Local Correlation Methods: From Molecules to Crystals

Dresden, September 12-15, 2007

Coupling between nuclear and electronic motion Experimental proofs and theoretical interpretation

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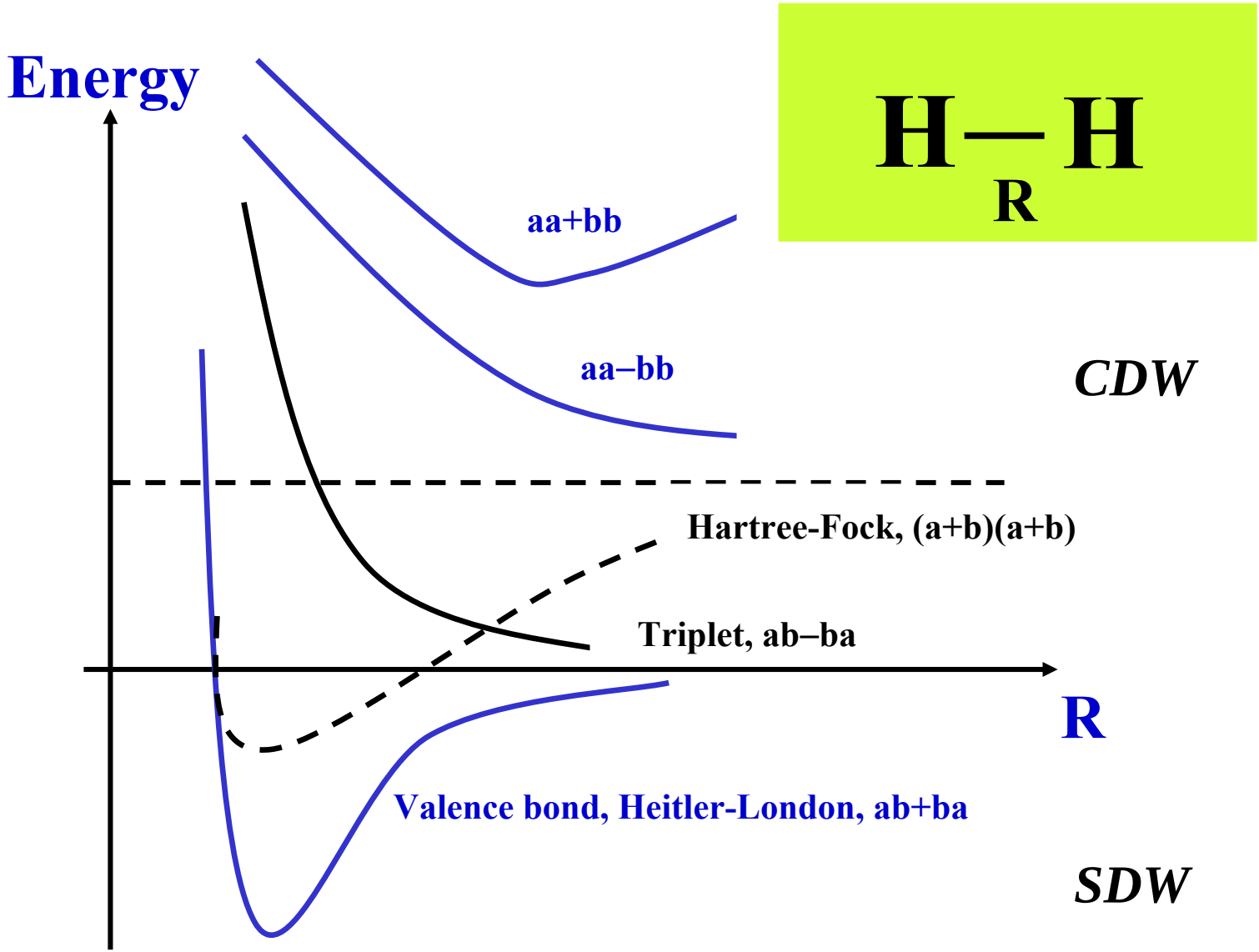
1. Mixed valence ”obvious” model for GMR and SC

2. F. Bloch: ”Spontaneous currents cannot exist in one-electron theory” (D. Bohm)

3. “Strongly correlated systems” - What does it mean?

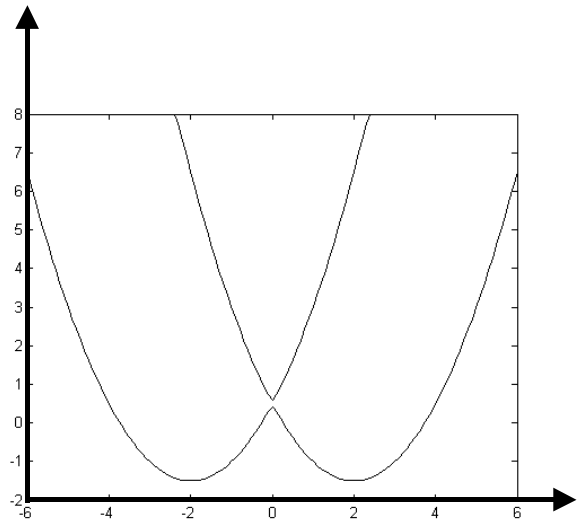
4. P. W. Anderson: ”There is no electron-phonon coupling”

5. L. Pintschovius, K. A. Müller and others find electron-phonon coupling


Energy
H—H
R
aa+bb
aa–bb
CDW
Hartree-Fock, (a+b)(a+b)
Triplet, ab–ba
R
Valence bond, Heitler-London, ab+ba
SDW

