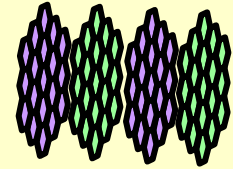




Some issues concerning
DISPERSION INTERACTIONS



ISSP Kashiwanoha, July 2012

John Dobson, Tim Gould, Griffith U., Nathan, Qld, Australia

Funding: CSIRO, FAST, ARC

Recent review: Dobson + Gould, J Phys Cond Matt 24 073201 (2012)

Simple pairwise models of dispersion (van der Waals) interaction

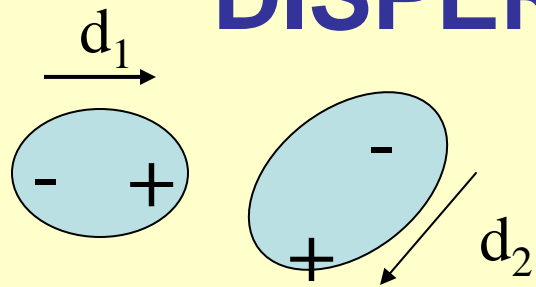
Importance of **non-pairwise-additive** parts of van der Waals interaction between polarizable anisotropic nanostructures (graphene, nanotubes, proteins, etc).

High level theory such as Lifshitz (macro) or RPA (micro)

vdW-DF theory (Langreth et al)

RPA+Response from electron “Continuum Mechanics” \Rightarrow vdW

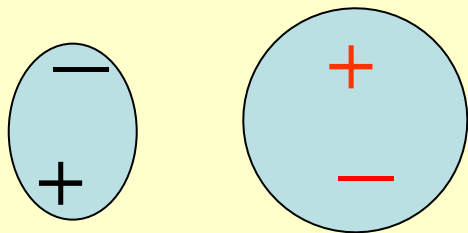
DIPOLE-DIPOLE, INDUCTION AND DISPERSION ENERGIES



Fixed dipole - fixed dipole

$$E \sim -\mathbf{d}_1 \cdot \mathbf{T} \cdot \mathbf{d}_2 / R^3$$

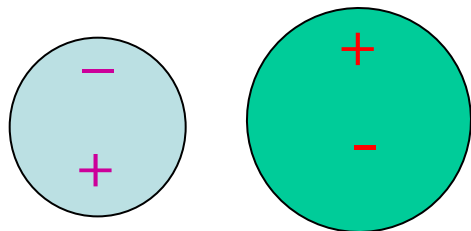
✓ HF, ✓ LDA



Fixed dipole - induced dipole

$$E \sim -d_1^2 \alpha / R^6 \quad \text{"induction energy"}$$

✓ HF, ✓ LDA



d_1

$$E \sim -\langle \mathbf{d}_1^2 \rangle \alpha / R^6 \quad \text{"vdW, dispersion"}$$

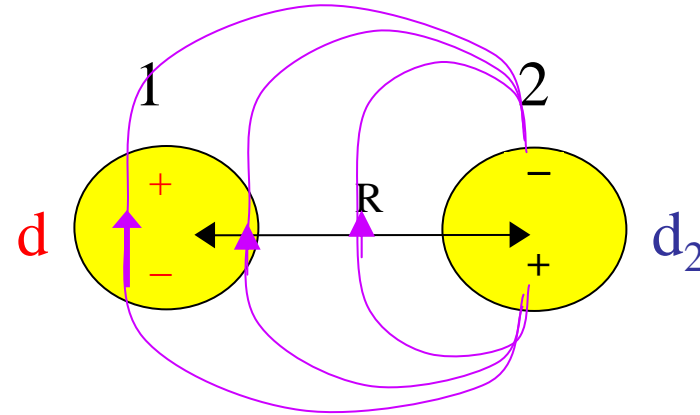
✗ HF, ✗ LDA

vdW betw. spherical atoms: fluctuation approach

Random zero-point (or thermal) dipole \mathbf{d} on #1 initiates the process

$$F_2 = -\frac{d}{R^3}$$

Field on #2:



Field Induces dipole on #2: $d_2 = -\alpha_2 \frac{u}{R^3}$

d_2 generates back-field on #1: $F_1 = -\frac{d_2}{R^3} = \frac{d\alpha_2}{R^6}$

Energy of F_1 with original dipole: $E \propto -F_1 d = -\frac{d^2 \alpha_2}{R^6}$

Time-averaged energy $\langle E \rangle = -\frac{\langle d^2 \rangle \alpha_2}{R^6} \approx -\frac{(\alpha_1 \hbar \omega_0) \alpha_2}{R^6}$ by *SHO* model

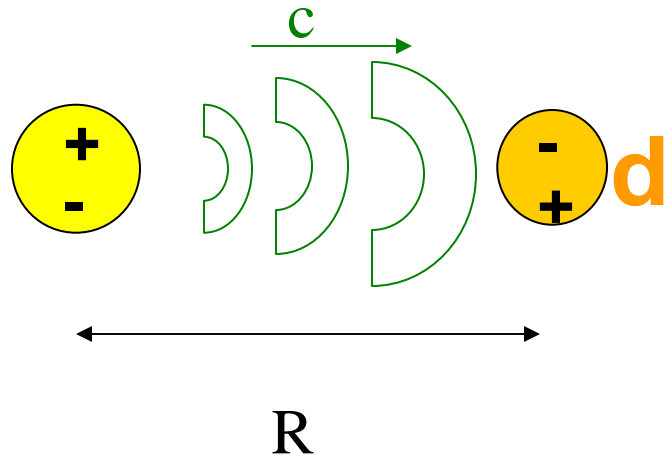
More accurate: $E = -C_6 R^{-6}$, $C_6 = \frac{3\hbar}{\pi} \int_0^\infty \alpha_1(iu) \alpha_2(iu) du$

From 2nd order Pertn th.

Incl. ZP KE

This form isotropic only

Electromagnetic retardation



Above treatments assumed instantaneous Coulomb interaction. In fact there is a delay $\tau_{\text{light}} \approx R/c$

If $\tau_{\text{light}} \gg \tau_{\text{el resp}}$, then the original random dipole has decayed by the time a return signal arrives, resulting in a smaller attractive energy.

End result is to replace ω in previous results by $1/\tau_{\text{light}}$ so that

$$E^{\text{retarded regime}} \approx -\frac{\alpha_1 \alpha_2 \hbar c}{R^7}$$

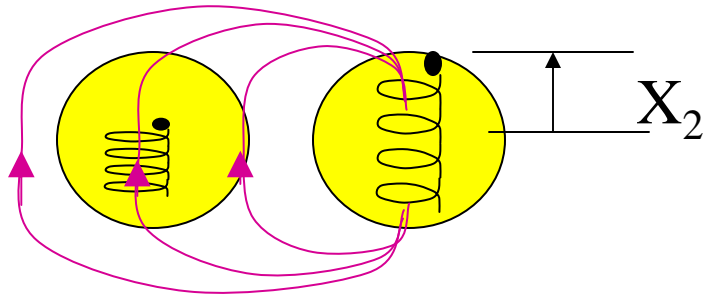
Condition for this to occur:

$$R \gg c\tau_{\text{el resp}} \approx (3 \cdot 10^8)(2\pi \cdot 10^{-15}) \approx 2 \cdot 10^{-6} \text{ m}$$

Retarded case generally known as “Casimir effect”: can get from e.m. ZP energy.

