Non-additivity in metallic tri-wire binding

Quantum Monte Carlo study

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vdW in Nano Wire

- Difficulty of conventional DFT

  XC functionals for Dispersion force

- Metallic Wire？ (Different Power law)

  → local polarization not well be defined...
  (Screening Length)

- Non-additivity

  Additive modeling ... valid only for local polarizations

Previous Studies

Between Insulating wires $\sim \frac{1}{z^5}$

Metal wires/RPA $\sim \frac{1}{z^2 (\ln z)^{3/2}}$ J.F. Dobson et.al., PRL**96**, 073201 (2006)

Metal-Semiconductor/SAPT $\sim \frac{1}{z^\alpha}$ $\alpha = 2 \sim 5$

Huckel J. Spencer and A. Alavi, (thesis)

SAPT (TB + Perturbation) A. Misquitta et.al., Phys. Rev. B, 82 , 075312, (2010).

Metal/QMC $\sim \frac{1}{z^\alpha (\ln z)^{3/2}}$ $\alpha = \alpha(r_s) \sim 2$

N.D. Drummond et.al., Phys. Rev. Lett. 99, 247401 (2009).

Much earlier works for 1-dim.

- Coulson and Davies, Trans. Faraday Soc. (1952).
- Longuet-Higgins and Salem, Proc. R. Soc. A. (1961).

Asymptotic Behavior

Density Matrix ; Power Decay ; Metals
Exponential Decay ; Insulators

- Local Polarization → z^{-6} → Inter-wire Interaction with z^{-5}
- Metals/ No local polarization defined...

RPA treatment ; $U(z) = \dfrac{\sqrt{r_S}}{16\pi z^2 \left[\log\left(2.39 z/b\right)\right]^{3/2}}$

Valid for Dense Gas

J.F. Dobson et.al., Phys. Rev. Lett. **96**, 073201 (2006)

Dilute region ... QMC treatment

'vdW' in Metallic systems

No local polarization well defined.

1) Zero point motion of the Plasmon

interaction between induced charge by quantum fluctuation

Frequency shift depending on distance (stabilization)

RPA evaluation

$$\delta\left[\hbar\omega_p(z)\right] \sim \frac{1}{z^{\alpha}}$$

$$U(z) = \frac{\sqrt{r_S}}{16\pi z^2\left[\log\left(2.39z/b\right)\right]^{3/2}}$$

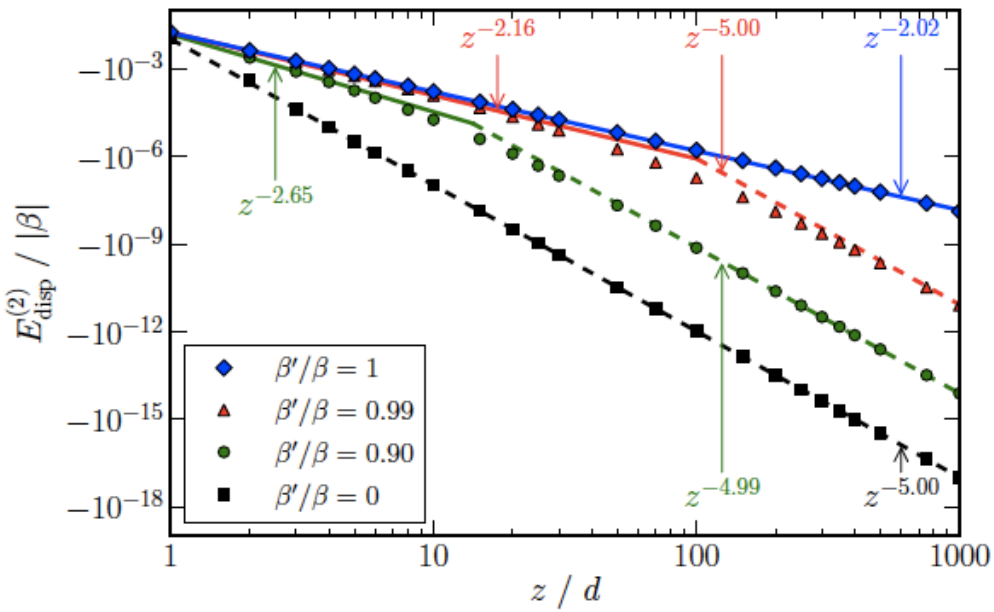
J.F. Dobson et.al., Phys. Rev. Lett. **96**, 073201 (2006)