Potential Energy Surface, PES

Energy



Nuclear Configuration

$*Mn^{3+} + Mn^{4+} \leftrightarrow *Mn^{4+} + Mn^{3+}$

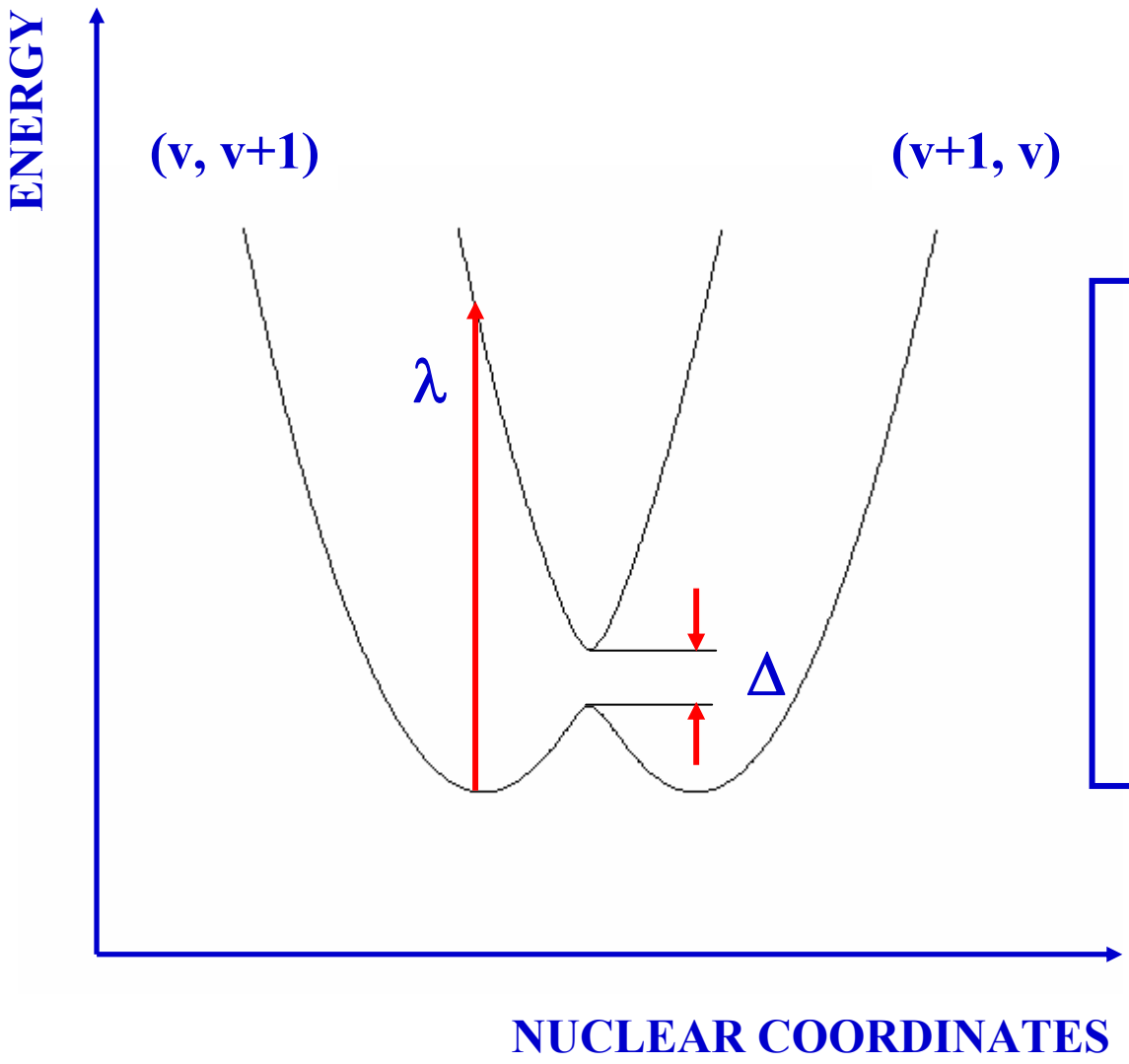
$*Ni^{2+} + Ni^{3+} \leftrightarrow *Ni^{3+} + Ni^{2+}$

$*Cu^{2+} + Cu^{3+} \leftrightarrow *Cu^{3+} + Cu^{2+}$

$*Cu^{+} + Cu^{3+} \leftrightarrow *Cu^{3+} + Cu^{+}$

$*Bi^{5+} + Bi^{3+} \leftrightarrow *Bi^{3+} + Bi^{5+}$

(2 electrons)



$H_{11} = \frac{1}{2}k\,(Q + Q_0)^2$

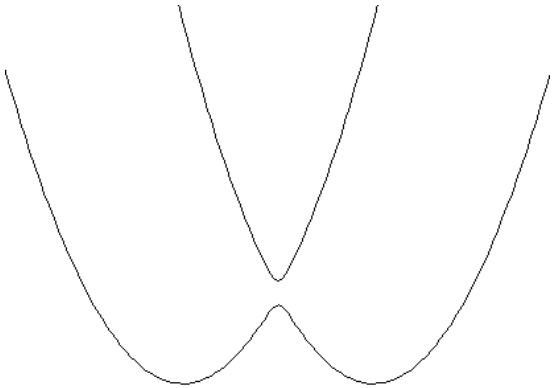
$H_{22} = \frac{1}{2}k\,(Q - Q_0)^2$

$\lambda = 2kQ_0^2$

$$\begin{vmatrix} H_{11} - E & H_{12} \\ H_{12} & H_{22} - E \end{vmatrix} = 0$$

$2H_{12} = \Delta/2$

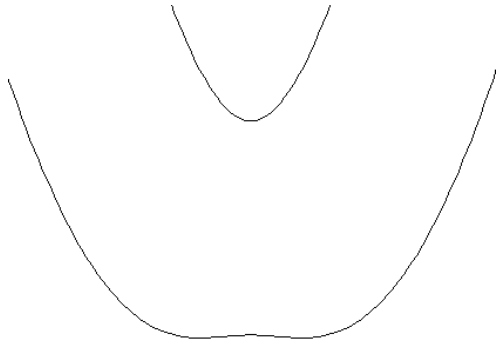
$MM^+ \leftrightarrow M^+M$ (MV-2 model)



