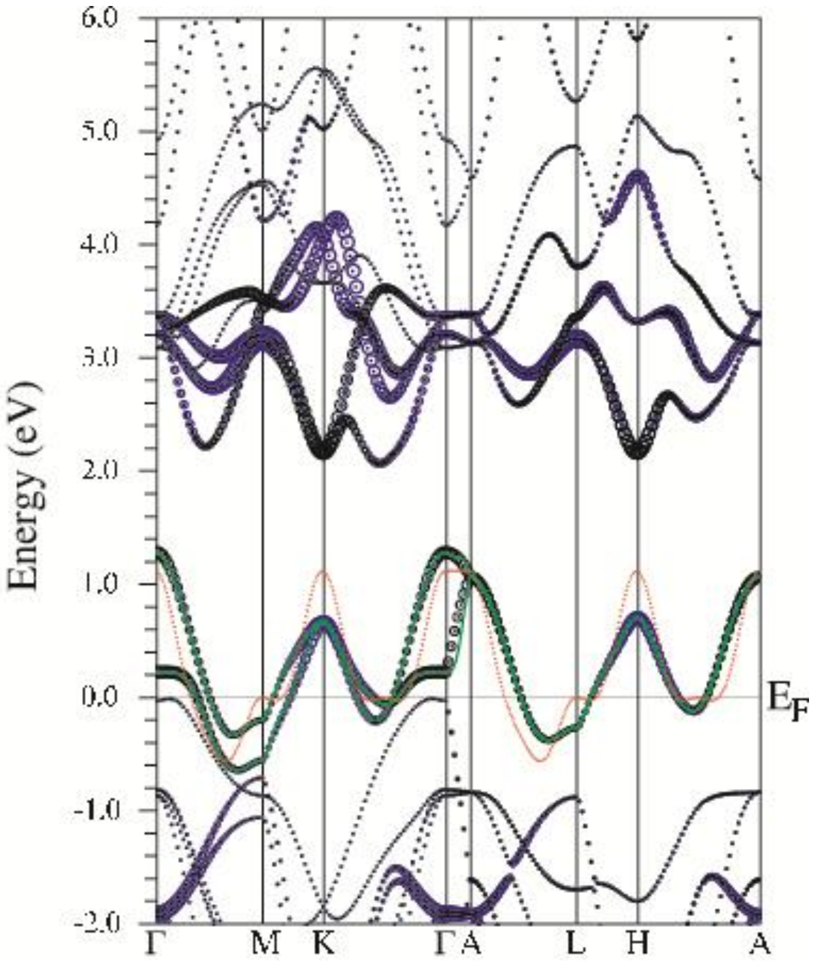
$$t_1 = 38\,(\text{meV})$$

$$t_2 = 115\,(\text{meV})$$

$$t_{\perp,1} = 29\,(\text{meV})$$

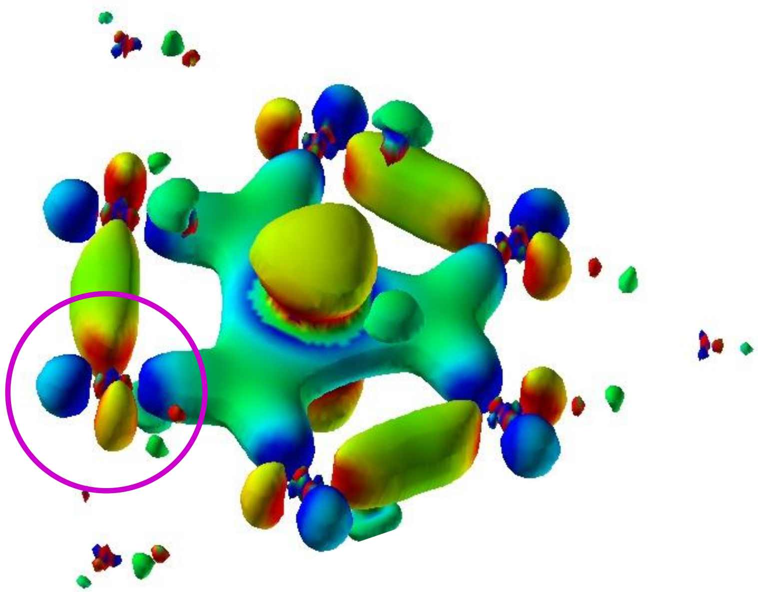
$$t_{\perp,2} = 23\,(\text{meV})$$

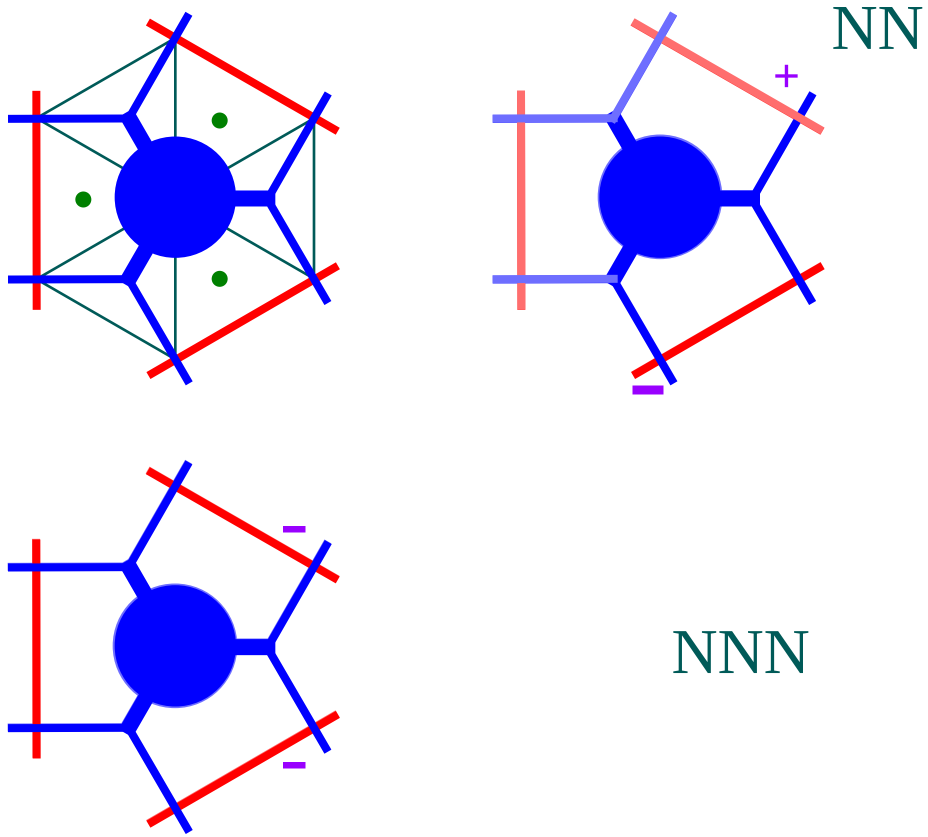
$$t_2 \gg t_1 !$$



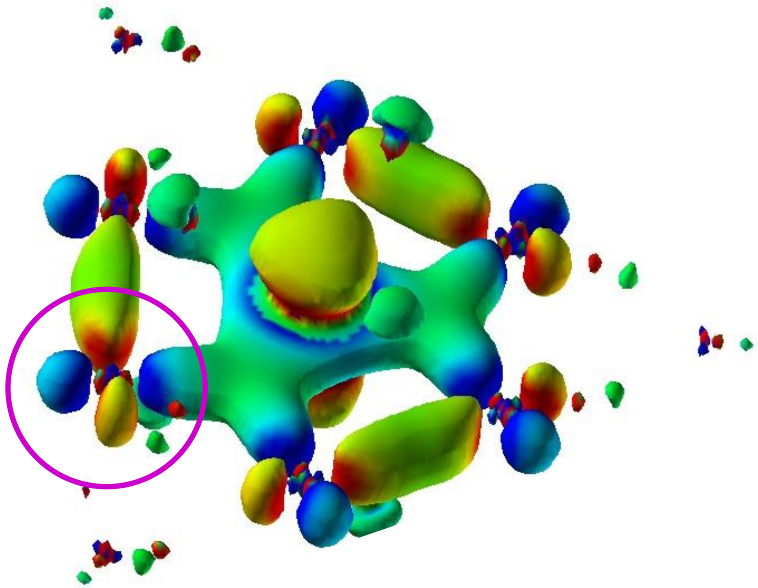
- perfect tight-binding "fit" to the band structure
- surprising hopping strength to 2nd nearest neighbors

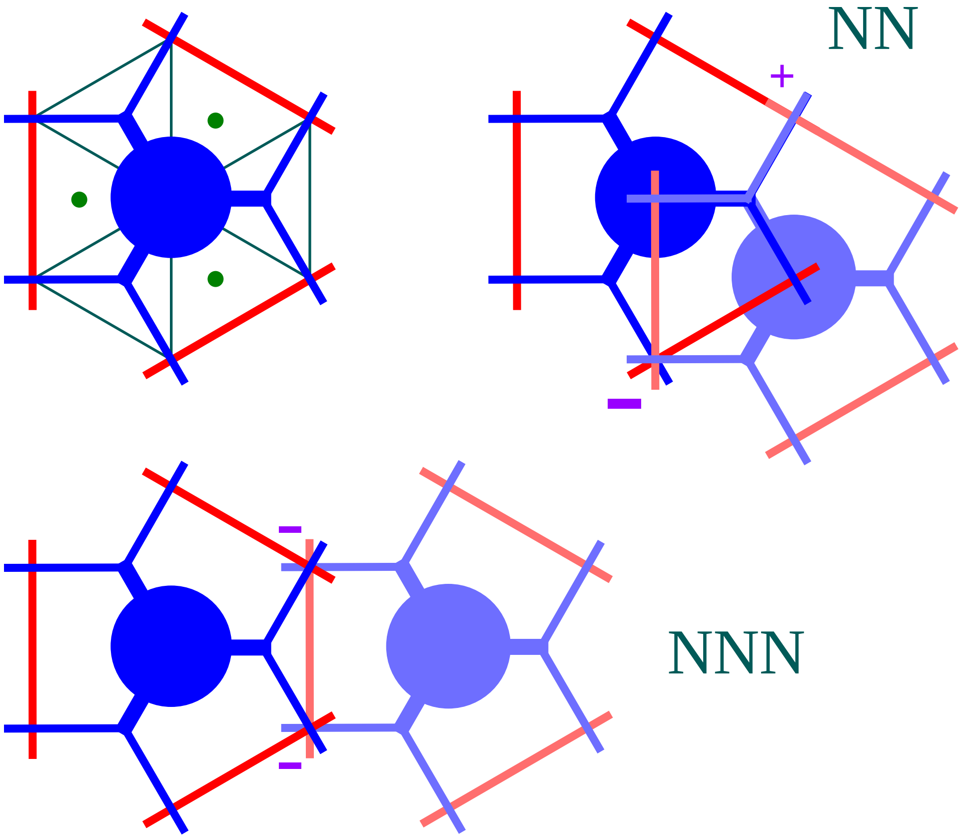
Why $t_2 >> t_1$?