2) 2nd order Perturbation

… shown later …

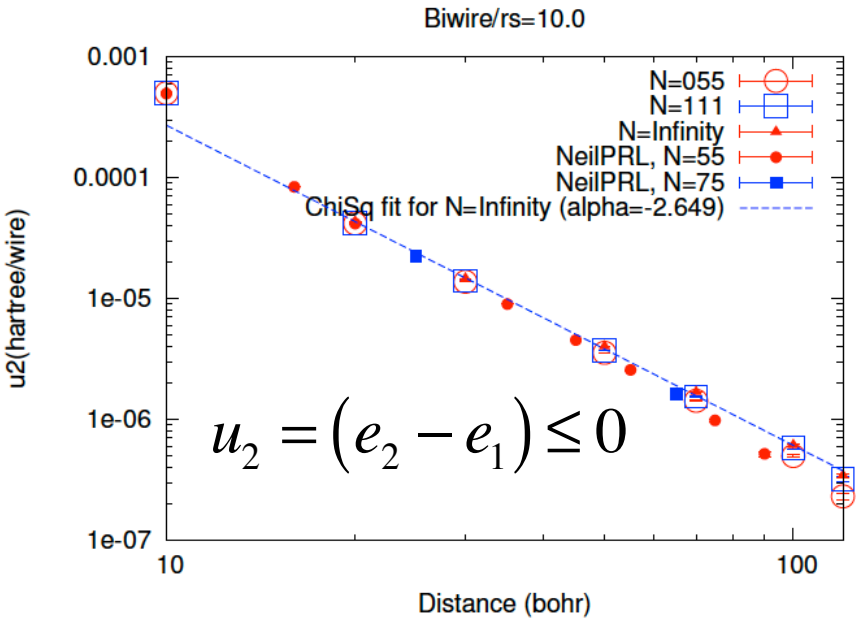
Kink in the exponent

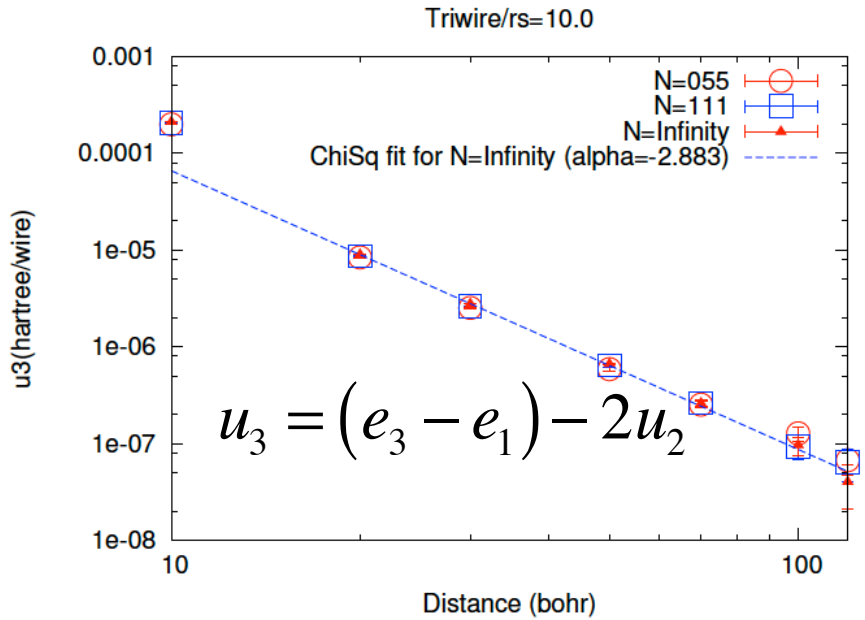
James Spencer & Ali Alavi: Interactions between parallel wires. Huckel



Note; correlation effect makes kink broader [Misquetta/SAPT, 2010]

Rs = 10.0



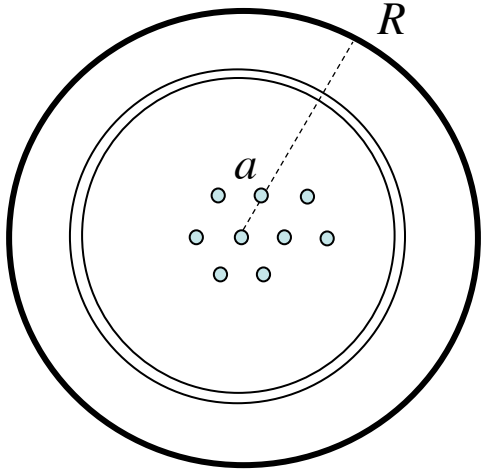


$$|u_{2,3}(z)| = \frac{C}{z^{\alpha}}$$

Exponents of Decay

Summing up interactions…

We expect it not diverging.



