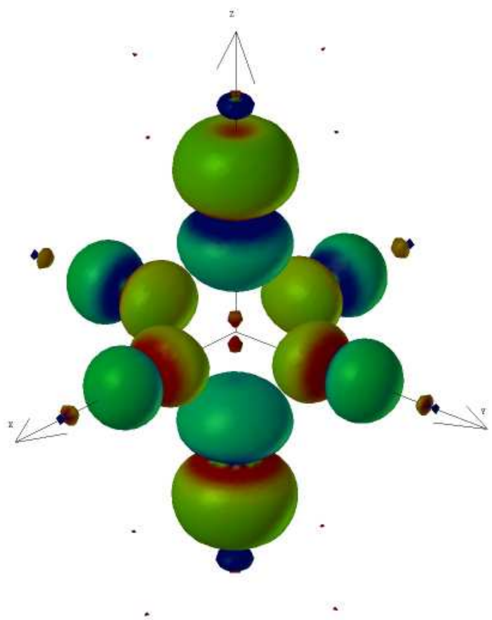
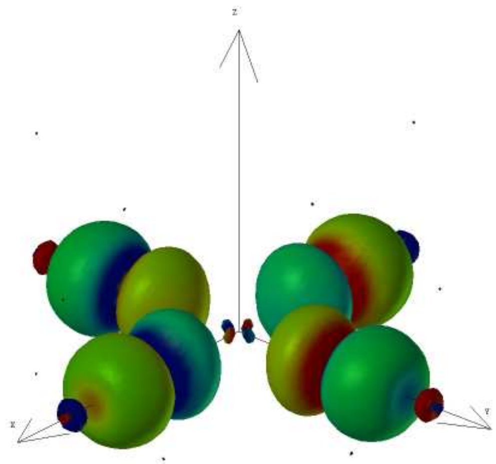
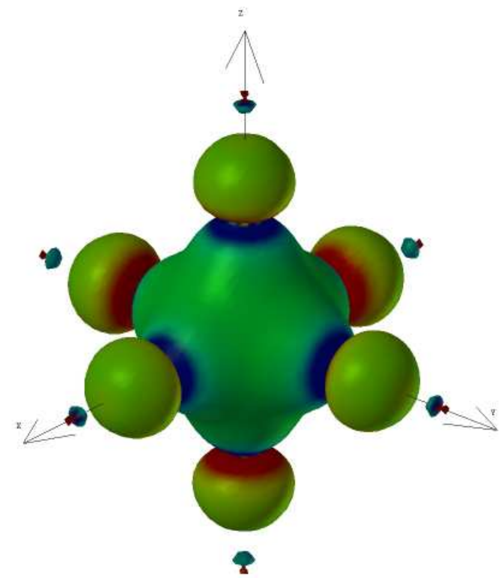
"Super atom" approach to local excitations in strongly correlated systems

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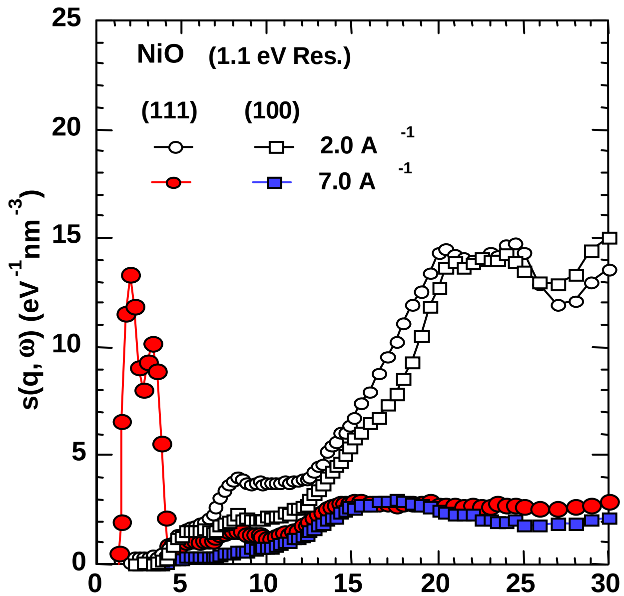
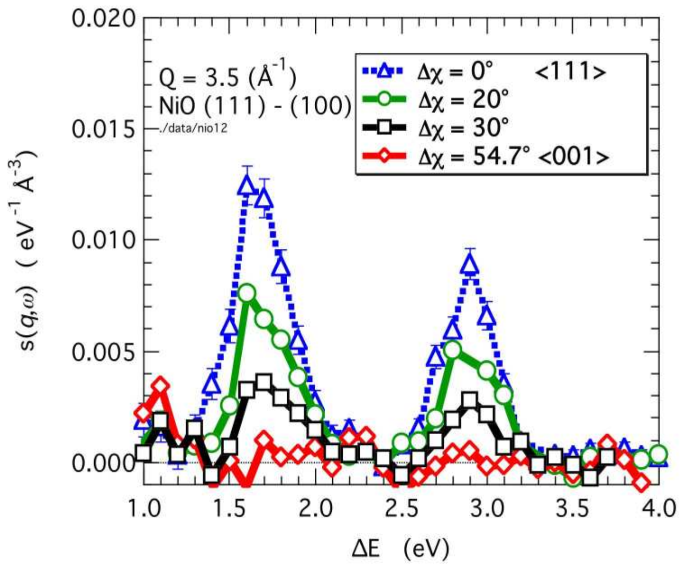
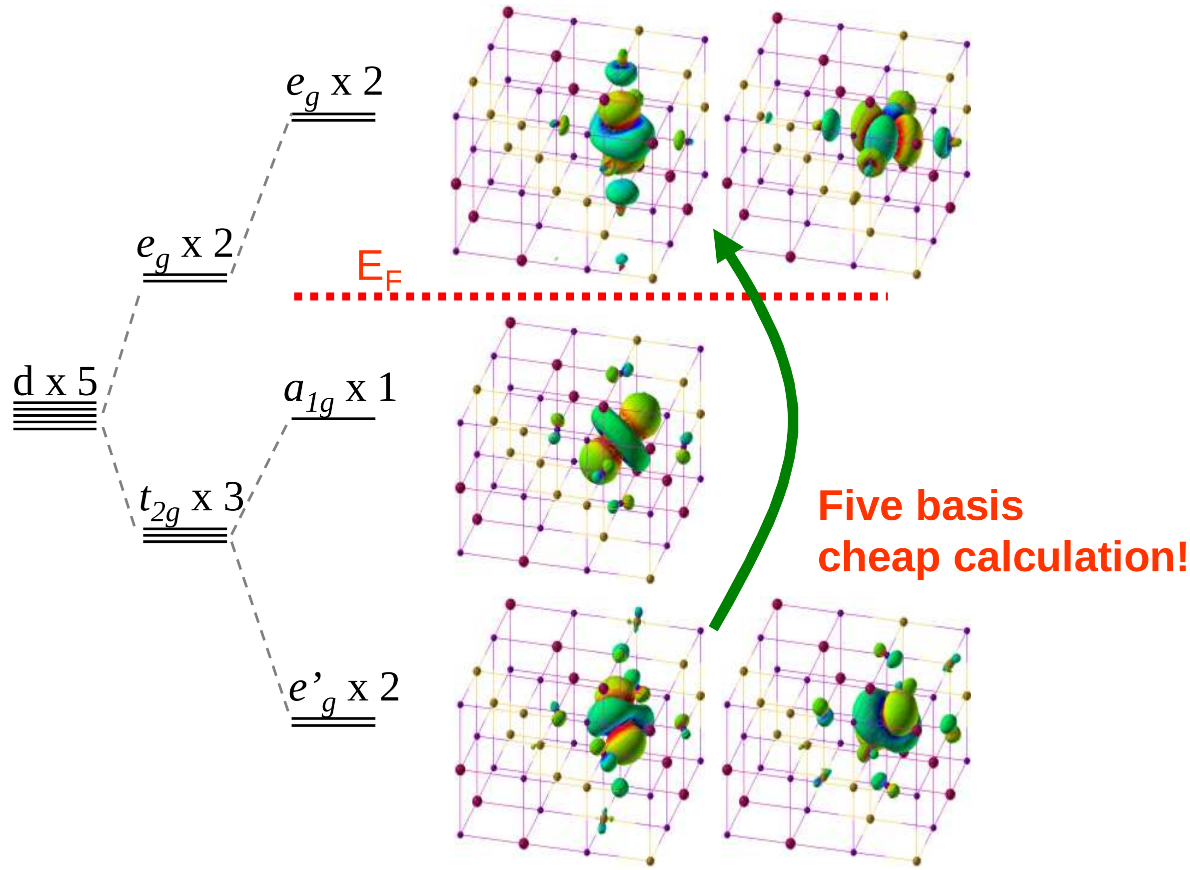
Introduction

- NIXS found in-gap *d*-*d* excitation in Mott-insulator NiO
- BSE with Hartree-Fock-type kernel not working
- Local many-body Hamiltonian investigation
- Super atom concept in Wannier basis
- Many-body excitation and density response function