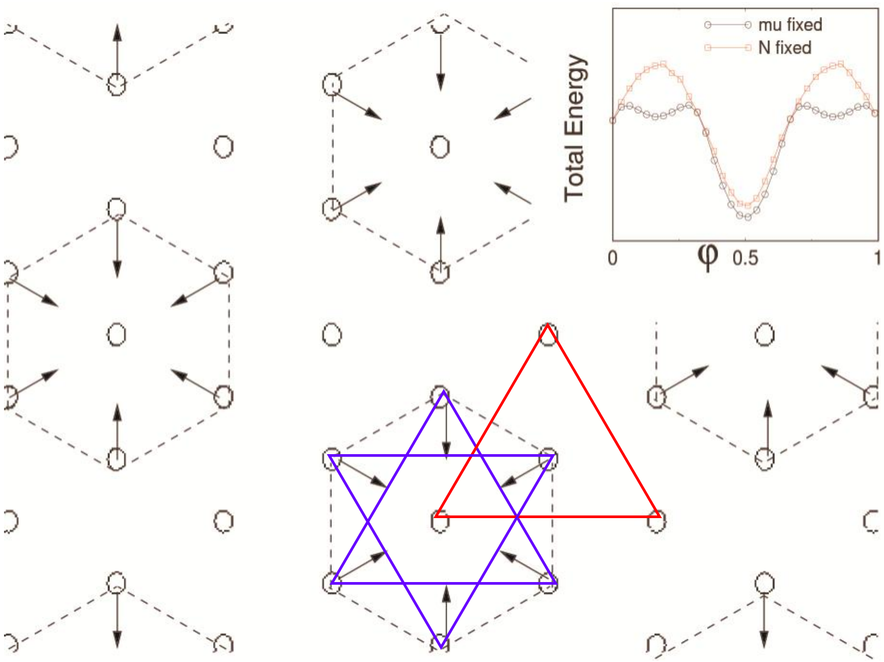
Why $t_2 >> t_1$?

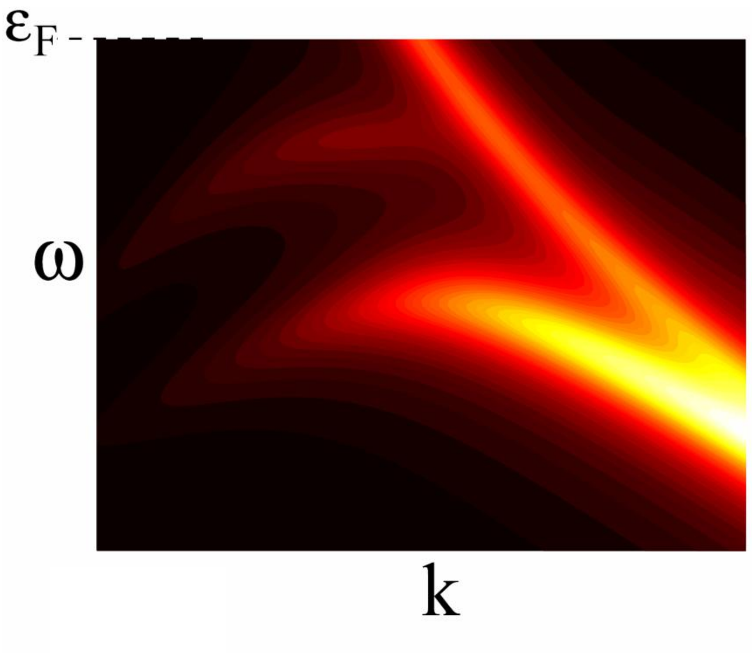




- phase interference from e_g' hybridization tail → $t_2 \gg t_1$

Gapless Charge-Density Wave in $TaSe_2$





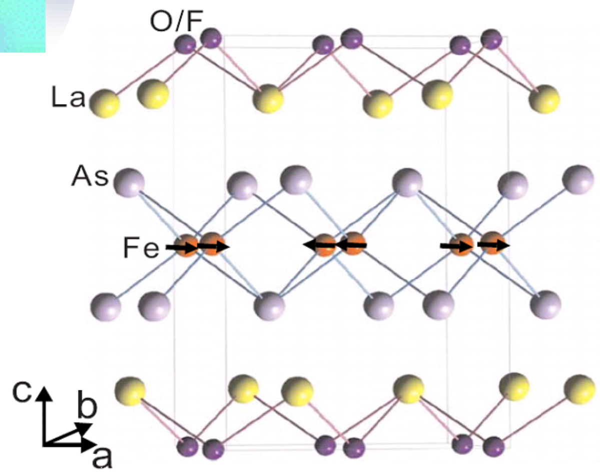
- x^2-y^2 hybridization → $t_2 \gg t_1$ → decoupling of 3 sublattices
- minimization of tight-binding *H* against distortion
  - → one sublattice undistorted
  - → gapless band structure

Spin & orbital: Ferro-orbital order & anisotropic magnetic structure in 1111 (&122)

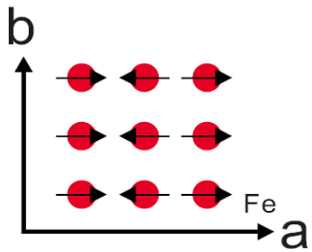
Chi-Cheng Lee, Wei-Guo Yin & Wei Ku

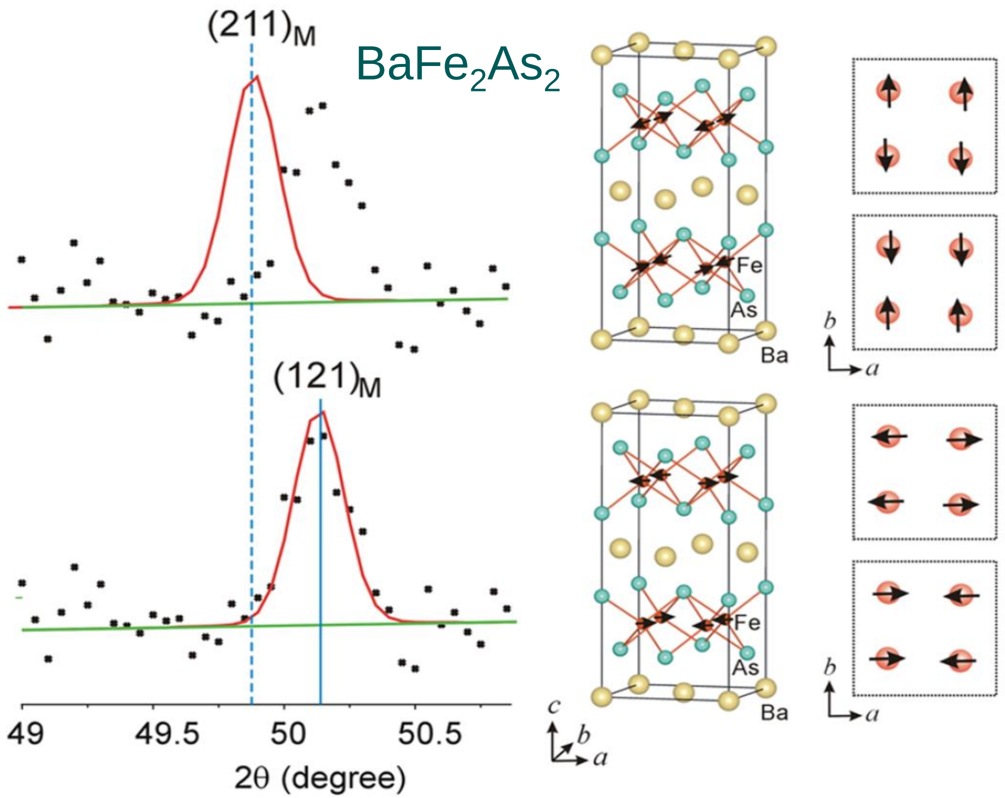
Phys. Rev. Lett. **103**, 267001 (2009)

Stripy magnetic and lattice structure



Phys. Rev. B **78**, 054529 (2008)

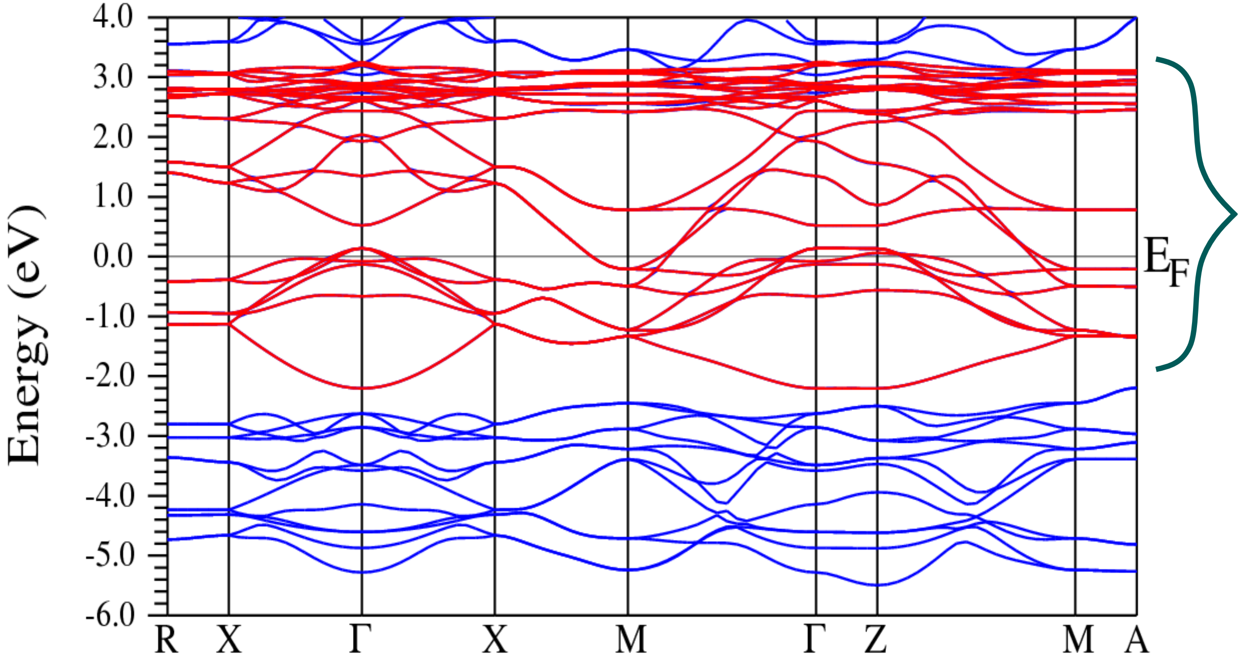




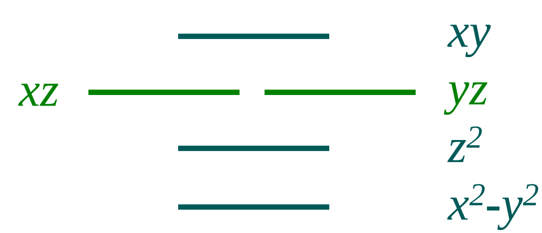
Q. Huang et al., PRL **101**, 257003 (2008)

- Structure transition at 155k; Stripy AFM order at 137K (AF bond longer?)
- What drives the magnetic transition?
  Fermi surface instability? (SDW due to nesting?)
- What drives the structural transition?
  Transition temperature so close to magnetic T_N : related?
- Implications to electronic structure and superconductivity?