ρ ; Num. of wires per unit area

$$dN(r) = \rho \cdot 2\pi r \cdot dr$$

$$\frac{E_M}{M} \sim \int_a^R u(r) \cdot dN(r) = \rho \int_a^R u(r) \cdot 2\pi r \cdot dr$$; Energy per wire

$u(r) \sim \dfrac{1}{r^\alpha}$ 、$R \to \infty$

$\alpha = 3$; $\int_a^R u(r) \cdot 2\pi r \cdot dr \sim \left[\dfrac{1}{r}\right]_a^R$ → Finite

$\alpha = 2$; $\int_a^R u(r) \cdot 2\pi r \cdot dr \sim [\ln r]_a^R$ → Diverge !

Exponents of Decay

Possible mechanisms making it finite.

1）Divergence of u_2 cancelled by u_3 and higher.

(c.f., Our equilateral triangle gives repulsive u_3)

2）Exponent falls off more rapidly at larger distances.

(at which we cannot perform accurate calculations)

3）Relativistic retardation reducing the interaction

at larger distances.

Non-additivity

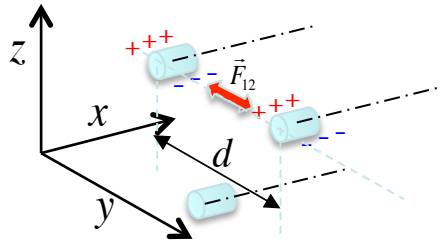
Interaction due to induced polarizations

Forces not superpose...

More remarkable in Metallic wires

Possible in Nano Tube systems

Equilateral Triangle Geometry



J.F. Dobson et.al., Surf. Sci. 601, 5667 (2007).

<What are clarified in this work>

- Non additive contribution well fitted by power law.
- Long-ranged ($\alpha < 3$), physically important.

Modeling

DMC (diffusion Monte Carlo) method

- Intra-Wire ; Anti-symetrized products of PW orbitals

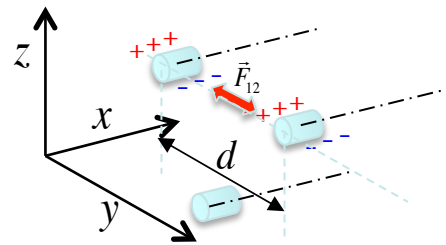
  1D HEG → No Nodal problem.

- Inter-Wire ; treated as Distinguishable particles

- Odd number of electrons ; Real WF.