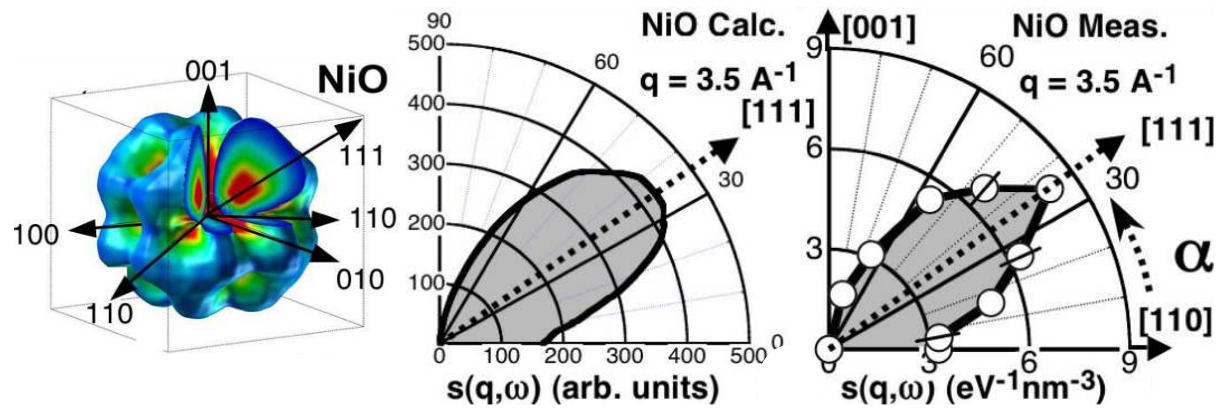
NIXS experiment for NiO*







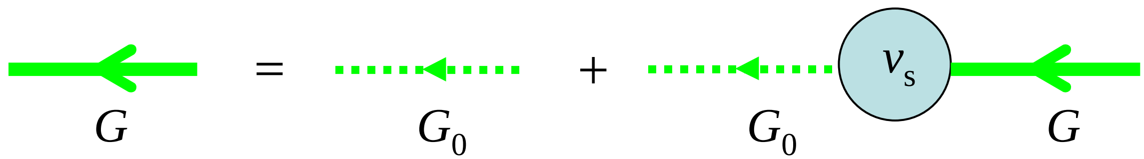
$$\chi(\mathbf{q},\mathbf{q}';w)=\sum_{11'}\left\langle 1\left|e^{-i\mathbf{q}\cdot\hat{\mathbf{x}}}\right|1'\right\rangle\left\langle 1'\left|e^{i\mathbf{q}'\cdot\hat{\mathbf{x}}}\right|1\right\rangle L(1,1';1',1;w)$$

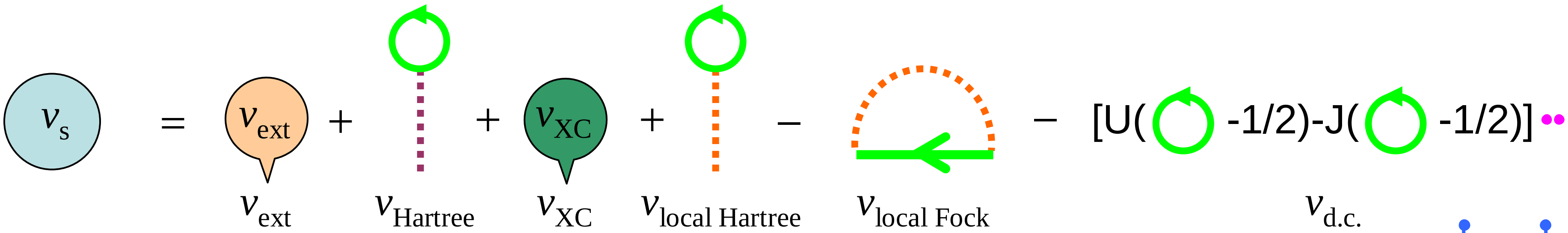


*B. C. Larson *et al.*, PRL **99**, 026401 (2007)

Linear response within TDDFT via LDA+U energy functional (TDLDA+U)