Energy resolved, symmetry respecting Wannier function

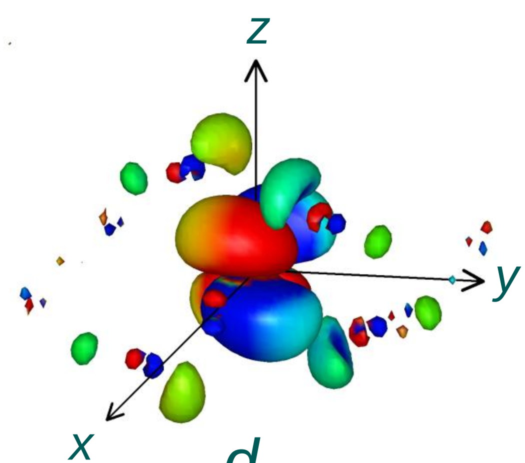


$$
\begin{aligned}
|\vec{R}n\rangle &= \sum_{\vec{k}m}^{\text{(energy window)}} |\vec{k}m\rangle\langle\vec{k}m|\vec{R}n\rangle \\
&= \frac{1}{\sqrt{N_{cell}}} \sum_{\vec{k}m} |\vec{k}m\rangle e^{-i\vec{k}\cdot\vec{R}} U_{mn}^{(\vec{k})} \\
&= \frac{1}{\sqrt{N_{cell}}} \sum_{\vec{k}} \left(\sum_{m} U_{mn}^{(\vec{k})} |\vec{k}m\rangle \right) e^{-i\vec{k}\cdot\vec{R}}
\end{aligned}
$$

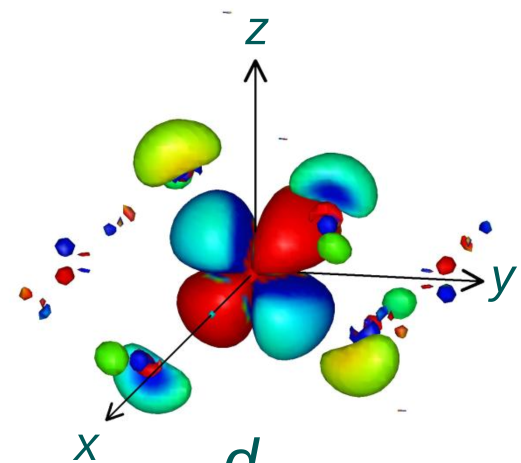


NM onsite energy (eV)

z^2	-0.03
x^2-y^2	-0.20
yz	0.10
xz	0.10
xy	0.34



d_{xz}



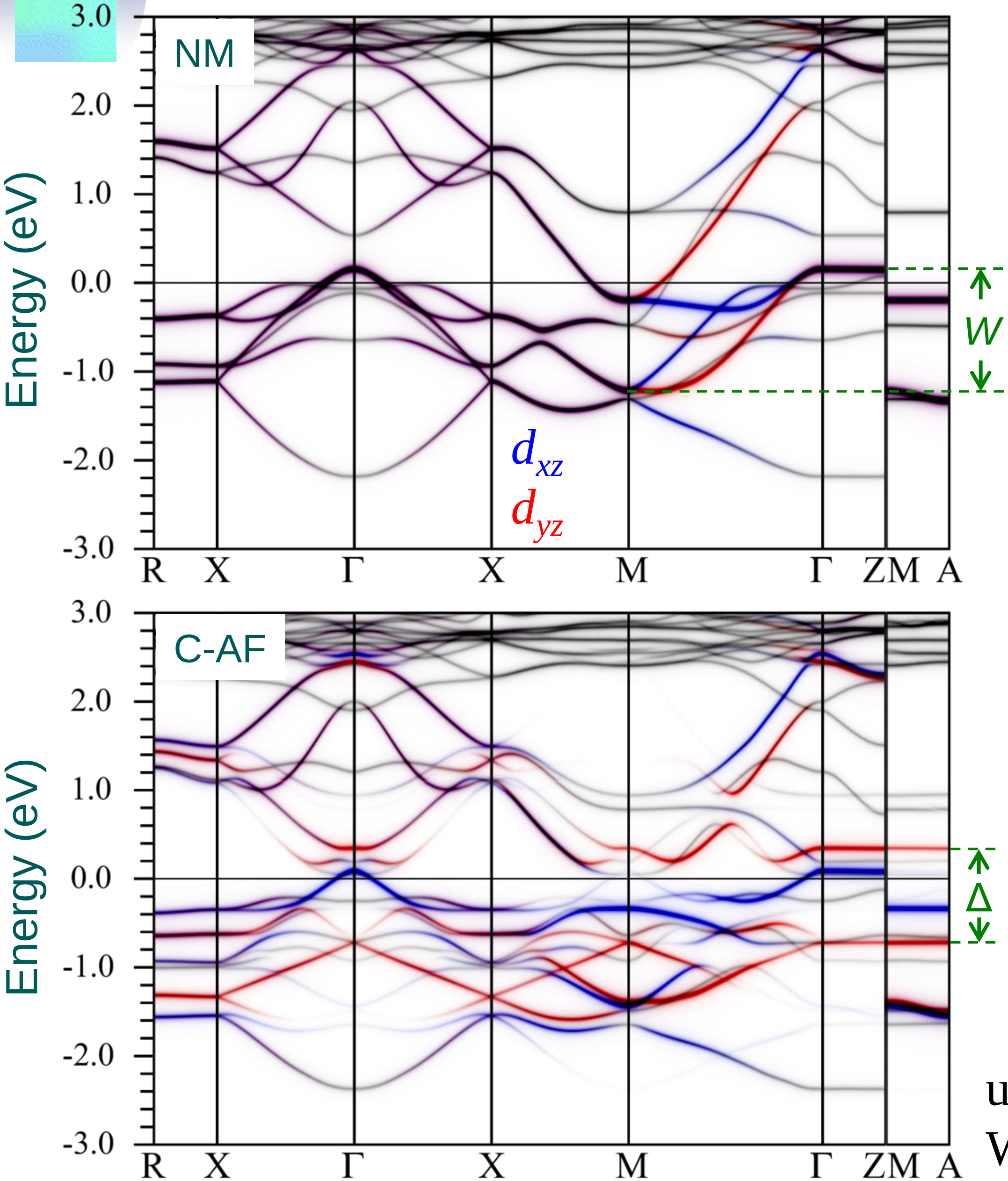
d_{yz}

- small crystal field splitting
- degenerate xz and yz

→ orbital freedom !

methods see: W. Ku et al., PRL **89**, 167204 (2002); W. Yin et al., PRL **96**, 116405 (2006)

Comparing LDA band structures



- in NM 1st-BZ
- d_{xz} & d_{yz} most relevant to the low-E
- Only d_{yz} splits strongly near E_F
- d_{yz} more spin polarized ~$0.34\mu_B$ than d_{xz} (~$0.15\mu_B$)
- more different with U=2eV
  0.58 vs. $0.23\mu_B$

→ orbital symmetry broken

- Δ ~ W

→ large (ω,**k**)-space involved

→ local picture more suitable

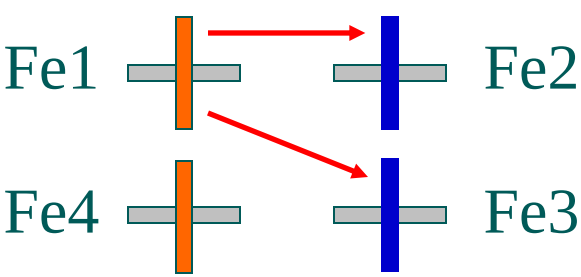
→ Fermi surface nesting not essential

→ SDW less convenient

unfolding methods see:
Wei Ku *et al.*, PRL **104**, 216401 (2010)

Anti-intuitive hopping parameters

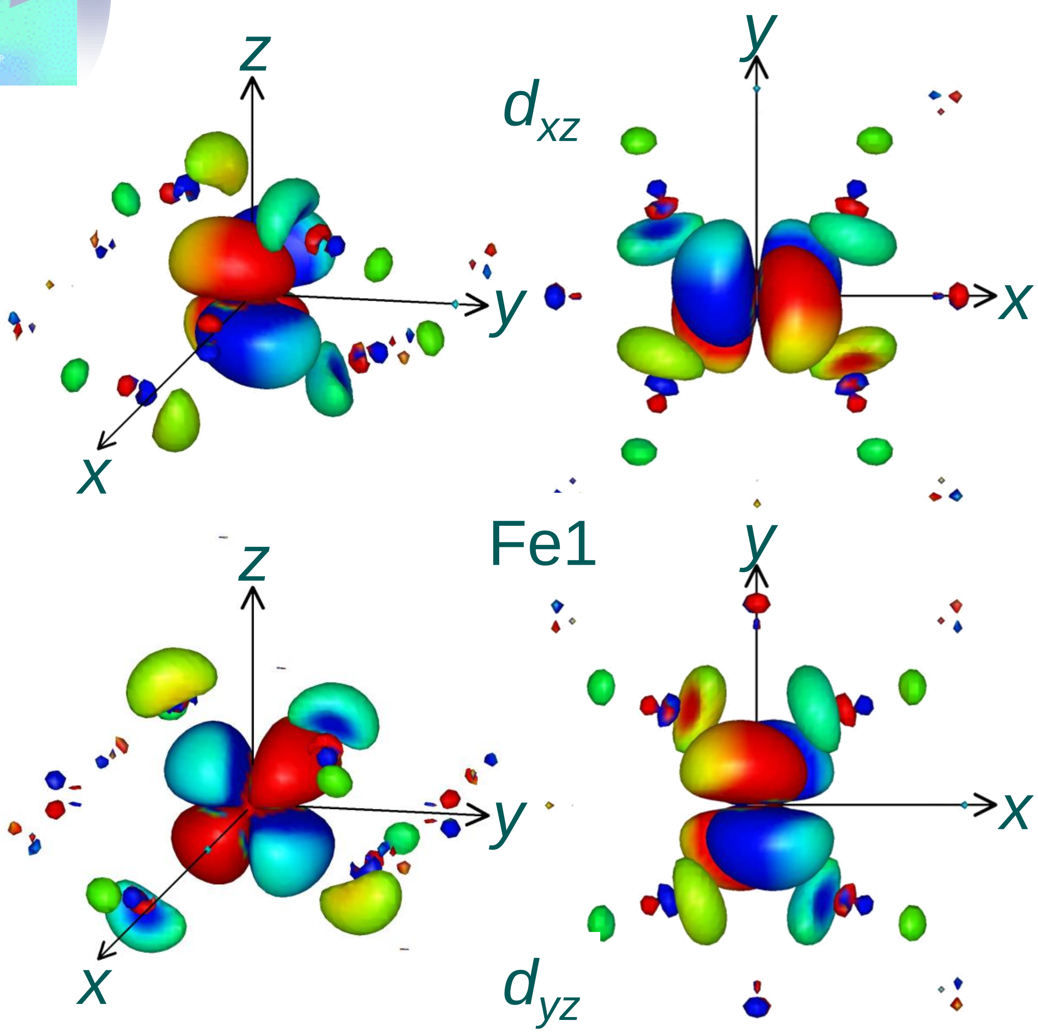
$\langle \mathrm{WFs}\vert H\vert \mathrm{WFs}\rangle$	Fe1 z^2	x^2-y^2	yz	xz	xy
Fe2 (Fe4) z^2	0.13	0.31 (-0.31)	-0.10 (0.00)	0.00 (0.10)	0.00
x^2-y^2	0.31 (-0.31)	-0.32	0.42 (0.00)	0.00 (0.42)	0.00
yz	-0.10 (0.00)	0.42 (0.00)	-0.40 (-0.13)	0.00	0.00 (0.23)
xz	0.00 (0.10)	0.00 (0.42)	0.00	-0.13 (-0.40)	-0.23 (0.00)
xy	0.00	0.00	0.00 (0.23)	-0.23 (0.00)	-0.30
Fe3 z^2	0.06	0.00	-0.08	0.08	0.26
x^2-y^2	0.00	-0.10	0.12	0.12	0.00
yz	0.08	-0.12	0.25	-0.07	-0.05
xz	-0.08	-0.12	-0.07	0.25	0.05
xy	0.26	0.00	0.05	-0.05	0.16

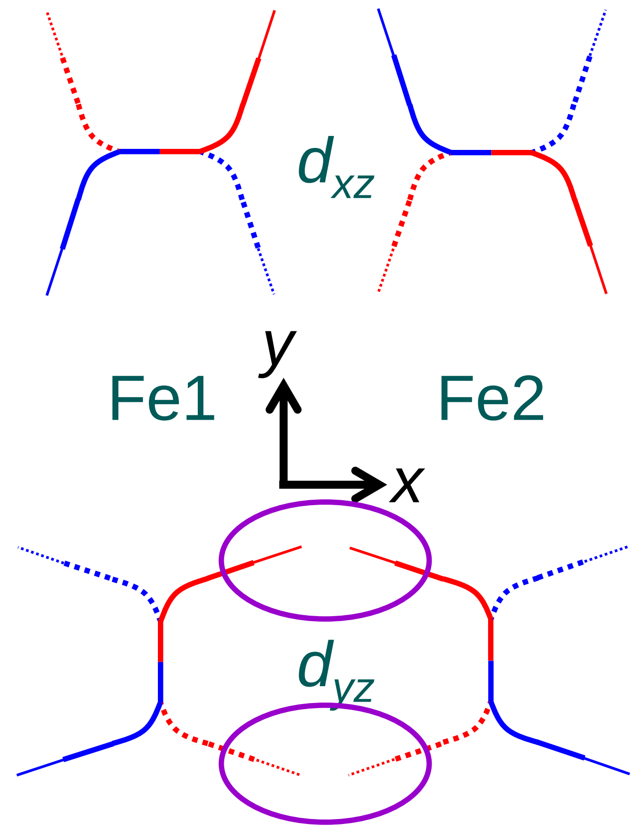


- Unusual coupling direction
- Cubic symmetry broken seriously by As
  → Fe-As phonon modes important
- Perpendicular hopping direction!