  N=55, 111

Equilateral Triangle Geometry



Bi-wire interaction

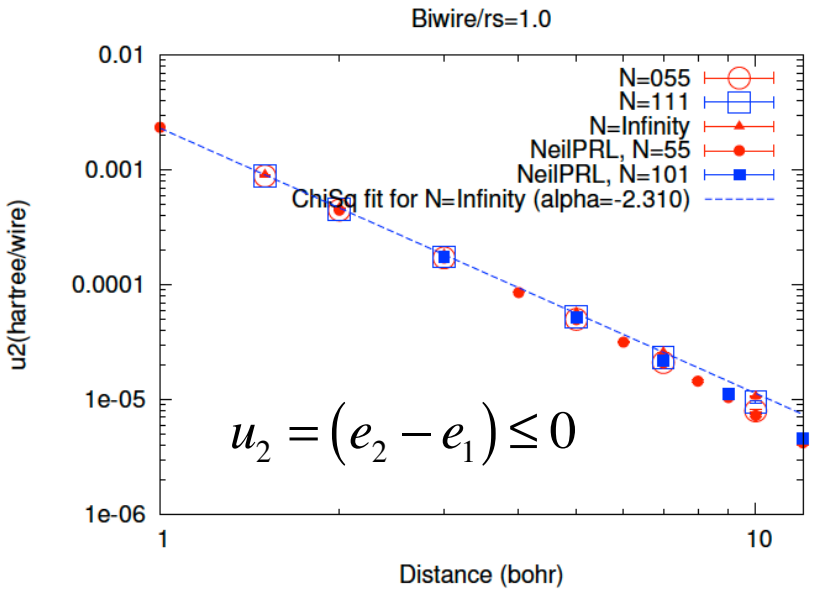
$$u_2 = (e_2 - e_1) \leq 0$$

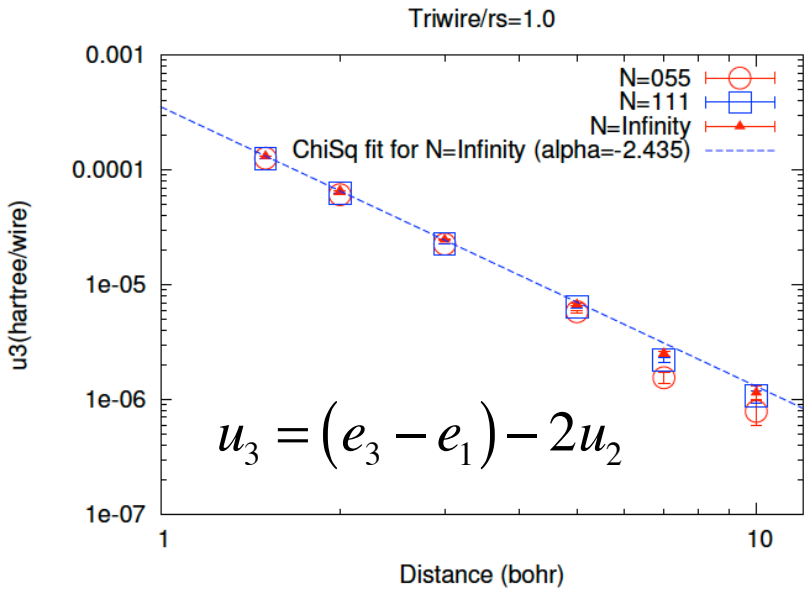
Non-additive contribution

$$u_3 = (e_3 - e_1) - 2u_2$$

$e_{2,3}$; Energy/wire @ Bi (Tri)-wire system

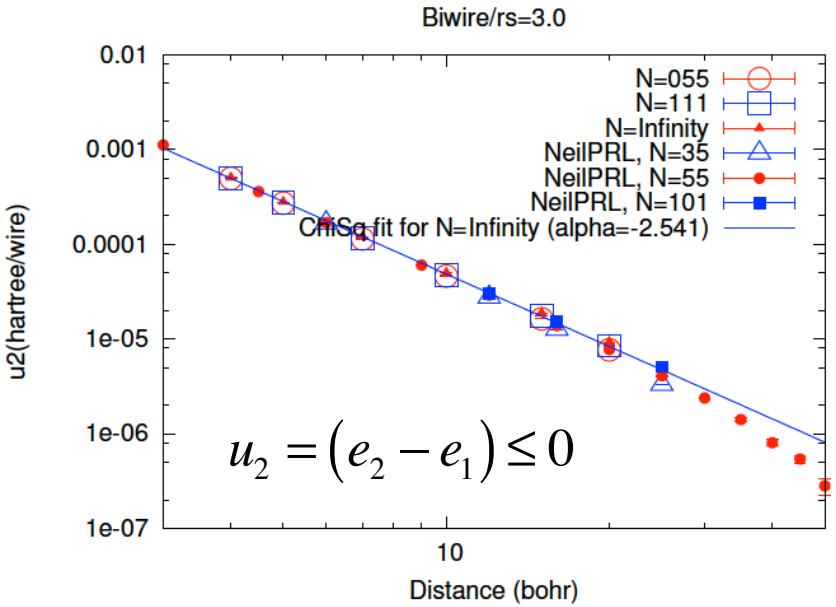
Rs = 1.0

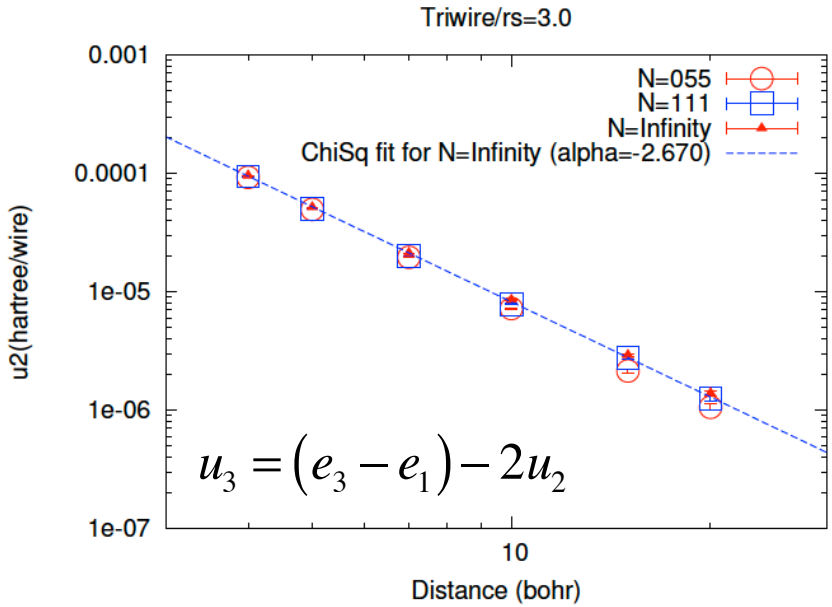




$$\left|u_{2,3}(z)\right| = \frac{C}{z^{\alpha}}$$

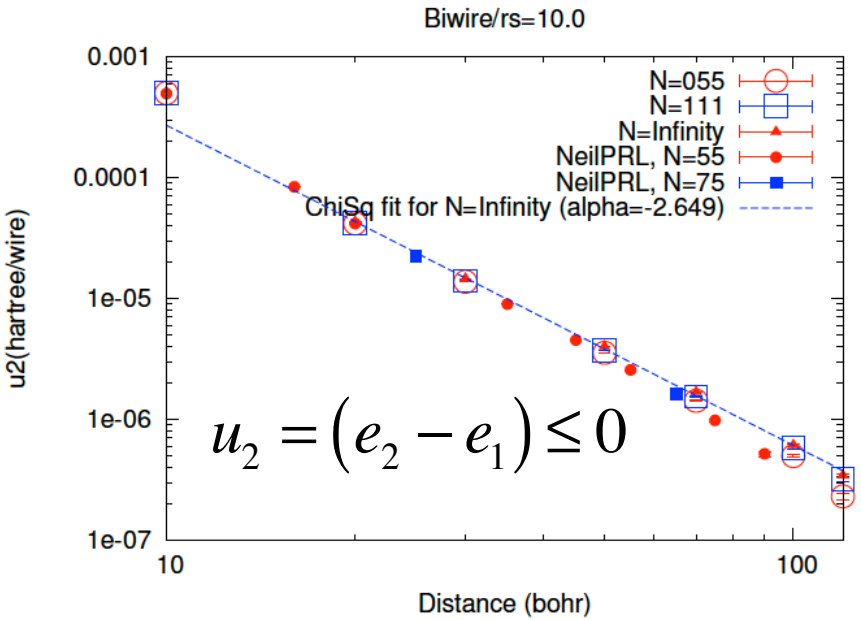
Rs = 3.0