Treat non-retarded case from here on

vdW attraction from coupled plasmons



Toy version of the theory

$$m\ddot{x}_1 = -m\omega_0^2 x_1 - \frac{e^2}{R^3} x_2$$

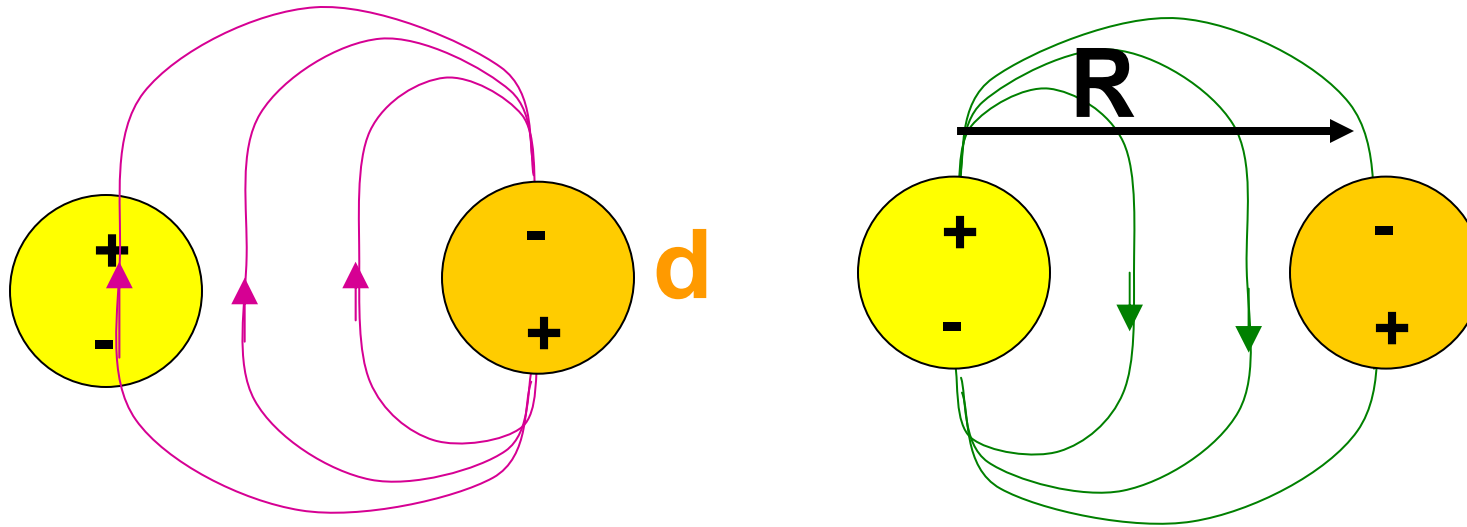
$$\begin{pmatrix} m(\omega_0^2 - \omega^2) & \frac{e^2}{R^3} \\ \frac{e^2}{R^3} & m(\omega_0^2 - \omega^2) \end{pmatrix} \begin{pmatrix} x_1 \\ x_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix} \quad \omega = \omega_{\pm} = \omega_0 \left(1 \pm \frac{e^2}{m\omega_0^2 R^3}\right)^{1/2}$$

Zero point plasmon energy: $E^{\text{vdW}} = \frac{\hbar}{2} (\Delta\omega_+ + \Delta\omega_-) \approx -\frac{\hbar e^4}{8\omega_0^3 R^6} = -\frac{\hbar\omega_0 \alpha_1 \alpha_2}{8R^6}$

ZP plasmon method works also for large systems where zero energy denominators make perturbation theory difficult. See Langbein's book 1974.

A more rigorous method, ACF/FDT, generalizes this approach:

ORIGIN OF VDW (DISPERSION) FORCE



$$E^{(2)} = -\frac{\alpha_2 \langle d^2 \rangle}{R^6} \approx -\frac{\alpha_2 \alpha_1 \hbar \omega_0}{R^6}$$

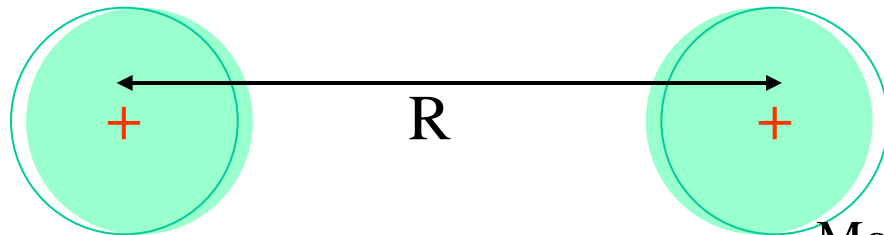
A **correlation** effect, highly **nonlocal** so **LDA & GGA FAIL**

Get from 2nd order perturbation theory (for small systems)

Or via theory of **response** (polarisability, **coupled plasmons**)

Weak but ubiquitous - additional to covalent, ionic bonds

Static vs. Dynamic e⁻ density distortions as the source of vdW interaction



Static distortion: Allen +Tozer, J. Chem. Phys. 117, 11113 (2002);

Both distortions strongly R dependent

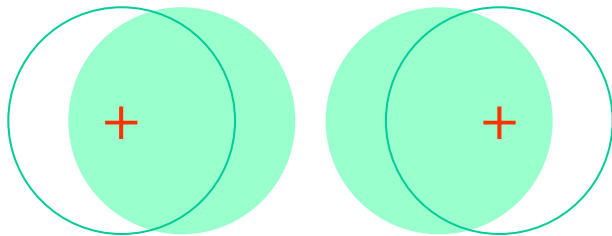
Moves electrons toward other atom

Requires wavefunction to 2nd order in W_{12}

Directly causes Feynman-vdW coulomb

force on nuclei: See Allen & Tozer JCP '02

NOT direct Coulomb interaction $dn_1 * W_{12} * dn_2$



Dynamic (ZP+Ind) distortions:

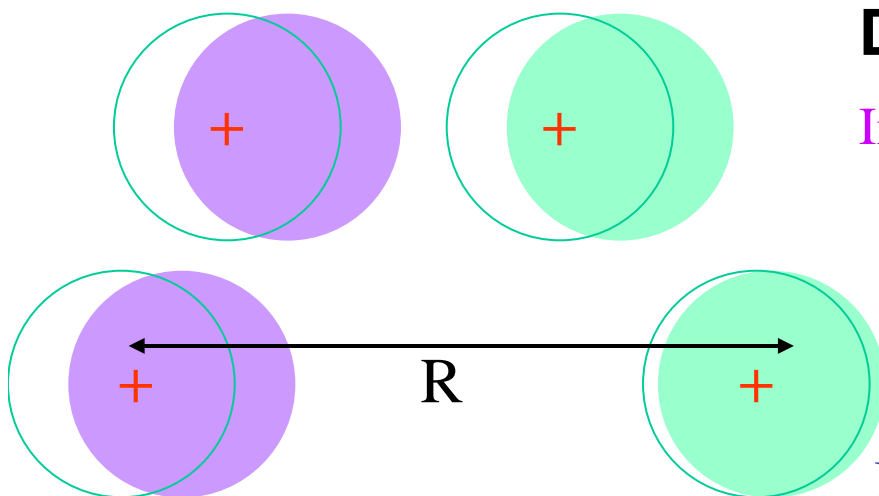
Initiating ZP distortion **NOT** R dependent

Moves **electrons away** from **initial distortion**

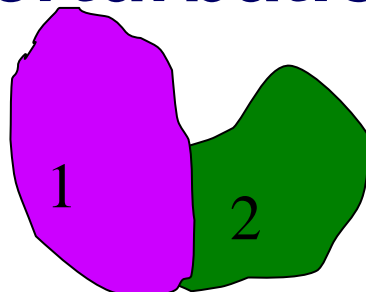
Needs (TD) wavefunct. to 1st order in W_{12}

Gives total energy change of $O(W_{12}^2)$

IS direct Coulomb interaction $dn_1 * W_{12} * dn_2$



Overlapping finite systems: Symmetry Adapted Perturbation Theory (SAPT)



Once overlap occurs, we can't distinguish electrons as belonging to one side or the other

SAPT introduces Projection Operator to enforce the Pauli principle while still treating cross-coulomb interaction as a perturbation.

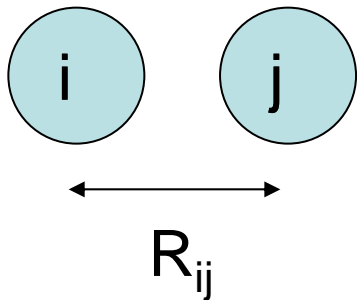
Expands coulomb in multipoles, includes higher order pertⁿ theory

Jeziorski +, Chem Rev **94**, 1887 ('94):

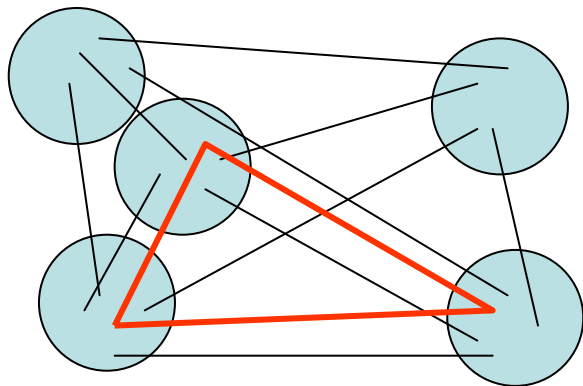
Hesselman +, JACS **128**, 11730 ('06)

This method is probably the state of the art for prediction of vdw interaction between molecules of modest size: but not yet feasible for extended nansystems, so not considered further here.

Conventional view in nano-community: “universality” of asymptotic vdW



“Take vdW as given between atoms or sub-units: $E_{ij} \approx -C_6^{(ij)}R_{ij}^{-6}$, $R_{ij} \rightarrow \infty$.”