$\Delta/\lambda = 0.01$

class 2

localized



$\Delta/\lambda = 1$

class 3

delocalized

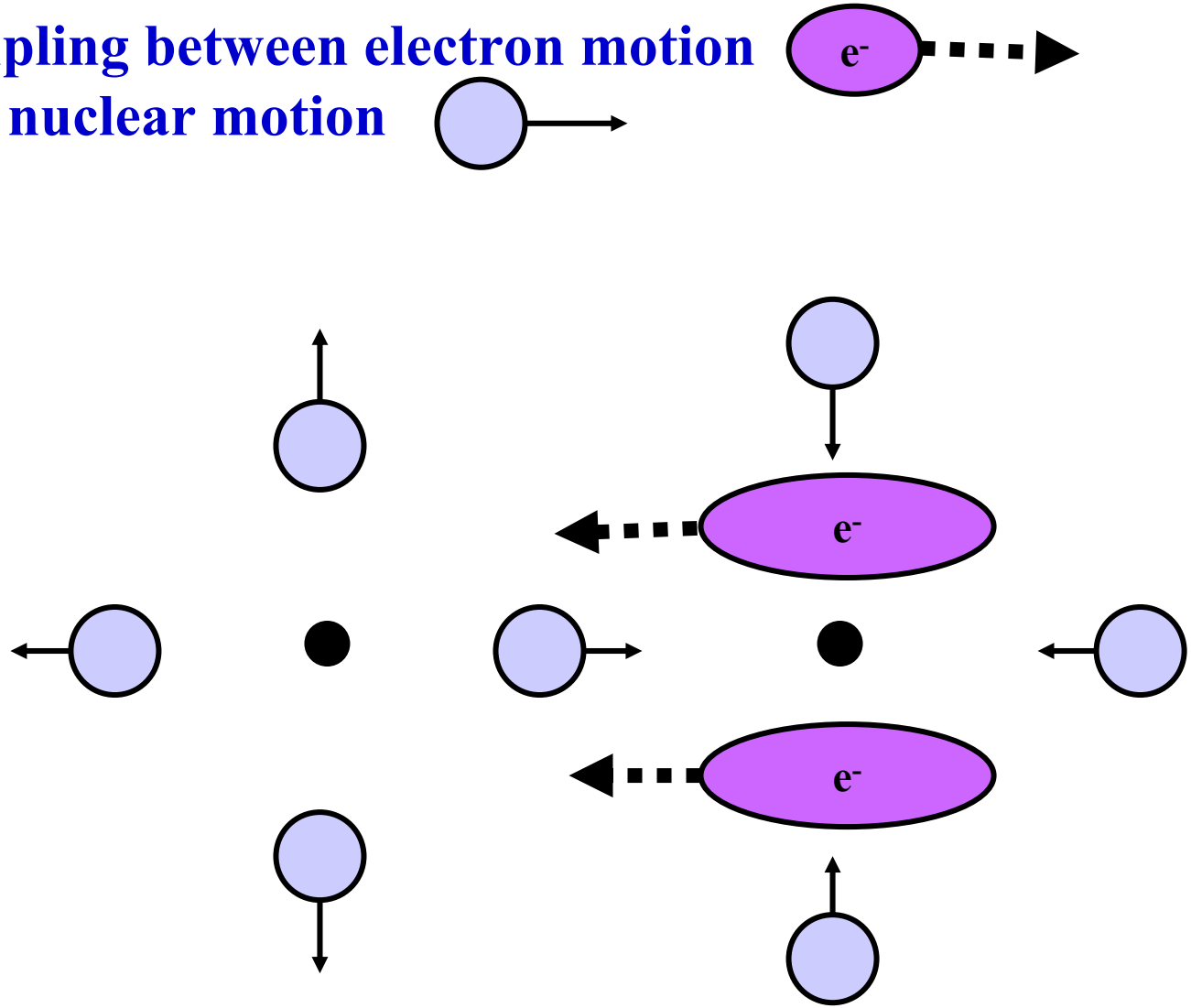
$\Delta/\lambda \rightarrow \infty$

band

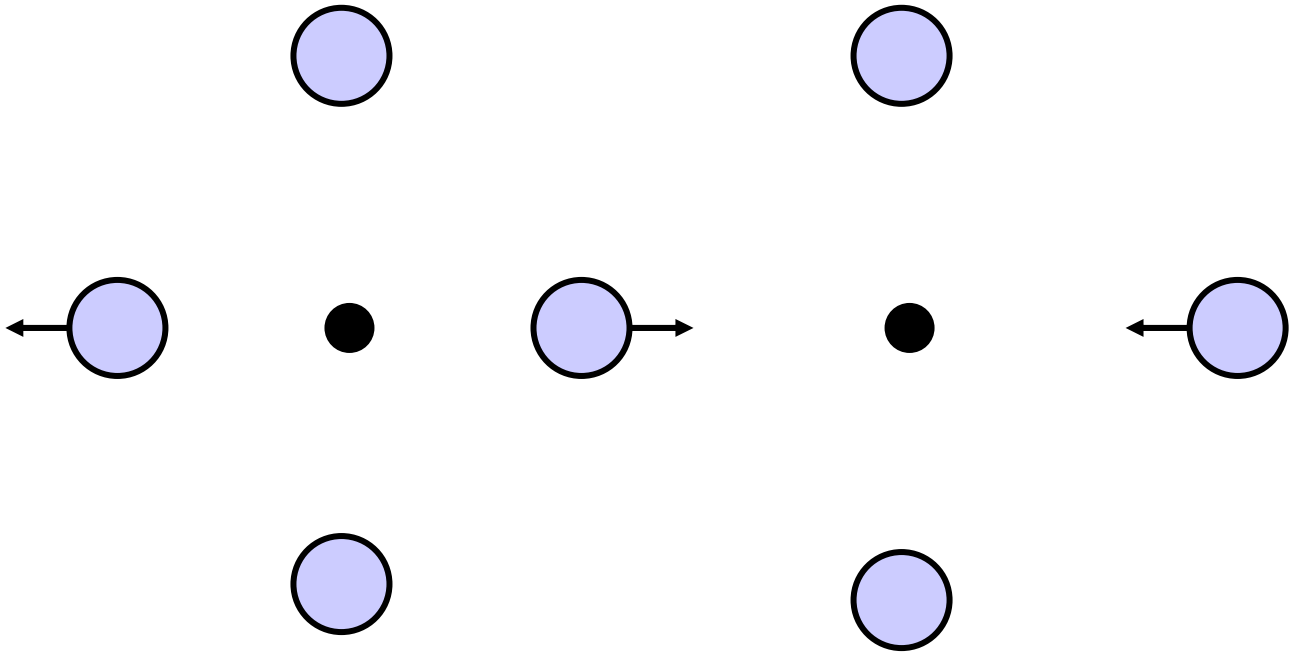
(Robin – Day class)

(Hush-Robin-Day delocalization)

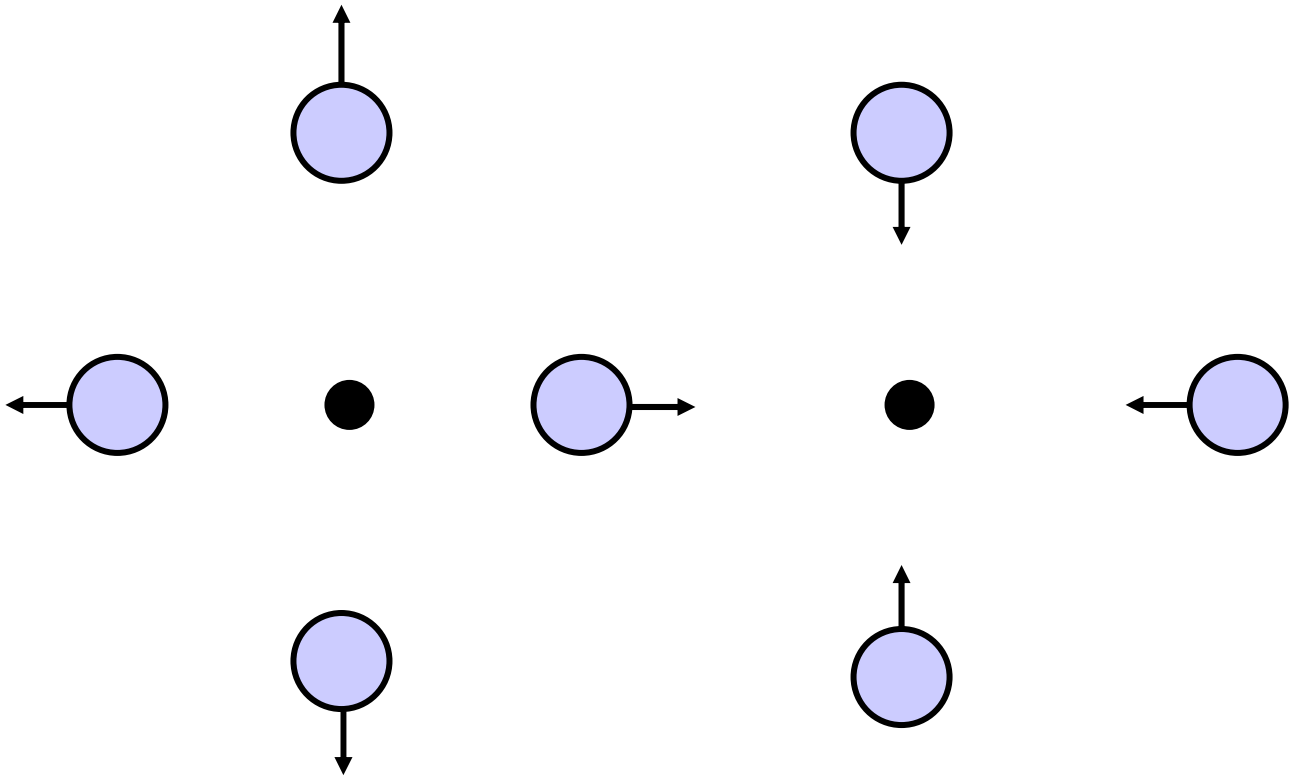
Coupling between electron motion and nuclear motion



