Ab initio derivation of multi-orbital extended Hubbard model for molecular crystals

Intra-Molecular Charge Ordering in (TTM-TTP)I_3

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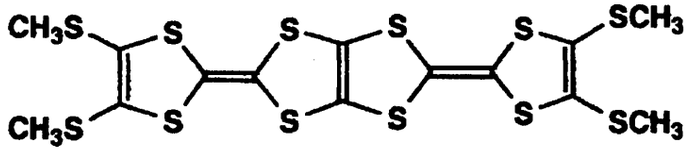
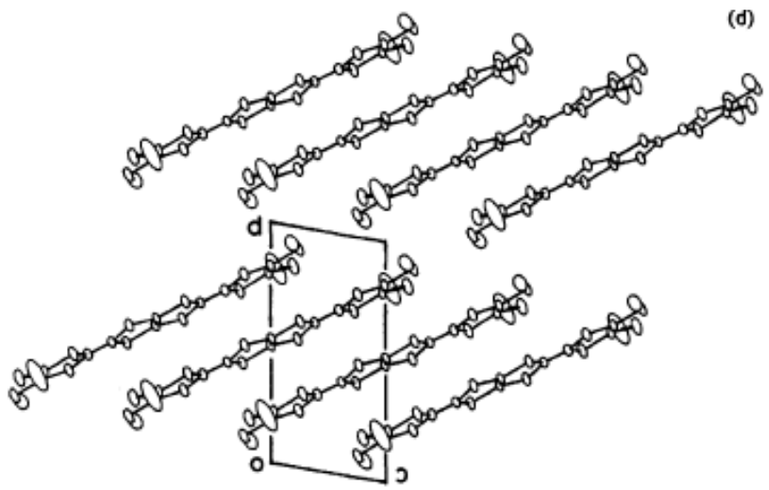
TTM-TTP molecule

Y. Misaki et al., Chem. Lett. (1994) 2321



crystal structure

T. Mori et al. Bull. Chem. Soc. Jpn. **67** (1994) 661

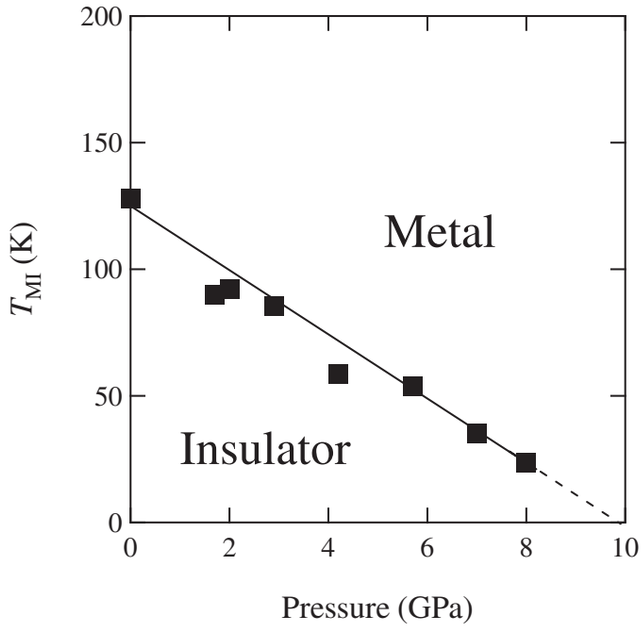


nominal charge

$(TTM\text{-}TTP)^{+}$ I_3^{-}

phase diagram

S. Yasuzuka et al., JPSJ 75 (2006) 053701



Resistivity measurement

T. Mori et al. PRL 79 (1997) 1702

S. Yasuzuka et al., JPSJ 75 (2006) 053701

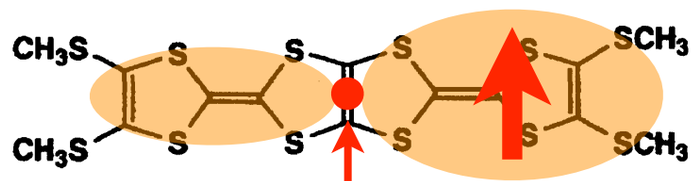
Raman scattering measurement

K. Yakushi et al .Synth. Met. **135-136** (2003) 583

X-ray measurement

Y. Nogami et al .Synth. Met. **135-136** (2003) 637

Intra-molecular charge ordering (ICO)