“Then total E_{vdW} is the sum of pairwise contributions

$$E_{vdW} = - \sum_{i,j: i \neq j} C_6^{(ij)} R_{ij}^{-6}$$

“Triplet and higher terms – e..g.

$$E_{vdW}^{(3)} = - \sum_{i,j,k} C_9^{(ijk)} R_{ij}^{-3} R_{jk}^{-3} R_{ik}^{-3}$$

do not make a qualitative difference.”

XX

ASYMPTOTICS $D \rightarrow \infty$

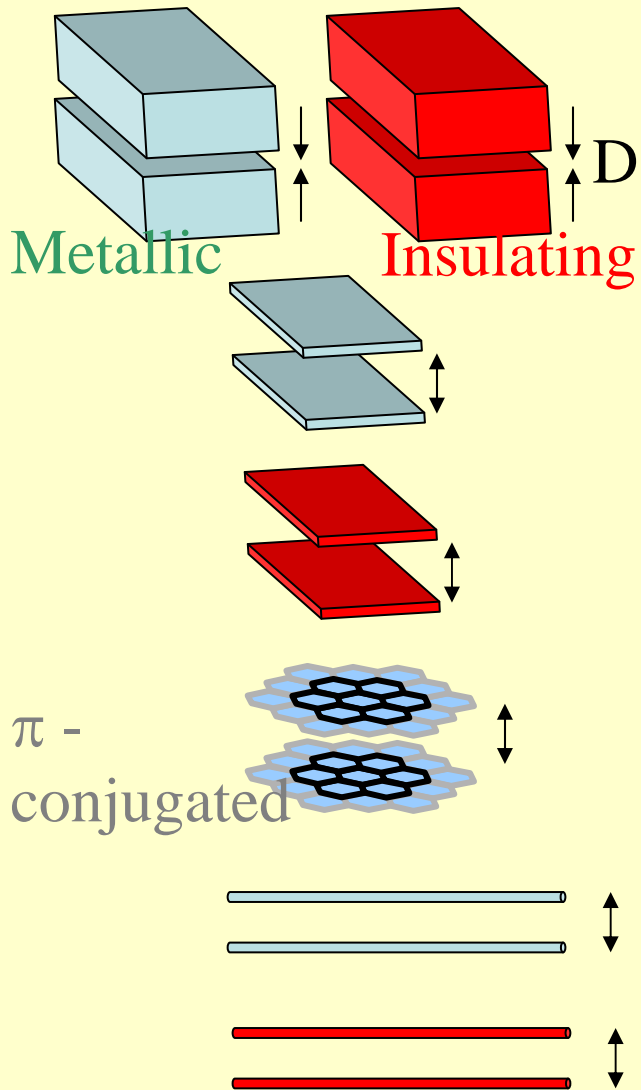
Present theory

Conv. theories

ΣR^{-6} , "vdW-DFT"

Coupled plasmon, RPA

Dobson White Rubio PRL **96**, 07320 (2006).



$$E \propto -D^{-2}$$

$$E \propto -D^{-2}$$

$$E \propto -D^{-5/2}$$

$$E \propto -D^{-4}$$

$$E \propto -D^{-4}$$

$$E \propto -D^{-4}$$

$$E \propto -D^{-3}$$

$$E \propto -D^{-4}$$

$$E \propto -D^{-2} (\ln D/b)^{-3/2}$$

$$E \propto -D^{-5}$$

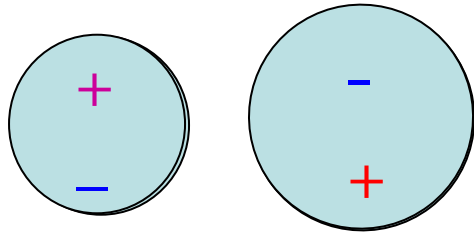
$$E \propto -D^{-5}$$

$$E \propto -D^{-5}$$

See also Dobson, Gould et al PRB '08, '09, PRA '09, Lebegue et al PRL **105**, 196401 (2010), JFD Surf Sci 2011, R Liu et al JCP **134**, 114106 (2011) 2011

WHY THE DIFFERENT POWER LAWS FOR LOW-DIM METALLIC SYSTEMS?

Strong non-pairwise-additivity of vdW interactions



vdW interaction between two “atoms”

Arises from correlations between dipole fluctuations.

Depends on polarizability of atoms

Can also be obtained from coupled plasmon z.p.e




Extended structures: individual atom pairs do not correlate independently.

Rather, correlation is between extended charge density fluctuations (plasmons).

In metallic 1D structures, long-wavelength plasmons have low energy, easily excited.

Nanotube attraction I: single wire/tube

(a) Conducting



$\lambda = 2\pi/q$

$2A$

$\frac{\delta n}{\delta V^{\text{tot}}} \equiv \chi_0(q, \omega) = n_{1D} q^2 (m\omega^2)^{-1}$

(b) semiconducting



$\chi_0(q, \omega) = n_{1D} q^2 (m(\omega^2 - \omega_0^2))^{-1}$

RPA equ.: $\delta n(q, \omega) = \chi_0(q, \omega) (\delta V^{\text{ext}} + W_{01D}(q) \delta n(q, \omega))$

$\frac{\delta n}{\delta V^{\text{ext}}} = \chi^{\text{RPA}} = \frac{\chi_0(q, \omega)}{1 - W_{01D}(q) \chi_0(q, \omega)}, \quad W_{01D}(q) = 2e^2 |\ln(qA)|$

Plasmon freqs are zeros of $\epsilon^{\text{RPA}} = 1 - W_{01D} \chi_0 = 1 - (\text{const})q^2 |\ln(qb)| / \omega^2$

c.f. $\epsilon^{3D} = 1 - \frac{4\pi e^2}{q^2} \frac{q^2}{m\omega^2} = 1 - \frac{\omega_{P3D}^2}{\omega^2}$ indep of $q \therefore$ spatially local

$\omega^{\text{RPA}} = \omega_{1D}(q) \equiv q \sqrt{2n_{1D} e^2 m^{-1} \ln(b^{-1} q^{-1})}$

quasi-acoustic plasmon

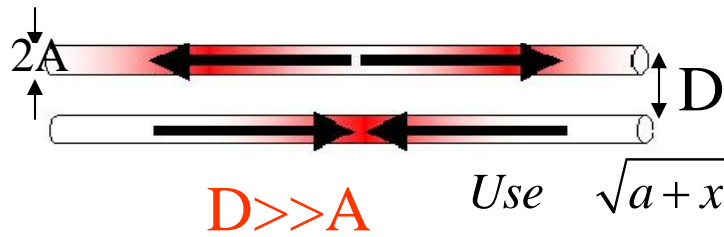
$\omega^{\text{RPA}} = \sqrt{\omega_{1D}^2 + \omega_0^2}$

optical plasmon

Nanotube attraction III: conducting case ($\omega_0=0$)

vdW energy in RPA $\frac{1}{L} E^{\text{vdW}}(D) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \frac{\hbar}{2} (\omega_+(q) + \omega_-(q) - 2\omega_{\text{wire}}(q)) dq$

$$\frac{E}{L} = \frac{\hbar \sqrt{2e^2 n_{1D} / m}}{4\pi} \int_{-\infty}^{+\infty} |q| \left(\sqrt{\tilde{V}(q,0) + \tilde{V}(q,D)} + \sqrt{\tilde{V}(q,0) - \tilde{V}(q,D)} - 2\sqrt{\tilde{V}(q,0)} \right) dq$$