Chi-Cheng Lee *et al.*, PRL **103**, 267001 (2009)

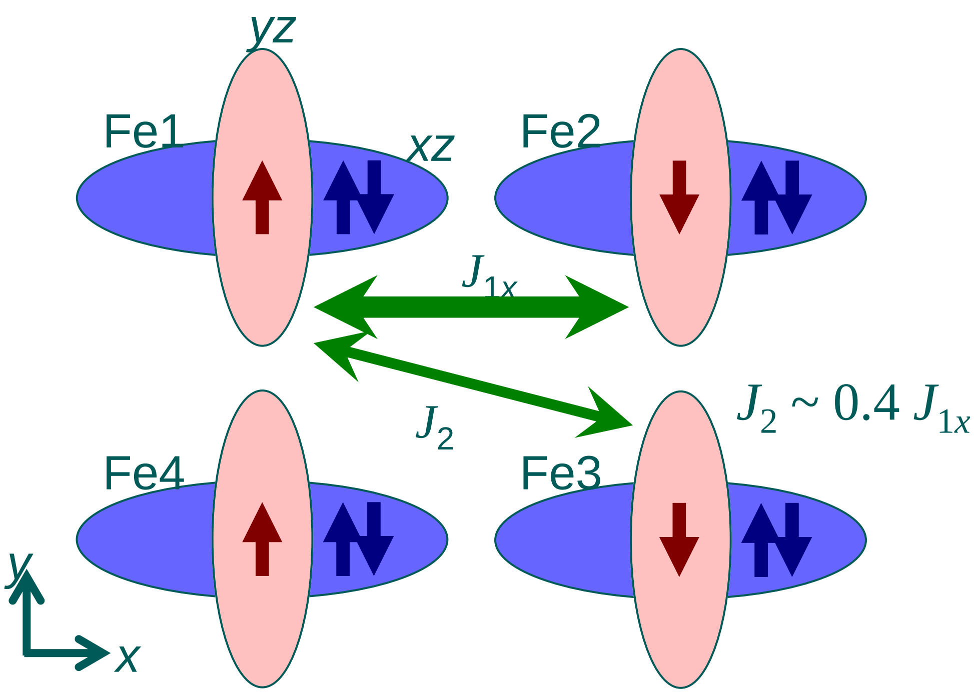
Examples of low-E Wannier functions

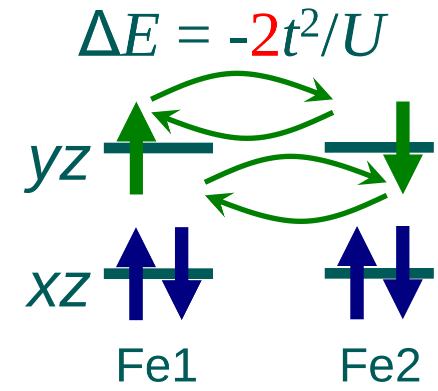


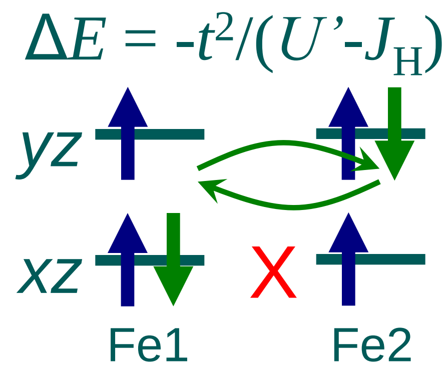


- Most relevant to the low-E
- The only ones that knows x != y
- Perpendicular extension of the hybridization tail due to As atoms !

C-AF magnetic structure and ferro-orbital order







- Strongly anisotropic super-exchange: $J_{1x} > J_2 >> J_{1y}$
  → no competition with G-AF at all ! $J_1 \sim 2J_2$ irrelevant !
  → Heisenberg model inadequate
- Orbital polarization and ferro-orbital correlation important
  Unusual coupling direction and strong anisotropic hoppings !
  → $a > b$: AF across long bond (rare)
  → strong in-plane nematic-like anisotropic response
  transport, optical, and lattice properties

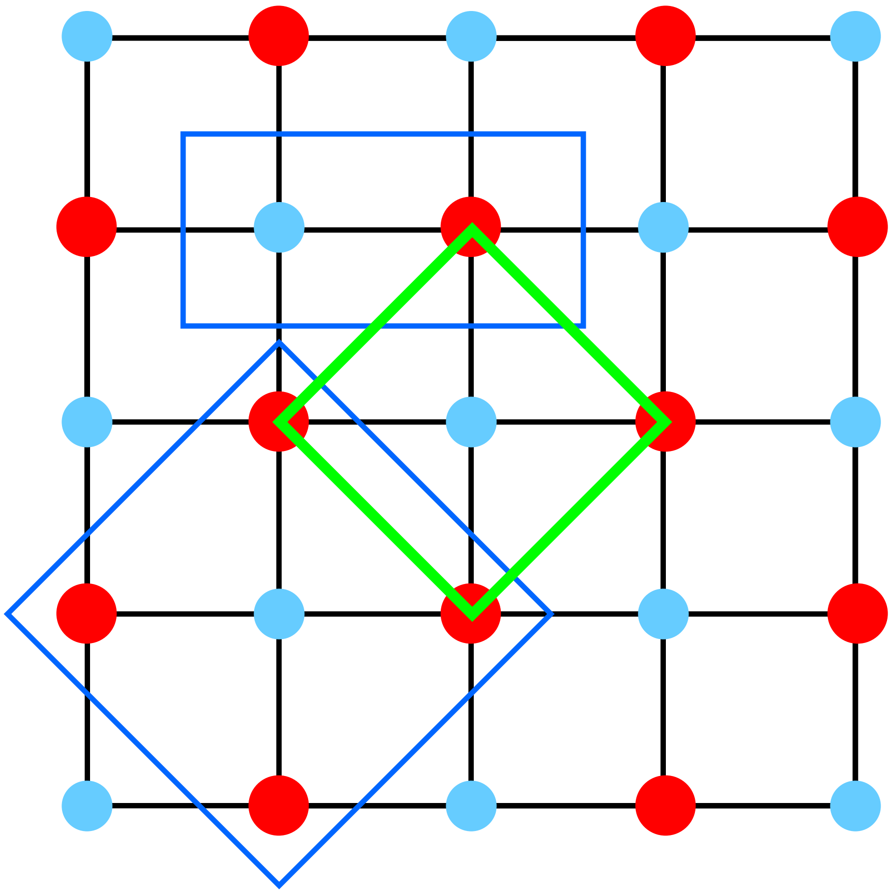
Chi-Cheng Lee *et al.*, PRL **103**, 267001 (2009)

Local Picture for Strongly Correlated Systems

$$H = H_0 + V = \boxed{H_{local}} + H_{nonlocal}$$

- V too big for perturbation
- Maximize the terms in the "local" part
  → symmetric Wannier Representation → defines "local"
- Treat local part "accurately"
- Add non-local part as modification

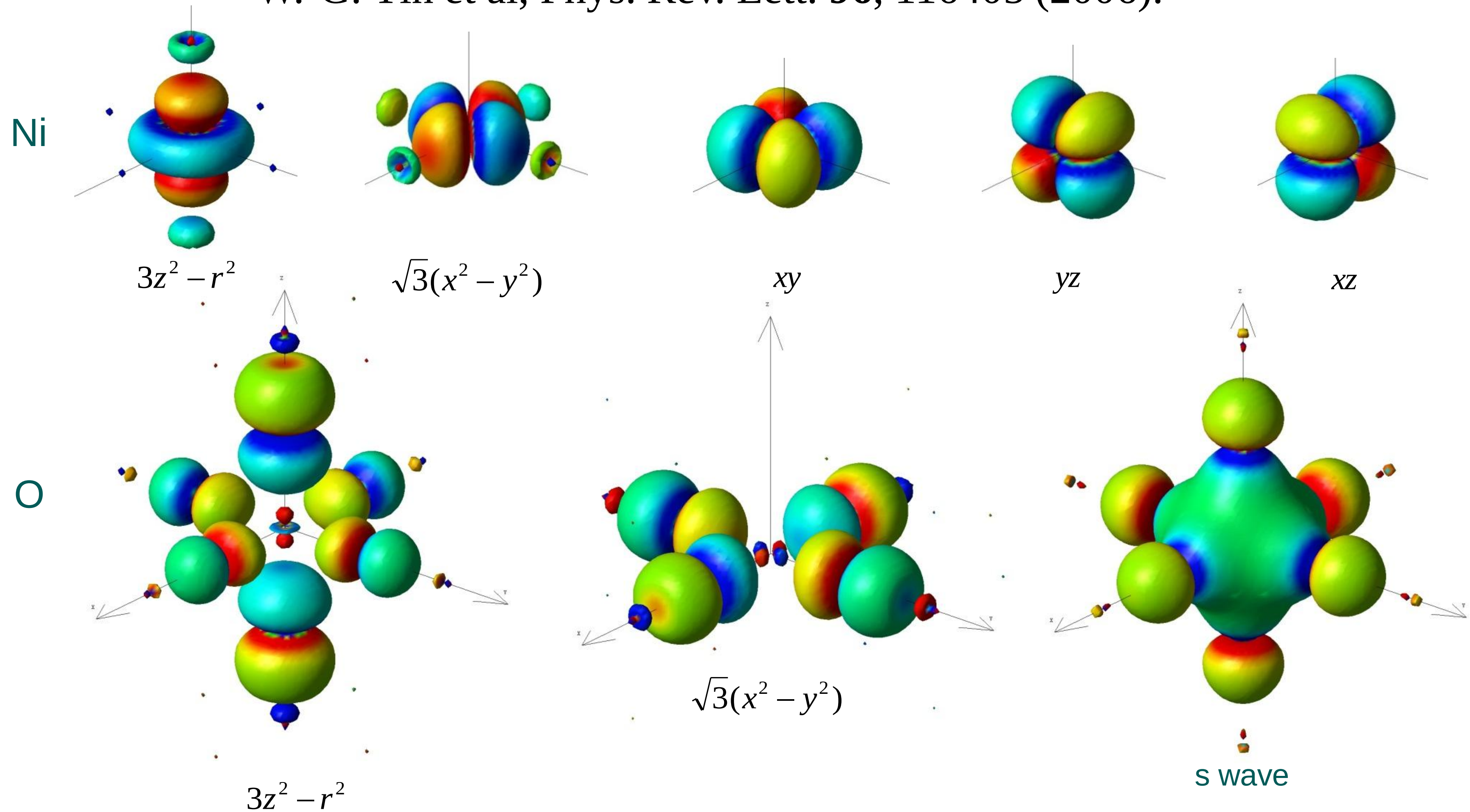
How to define “local” in CT-insulators?