inversion center is lost in the low-T phase

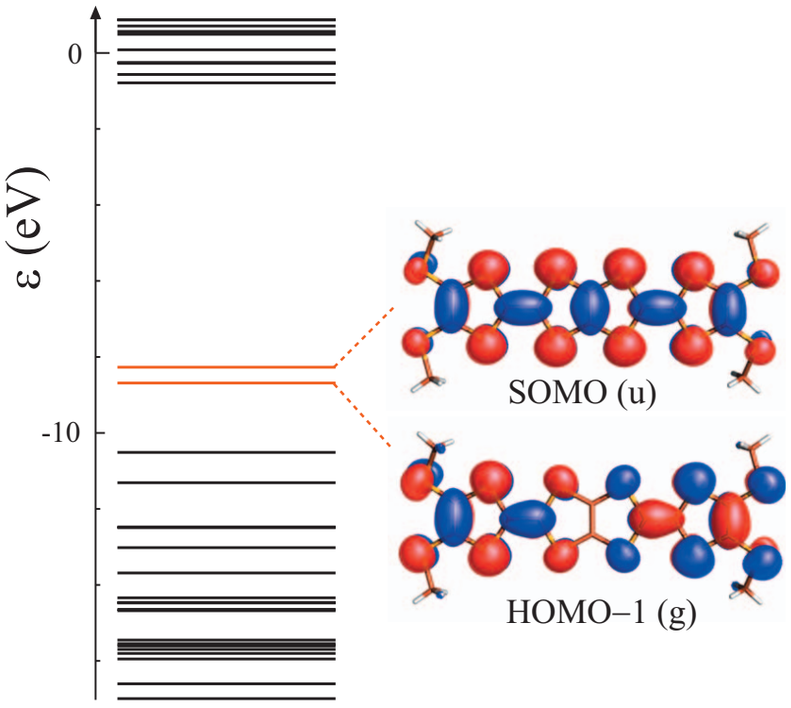
ICO pattern was unknown and origin of spin gap was unclear

molecular orbitals of TTM-TTP

ab initio calculation

(restricted open-shell HF)

M.-L.Bonnet, V. Robert, M.Tsuchiizu, Y. Omori, Y. Suzumura:
J. Chem. Phys. 132, 214705 (2010)

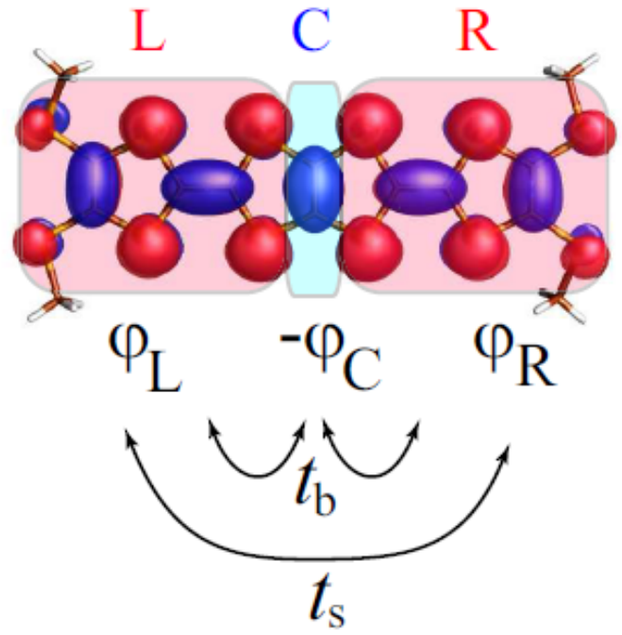


$$\varepsilon_{\mathrm{u}} = -8.2\mathrm{eV}$$
$$\varepsilon_{\mathrm{g}} = -8.6\mathrm{eV}$$