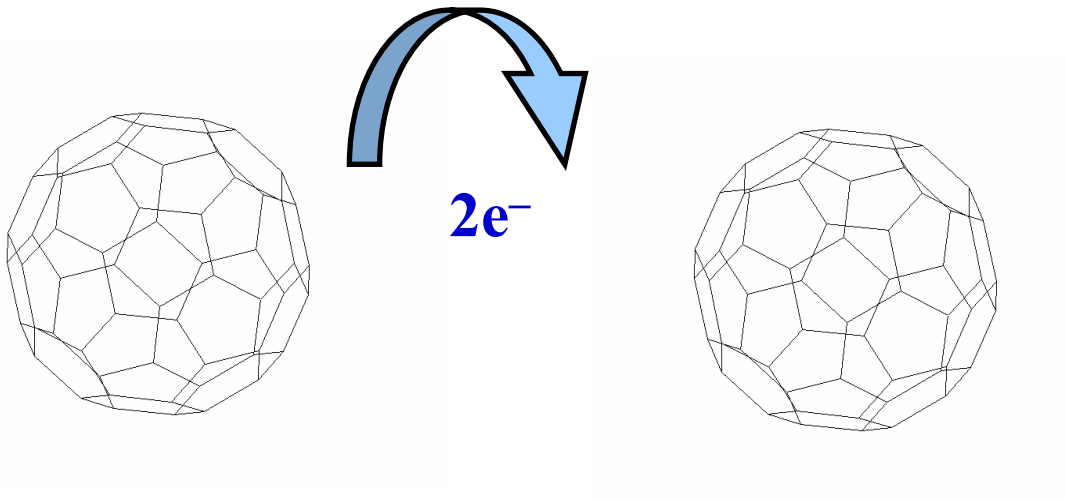
Half-breathing mode



Full-breathing mode

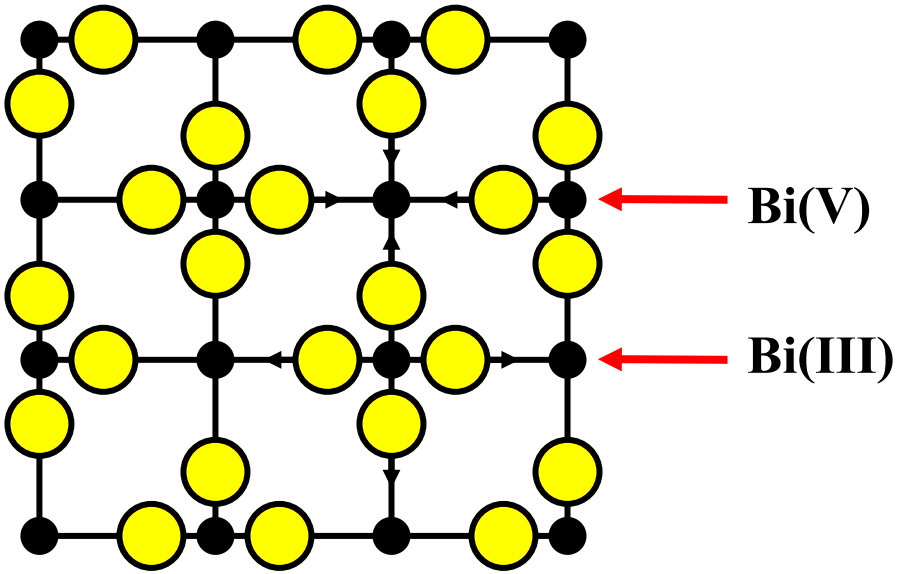


Rb_3C_{60}



C_{60}^{2-} C_{60}^{4-}

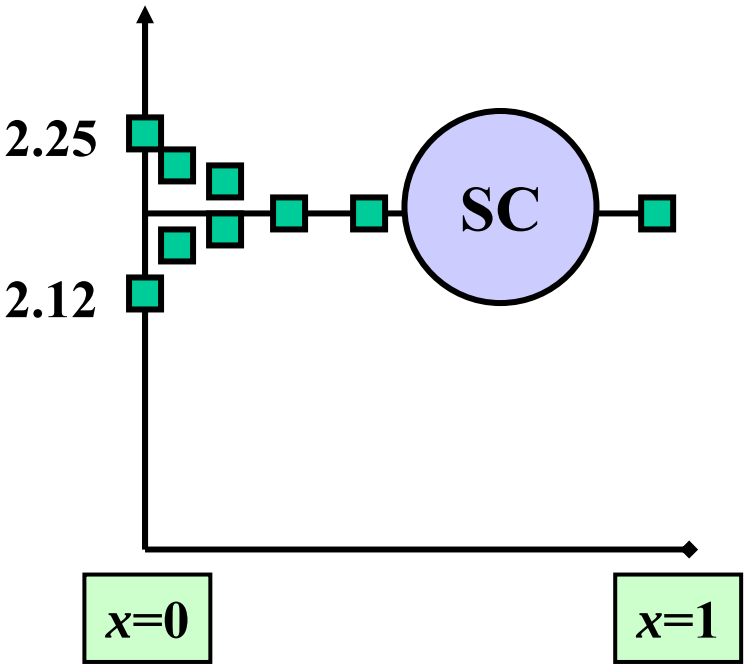
$$2\ C_{60}^{3-} \leftrightarrow C_{60}^{2-} + C_{60}^{4-}$$



$BaBiO_3$

oxygen

bismuth



$Ba_{1-x}K_xBiO_3$

ΔR = Bi-O bond length change

Batlogg, et al. IBM J Res Dev **33**, 208-214 (1989)