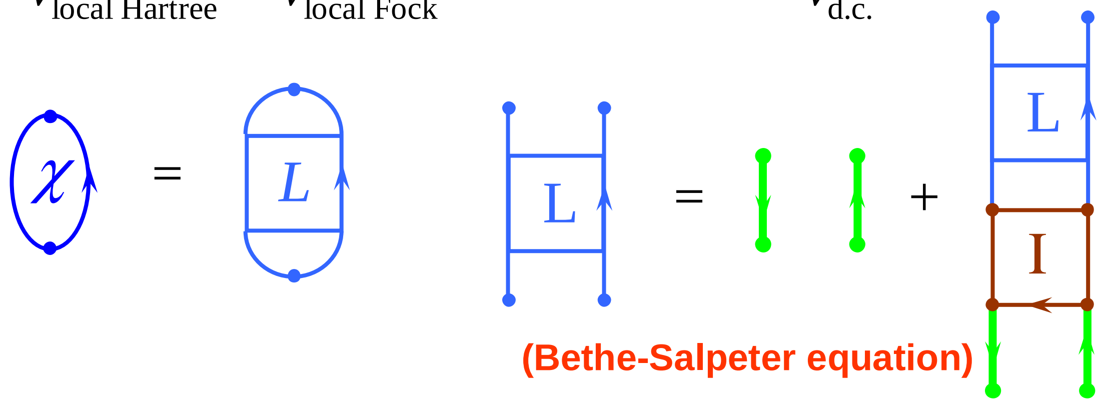
equation of motion

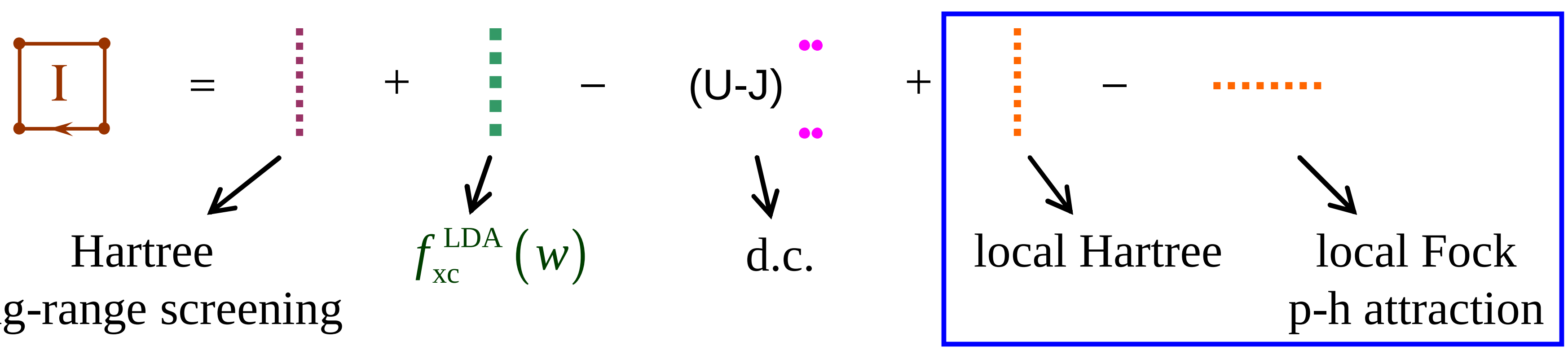




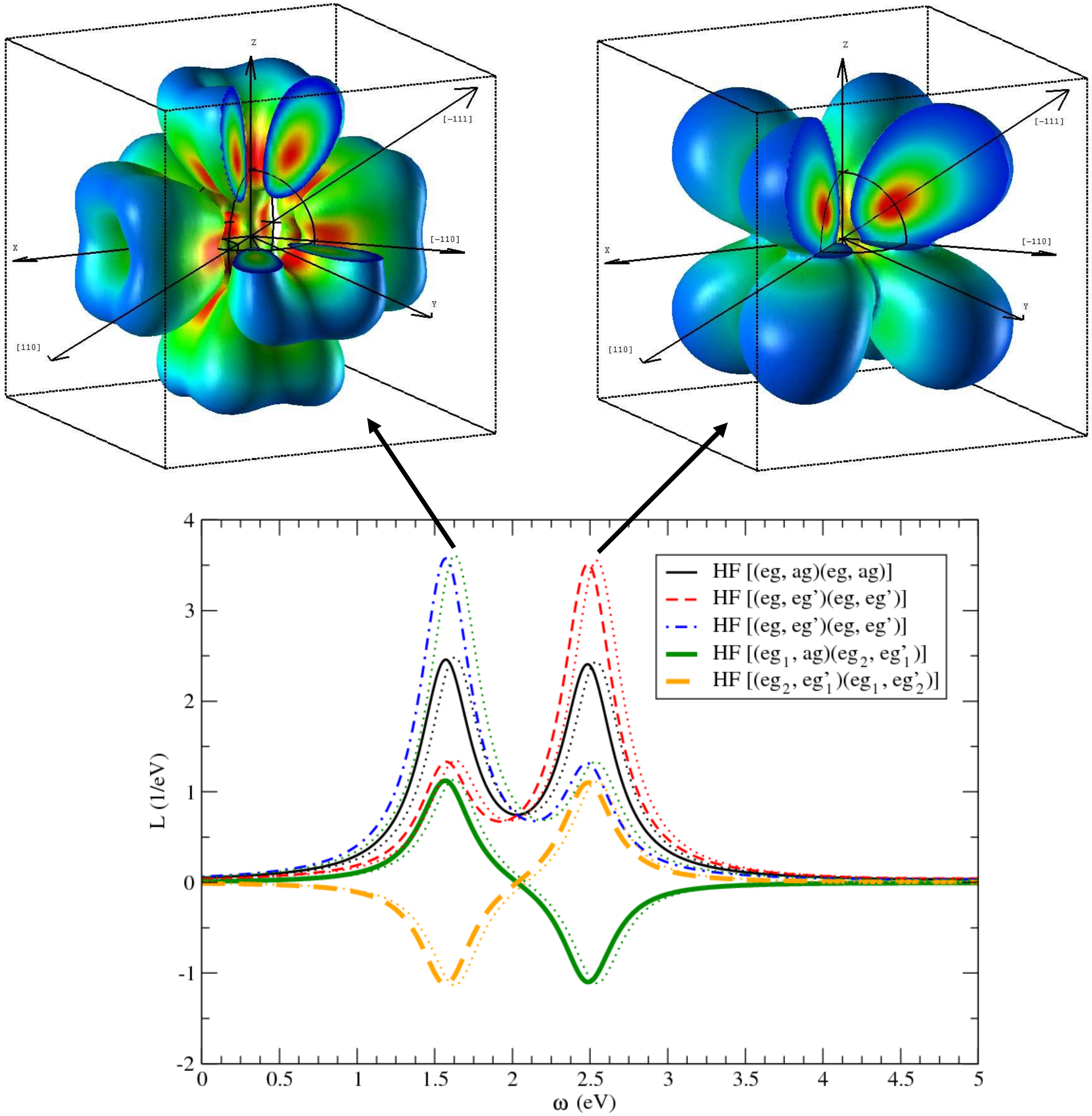
response function

$$L = \frac{\delta G}{\delta v_{ext}} = -G\frac{\delta G^{-1}}{\delta v_{ext}}G$$





Bethe-Salpeter solution with local Hartree-Fock interaction



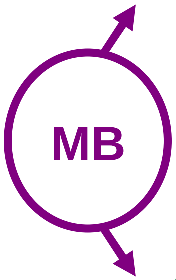
Perturbation not working ! ➔ Many-body diagonalization is necessary !

Local many-body Hamiltonian for strongly correlated systems

H_{LDA+U} :

$$E^{LDA+U}[\rho^\sigma(\vec{r}),\{n^\sigma\}] = E^{LSDA}[\rho^\sigma(\vec{r})] + E^U[\{n^\sigma\}] - E_{dc}[\{n^\sigma\}]$$

$$E^U[\{n\}] = \frac{1}{2}\sum_{\{m\},\sigma}\{<m,m''|V_{ee}|m',m'''> n^\sigma_{mm'} n^{-\sigma}_{m''m'''} + (<m,m''|V_{ee}|m',m'''> - <m,m''|V_{ee}|m''',m'>) n^\sigma_{mm'} n^\sigma_{m''m'''}\}$$



$$V^\sigma_{mm'} = \sum_{m''m'''}\{<m',m''|V_{ee}|m,m'''> n^{-\sigma}_{m''m'''} + (<m',m''|V_{ee}|m,m'''> - <m',m''|V_{ee}|m''',m>) n^\sigma_{m''m'''}\}$$
$$-U(n-\frac{1}{2}) + J(n^\sigma - \frac{1}{2})$$

$$H_{LDA+U} = \sum_{Rm,R'm',\sigma} \underline{t^\sigma_{Rm,R'm'}} C^+_{Rm\sigma} C_{R'm'\sigma} = \sum_{Rm,R'm',\sigma} \underline{\langle WF_{Rm}|\hat{H}^\sigma_{LDA+U}|WF_{R'm'}\rangle} C^+_{Rm\sigma} C_{R'm'\sigma}$$

$$H = H_{local} + H_{nonlocal} = T^\sigma_{ij} C^+_{i\sigma} C_{j\sigma} + \frac{1}{2} V_{ijkl} C^+_{i\sigma} C^+_{j\sigma'} C_{l\sigma'} C_{k\sigma} + T^\sigma_{ij} C^+_{i\sigma} C_{j\sigma}$$

H_{SCHF} :

$$H^{HF}_{local} = T^\sigma_{ij} C^+_{i\sigma} C_{j\sigma} + (V^{eff}_{kilj} < C^+_{k\sigma'} C_{l\sigma'} > - \delta_{\sigma\sigma'} V^{eff}_{kijl} < C^+_{k\sigma} C_{l\sigma} >) C^+_{i\sigma} C_{j\sigma}$$

$$H^{HF}_{local} = \underline{T^\sigma_{ij}} C^+_{i\sigma} C_{j\sigma} + \underline{\varepsilon^{-1}} U^\sigma_{ij} C^+_{i\sigma} C_{j\sigma} \; ; \; U^\sigma_{ij} = (V^{eff}_{kilj} - \delta_{\sigma\sigma'} V^{eff}_{kijl}) < C^+_{k\sigma'} C_{l\sigma'} >$$ ← **LDA+U**

Fitting :

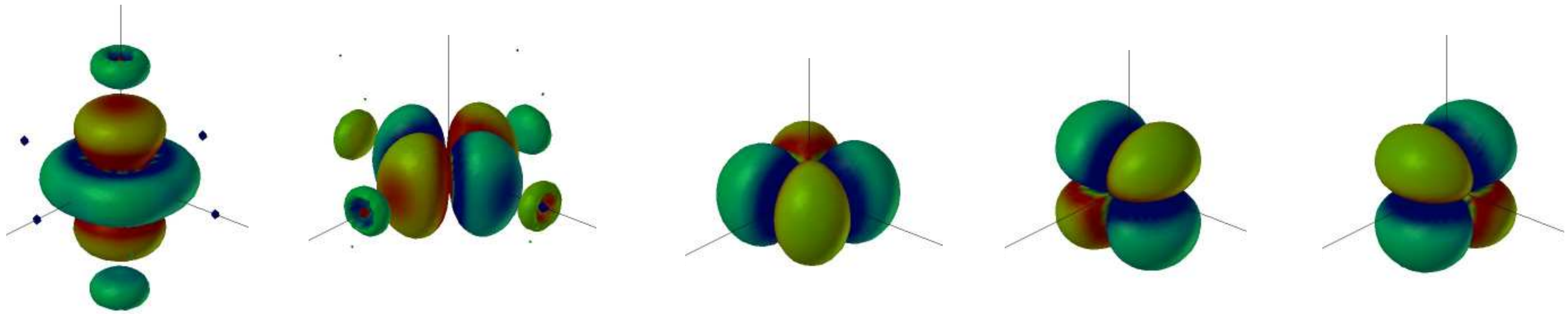
$$F = \sum_{ij\sigma} (\underline{t^\sigma_{ij}} - \underline{T^\sigma_{ij}} - \underline{\varepsilon^{-1}} \underline{U^\sigma_{ij}})^2 \; ; \; T^\uparrow_{ii} = T^\downarrow_{ii}$$

Dielectric constant ~ 1

We can safely choose atomic Coulomb matrix elements in many-body Hamiltonian

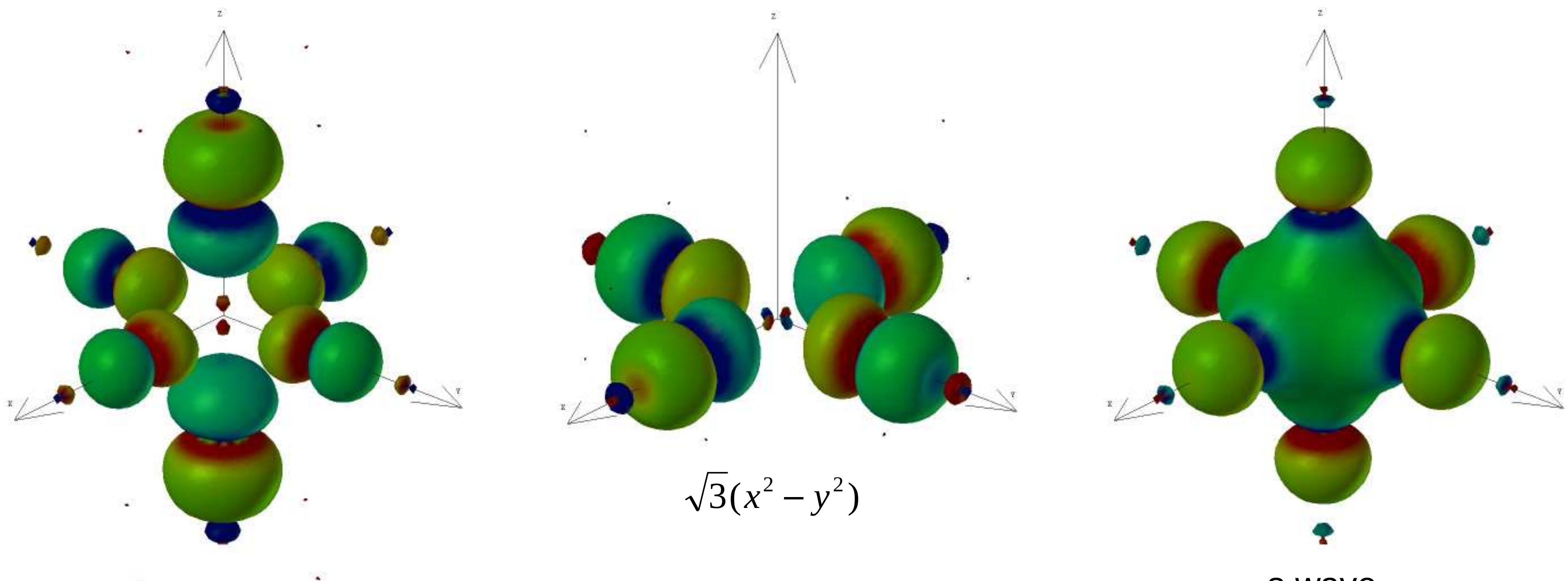
Super atom for charge transfer insulator