SOMO and HOMO-1
quasi-degenerate

origin of quasi-degeneracy

virtual fragment MOs



t_{b}: through-bond interaction ~ 1.3 eV
t_{s}: through-space interaction ~ -0.04 eV

$$\varphi_{\mathrm{u}} = \frac{1}{\sqrt{2+a^2}}(\varphi_{\mathrm{L}} - a\varphi_{\mathrm{C}} + \varphi_{\mathrm{R}})$$

$$\varphi_{\mathrm{g}} = \frac{1}{\sqrt{2}}(\varphi_{\mathrm{L}} - \varphi_{\mathrm{R}})$$

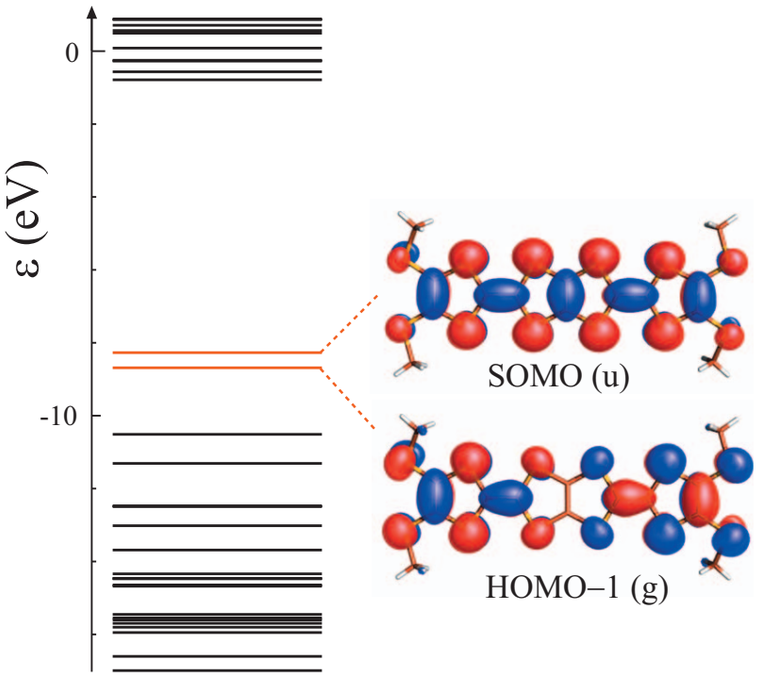
$$\varepsilon_{\mathrm{u}} - \varepsilon_{\mathrm{g}} \approx \frac{2t_{\mathrm{b}}^2}{\Delta\varepsilon} \approx 0.4\,\mathrm{eV}$$

The presence of the C fragment is crucial
for realization of quasi-degenerate MOs

model construction and parameter evaluation

two-orbital model derived from
configuration-interaction (CI) ab initio calculation

M.Tsuchiizu, Y.Omori, Y.Suzumura, M.-L.Bonnet, V.Robert,
S.Ishibashi, and H.Seo, J. Phys. Soc. Jpn. 80 (2011) 013703



intra-mol.

	(eV)
level energy ε_{g}	-8.63
level energy ε_{u}	-8.21
U_{g}	3.70
U_{u}	3.90
U'	2.82
J'_{H}	3.19