- Periodic symmetry
- Point group symmetry
- Simultaneously keep both? How to split the Hilbert space?

Symmetric Wannier Functions for CT-Insulators

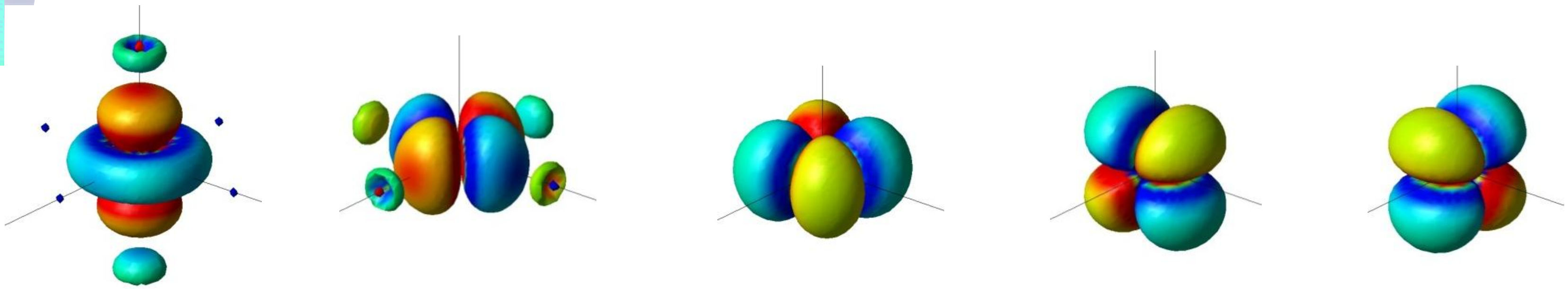
W. Ku et al., Phys. Rev. Lett. **89**, 167204 (2002).
R. L. Barnett et al., Phys. Rev. Lett. **96**, 026406 (2006).
W.-G. Yin et al, Phys. Rev. Lett. **96**, 116405 (2006).



- O-*p* orbitals → additional Ni-*d* orbitals (no double counting of O orbitals)
- “local” is now defined by this “super-atom”

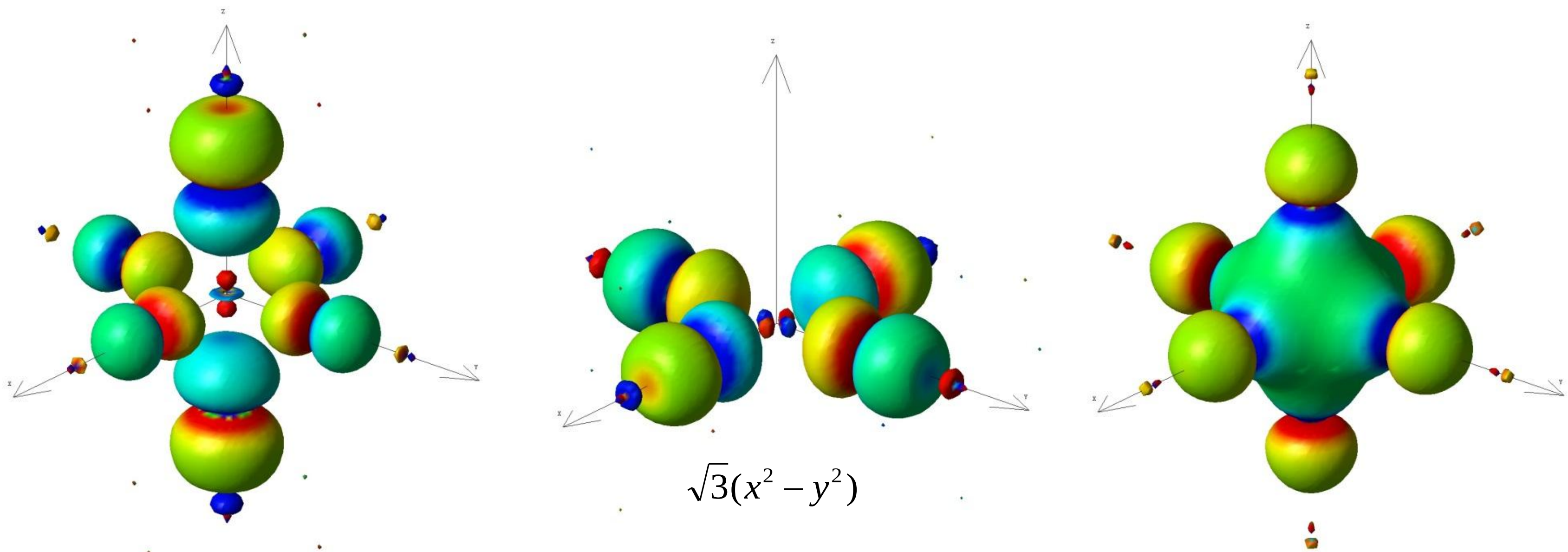
Super Atom for Charge Transfer Insulator

Ni



$3z^2-r^2$ $\sqrt{3}(x^2-y^2)$ xy yz xz

O



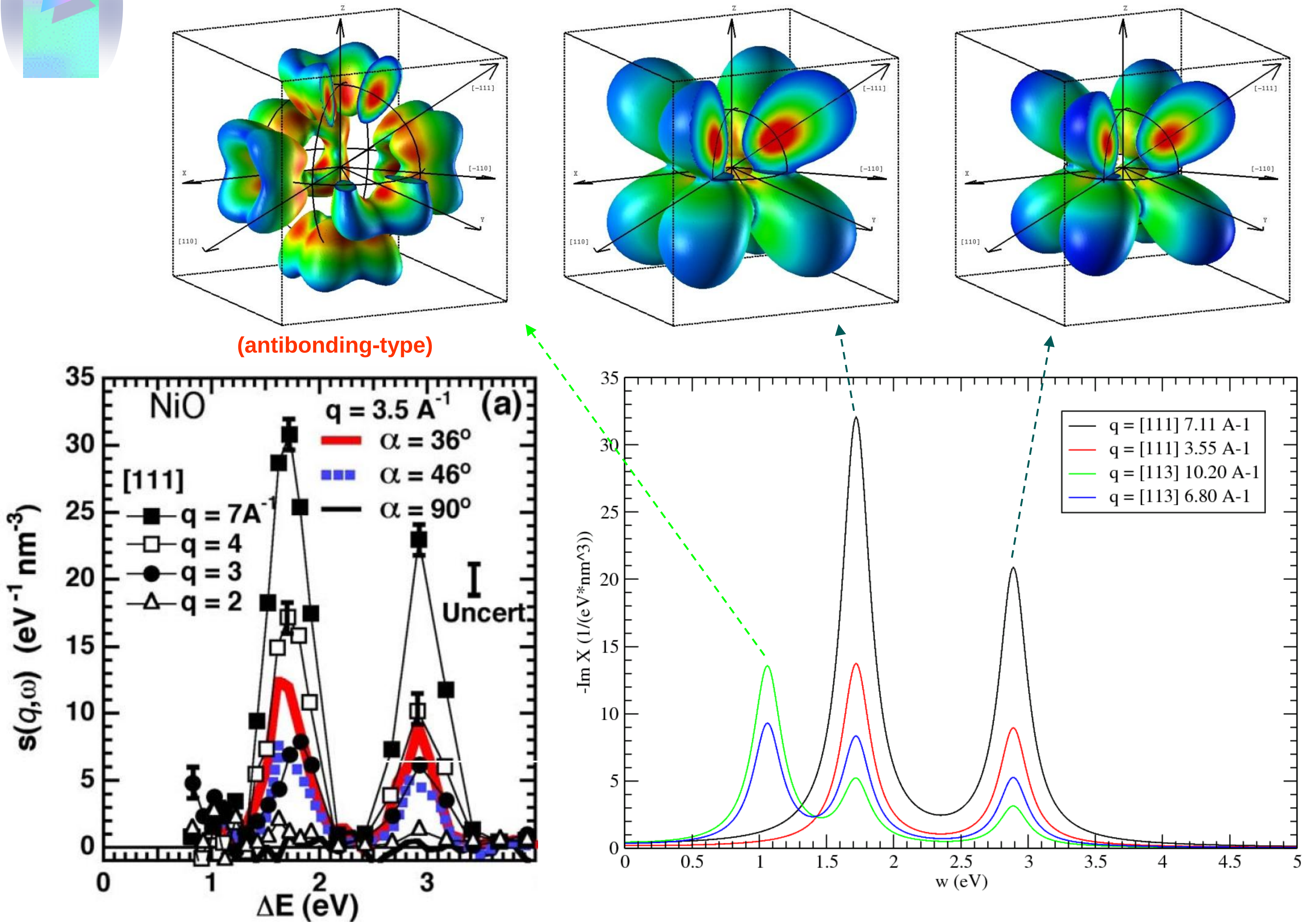
$3z^2-r^2$ $\sqrt{3}(x^2-y^2)$ s wave

$$H = H_{local} + H_{nonlocal}$$

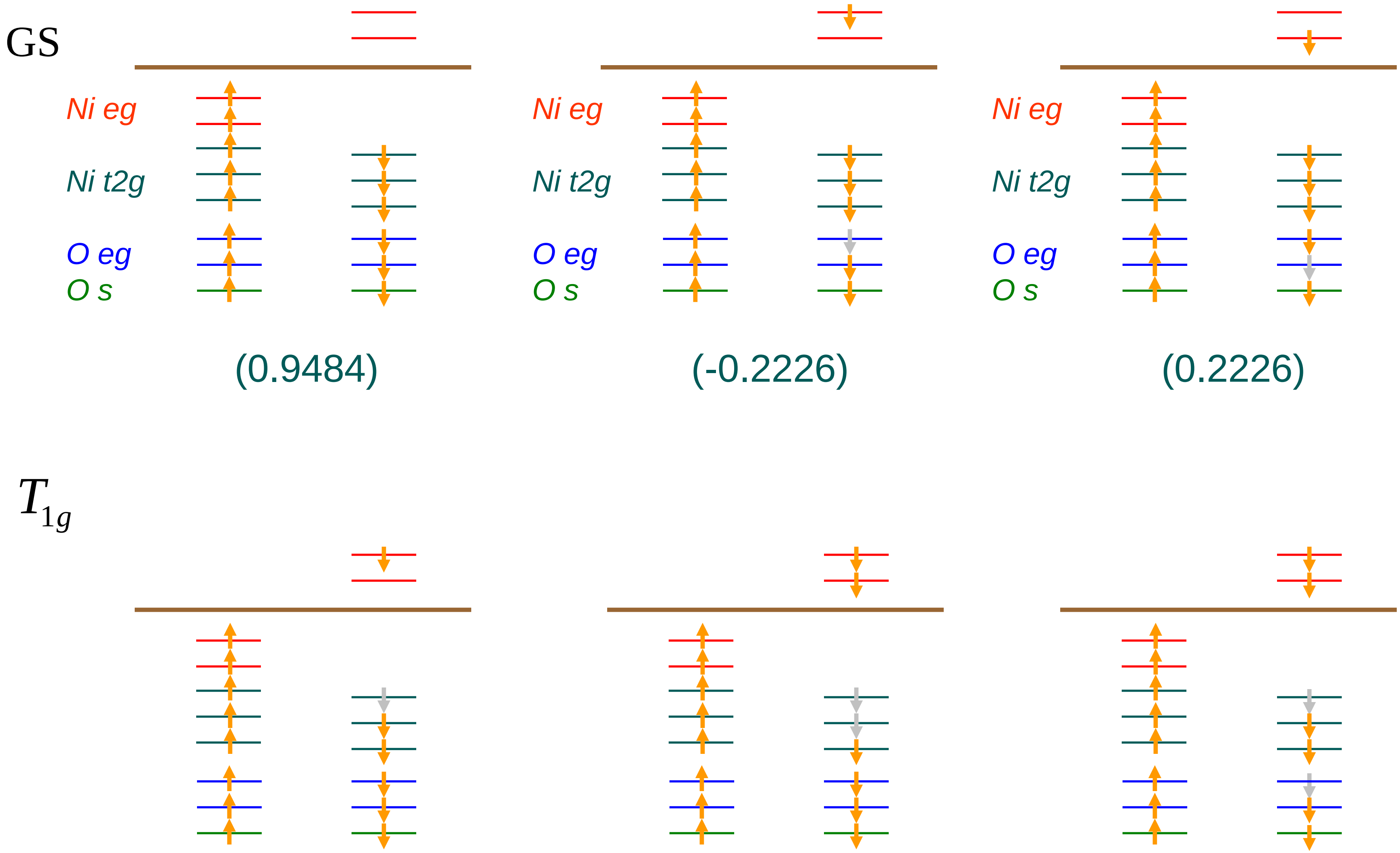
(exact) **(modification)**

Maximize the contributions of "local atom"