$\Delta \approx 0$ for two electrons => third state

MV-3 - model

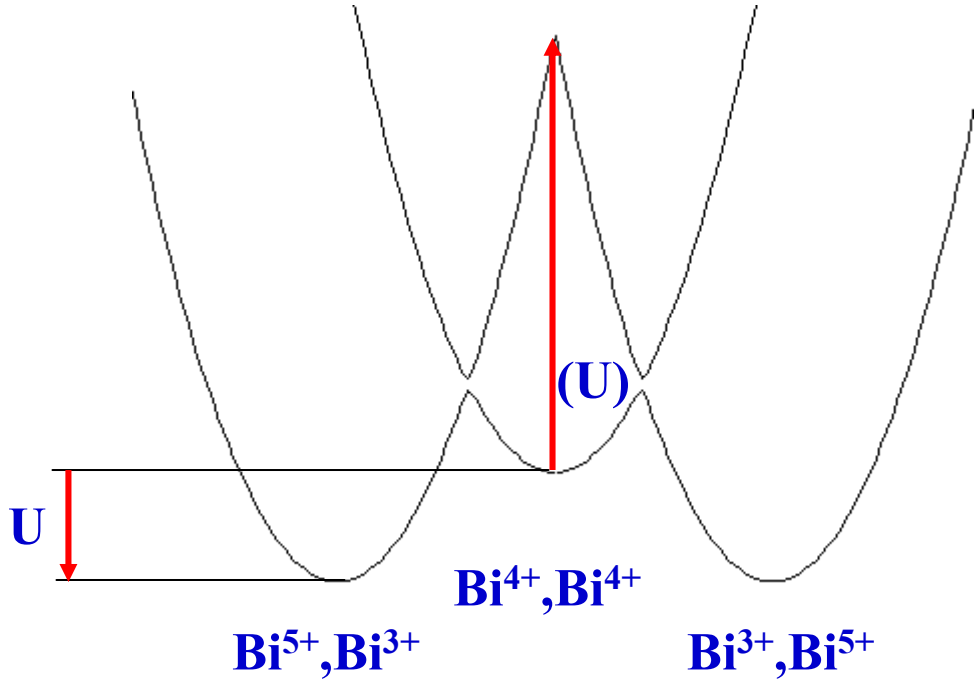
Disproportionation:

$2MM \leftrightarrow M^{+}M^{-} + M^{-}M^{+}$, $\Delta G^{0} = U$

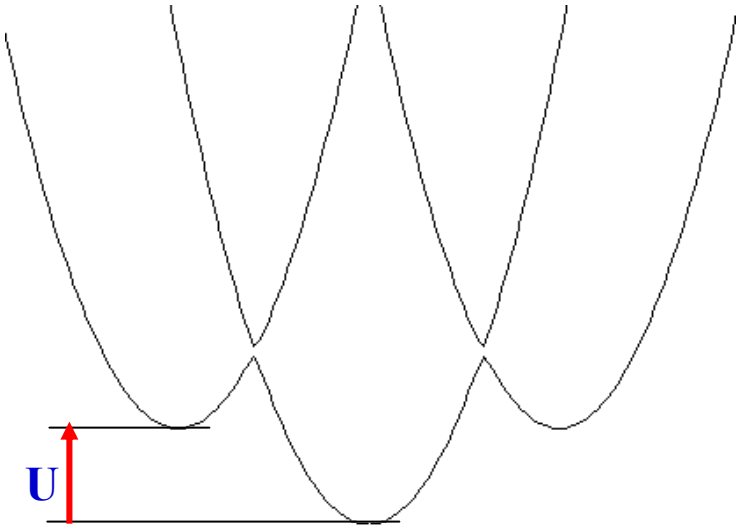
Mott U ?

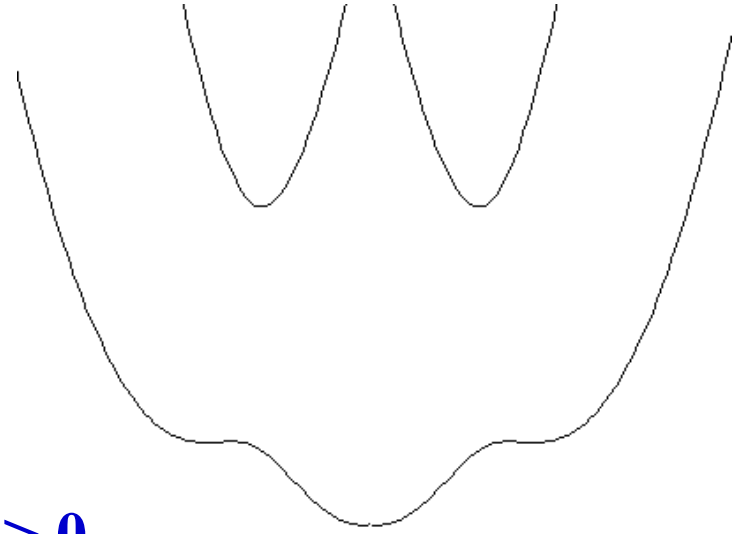
MV-3 model, U < 0

($BaPb_xBi_{1-x}O_3$ and $Ba_{1-x}K_xBiO_3$)