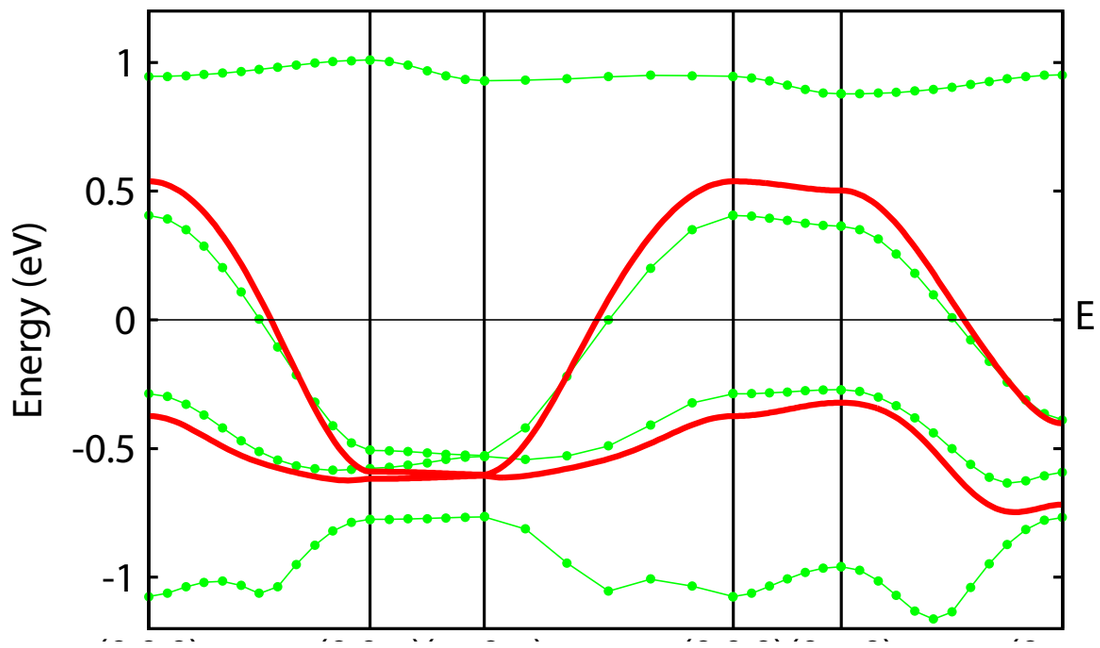
inter-mol.

	[001]	⋯
t_{gg}	-0.04	
t_{uu}	-0.29	
t_{gu}	-0.13	
V_{gg}	2.12	
V_{uu}	2.30	
V_{gu}	2.21	

- focus on two orbitals
- parameters are determined
  in order to reproduce CI matrix

no fitting parameters

band structure



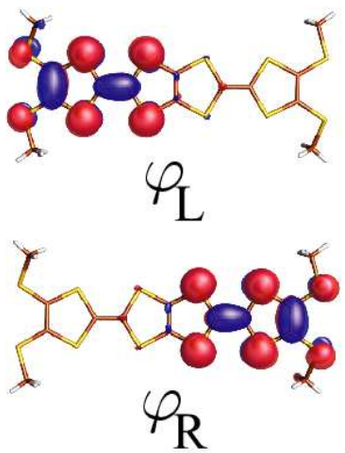
CI ab initio calcualtion

direct crystal calculation by DFT(GGA)

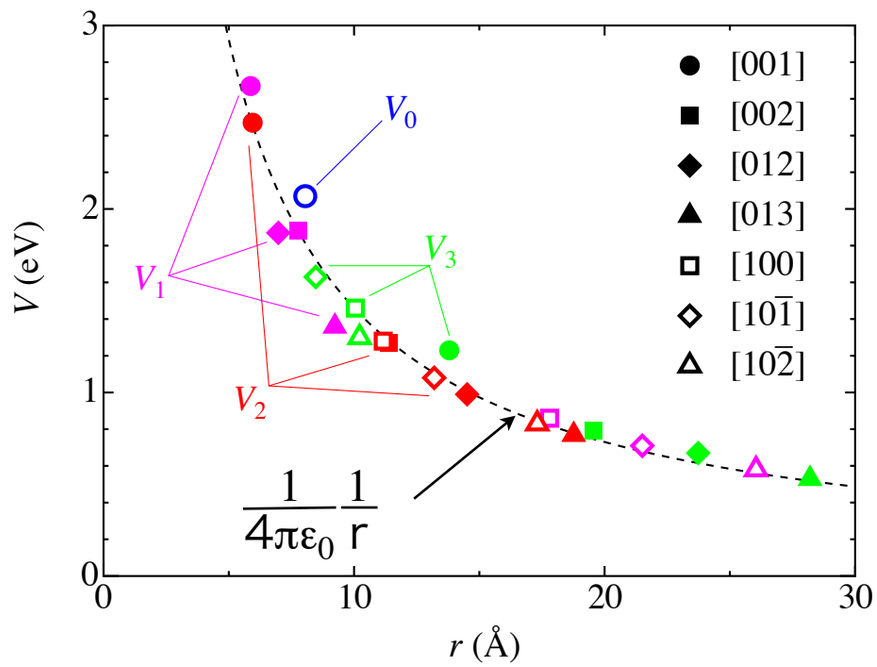
transformation into the fragment MO picture