Density response for super atom (eg-t2g=0.65eV)



Multiplet Splitting Made Possible with MB Hilbert Space

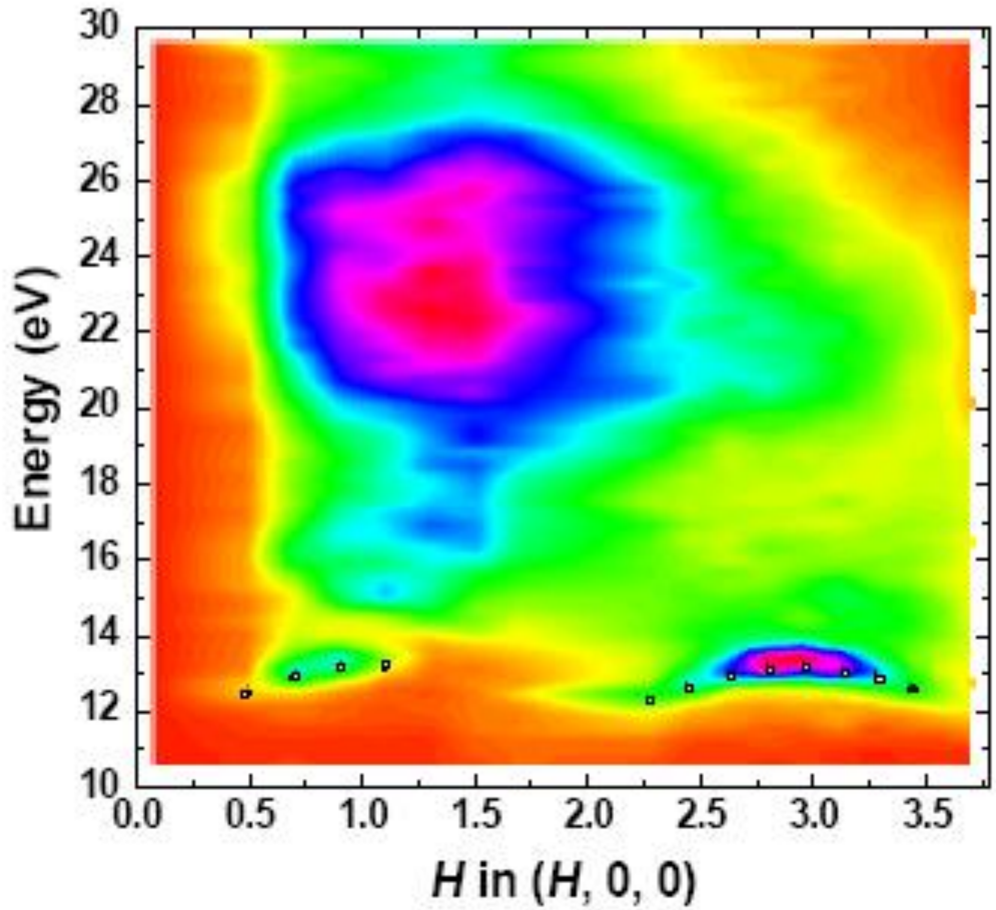


Propagation of Tightly-Bound Excitons: case study of LiF

- Tightly bound exciton
- Charge transfer insulator
  → p-h in different atoms
- Frenkel or Wannier exciton ?
- Dispersion
  → propagation in space/time

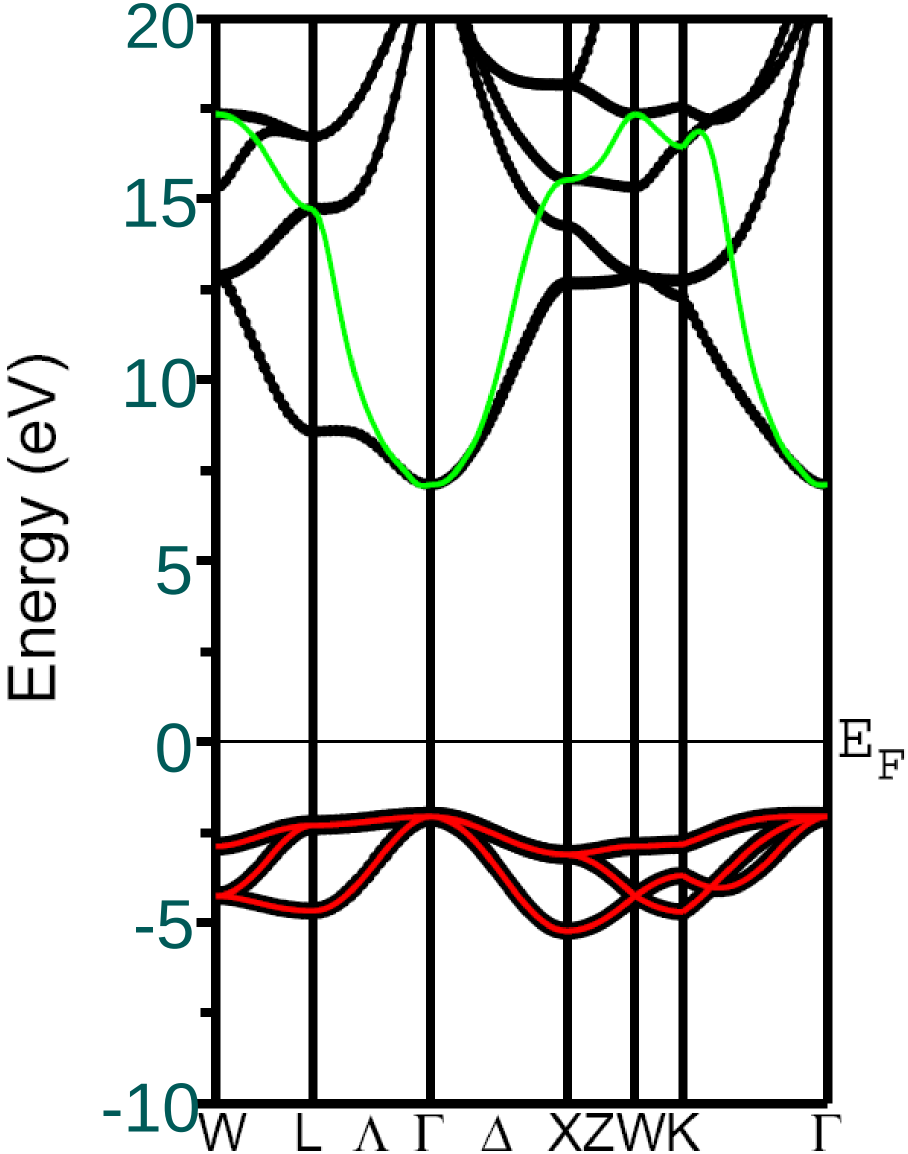
Inelastic X-ray scattering

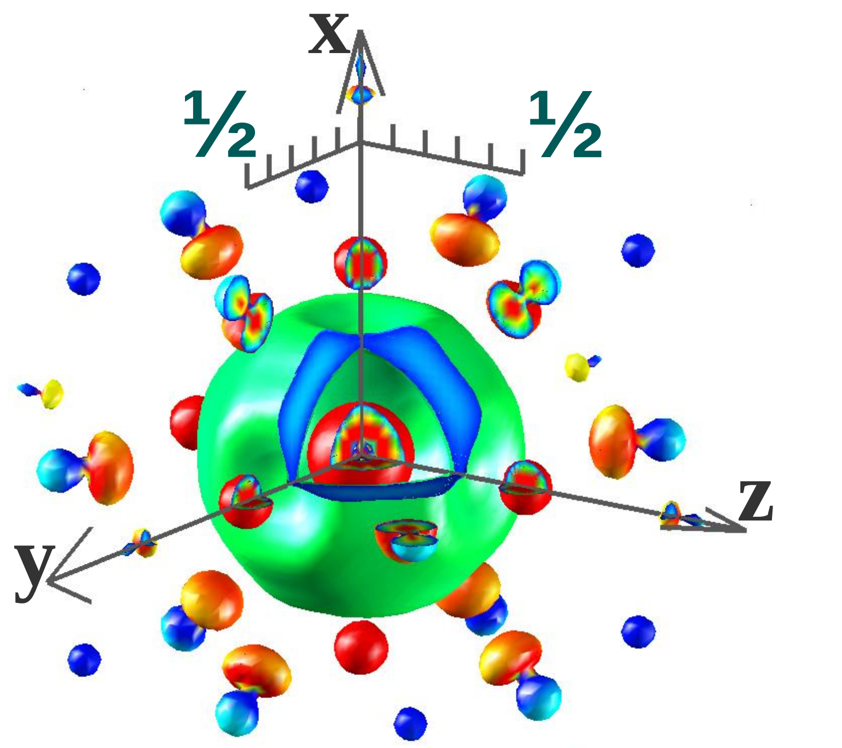
- Structured spectral weight
- Clear dispersion at large *q* !
- observe *fs* dynamics