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

Enlarge the contribution of "local atom"

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

(exact) **(perturbation)**

$\langle WF_{0m} | \hat{H}^{\sigma}_{LDA+U} | WF_{0m'} \rangle$:

(up)

	$3z^2-r^2$	$\sqrt{3}(x^2-y^2)$	yz	xz	xy	O s	O $3z^2-r^2$	O $\sqrt{3}(x^2-y^2)$
$3z^2-r^2$	4.06	0.00	0.00	0.00	0.00	0.00	1.84	0.00
$\sqrt{3}(x^2-y^2)$	0.00	4.06	0.00	0.00	0.00	0.00	0.00	1.84 → t_{pd}
yz	0.00	0.00	-2.95	0.00	0.00	0.00	0.00	0.00
xz	0.00	0.00	0.00	-2.95	0.00	0.00	0.00	0.00
xy	0.00	0.00	0.00	0.00	-2.95	0.00	0.00	0.00
O s	0.00	0.00	0.00	0.00	0.00	-4.01	0.00	0.00
O $3z^2-r^2$	1.84	0.00	0.00	0.00	0.00	0.00	-2.02	0.00
O $\sqrt{3}(x^2-y^2)$	0.00	1.84	0.00	0.00	0.00	0.00	0.00	-2.02

(down)

	$3z^2-r^2$	$\sqrt{3}(x^2-y^2)$	yz	xz	xy	O s	O $3z^2-r^2$	O $\sqrt{3}(x^2-y^2)$
$3z^2-r^2$	-5.06	0.00	0.00	0.00	0.00	0.00	1.81	0.00
$\sqrt{3}(x^2-y^2)$	0.00	-5.06	0.00	0.00	0.00	0.00	0.00	1.81
yz	0.00	0.00	-3.69	0.00	0.00	0.00	0.00	0.00
xz	0.00	0.00	0.00	-3.69	0.00	0.00	0.00	0.00
xy	0.00	0.00	0.00	0.00	-3.69	0.00	0.00	0.00
O s	0.00	0.00	0.00	0.00	0.00	-4.06	0.00	0.00
O $3z^2-r^2$	1.81	0.00	0.00	0.00	0.00	0.00	-2.02	0.00
O $\sqrt{3}(x^2-y^2)$	0.00	1.81	0.00	0.00	0.00	0.00	0.00	-2.02

Local density-density response function

$$H_{local} = T_{ij}^{\sigma} C_{i\sigma}^{+} C_{j\sigma} + \frac{1}{2} V_{ijkl} C_{i\sigma}^{+} C_{j\sigma'}^{+} C_{l\sigma'} C_{k\sigma}$$ (in Wannier basis)

one-particle Green's function
two-particle Green's function

$$\chi(\vec{q},\vec{q};\omega) = \sum_m \left(\frac{\left|\langle \Psi_m | \hat{\rho}(-\vec{q}) | \Psi_0 \rangle\right|^2}{\hbar\omega - (E_m - E_0) + i\eta} - \frac{\left|\langle \Psi_m | \hat{\rho}(\vec{q}) | \Psi_0 \rangle\right|^2}{\hbar\omega - (E_0 - E_m) - i\eta} \right)$$

T_{ij}^{local} :

$3z^2-r^2$	$\sqrt{3}(x^2-y^2)$	yz	xz	xy	O: s	O: $3z^2-r^2$	O: $\sqrt{3}(x^2-y^2)$
eg	0.00	0.00	0.00	0.00	0.00	1.84	0.00
0.00	eg	0.00	0.00	0.00	0.00	0.00	1.84
0.00	0.00	t2g↕	0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	t2g↕	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	t2g↕	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	-4.03↕	0.00	0.00
1.84	0.00	0.00	0.00	0.00	0.00	-2.02↕	0.00
0.00	1.84	0.00	0.00	0.00	0.00	0.00	-2.02↕

(up)

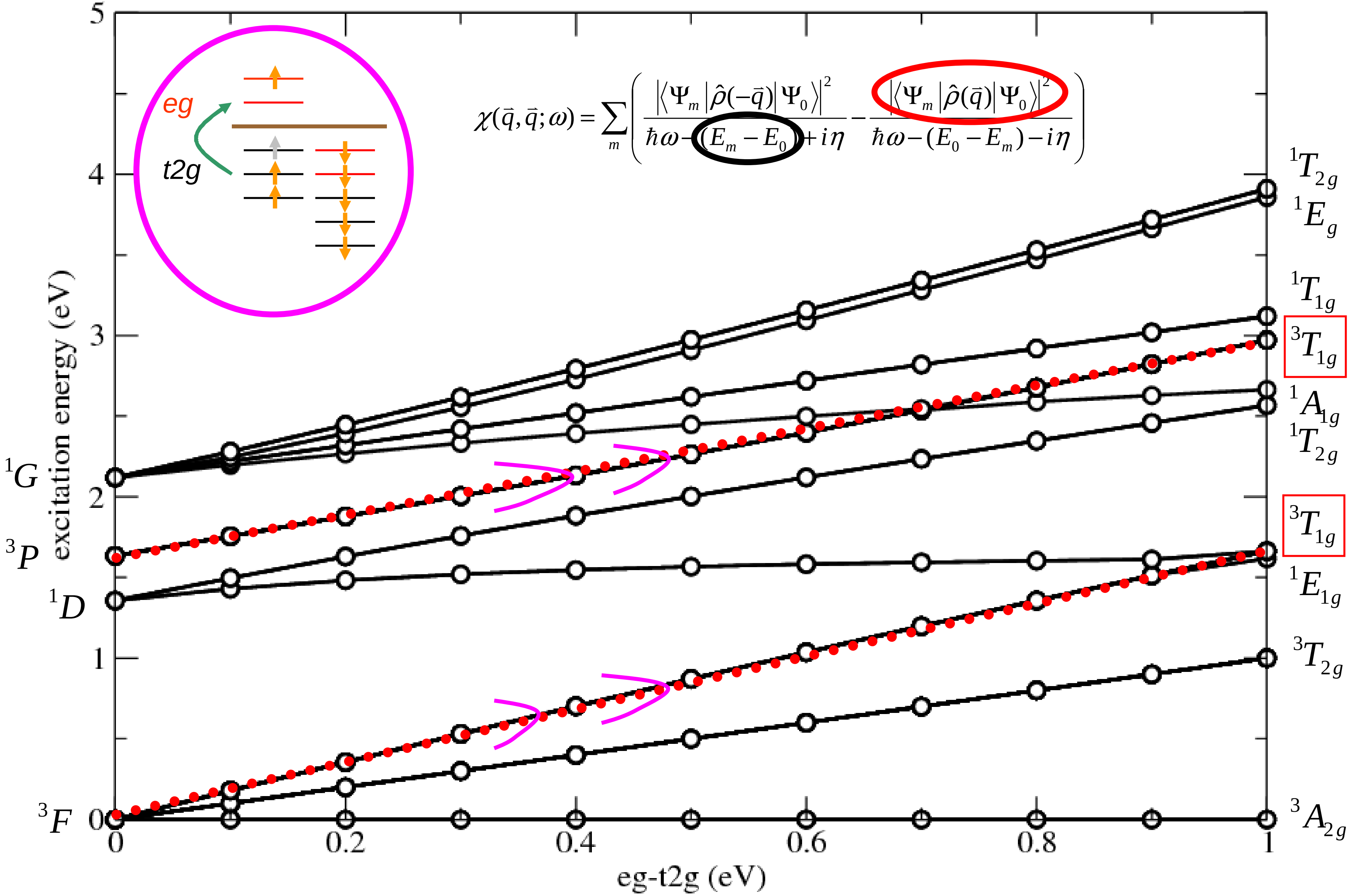
eg	0.00	0.00	0.00	0.00	0.00	1.81	0.00
0.00	eg	0.00	0.00	0.00	0.00	0.00	1.81
0.00	0.00	t2g	0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	t2g	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	t2g	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	-4.03	0.00	0.00
1.81	0.00	0.00	0.00	0.00	0.00	-2.02	0.00
0.00	1.81	0.00	0.00	0.00	0.00	0.00	-2.02

(down)