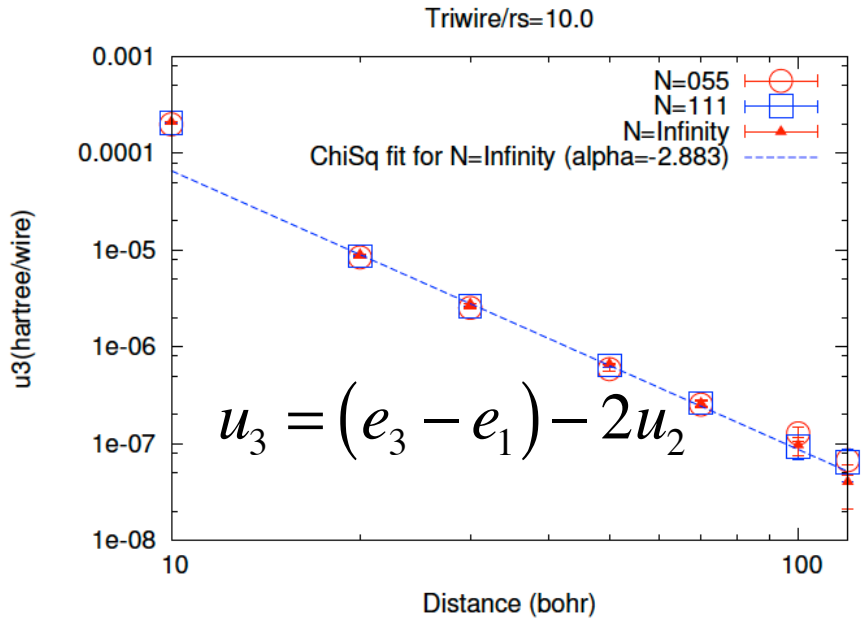




$$\left|u_{2,3}(z)\right| = \frac{C}{z^{\alpha}}$$

Rs = 10.0





$$|u_{2,3}(z)| = \frac{C}{z^{\alpha}}$$

Exponents

TABLE II: Fitted parameters (extrapolated to $N \to \infty$).

	u_2		u_3	
	C	α	C	α
$r_s = 1.0$	-6.0685(6)	2.310(1)	-7.942(5)	2.435(8)
$r_s = 3.0$	-4.084(1)	2.5410(7)	-5.565(8)	2.670(5)
$r_s = 10.0$	-2.114(6)	2.649(2)	-2.98(5)	2.88(2)

$$\left|u_{2,3}(z)\right| = \frac{C}{z^{\alpha}}$$

Long-ranged interactions ; $\alpha < 3$