model on the fragment MO basis

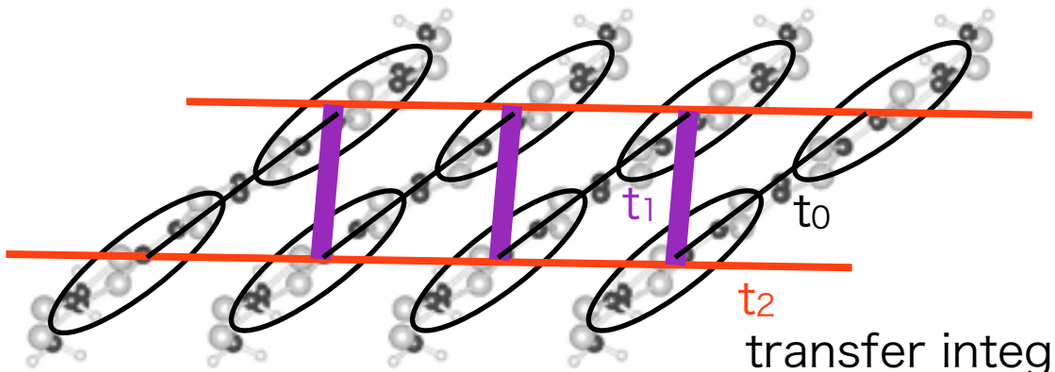
$$\begin{cases} \varphi_u \approx \frac{1}{\sqrt{2}}(\varphi_L + \varphi_R) \\ \varphi_g \approx \frac{1}{\sqrt{2}}(\varphi_L - \varphi_R) \end{cases}$$