where $\tilde{V}(q,0) = (2e^2)^{-1} V_0(q) = -\ln(A|q|)$ for $|Aq| \ll 1$

$$\tilde{V}(q,D) = (2e^2)^{-1} V_D(q) = K_0(qD)$$

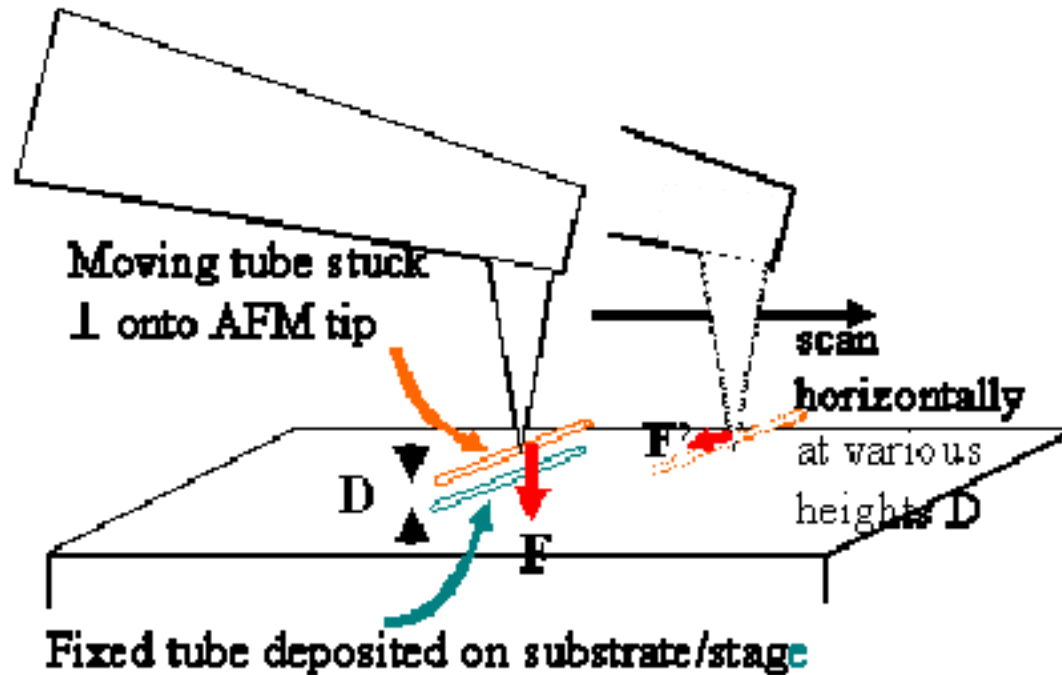
Use $\sqrt{a+x} + \sqrt{a-x} - 2\sqrt{a} \approx -\frac{x^2}{4a^{3/2}}, \quad |x| \ll a$

$$4\pi \hbar^{-1} (2e^2 n_{1D} / m)^{-1/2} \frac{E}{L} = 2 \int_0^{\infty} q \left(-\frac{K_0^2(qD)}{4|\ln(Aq)|^{3/2}} \right) dq = -\frac{1}{2D^2} \int_0^{\infty} x K_0^2(x) (\ln(xD/A))^{-3/2} dx$$

$$\approx -\frac{(\ln(\bar{x}D/A))^{-3/2}}{2D^2} \int_0^{\infty} x K_0^2(x) dx = -\frac{(\ln(\bar{x}D/A))^{-3/2}}{4D^2}$$

$$\bar{x} = \exp \left(\int_0^{\infty} x K_0^2(x) (-\ln x) dx / \int_0^{\infty} x K_0^2(x) dx \right) = 2.3,$$

DIRECT AFM MEASUREMENT OF CNanoTube-CNT FORCE?



JFD, experimental design in progress

Need to consider nonparallel tubes: JFD et al, PRA **80**, 012506 (2009)

vdW force from conducting e^- s exceeds "majority" transitions only for $D > 5$ nm

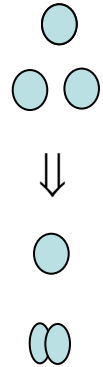
Fixed end dipoles exist – keep them apart with unequal-length tubes

Conclusions for the AFM expts: **"Weird" Force of a few picoNewtons measurable for**

(6,6) Tubes $L \sim 2$ microns long, 20 nm apart

High vacuum, $T = \text{few K}$, unequal tube lengths $L_1 \neq L_2$

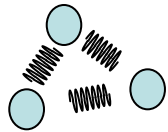
THREE DISTINCT CAUSES OF NON-PAIRWISE-ADDITIVE DISPERSION ENERGY



TYPE A NONADDITIVITY.

When atoms come together to make a molecule or solid, electron clouds overlap and may be compressed by Pauli effects, and also because additional positive nuclei are nearby. This often makes the electrons less polarizable, reducing vdW energy with a second molecule, compared with a sum of free-atom pairs. .

TYPE B NONADDITIVITY.



The presence of a nearby polarizable atom may affect (Coulomb-screen) the response of a second atom to fluctuations occurring on a third atom/molecule. This can either reduce or enhance the vdW interaction depending on geometry. It does not rely on overlap of atoms/molecules

TYPE C NONADDITIVITY.

+
-
This occurs in cases of degeneracy which favours large electron density fluctuations related to hopping of electrons between neighbouring atoms. A **metal** is an extreme case of this. The longer electronic motions permit large dipoles to be induced, tending to increase the vdW interaction. This is however strongly suppressed by Type B effects for the case of 3D metals, but less so for 2D or 1D metals.

IMPORTANCE OF NON-PAIRWISE ADDITIVITY

Note: **Don't** need metallic systems to see type B non-additivity.

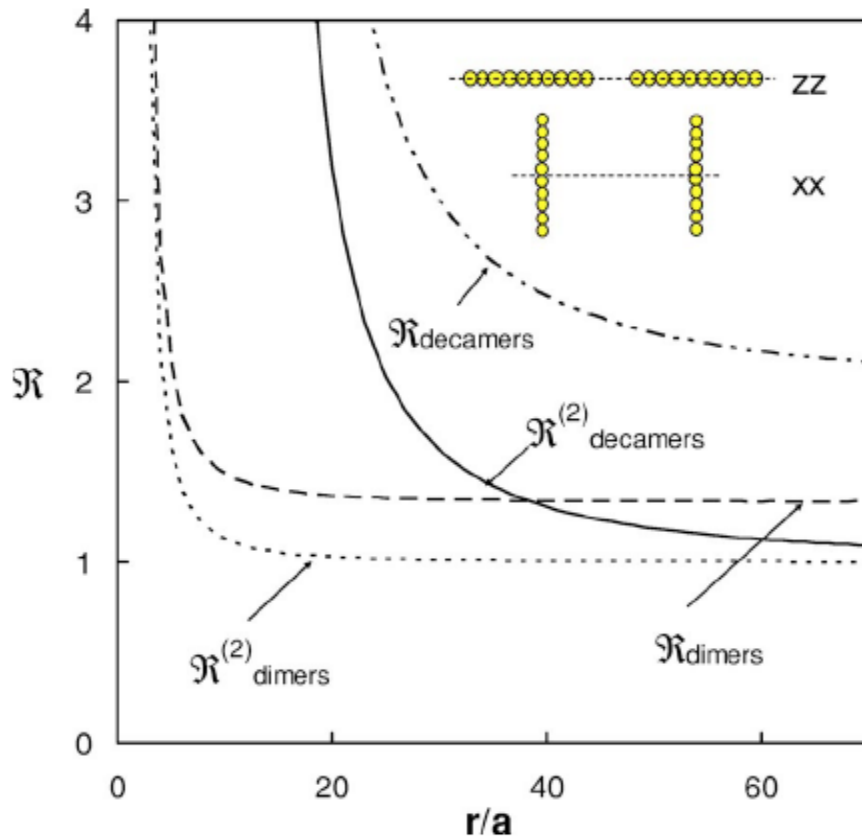


FIG. 1. Anisotropy ratio $\mathcal{R} = V_{zz}/V_{xx}$ for various cluster pairings as a function of center-to-center separation r . Ratios with the superscript (2) are computed by summing pair interactions. The other curves include all MB interactions.

Chains of SiO_2 spheres (B):
Kim et al, JCP 124, 074504 (2006)

consistent coupled dipole equations,

$$\frac{1}{\alpha(\omega)} \mathbf{p}_i - \sum_{j \neq i} \mathbf{T}_{ij} \cdot \mathbf{p}_j = 0.$$

$$\alpha(\omega) = \frac{\alpha_0}{1 - \omega^2 \omega_0^{-2}}$$

$$E_{vdW} = \sum_n \frac{\hbar}{2} (\omega_n - \omega_n^{(R \rightarrow \infty)})$$

(Discrete RPA method)

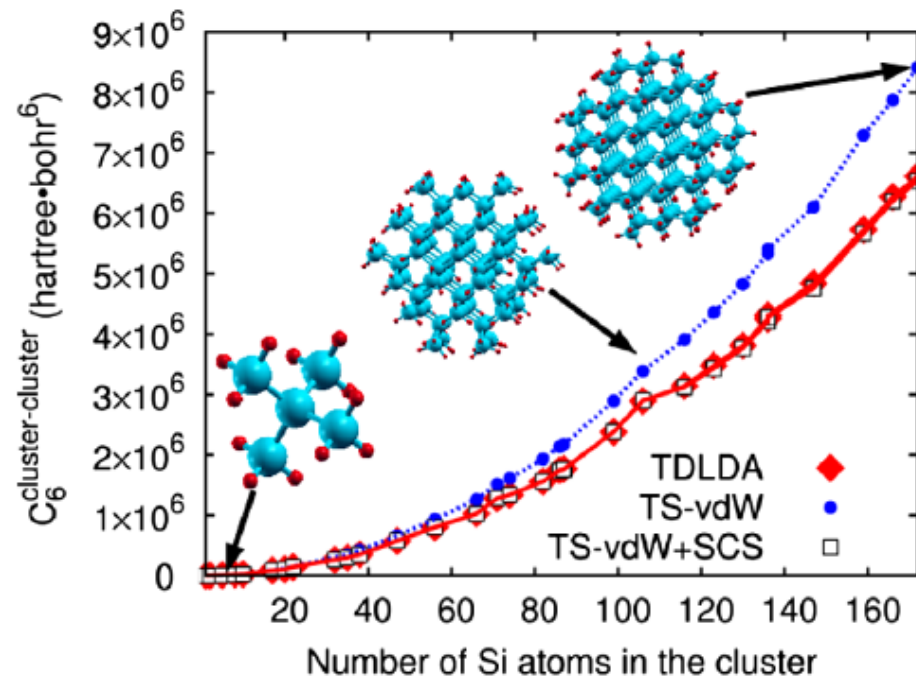
Kim et al also concluded that adding triplet (Axilrod-Teller) terms is not enough.