Exponents of Decay

Possible mechanisms making it finite.

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(c.f., Our equilateral triangle gives repulsive u_3)

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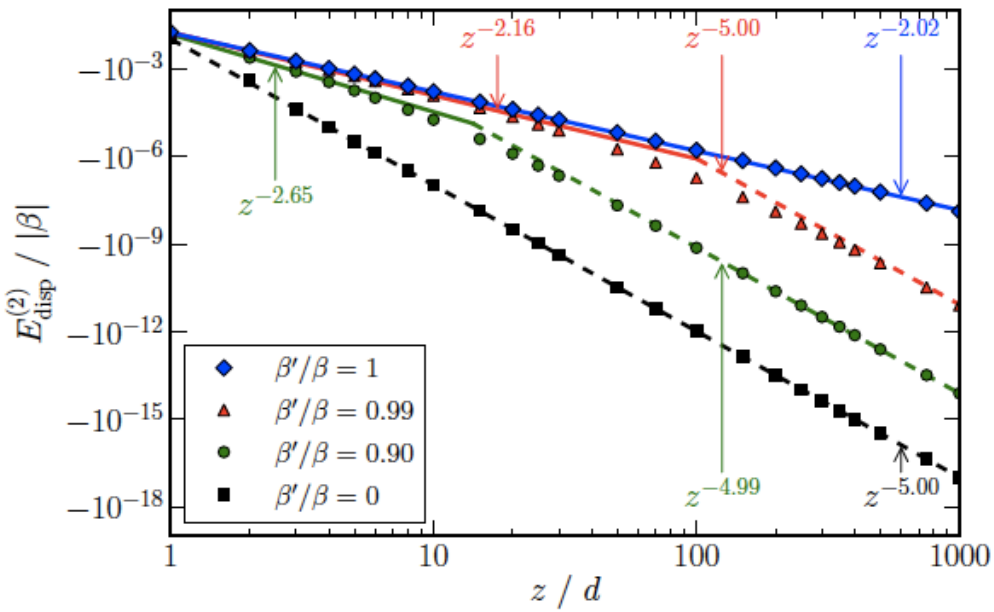
Kink in the exponent

James Spencer & Ali Alavi: Interactions between parallel wires. Huckel



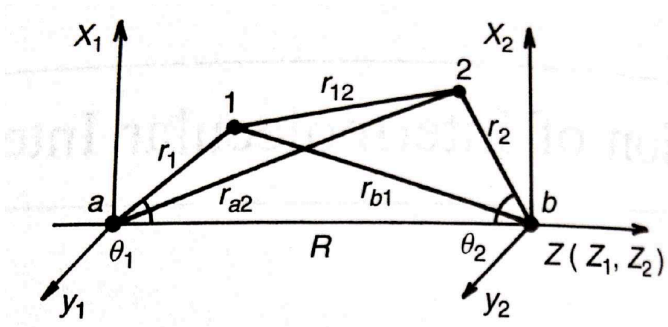
Note; correlation effect makes kink broader [Misquetta/SAPT, 2010]