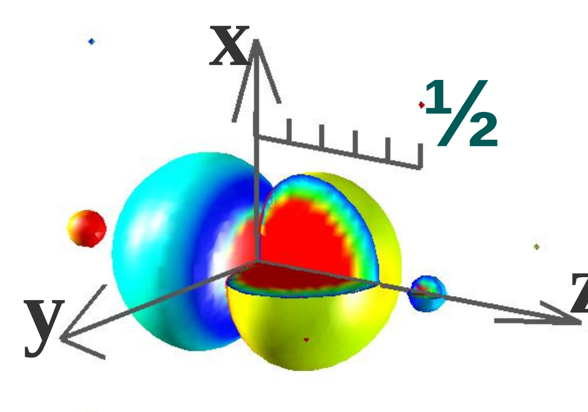


P. Abbamonte *et. al.*, PNAS 2008

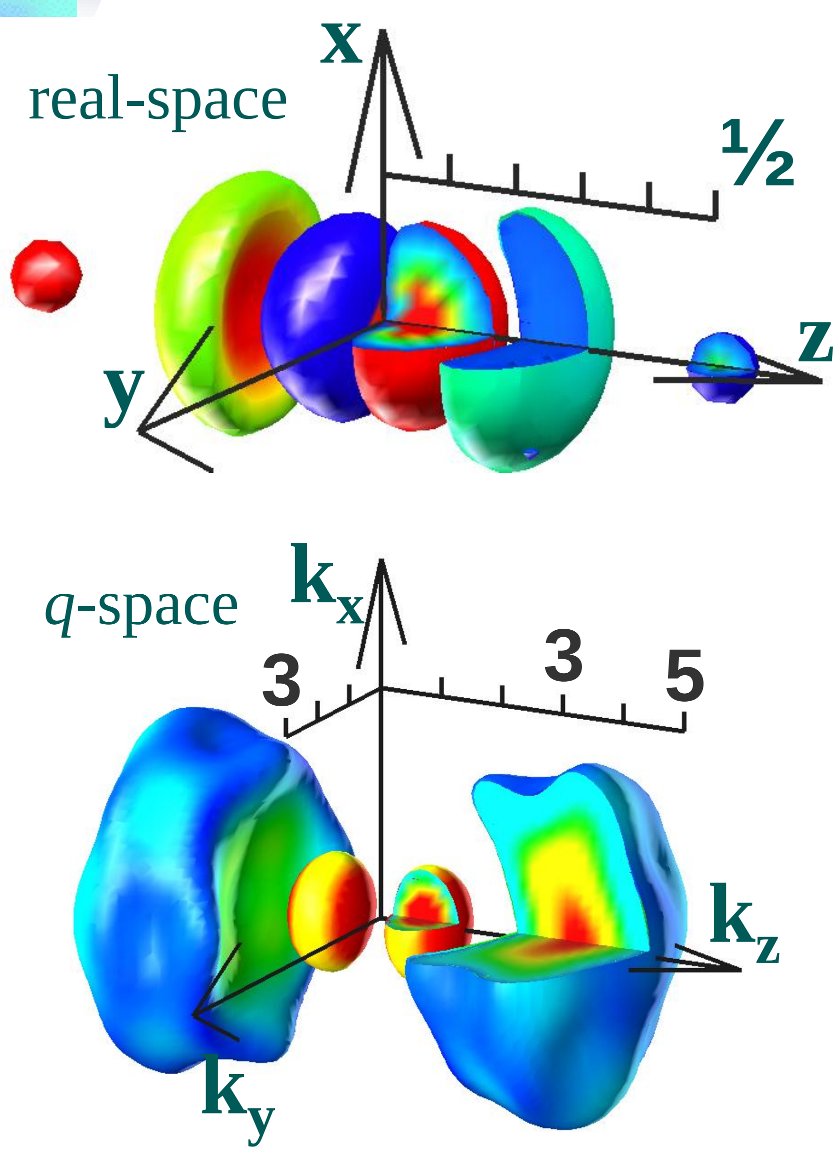
Excitons in LiF as a Frenkel Exciton in a “Super Atom”

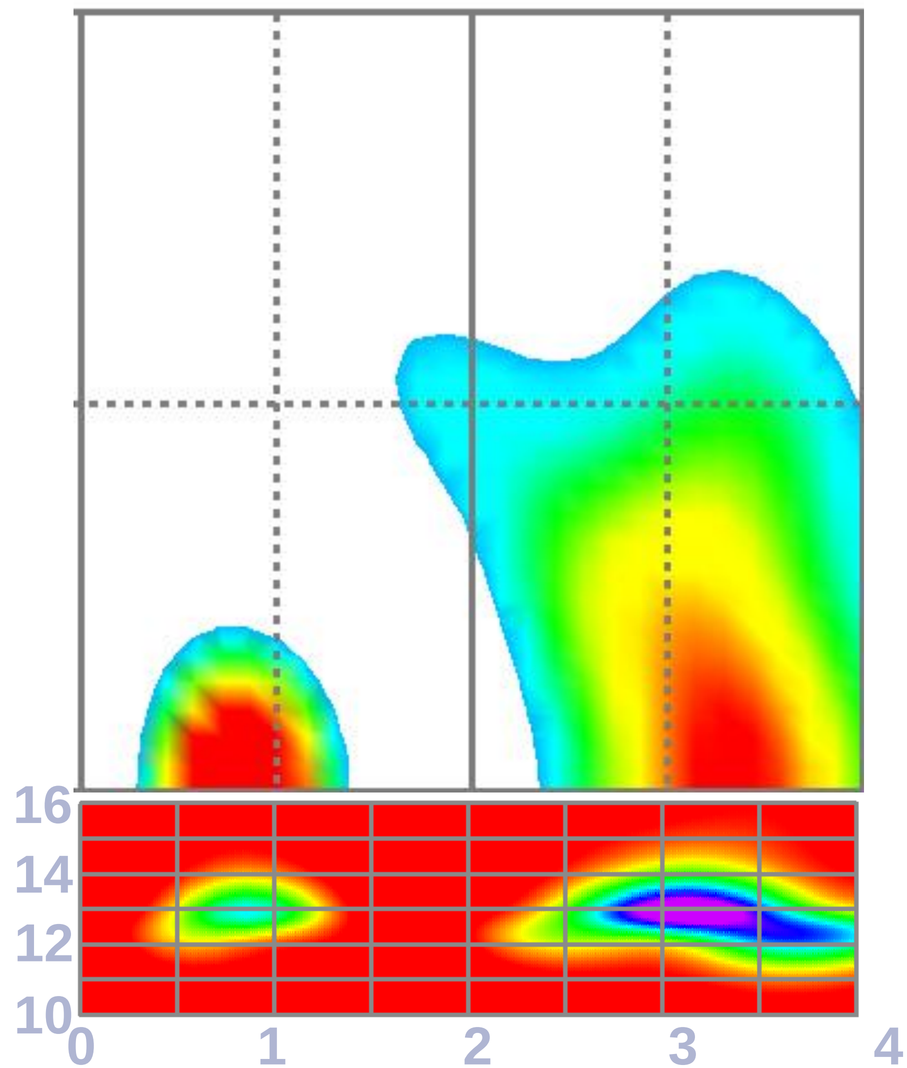






Matrix Element and Structure in *q*-space





q = 0~1.5 Intensity divided by 2.6

P. Abbamonte *et al.*, PNAS 2008

Propagation of tightly bound excitons

- Treat tightly bound excitons (and other local excitations) as a composite boson. Define its propagation kinetic kernel T via local and full propagator $D[H_L]$ and $D[H]$:

$$D[H] = D[H_L] + D[H_L]\,T\,D[H]$$

- T integrates out all the pair fluctuation in space and encapsulates propagation and decay processes.
- We then approximate T using unbound exciton propagator

$$T = D^{-1}[H_L] - D^{-1}[H] \sim D_0^{-1}[G[H_L]] - D_0^{-1}[G[H]]$$

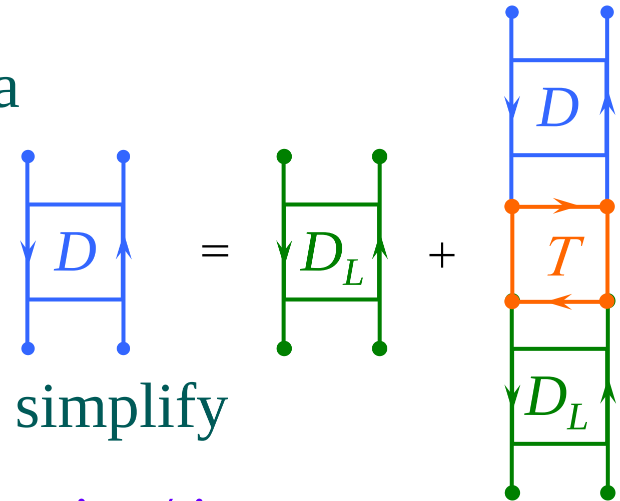
- Separation of local many-body problem from non-local propagation
- Many orders of magnitudes cheaper than Bethe-Salpeter equation

C-C Lee *et al.*, Phys. Rev. Lett. **111**, 157401 (2013)

Effective Two-Particle Hopping

Define effective two particle kinetic kernel T via

$$D[H] = D[H_L] + D[H_L]TD[H]$$



in the basis of local bound pair $b^+_{RN} \equiv c^+_{Rp} c_{Rh}$ and simplify

same location/time $Rpt\ Rht$

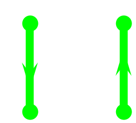
$$T = D^{-1}[H_L] - D^{-1}[H]$$

$$= \left(D_0^{-1}\left[G[H_L]\right] - I[H_L]\right) - \left(D_0^{-1}\left[G[H]\right] - I[H]\right)$$

$$\simeq D_0^{-1}\left[G[H_L]\right] - D_0^{-1}\left[G[H]\right]$$

using the empty bubble

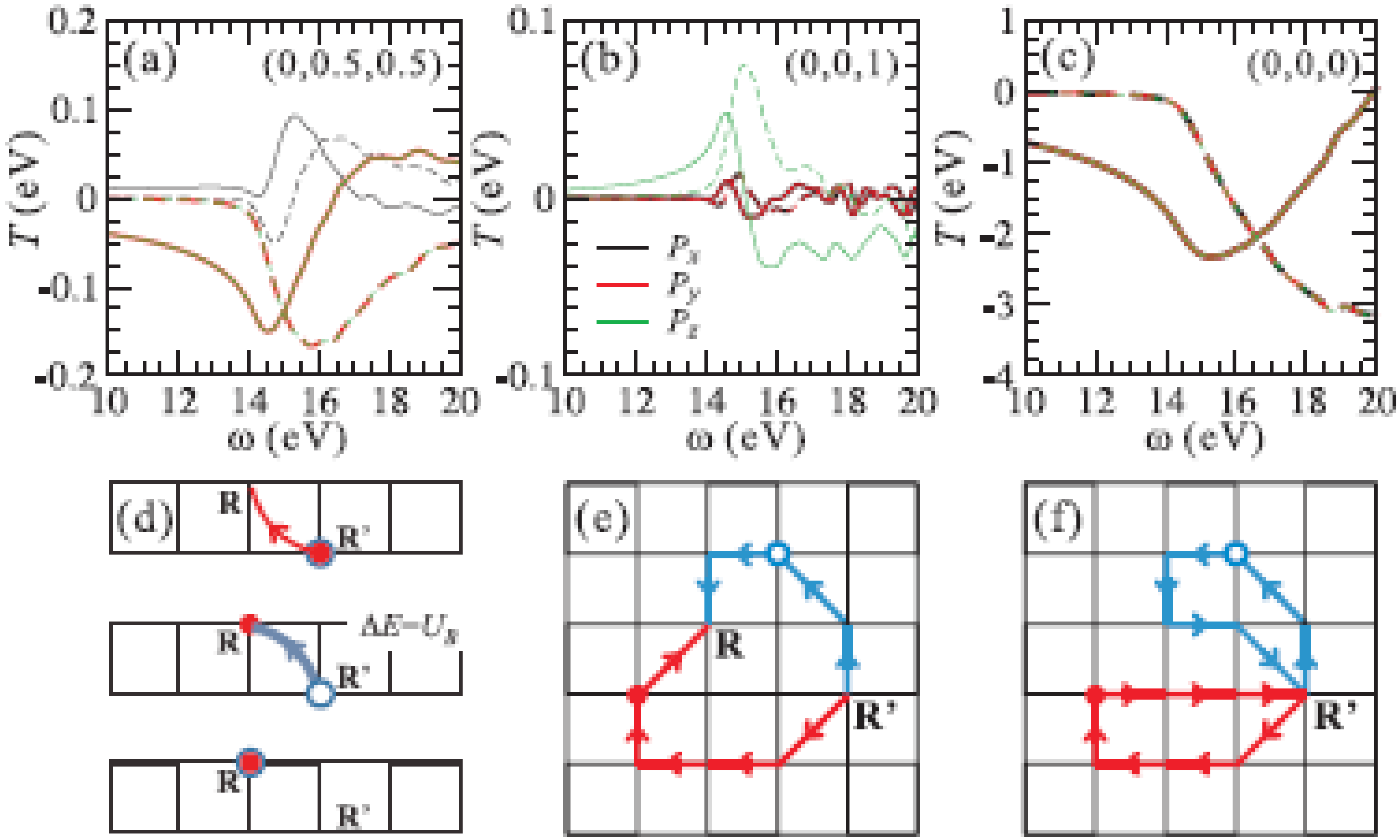
$$D_0(RN, R'N'; t, t') = G(Rp, R'p'; t, t')\, G(R'h', Rh; t', t)$$