CDW, localized, U < 0





MV-3, U > 0

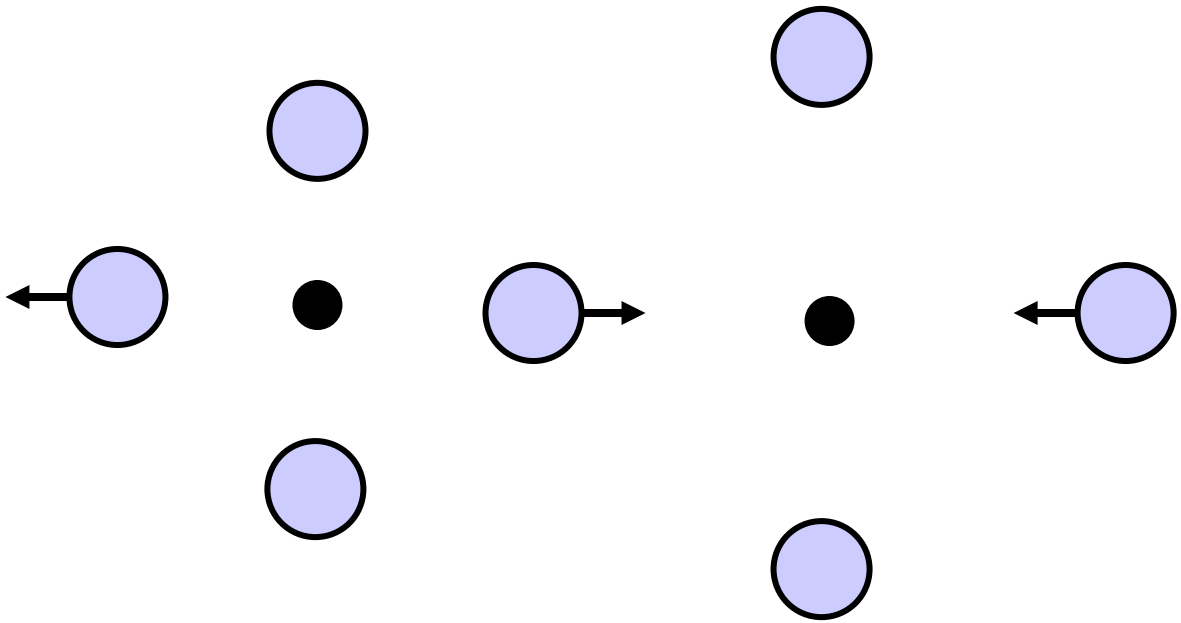
SDW,
localized

SDW,
Hush delocalized
Mott localized

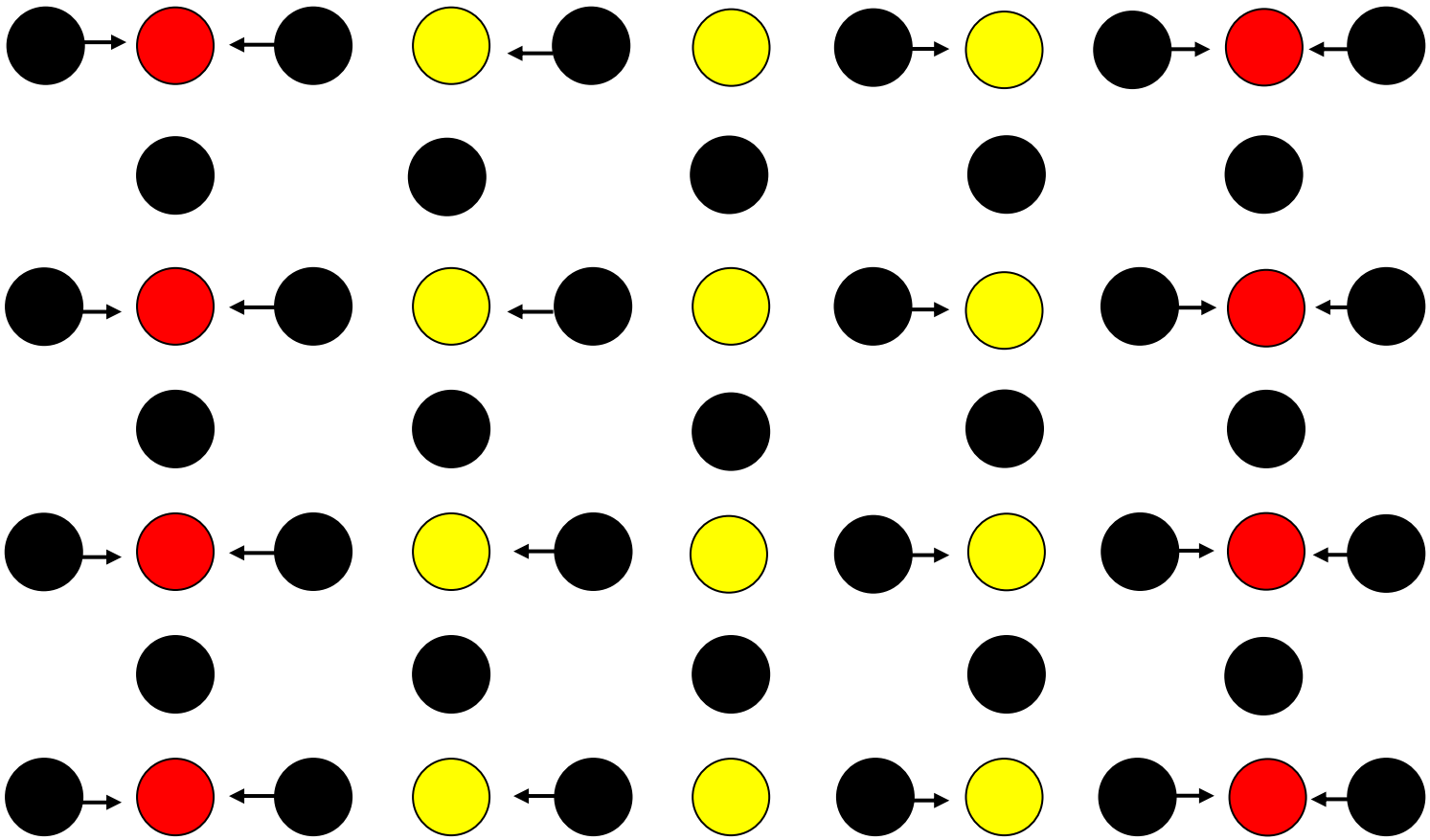
Mott insulators: CuO, NiO, CoO,...

1. D. Reznik, L. Pintschovius, M. Ito, S. Iikubo, M. Sato, H. Goka, M. Fujita, K. Yamada, G.D. Gu, and J.M. Tranquada, *Nature* 440, 1170-1173 (2006).
2. L. Pintschovius, *Phys. Stat. Sol. (b)* 242, 30-50 (2005).

Half-breathing mode; softening:

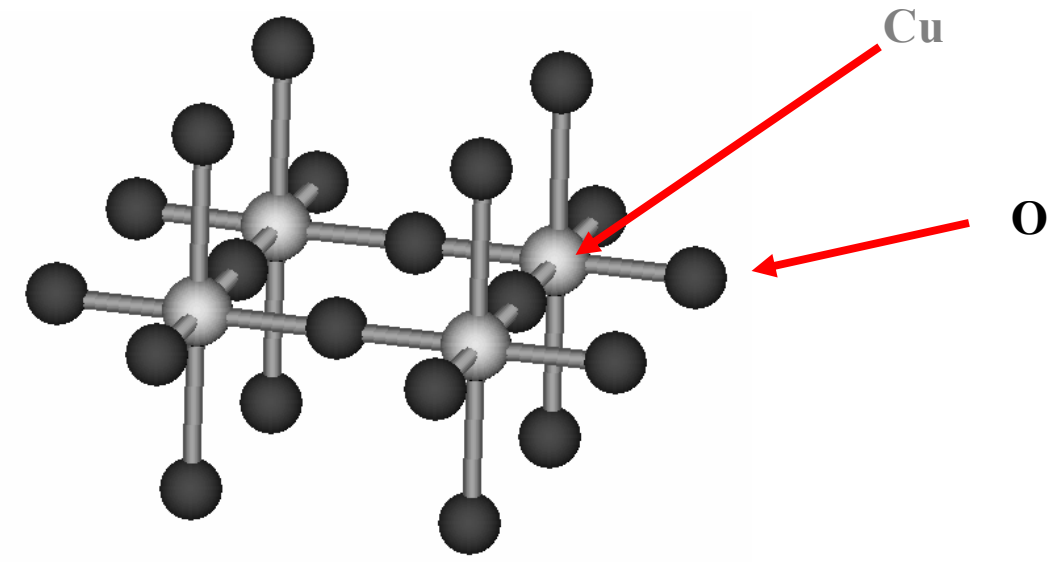


(Full-breathing mode; no softening)