inter-fragment Coulomb repulsions



effective two-leg ladder



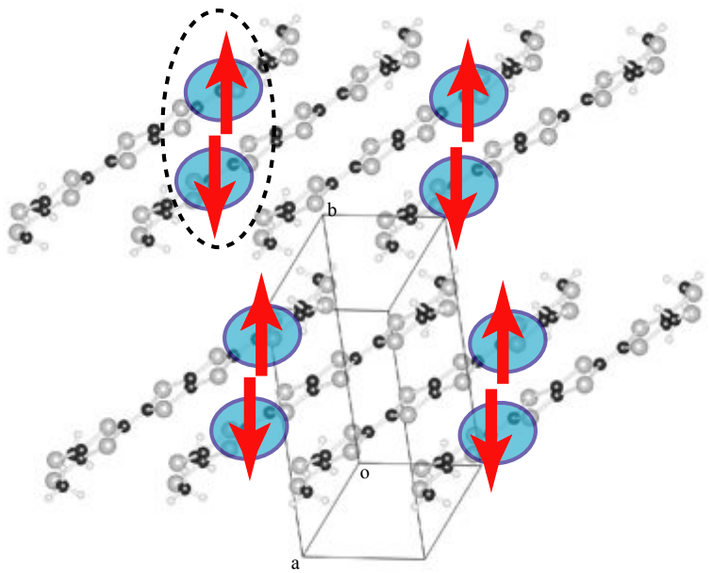
transfer integrals

t_0=-0.17 eV

t_1=-0.26 eV

t_2=-0.17 eV

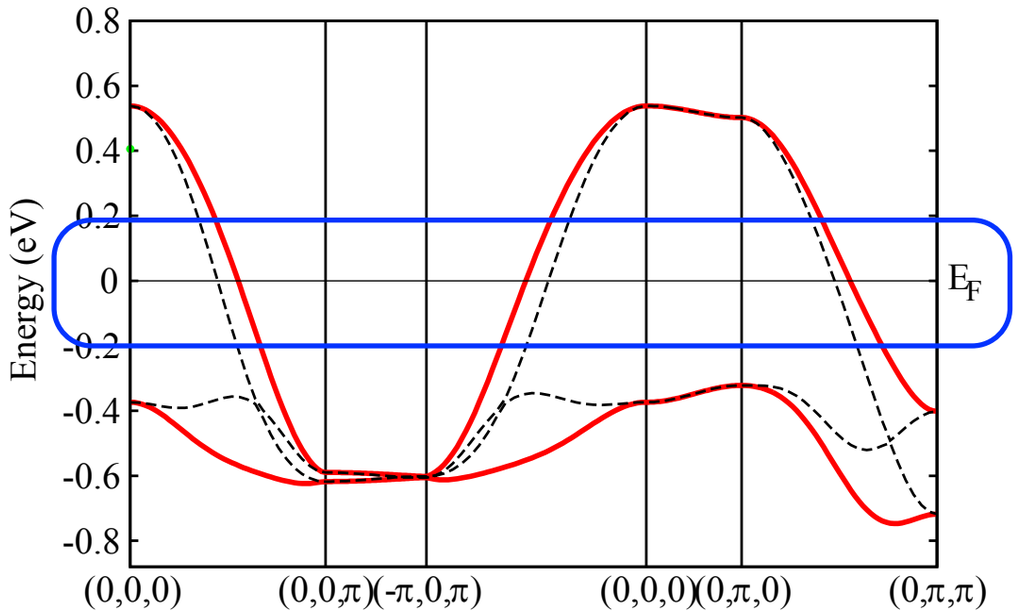
strong-coupling (atomic limit) analysis



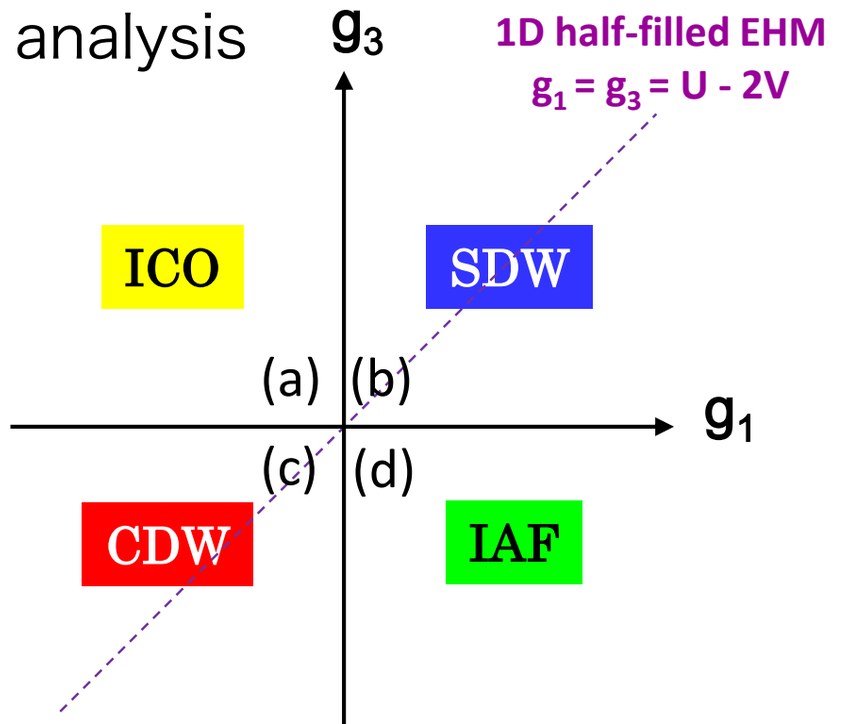
intra-molecular charge ordering with spin gap