H chains via SAPT: R.-F.Liu, J. Angyan, J. Dobson, JCP. **134**, 114106 (2011) (B,C)

Large molecules: A. Tkatchenko et al, PRL 108, 236402 (2012) (gap $\neq 0$: A,B)

Tkatchenko et al, PRL 108, 236402 (2012)

Non-pairwise additivity in spherical Si clusters

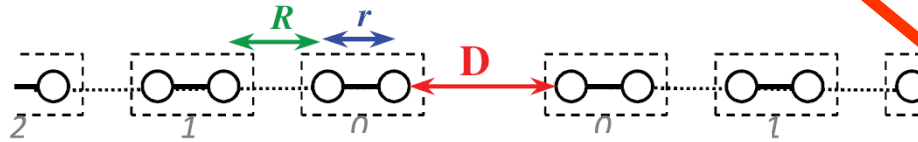


20%
effect

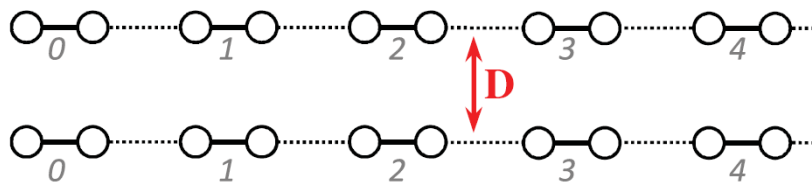
H CHAINS LIU+ANGYAN+DOBSON JCP 2011

Type C
nonadditivity

Type B nonadditivity

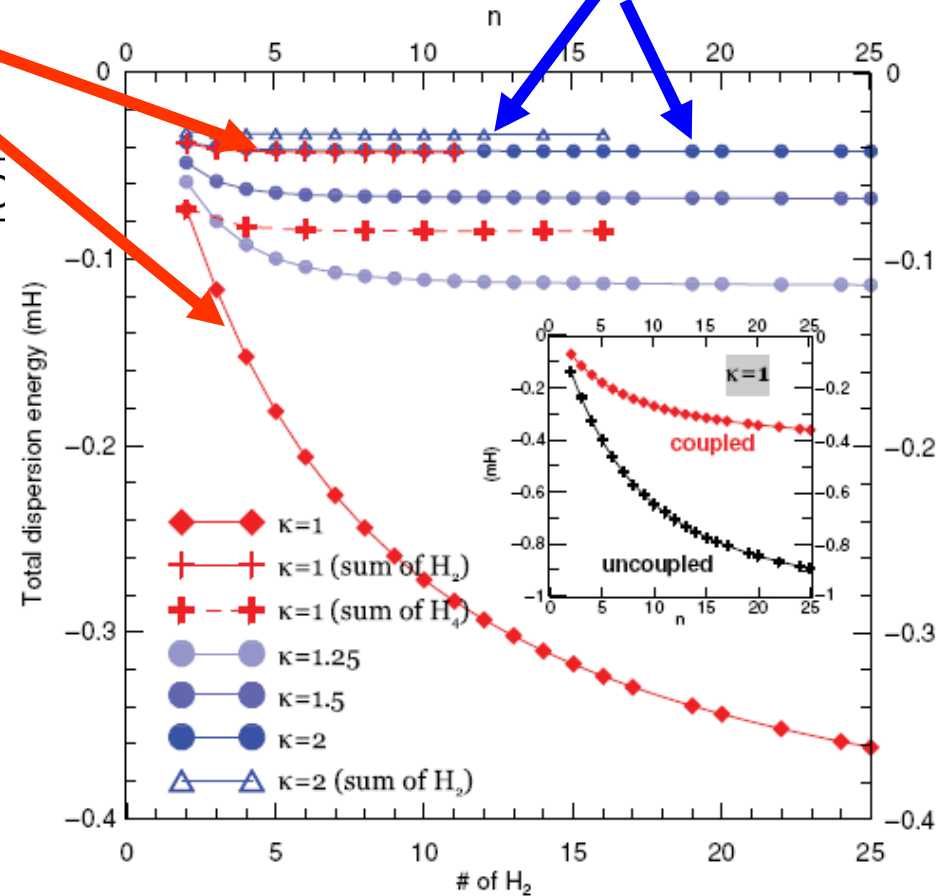


(a) Pointing chains



(b) Parallel chains

$$D = 8a_0, \quad r = 1.84a_0$$



Uneven chain spacing. $r \neq R$ (i.e. $K=R/r > 1$) gives insulator, semiconductor:

$r=R$ (i.e. $K=1$) gives metal

BEYOND ATOMIC PAIRWISE ADDITIVITY: TYPE A

Type A nonadditivity: Nearby atoms cause Pauli compression, atomic level spacing increases $\Rightarrow \chi$ decreases $\Rightarrow C_6^{\text{in molecule}} < C_6^{\text{isolated atoms}}$

Usually treated by empirical C_6 fitting to molecular or SS data:

$$\text{Wu \& Yang JCP 116 515 (2002) } E = E^{\text{LDA}} - \sum f(r_{ij}) R_{ij}^6$$

$$\text{e.g. Grimme JCP 132, 154104 (2010): } E^{\text{DFT-D}} = E_{\text{GGA}} - \sum f(R_{ij}) C_{6ij} R_{ij}^{-6}$$

$$\text{Tkatchenko, Scheffler PRL 102, 073005 (2009) } C_6 = \left(\frac{V_{\text{atom}}^{\text{in mol}}}{V_{\text{atom}}^{\text{free}}} \right)^2 C_6^{\text{free atom}}$$

Fitted potentials for larger & layered systems

$$\text{e.g. "Univ, Graphitic Potential" (Lennard Jones) } E = 4\epsilon \left(-\left(\frac{\sigma}{R} \right)^{-6} + \left(\frac{\sigma}{R} \right)^{-12} \right)$$

Girifalco+, Phys. Rev. B 62, 13104 (2000)
Also Brenner, Tersoff

e.g.. Hasegawa & Nishidate PRB 76, 115424 (2007) graphite layers

TYPES B AND C NONADDITIVITY

Type B nonadditivity: (e.m. effect) polzⁿ of additional atoms screens vdW interaction between a pair. Esp. in large low-dimens^{nal} systems

Chains of SiO₂ beads: Kim et al JCP **124**, 074504 2006

H atom chain Liu+Angyan+JFD, JCP **134**, 114106 (2011): Misquitta

Tkatchenko et al PRL **108**, 236402 (2012): RPA with point polarizable dipoles representing atoms

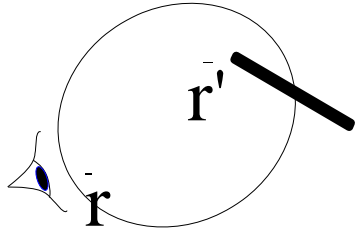
Type C nonadditivity: High symmetry \Rightarrow H-L gap $\rightarrow 0 \Rightarrow \chi$ increases

Chang, 1D conductors Phys Letts 37A, 311 (1971) (RPA/plasmon ZPE)

Parallel 2D metals Sernelius & Bjork **57**, 6592 (1998)

E.g. Low-D metals, graphene JFD+, Phys. Rev. Lett. **96**, 073201 (2006)

Interacting(λ) and KS ($\lambda=0$) dens response



Apply small potential $\delta V \exp(-i\omega t)$ at position r'
 e^- dens change at \underline{r} is $\delta n(\underline{r}, t) = \chi(\underline{r}, \underline{r}', \omega) \delta V \exp(-i\omega t)$

Operator for dens at \underline{r} : $\hat{n}(\vec{r}) = \sum_{\text{particles } a} \delta(\vec{r} - \hat{\vec{r}}_a) = n(\vec{r}) + \delta \hat{n}(\vec{r})$