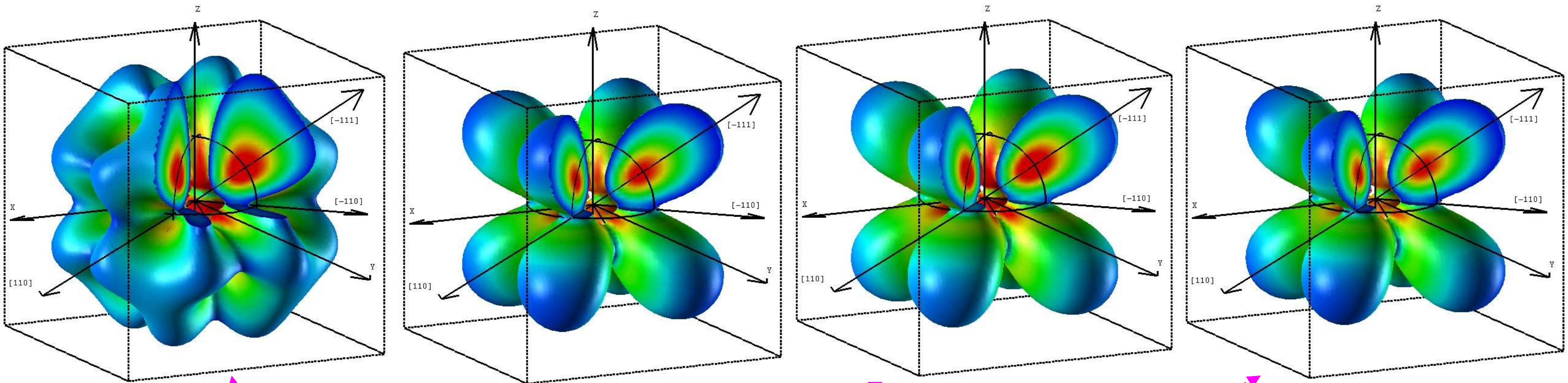
Many-body excitation for local atom

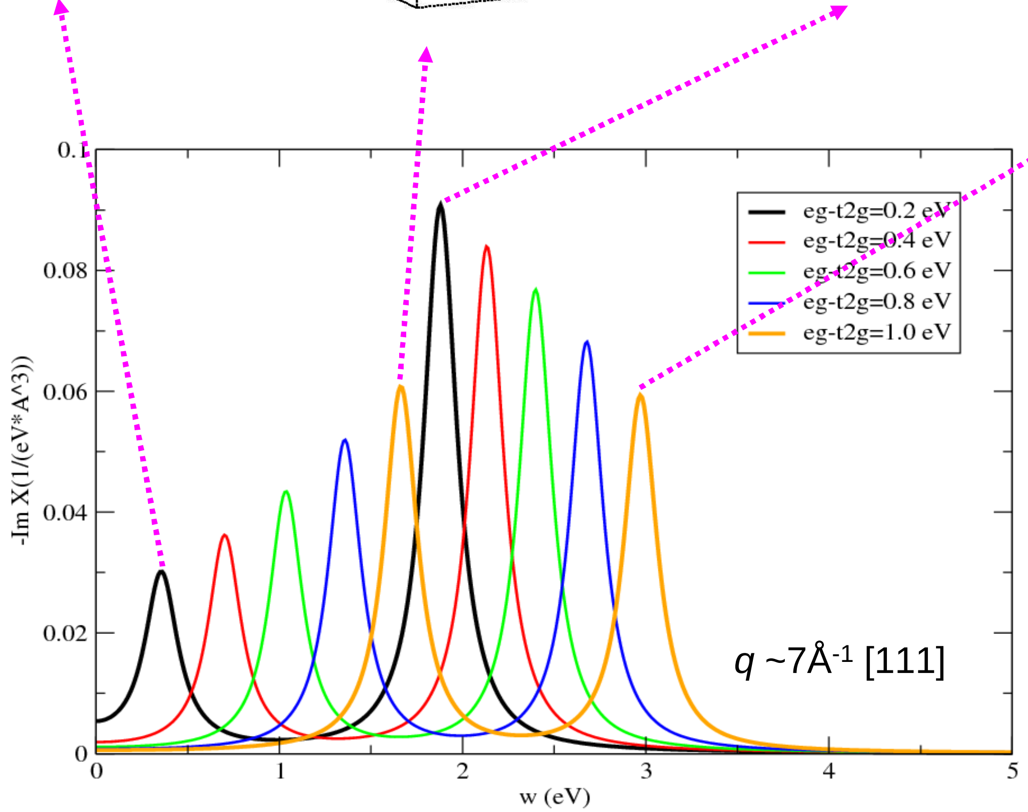
(eg-t2g=1eV to get experiment energy)

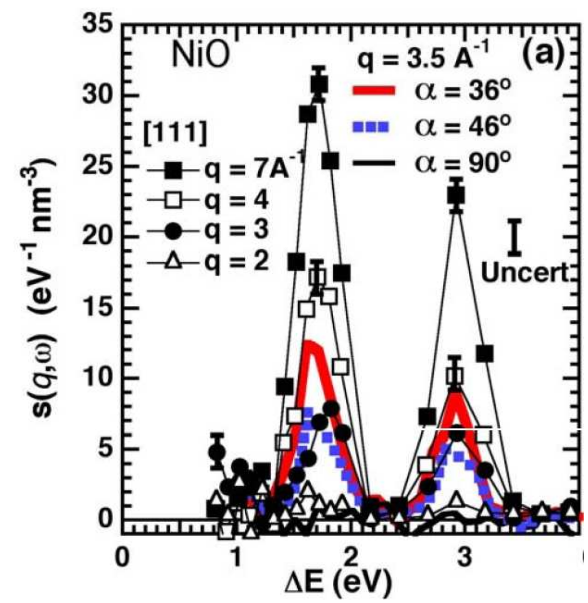
d **orbitals of Ni only, no super atom of O included**