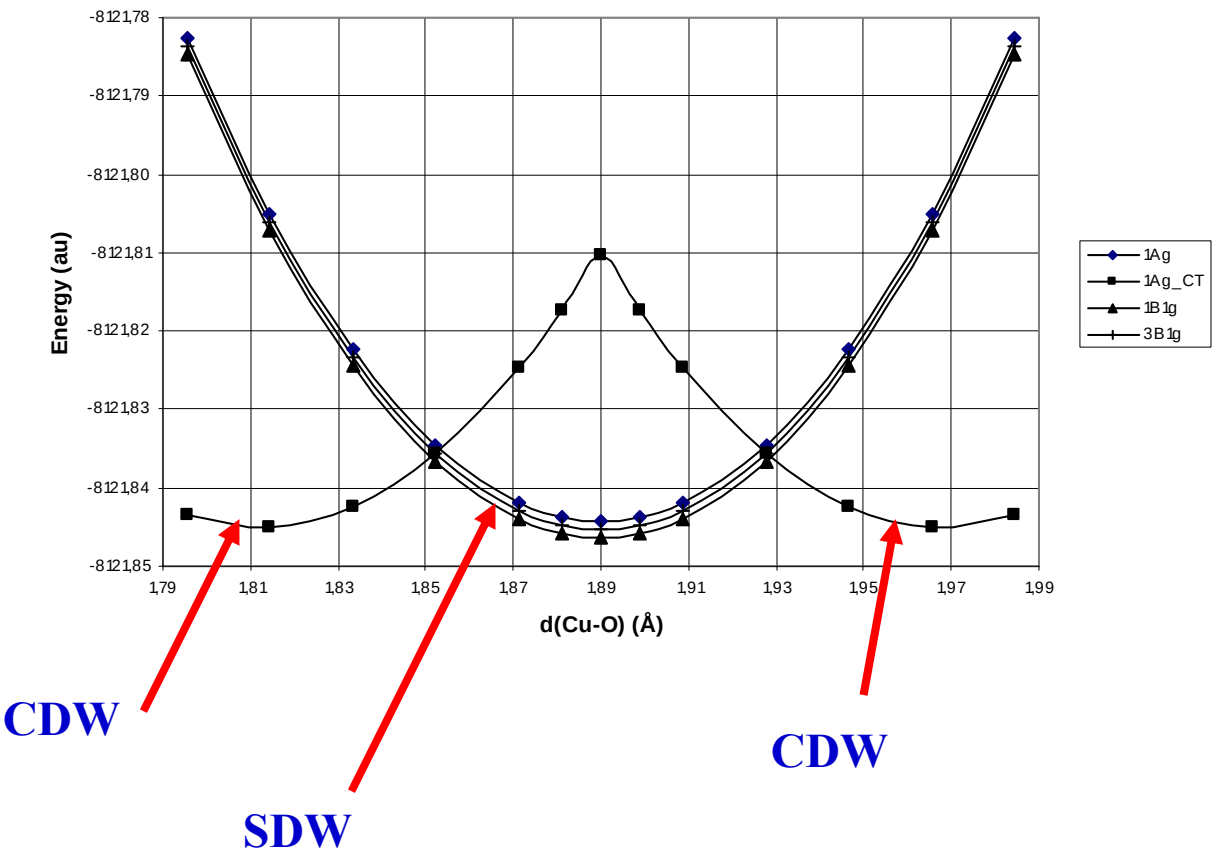


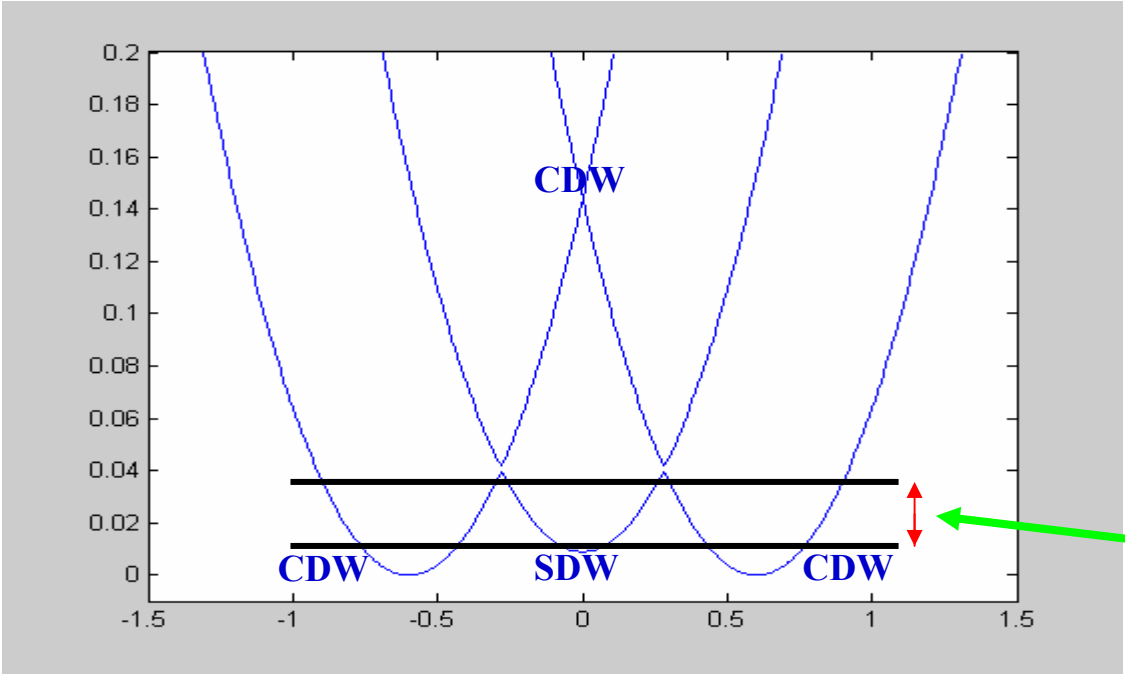
D. Reznik, L. Pintschovius *et al.*, *Nature*, April 2006, 1170.

System calculated using CASSCF (A. Klimkans, 2001)



Number of basis functions: 468
42396 configurations


-8121,78
-8121,79
-8121,80
-8121,81
-8121,82
-8121,83
-8121,84
-8121,85
Energy (au)
1,79
1,81
1,83
1,85
1,87
1,89
1,91
1,93
1,95
1,97
1,99
d(Cu-O) (Å)
1Ag
1Ag_CT
1B1g
3B1g
CDW
SDW
CDW



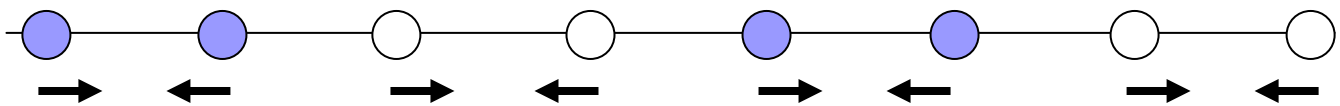
SDW $\longrightarrow \Psi(B_1) = (XX - YY)/\sqrt{2} = \left[(X+Y)(X-Y) + (X-Y)(X+Y)/2\sqrt{2}\right]$

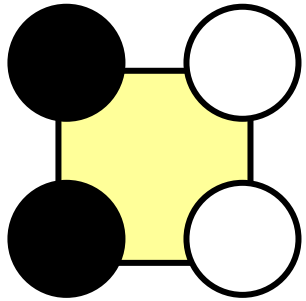
CDW $\longrightarrow \Psi(B_2) = (XY + YX)/\sqrt{2} = \left[(X+Y)(X+Y) - (X-Y)(X-Y)/2\sqrt{2}\right]$

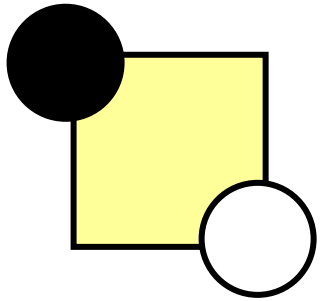
CDW $\longrightarrow \Psi(A_1) = (XX + YY)/\sqrt{2} = \left[(X+Y)(X+Y) + (X-Y)(X-Y)/2\sqrt{2}\right]$