Fully interacting M-B eigenstate

$$\chi_\lambda(\vec{r}, \vec{r}', \omega = iu) = - \sum_J \frac{\langle 0 | \delta \hat{n}(\vec{r}) | J \rangle_\lambda \langle J | \delta \hat{n}(\vec{r}') | 0 \rangle_\lambda}{E_0 - E_J - i\hbar u} = \chi_{\delta n(\underline{r}), \delta n(\underline{r}')}$$

Fully interacting M-B energy \rightarrow

Fermi factor \rightarrow Kohn-Sham orbital

$$\chi_{\lambda=0}(\vec{r}, \vec{r}', \omega = iu) = \sum_{ij} (f_i - f_j) \frac{\phi_i^*(\vec{r}) \phi_j^*(\vec{r}') \phi_j(\vec{r}) \phi_i(\vec{r}')}{\epsilon_i - \epsilon_j - i\hbar u}$$

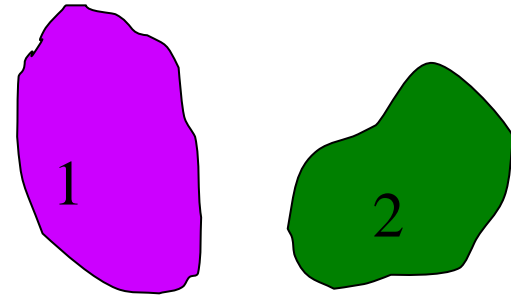
Bare or KS resp \rightarrow Kohn-Sham eigenvalue

Perturbation theory and vdW I

$$E_{12}^{(2)} = -\frac{\hbar}{2\pi} \int d^3r_1 d^3r_1' d^3r_2 d^3r_2' \frac{e^2}{r_{12}} \frac{e^2}{r'_{12}}$$

$$\times \int_0^\infty \chi_2(\vec{r}_1, \vec{r}_1', iu) \chi_2(\vec{r}_2, \vec{r}_2', iu) du$$

nonlocal dens-dens
resp of system 2



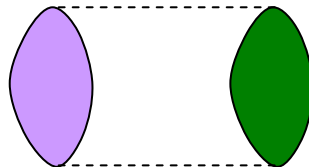
Nonoverlapping
finite systems

H.C. Longuet-Higgins, Disc. Faraday Soc. 40, 7 (1965).

E. Zaremba and W. Kohn, P.R.B 13 2270 (1976).

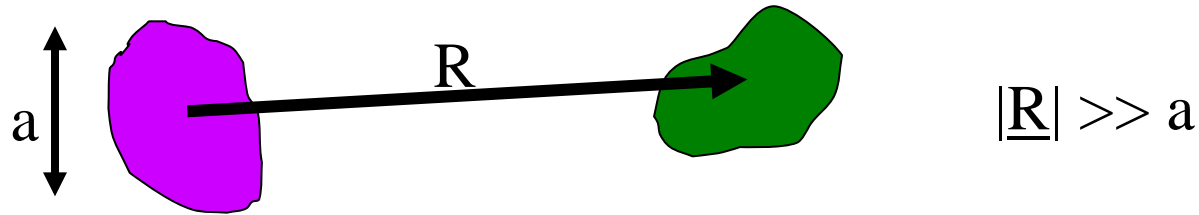
“Generalized Casimir-Polder formula”

$$E_{12}^{(2)} =$$



Feynman diagram for $E^{(2)}$

vdW energy: well separated systems



Make multipolar expansion of $e^2 / |\vec{r}_1 - \vec{r}_2|$ and $e^2 / |\vec{r}_1' - \vec{r}_2'|$

$$E^{(2)} = -\frac{\hbar e^2}{2\pi} \sum_{i,j} T_{ij} T_{kl} \int_0^\infty A_{ik}^{(1)}(iu) A_{jl}^{(2)}(iu) du, \quad T_{ij} = \frac{3R_i R_j - \delta_{ij} R^2}{R^5}$$

$$\vec{A}_1(iu) = \int \chi_1(\vec{r}, \vec{r}', \omega = iu) \vec{r} \vec{r}' d\vec{r} d\vec{r}'$$

isotropic case

$$E_{12}^{(2)} = -C_6 R^{-6}, \quad C_6 = \frac{3\hbar}{\pi} \int_0^\infty A_1(iu) A_2(iu) du$$

Dipole resp of 2

TDDFT/ACF/FDT CONTAINS ALL THE BASIC CHEMICAL AND PHYSICAL FORCES - I

$$E_{xc} = \frac{1}{2} \int_0^1 d\lambda \int d^3r d^3r' \frac{e^2}{|\vec{r} - \vec{r}'|} \left\{ \langle \delta \hat{n}(\vec{r}) \delta \hat{n}(\vec{r}') \rangle_\lambda - n(\vec{r}) \delta(\vec{r} - \vec{r}') \right\}$$

Fluct-dissipation thm

$$E_{xc} = \frac{1}{2} \int_0^1 d\lambda \int d^3r d^3r' \frac{e^2}{|\vec{r} - \vec{r}'|} \left\{ \left[-\frac{\hbar}{\pi} \int_0^\infty \chi_\lambda(\vec{r}, \vec{r}', \omega = iu) du \right] - n(\vec{r}) \delta(\vec{r} - \vec{r}') \right\}$$

ACF-FDT (exact)

$$E_x = \frac{1}{2} \int_0^1 d\lambda \int d^3r d^3r' \frac{e^2}{|\vec{r} - \vec{r}'|} \left\{ \left[-\frac{\hbar}{\pi} \int_0^\infty \chi_{KS}(\vec{r}, \vec{r}', \omega = iu) du \right] - n(\vec{r}) \delta(\vec{r} - \vec{r}') \right\}$$

Insert expr. for χ_{KS} from $\{\phi_i\} \Rightarrow E_x = E^{HF}(\{\phi_i\})$

Our E_{xc} contains EXACT DFT EXCHANGE

RPA Interaction energy related to sum of coupled plasmon zero-point energies

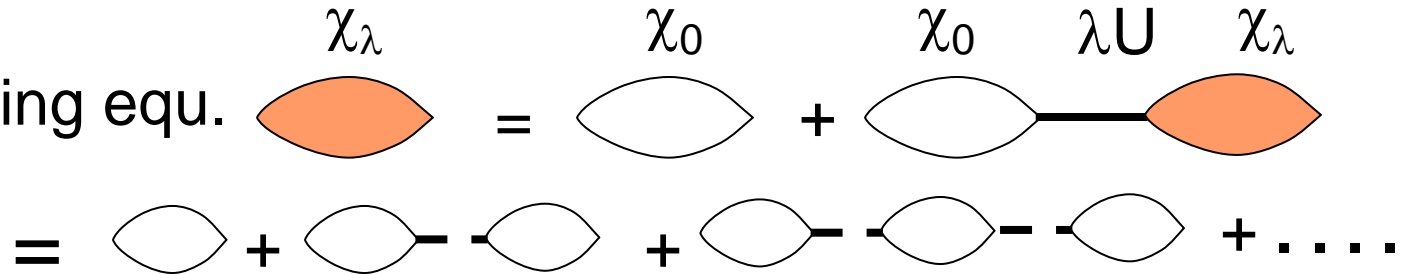
For generalization see Furche 129, 114105 (2008) $E_c^{dRPA} = \frac{\hbar}{2} \sum_n (\Omega_n - \Omega_n^D)$

DIAGRAMS, (d)RPA

Time dep Hartree approx

$$\chi_\lambda = \chi_0 + \chi_0 * \lambda U * \chi_\lambda$$

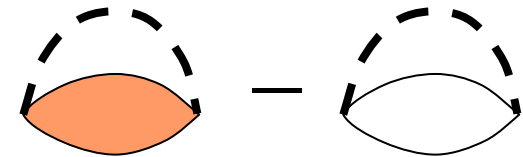
dRPA Screening equ.