weak-coupling analysis

scattering processes near Fermi energy



RG analysis

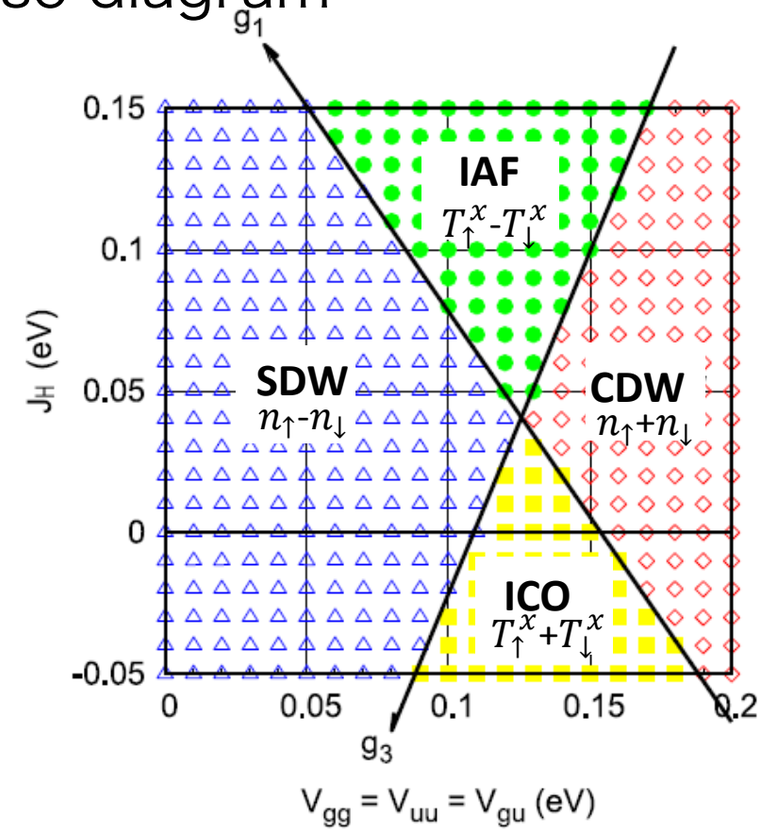


“g-ology” parameters

$$
\begin{aligned}
g_1 &= U_{\mathrm{eff}} - 2V_{\mathrm{eff}} + (J_{\mathrm{H}} - 4I)\,\frac{C}{2} \\
g_2 &= U_{\mathrm{eff}} + 2V_{\mathrm{eff}} \\
g_3 &= U_{\mathrm{eff}} - 2V_{\mathrm{eff}} - (J_{\mathrm{H}} - 4I)\,\frac{C}{2} \\
g_4 &= U_{\mathrm{eff}} + 2V_{\mathrm{eff}}
\end{aligned}
$$

$$
\begin{aligned}
U_{\mathrm{eff}} &= U_{\mathrm{g}}C_{\mathrm{g}} + U_{\mathrm{u}}C_{\mathrm{u}} + V_{\mathrm{gu}}C, \\
V_{\mathrm{eff}} &= V_{\mathrm{gg}}C_{\mathrm{g}} + V_{\mathrm{uu}}C_{\mathrm{u}} + \left(\frac{U'}{4} + \frac{J_{\mathrm{H}}}{16}\right)C.
\end{aligned}
$$

Phase diagram



Summary

we have analyzed the intramolecular charge ordering in (TTM-TTP)I_3 from the configuration-interaction (CI) ab initio calculation.

- characteristics of MOs
    - two-orbital system
- effective two-orbital Hubbard model from CI ab initio calculation
- transform into the fragment picture
    - we propose the two-leg ladder model
- analysis of the model
    - strong coupling & weak coupling analysis

collaborators

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Marie-Laure Bonnet	Univ. of Zurich, Switzerland
Shoji Ishibashi	AIST, Japan
Hitoshi Seo	RIKEN, Japan