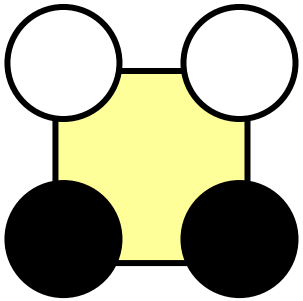
Peierls transition

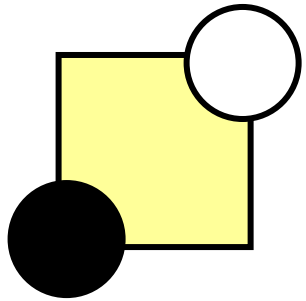
HOMO for one-dimensional chain:



X= 

X–Y= 

Y= 

X+Y= 

SDW $\longrightarrow \Psi(B_1) = (XX - YY)/\sqrt{2} = [(X+Y)(X-Y) + (X-Y)(X+Y)/2\sqrt{2}]$

CDW1 $\longrightarrow \Psi(B_2) = (XY + YX)/\sqrt{2} = [(X+Y)(X+Y) - (X-Y)(X-Y)/2\sqrt{2}]$

CDW2 $\longrightarrow \Psi(A_1) = (XX + YY)/\sqrt{2} = [(X+Y)(X+Y) + (X-Y)(X-Y)/2\sqrt{2}]$

Spin function: ↑ ↓ — ↓ ↑

Spin singlet in all cases

Angular momentum wave functions:

$\Psi_+ = ½ \; [XY + YX + i(XX - YY)]$

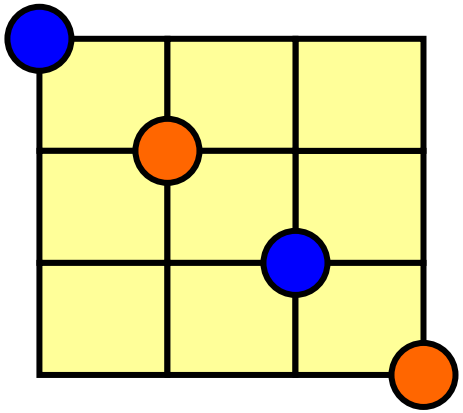
$\Psi_- = ½ \; [XY + YX - i(XX - YY)]$

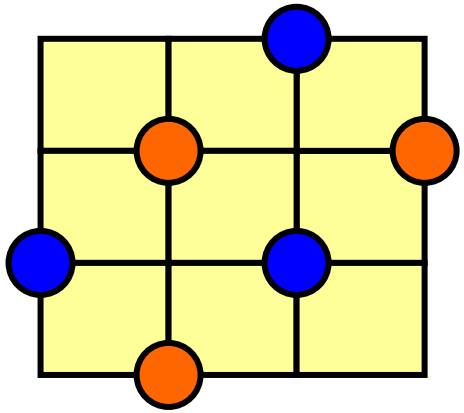
(=ground state currents of electron pairs)

Orbital Generators

$(X-Y)_1$

$= (-1)$



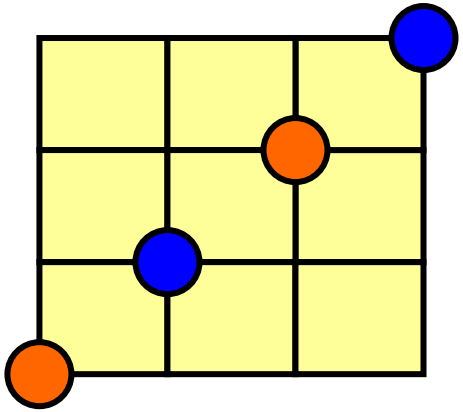


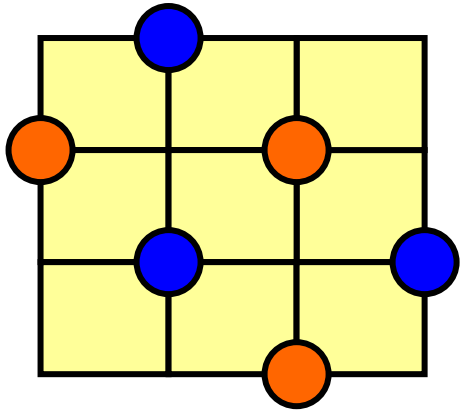
$(X+Y)_2$

$= (+2)$

$(X+Y)_1$

$= (+1)$





$(X-Y)_2$

$= (-2)$

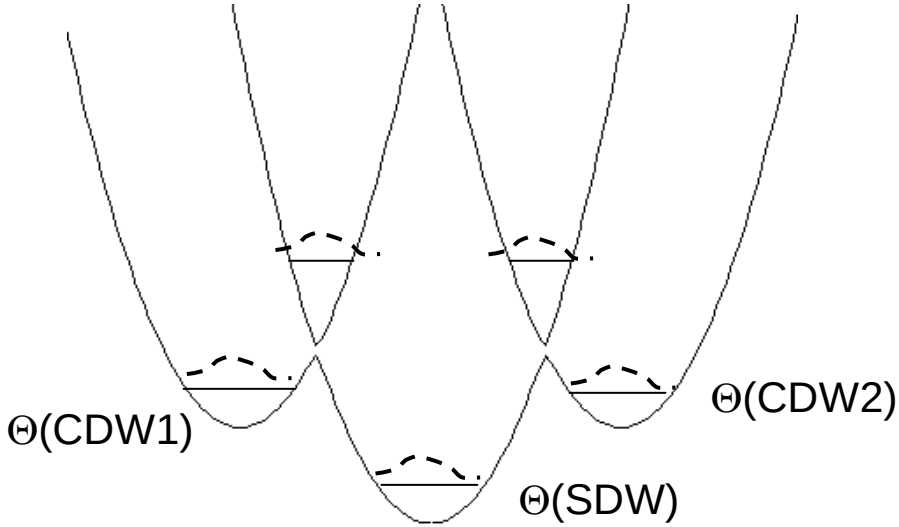
SDW wave function:

$$\Psi(\text{SDW}) = S_1\,[(+1)(-1) + (-1)(+1)] + S_2\,[(+2)(-2) + (-2)(+2)]$$

CDW wave function:

$$\Psi(\text{CDW}) = C_1[(+1)(+1) + (-1)(-1)] + C_2[(+2)(+2)] + (-2)(-2)$$

Can be combined to Ψ_+ and Ψ_- wave functions



Vibrational wave functions:

Θ(SDW), Θ(CDW1)), Θ(CDW2), etc.

Final wave function:

$$\Psi = \Psi(SDW)\,\Theta(SDW) + \Psi(CDW1)\,\Theta(CDW1) + \Psi(CDW2)\Theta(CDW2) + ...$$

Conclusions

1. **Pairing mechanism: MV-3, the same for cuprates and bismuthates, *etc.***
2. **Mott U ≈ 0 for superconductors. CDW + SDW interacting with phonons**

3. **INS softening is related to mixed valency**
4. **Detailed comparison between MV-3 and INS should be carried out**

5. **Hush – Robin – Day is the correct delocalization mechanism**
6. **Delocalized MV-2 delocalizes to an ordinary metal**
7. **Delocalized MV-3 delocalizes to a superconductor**

8. **Currents of electron pairs in the ground state**