Adiabatic conn

Fluct-diss theorem

$$E_c = \frac{1}{2} \int_0^1 d\lambda \int_0^\infty du \frac{\hbar}{\pi} \text{Tr}(U_{\lambda=1} * (\chi_\lambda - \chi_0))$$



$$= \text{[diagram of two ovals connected by two horizontal lines]} = \text{[diagram of two ovals connected by two vertical lines]} + \text{[diagram of a ring of four ovals]} + \dots \text{ Sum of rings}$$

MP2, MP3- like terms (no exch diags)

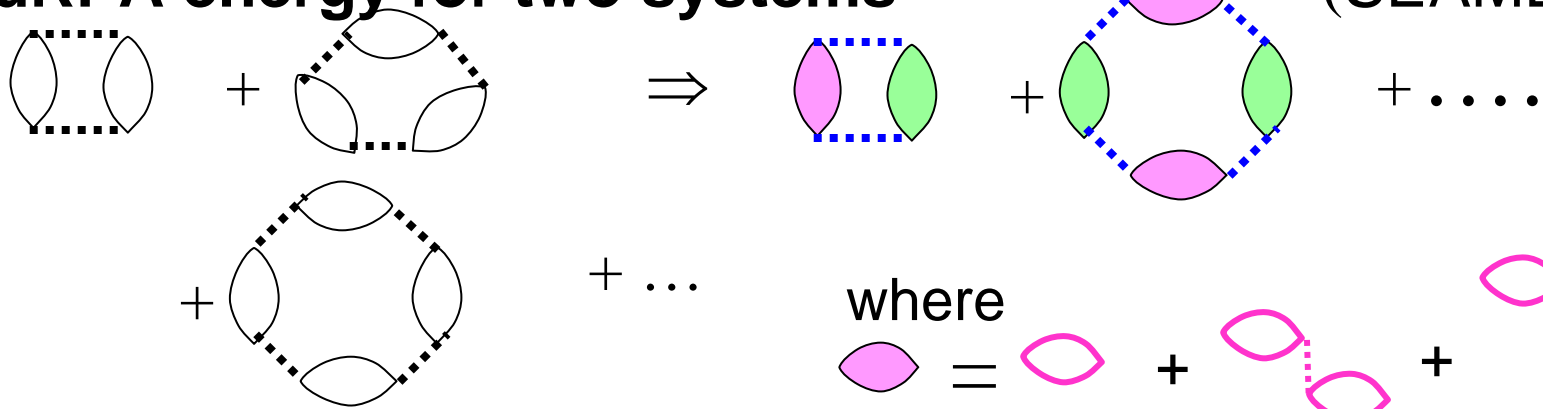
In dRPA:

pair (2-atom, Casimir-Polder) contributions come from diags with 2 inter-atom U lines

triplet (3-atom, Axilrod-Teller) contributions come from diags with 3 inter-atom U lines, etc

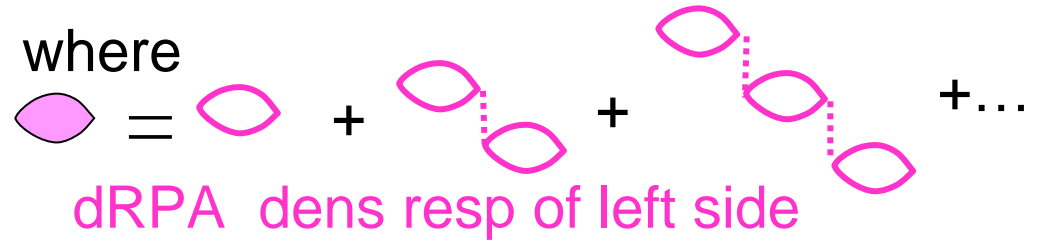
In extended or very anisotropic systems, beyond-pairwise vdW terms are large for low q

dRPA energy for two systems



(SEAMLESS)

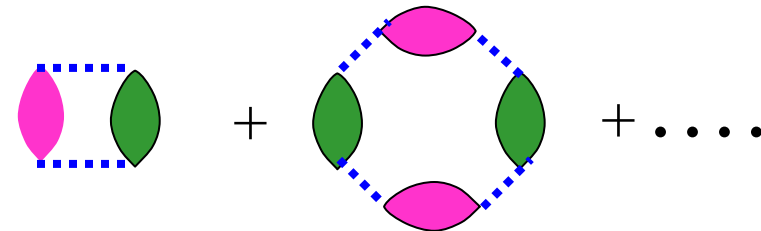
where



em nonretarded

Lifshitz-Dzyaloshinsky

=



NOT seamless – can't use down to bonding distance

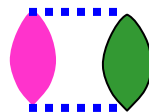
where



= exact dens resp of left side (usually evaluated only for $q \rightarrow 0$ and taken from expt^{al} dielectric fn)

Generalized Casimir-Polder

NOT seamless



Cohesive energy curves for noble gas solids calculated by adiabatic connection fluctuation-dissipation theory

Judith Harl and Georg Kresse*

TABLE III. Equilibrium lattice constants and cohesive energies of the noble gas fcc crystals Ne, Ar, and Kr. The DFT results are compared with ACFDT values and experiment. The zero-point energy is neglected, and the experimental lattice constants are extrapolated to zero temperature (see Ref. 30).

	DFT-LDA	ACFDT-LDA	DFT-PBE		Expt.	Expt (T=0 extrapolation)
	Lattice constant (Å)					
Ne	3.9	4.7	4.6		4.35	
Ar	4.9	5.4	6.0		5.23	
Kr	5.3	5.8	6.4		5.61	
	Cohesive energy (meV)					
Ne	83	11	20		27.3	
Ar	140	59	22		88.9	
Kr	165	88	25		122.5	

Accurate Bulk Properties from Approximate Many-Body Techniques

Judith Harl and Georg Kresse

PRL **103**, 056401 (2009)

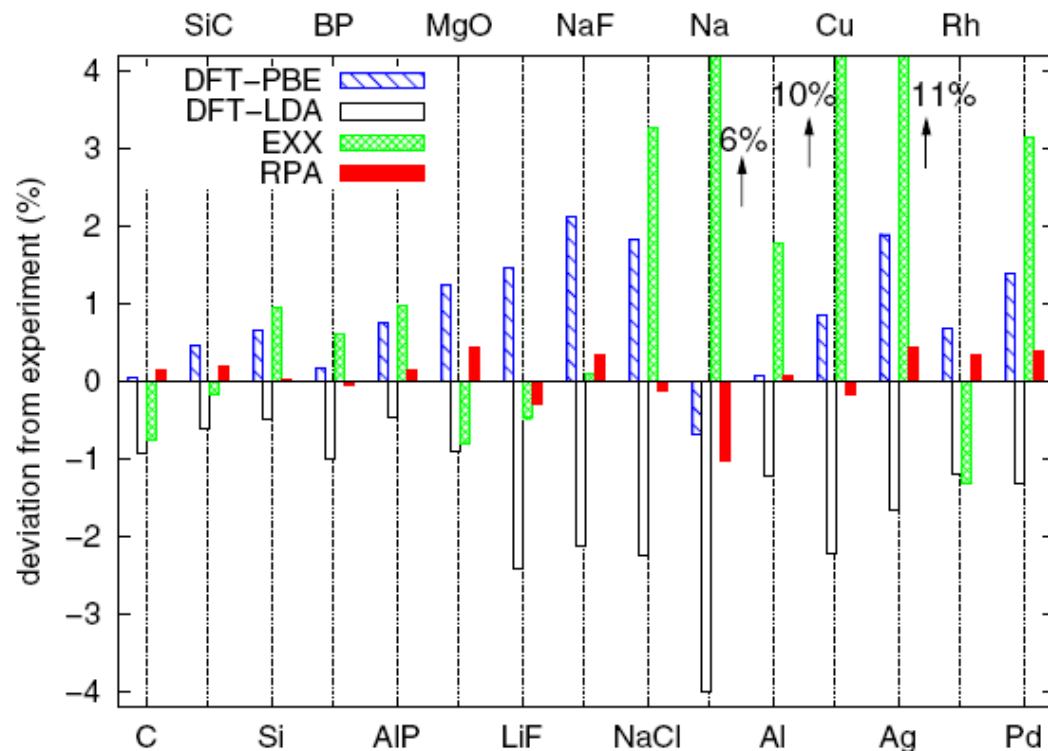
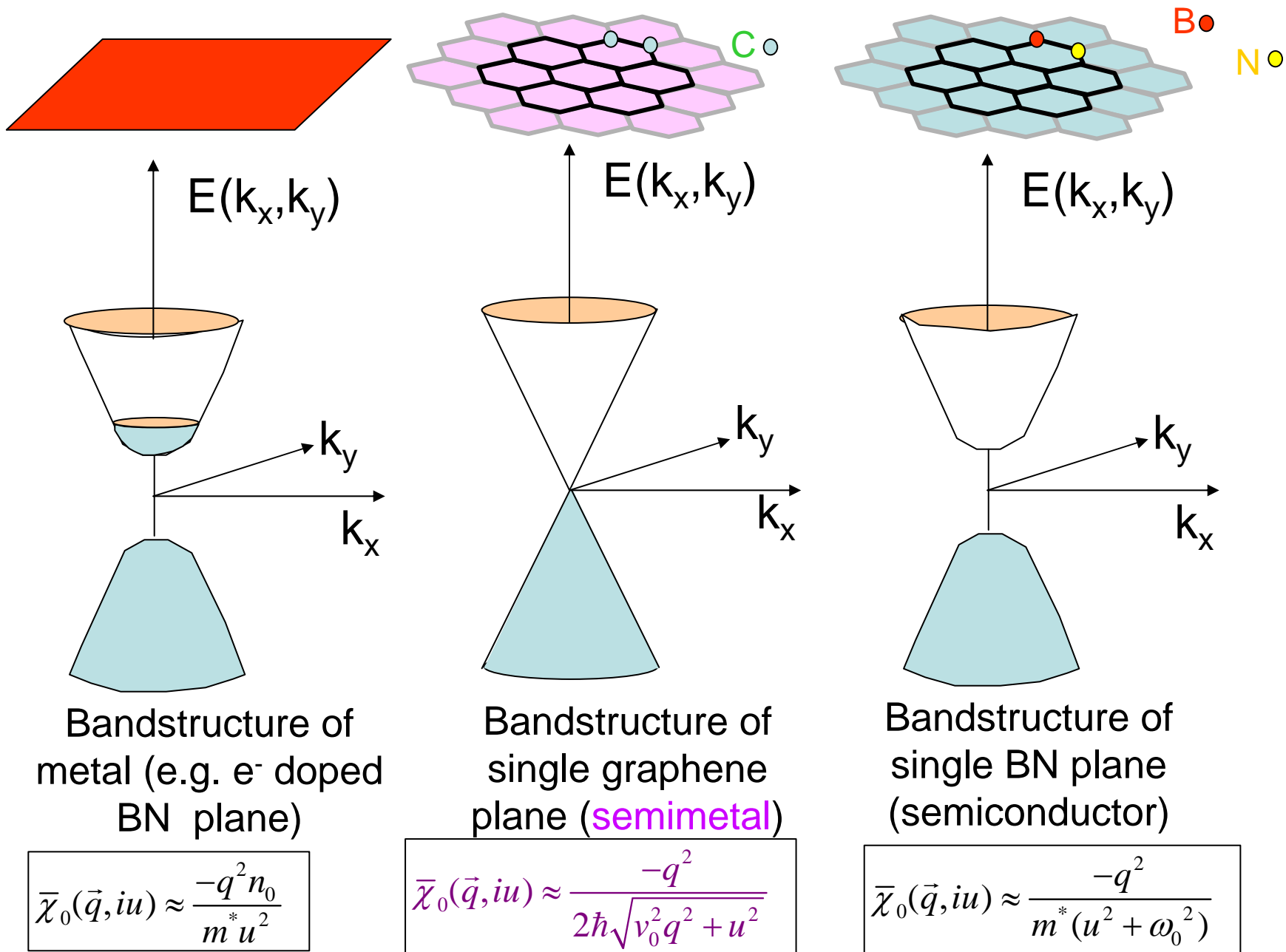