2nd order perturbation

$$E_{disp}^{(2)} = -\sum_{n\neq 0, m\neq 0} \frac{\left|\left\langle \Psi_n^A \Psi_m^B \middle| V_{AB} \middle| \Psi_0^A \Psi_0^B \right\rangle\right|^2}{\left(E_n^A + E_m^B\right) - \left(E_0^A + E_0^B\right)}$$

inter-molecular interactions

$$V_{AB} \sim \int_A d^3 r_A \int_B d^3 r_B \cdot \frac{\rho\left(\vec{r}_A\right)\rho\left(\vec{r}_B\right)}{\left|\vec{r}_A - \vec{r}_B\right|}$$



integral representation

$$\frac{1}{\left(E_n^A + E_m^B\right) - \left(E_0^A + E_0^B\right)} = \frac{1}{\omega_{n0}^A + \omega_{m0}^B} = \frac{2}{\pi}\int_0^\infty d\omega \cdot \frac{\omega_{n0}^A \omega_{m0}^B}{\left(\left(\omega_{n0}^A\right)^2 + \omega^2\right)\left(\left(\omega_{m0}^B\right)^2 + \omega^2\right)}$$

Longuet-Higgins Representation

of dispersion energy

$$E_{disp}^{(2)} = -\frac{1}{2\pi}\int_0^\infty d\omega \cdot \int_A d^3r_A' d^3r_A \int_B d^3r_B' d^3r_B \cdot \frac{\alpha\left(\vec{r}_B', \vec{r}_B; i\omega\right)\alpha\left(\vec{r}_A', \vec{r}_A; i\omega\right)}{\left|\vec{r}_A - \vec{r}_B\right| \cdot \left|\vec{r}_A' - \vec{r}_B'\right|}$$

H. C. Longuet-Higgins, Discuss. Faraday Soc. 40, 7 1965 .

non-local polarizability

$$\alpha\left(\vec{r}_A', \vec{r}_A; i\omega\right) = \sum_{n\neq 0} \frac{\omega_{n0}^A \left\langle \Psi_0^A \middle| \rho\left(\vec{r}_A'\right) \middle| \Psi_n^A \right\rangle \left\langle \Psi_n^A \middle| \rho\left(\vec{r}_A\right) \middle| \Psi_0^A \right\rangle}{\left(\omega_{n0}^A\right)^2 - \left(i\omega\right)^2}$$

multi-pole expansion

$$\frac{1}{\left|\vec{r}_A - \vec{r}_B\right|} \sim \frac{1}{R}\sum_{t,u} \tau_{t,u} \left(\frac{r_A}{R}\right)^{l_t} \left(\frac{r_B}{R}\right)^{l_u} = \frac{1}{R^{1+l_t+l_u}} \sum_{t,u} \hat{Q}_t^A \cdot T_{tu}^{AB} \cdot \hat{Q}_u^B$$

Exponent of decay

$$E_{disp}^{(2)} = -\sum_{n\neq 0, m\neq 0} \sum_{t,u} \sum_{t',u'} \frac{1}{R^{2+l_t+l_u+l_{t'}+l_{u'}}} T_{tu}^{AB} T_{t'u'}^{AB} \alpha_{tt'}^{A}(i\omega) \alpha_{uu'}^{B}(i\omega)$$

$$\alpha_{tt'}^{A}(i\omega) = \int_A d^3 r_A' d^3 r_A \cdot \hat{Q}_t'^{A} \alpha(\vec{r}_A', \vec{r}_A; i\omega) \hat{Q}_{t'}^{A}$$

$$\hat{Q}_t^A \sim r^{l_t}$$

Induced dipole-dipole int.

Rank of tensor $(l_t, l_{t'}) = (l_u, l_u) = (1,1)$ --> $E_{disp}^{(2)} \sim \frac{1}{R^{2+1+1+1+1}} = \frac{1}{R^6}$

lowest possible contribution

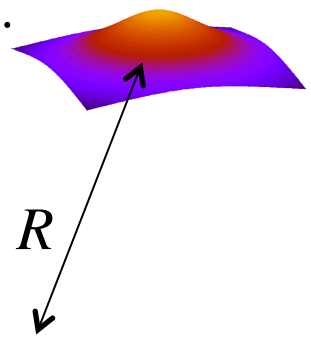
$(l_t, l_{t'}) = (l_u, l_u) = (0,0)$ --> $E_{disp}^{(2)} \sim \frac{1}{R^{2+0}} = \frac{1}{R^2}$