Density response for Ni only

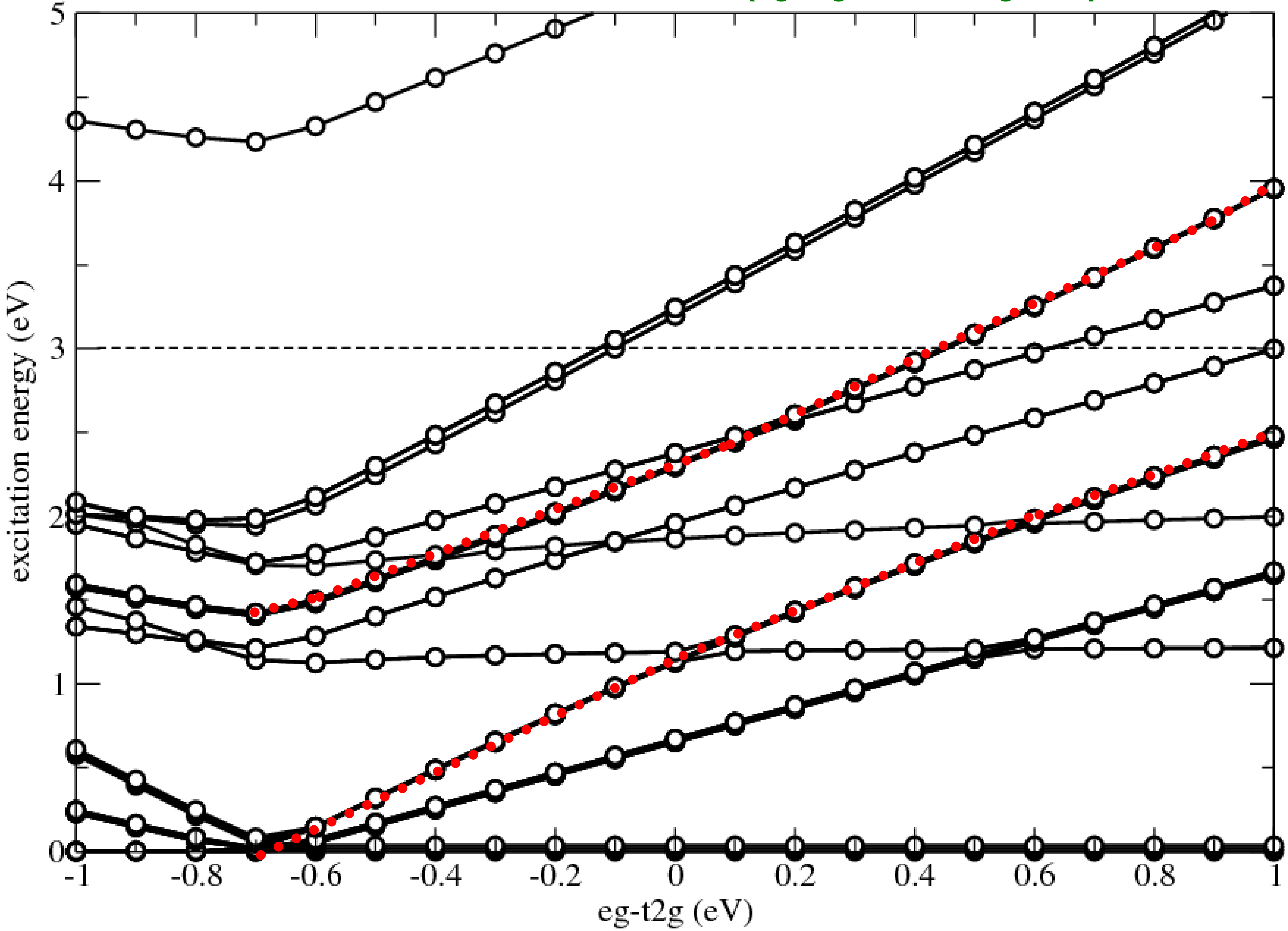




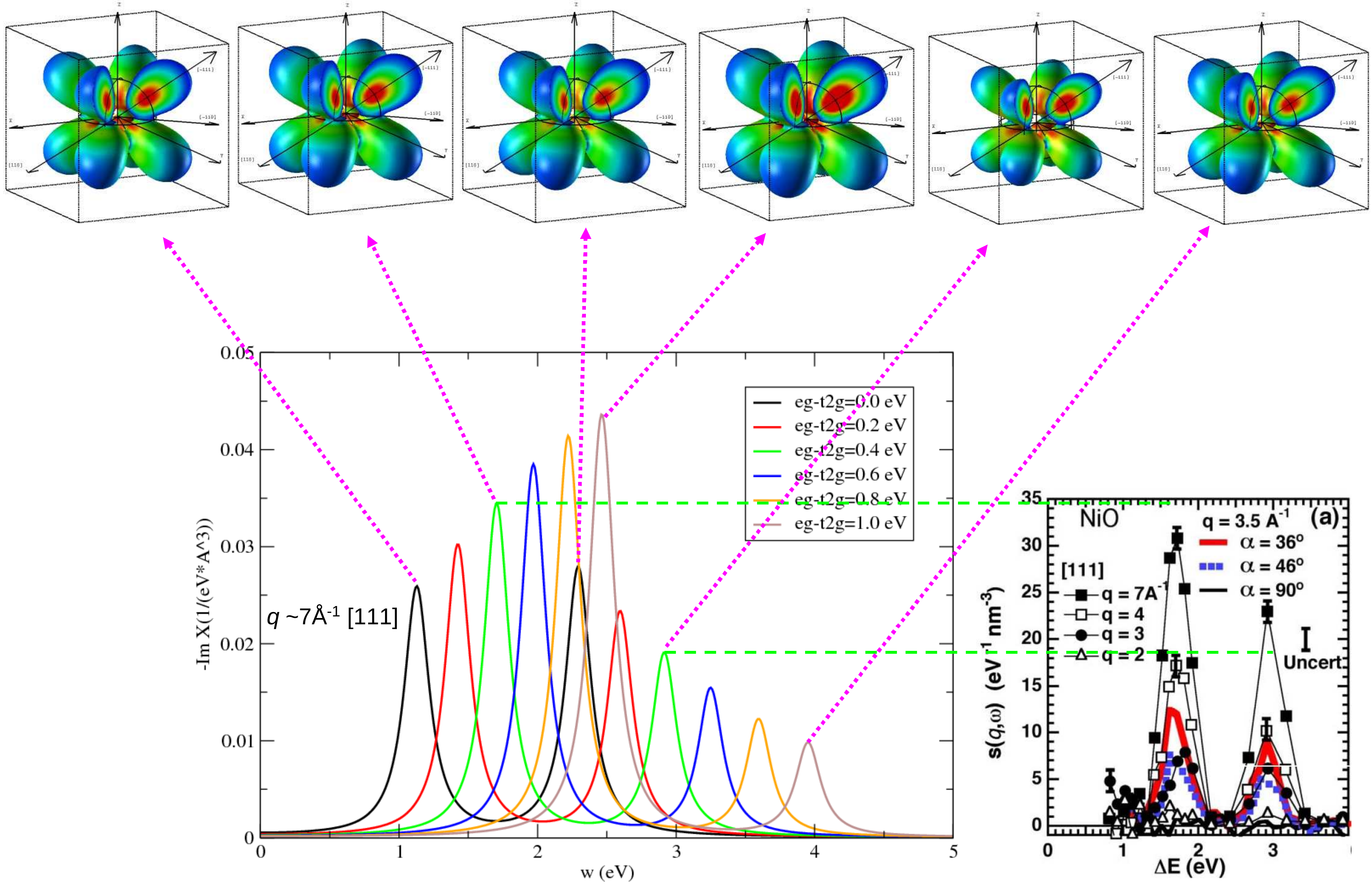


Many-body excitation with super atom of O

(eg-t2g=0.4eV to get experiment energy)