T gives hopping of p-h pair in real space → dispersion in q-space

C-C Lee *et al.*, Phys. Rev. Lett. **111**, 157401 (2013)

Effective Two-Particle Hopping in LiF

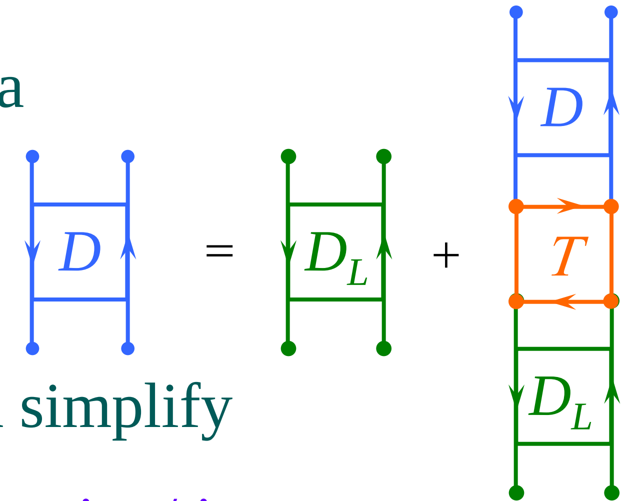


$T(\omega)$ is complex and strongly ω-dependent to fully account for

1. Landau continuum (integrating out virtual pair breaking processes) → exact for $E_b = 0$
2. Lower mobility with stronger p-h binding → correct t^2/E_b behavior
3. Renormalization of on-site energy from kinetic energy

Effective Two-Particle Hopping

Define effective two particle kinetic kernel *T* via



$$D[H] = D[H_L] + D[H_L]TD[H]$$

in the basis of local bound pair $b^+_{RN} \equiv c^+_{Rp} c_{Rh}$ and simplify

same location/time

Rpt Rht

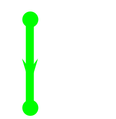
$$T = D^{-1}[H_L] - D^{-1}[H_L]$$

$$= \left(D_0^{-1}\left[G[H_L]\right] - I[H_L]\right) - \left(D_0^{-1}\left[G[H]\right] - I[H]\right)$$

$$\simeq D_0^{-1}\left[G[H_L]\right] - D_0^{-1}\left[G[H]\right]$$

using the empty bubble

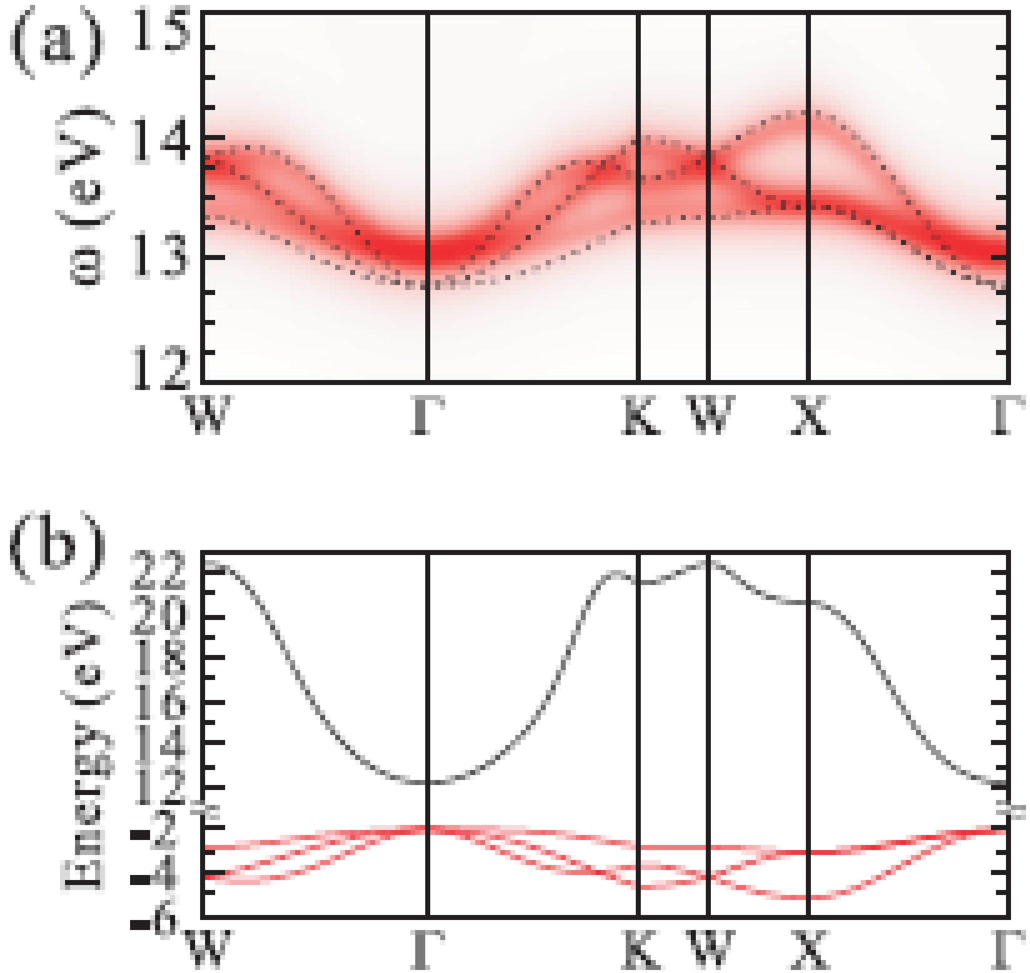
$$D_0(RN, R'N'; t, t') = G(Rp, R'p'; t, t')\,G(R'h', Rh; t', t)$$



T gives hopping of p-h pair in real space → dispersion in *q*-space

C-C Lee *et al.*, Phys. Rev. Lett. **111**, 157401 (2013)

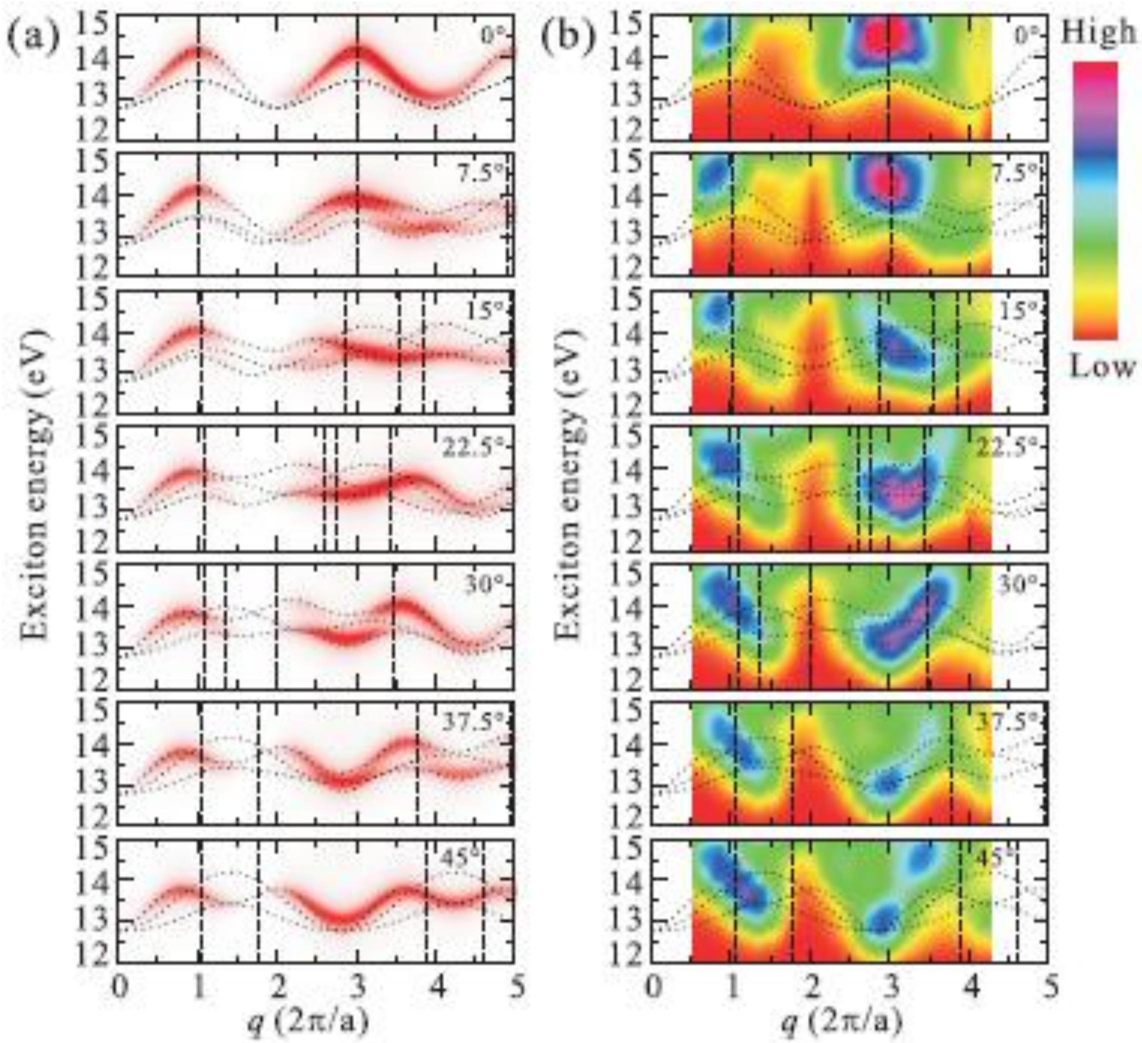
Exciton Band Structure



1. Full results similar to the diagonalization of $\omega_{exciton} + \mathrm{Re}\,T\left(\tilde{\omega}_{exciton}\right)$
2. Similar dispersion to the F *p*-bands (same symmetry)

C-C Lee *et al.*, Phys. Rev. Lett. **111**, 157401 (2013)

Observation of Multiple Exciton Bands



1. Similar weight in momentum space
2. Similar dispersion
3. Switching of bands (breaks in intensity)

Future development: systems with stronger correlation one scenario within DOE-CMSN

DFT (SIC, LDA+U)
→ Bloch states & eigenenergies

- complete basis in large energy scale
- reasonable energy resolution
- proper hybridization

Wannier Construction
→ Wannier states
→ full lattice Hamiltonian

- multiple energy resolution
- localized basis
- non-perturbative inclusion of hybridization

Numerical Canonical Transformation
→ reduced effective Hamiltonian

- numerical renormalization group
- effective inclusion of high-energy excitation
- 1st-principles derivation of few-band “model”

QMC, FLEX, DMFA, DCA
→ physical observables

- careful treatment of quantum correlation
- dynamical excitation spectrum
- long range order
- phase transition
- volume collapse