Inv.Sq. contribution

$$E_{disp}^{(2)} \sim -\frac{1}{R^{2+2l+2l'}} \int_A \left[r_A^l \times \rho(r_A) \right] d^3 r_A \cdot \int_B \left[r_B'^{l'} \times \rho(r_B') \right] d^3 r_B'$$

Insulator (localized) ; $\alpha(\vec{r}_A', \vec{r}_A; i\omega) \sim \exp\left[-\gamma \left| \vec{r}_A' - \vec{r}_A \right| \right]$

$\int_A d^3 r_A' d^3 r_A \cdots$



$\gamma^{-1} \sim L_c$; localization length

--> $\int_A d^3 r_A' \cdot \alpha(\vec{r}_A', \vec{r}_A; i\omega) = 0$

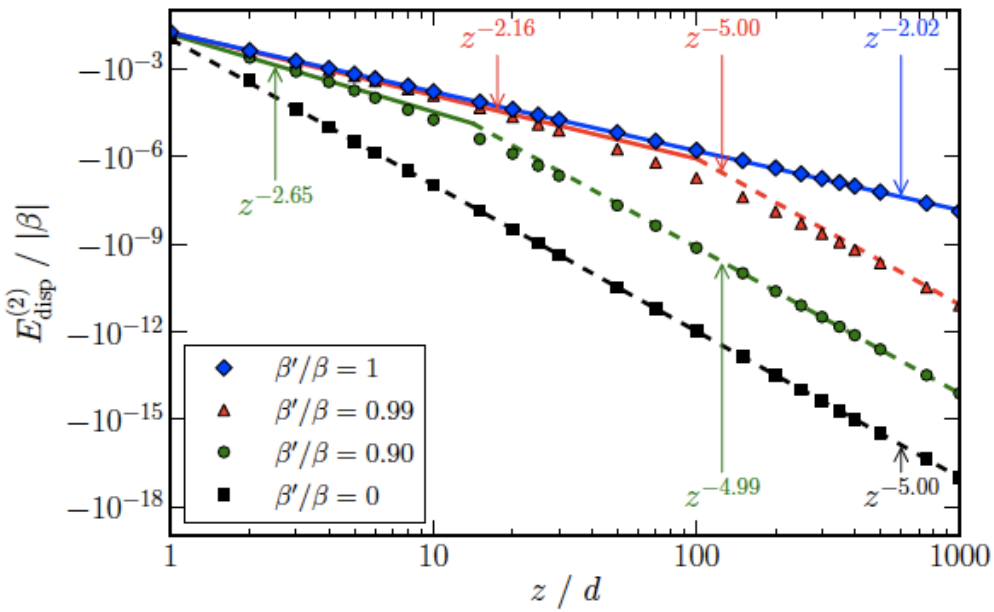
inv-sq. contribution vanishes

$R >> L_c$; integral region valid for multi-pole expansion

gets larger --> integral gets disappear

Kink in the exponent

James Spencer & Ali Alavi: Interactions between parallel wires.



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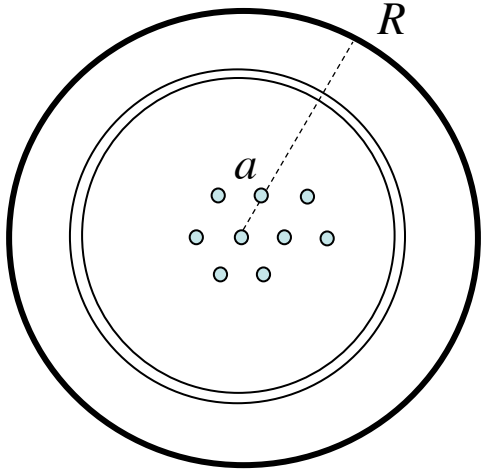

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Summary

Non-additivity of vdW investigated

on 1-dim. metallic tri-wire system.

1）Bi-wire interaction u_2

as well as non-additive contribution u_3

show long-ranged exponent $u \sim \frac{1}{z^{2.5}}$

2）Divergence of u_2 when we make a bunch of wire.

(not physical, should not occur)

cancelled by u_3 and higher？

(importance of non-additive contribution in metallic system)