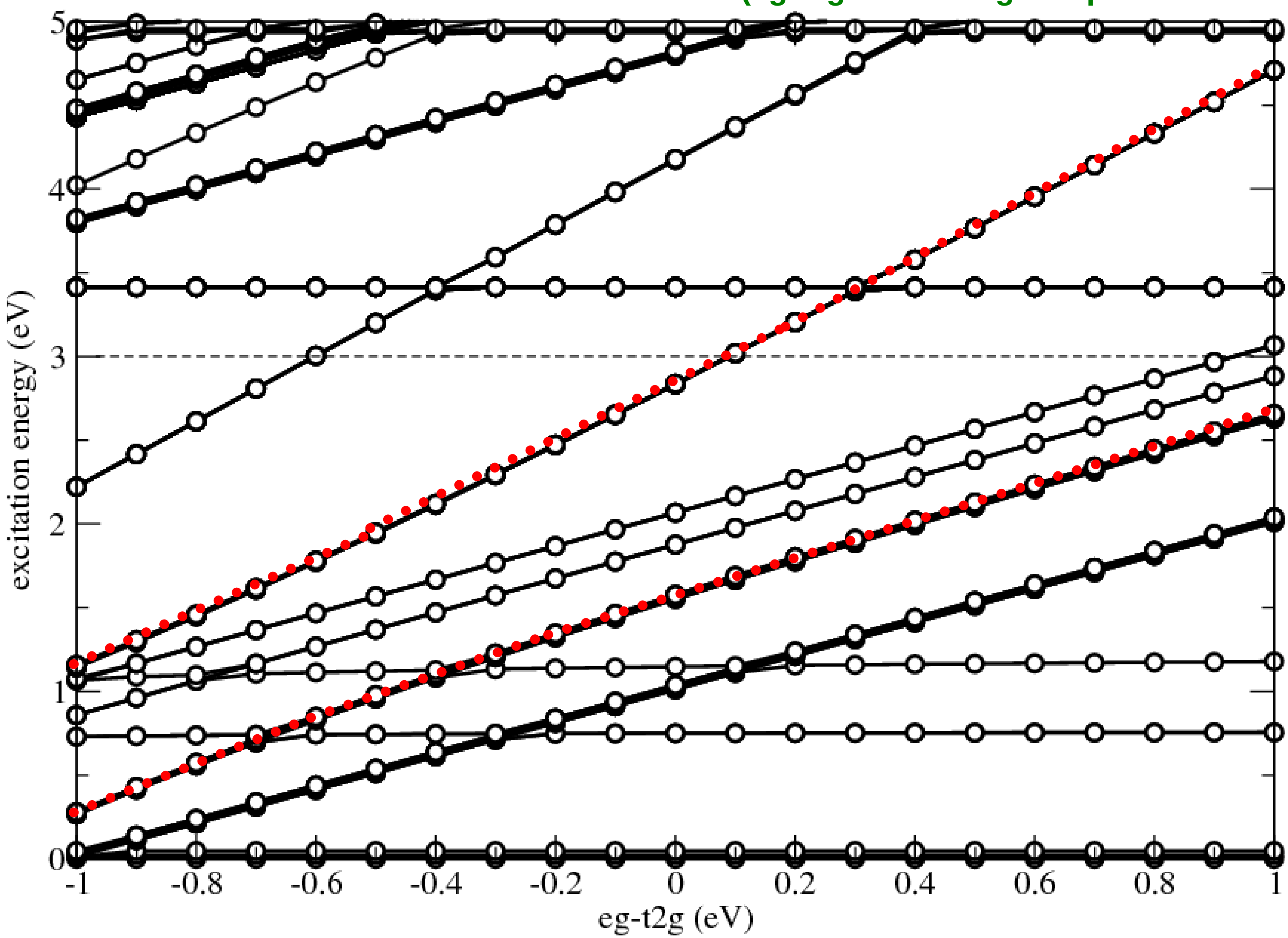


Density response with super atom

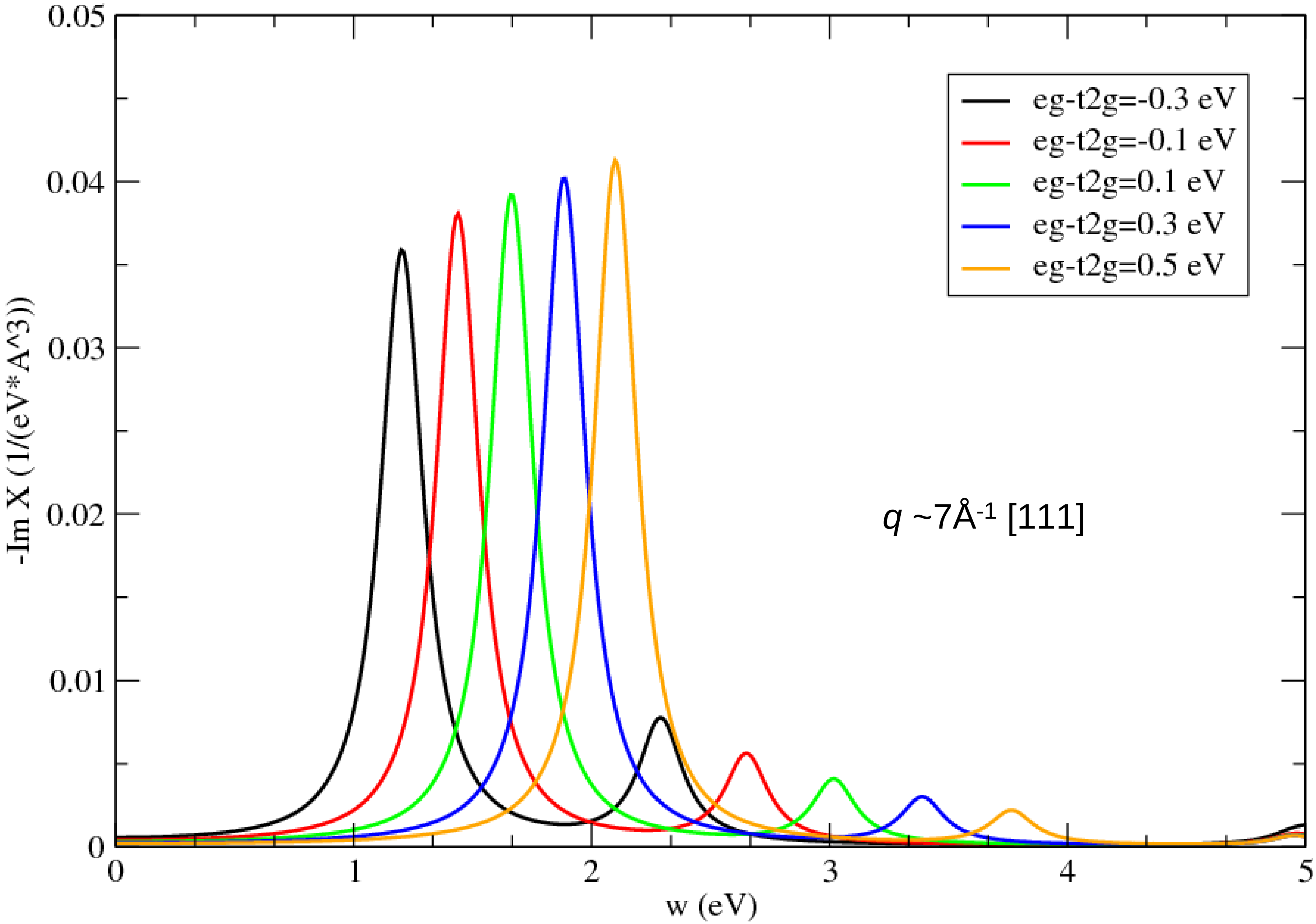


Many-body excitation with super atom of O (heighten O_{site} 3 eV)

(eg-t2g=0.1eV to get experiment energy)

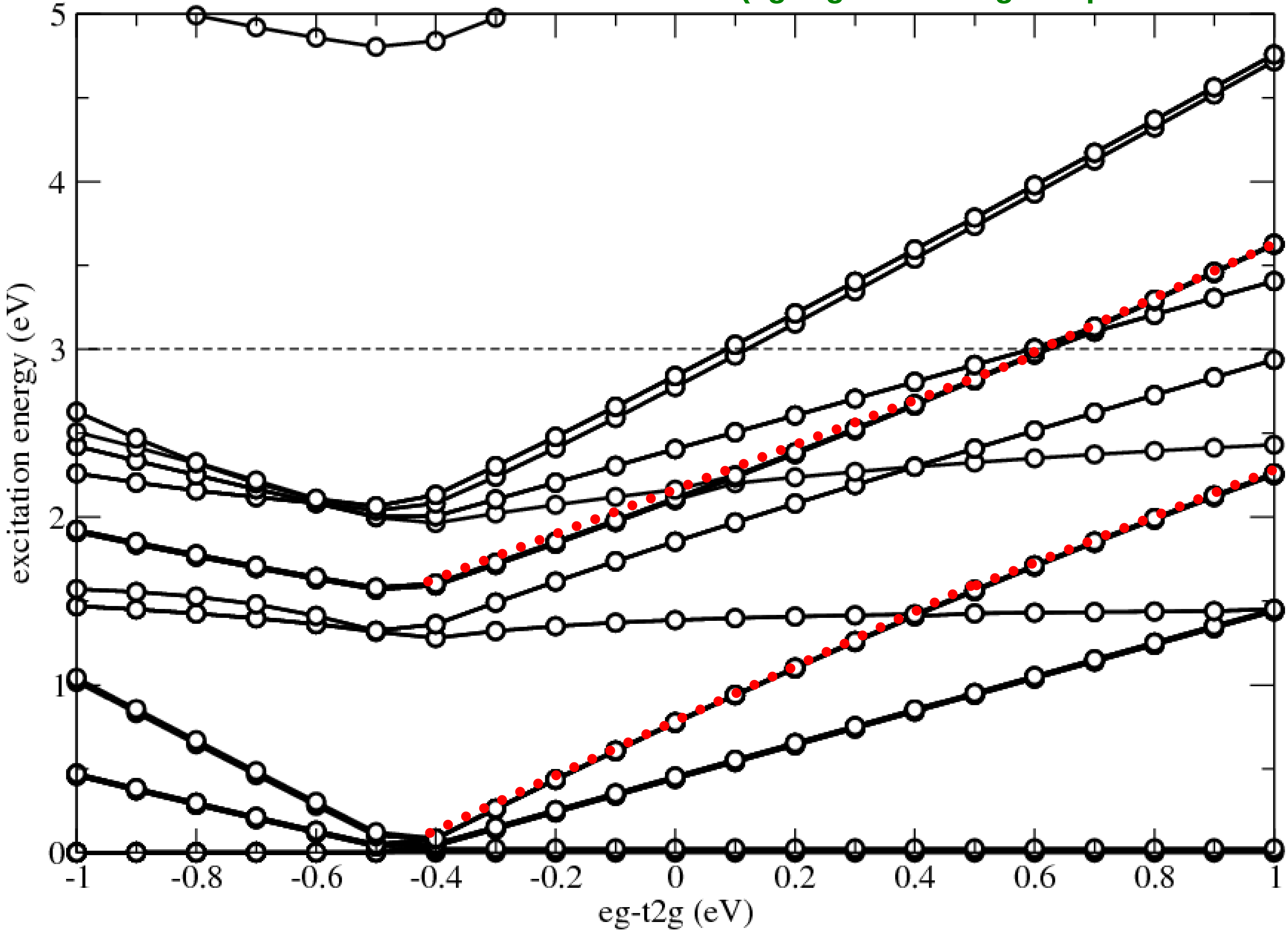


Density response with super atom (heighten O_{site} 3 eV)

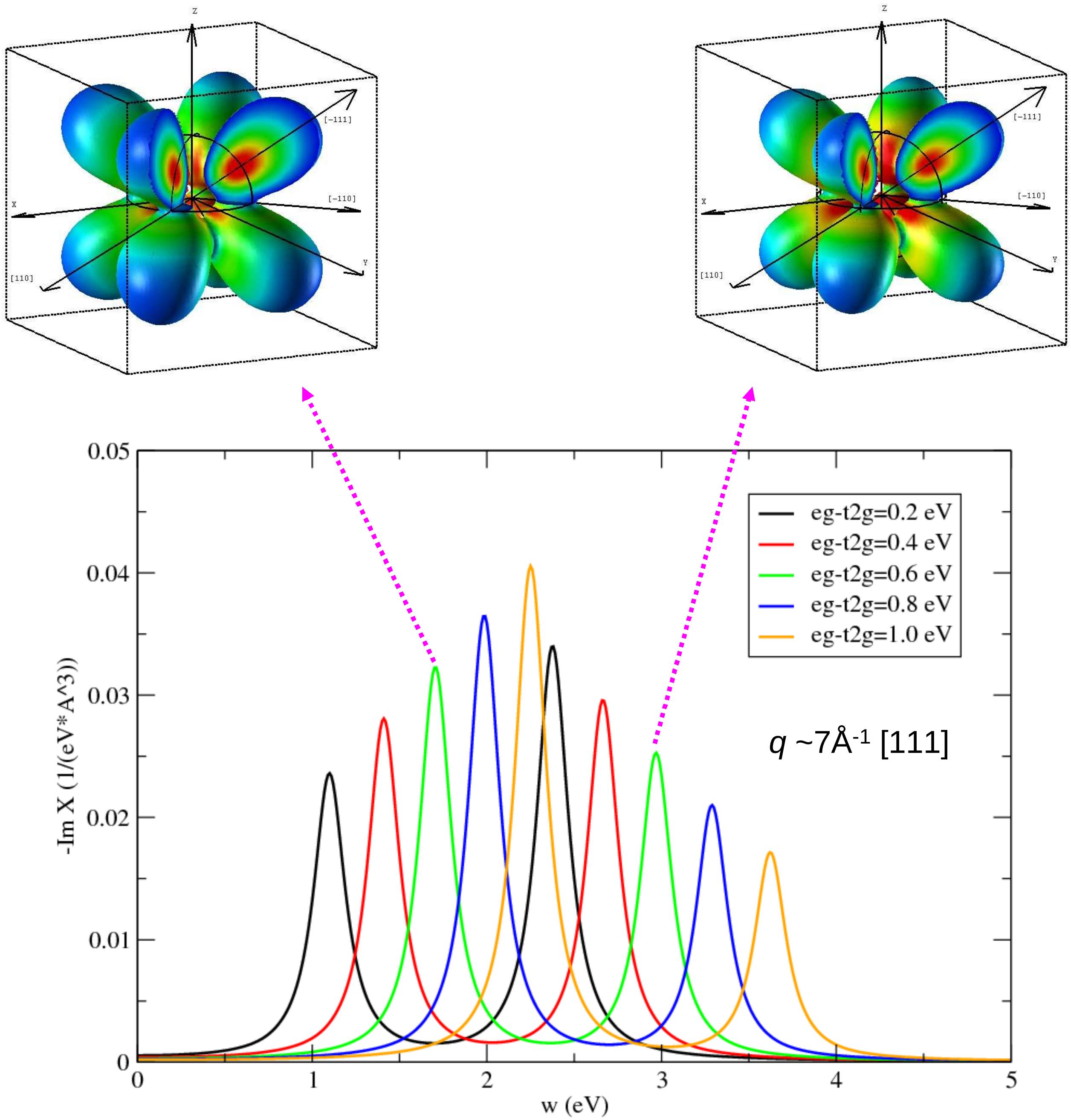


Many-body excitation with super atom of O (lower O_{site} 3 eV)

(eg-t2g=0.6eV to get experiment energy)

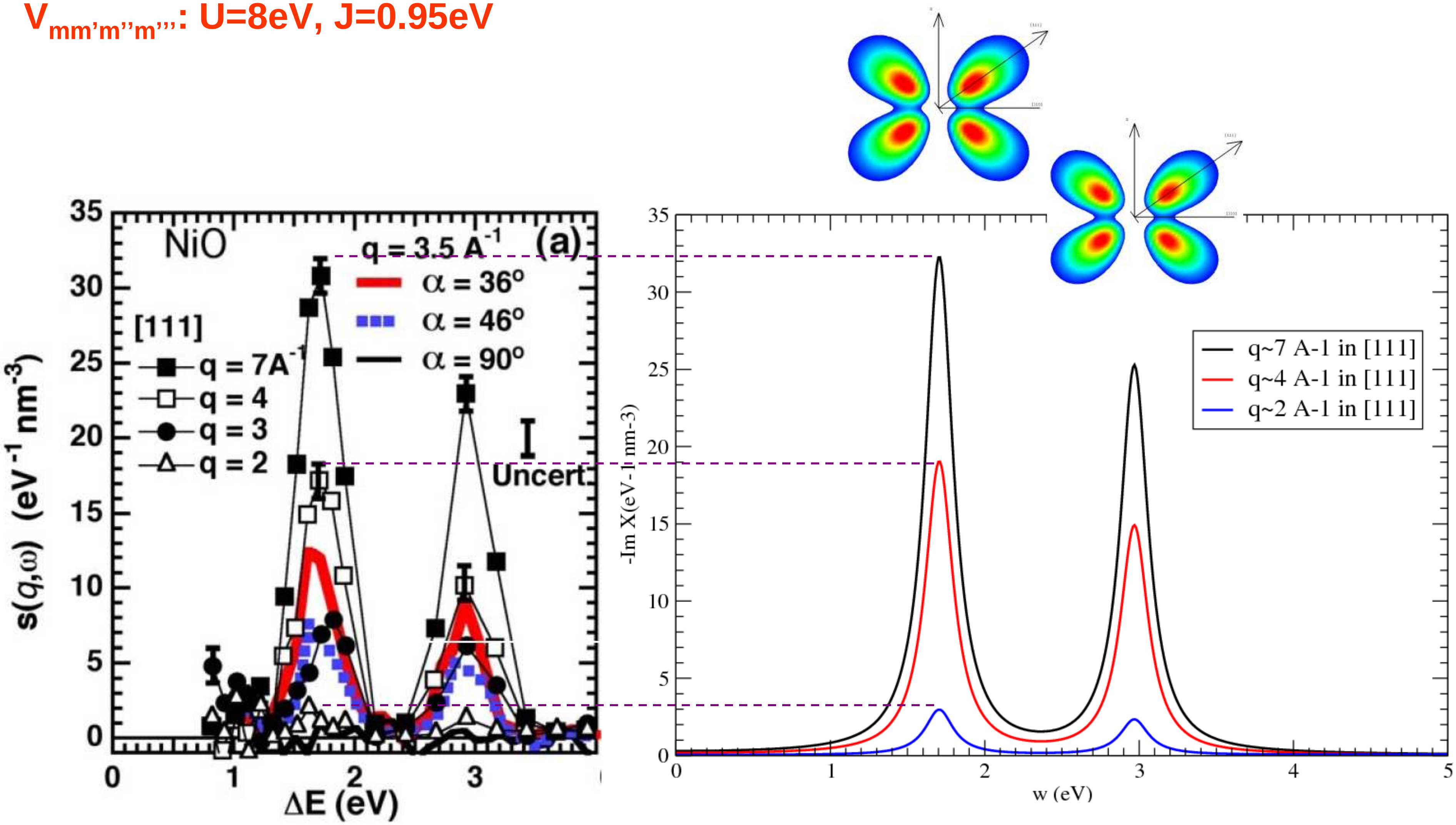


Density response with super atom (lower O_{site} 3 eV)



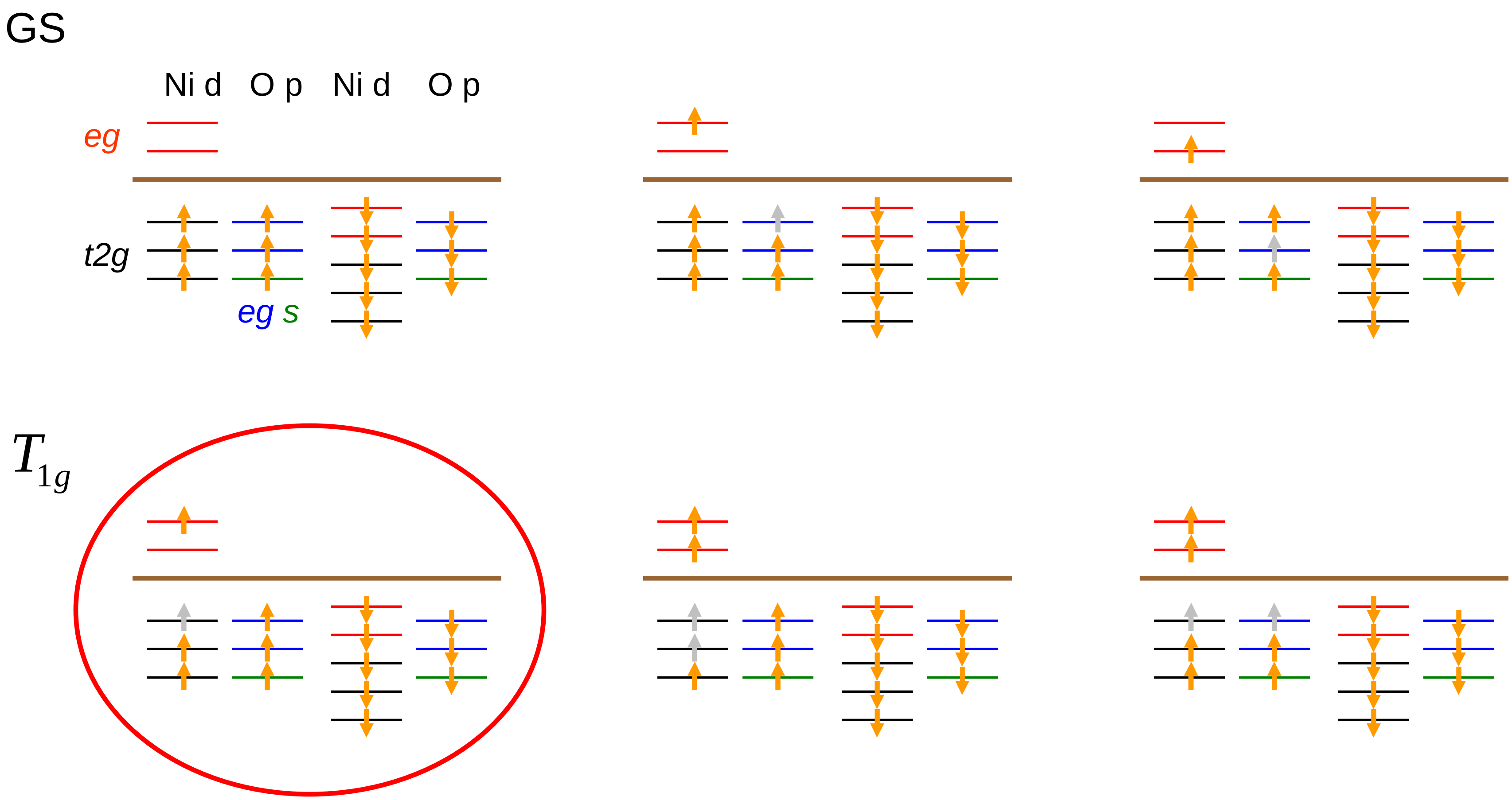
Density response with super atom

Ni_{eg}-Ni_{t2g}=0.6 eV
Ni_{eg}-O_{eg}=-54.62eV
$V_{mm'm''m'''}$: U=8eV, J=0.95eV



experiment calculation

Many-body basis



measured by NIXS

Summary

- Treat local Coulomb interaction as perturbation ➔ BSE ➔ not working
- Diagonalizing local Hamiltonian composed of super atom
- Traditionally 10Dq(=eg-t2g)=1eV provides correct excitation energy and *q*-dependence but not spectral weight
- Including oxygen changes the 10Dq to 0.6eV also help the spectral weight
- Many-body calculation of local Hamiltonian suggests same *q*-dependence for both peaks due to the contribution comes from the same many-body basis (one electron of t2g excites to one eg state)
- More possibility in investigating local many-body Hamiltonian e.g. quasiparticle calculation compared to ARPES

Next step

- First-principles site energies (eg, t2g)
- Inclusion of non-local effect to study self energy ➔ low-energy Hamiltonian