FIG. 1 (color online). Relative error (%) of the theoretical lattice constants of insulators, semiconductors, and metals. The experimental lattice constants are summarized in Ref. [33] and have not been corrected for zero-point vibrational effects.



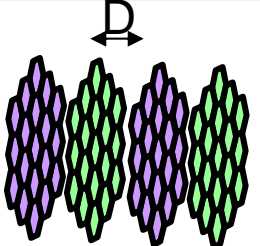
$\alpha = \chi_0 q^{-2}$ diverges if $u \rightarrow 0$

$\alpha = \chi_0 q^{-2}$ diverges if **BOTH** $q, u \rightarrow 0$

$\alpha = \chi_0 q^{-2}$ not divergent

LAYER BINDING PROPERTIES OF GRAPHITE

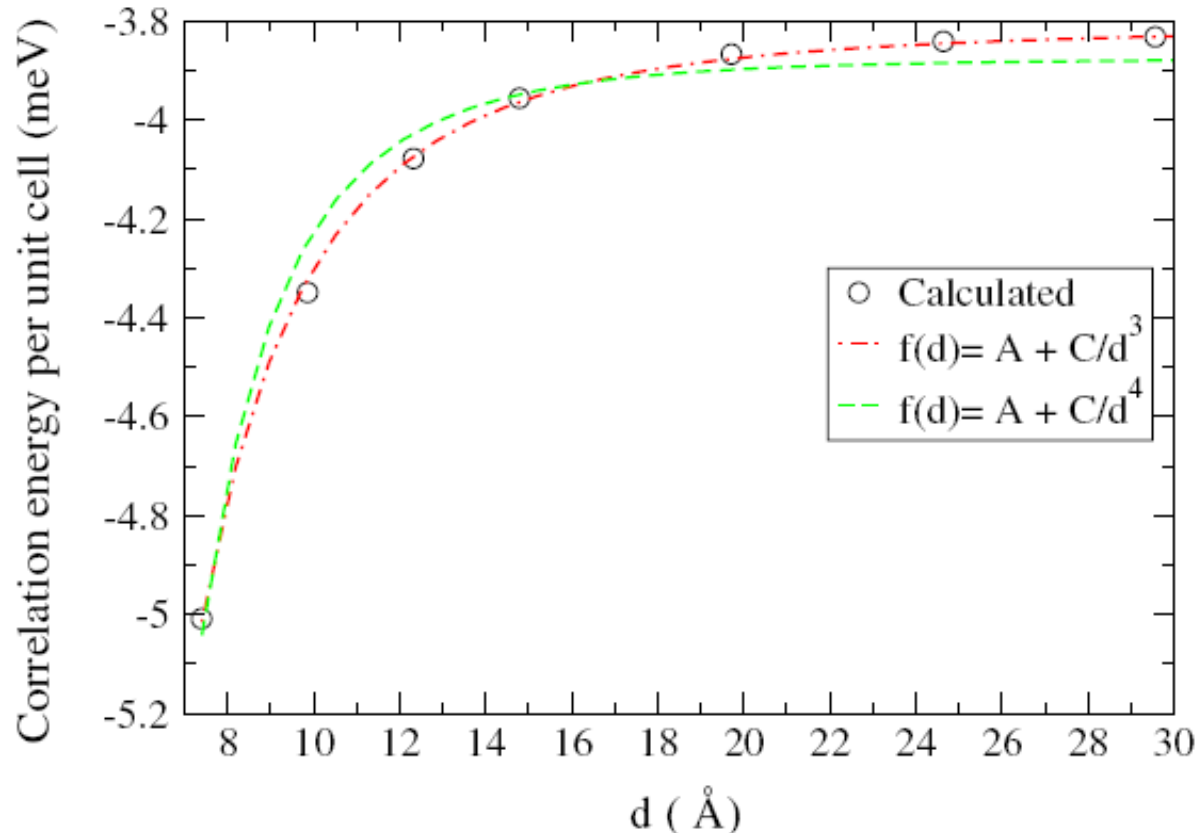
One of many RPA success stories for a_0 , E_{coh} , B of periodic solids

	LDA (Present)	vdW-DF	DMC	ACFDT- dRPA (present)	Expts
Equilibrium interplanar distance D_0	3.33	3.76 ^c 3.6 ^a 3.59 ^b	3.43 ^m	3.34	3.35
C_{33} (Gpa)	29.5	13 ^c , na, 27 ^b	?	37	40.7 ^e 36.5 ^{ef} 38.7 ^g 37 ^h
Binding energy (meV /atom)	24	24 ^c 45.5 ^a 50 ^b	56 ^m	48+	43 ⁱ 35 ^j 52 ^k (All suspect and involve assumptions of additive vdW forces)

Lebegue, Harl, Gould, Angyan, Kresse, Dobson, PRL 105, 196401 (2010)

Many other solids in RPA: Harl, Kresse PRL 103, 056401 (2009):

VERIFICATION OF D^{-3} POWER LAW FOR GRAPHITE, PRL 105, 196401 (2010)



Numerical $\Delta E = CD^{-3}$ law from dRPA (VASP) with transitions restricted to within 1.25 eV of E_F . (Excludes non- π_z transitions $\Rightarrow D^{-4}$ that still dominate here)

Coefficient C from this fit is much less than analytic RPA prediction but

- (i) ± 1.25 eV restriction removes some $\pi_z - \pi_z^*$ transitions \therefore C underestimated.
- (ii) Local-field screening effects neglected in analytic approach might matter

SOME WEAKNESSES OF dRPA ENERGY (ACFDT with $f_{xc} = 0$)

1. dRPA does not exclude incorrect orbital self-interaction in the dynamical response

This can be a big problem where one wants to describe correlations between s electrons eg He2, Be2. But SIC is not a major problem (e.g.) for spatially extended 2π orbitals that are important in graphitic cohesion. The SIC problem is largely fixed by **RPAx**, **RPA+SOSEX**, **ISTLS**,

2. dRPA gives a poor account of the short ranged part of the correlation hole.

It therefore often grossly overestimates the absolute correlation energy.

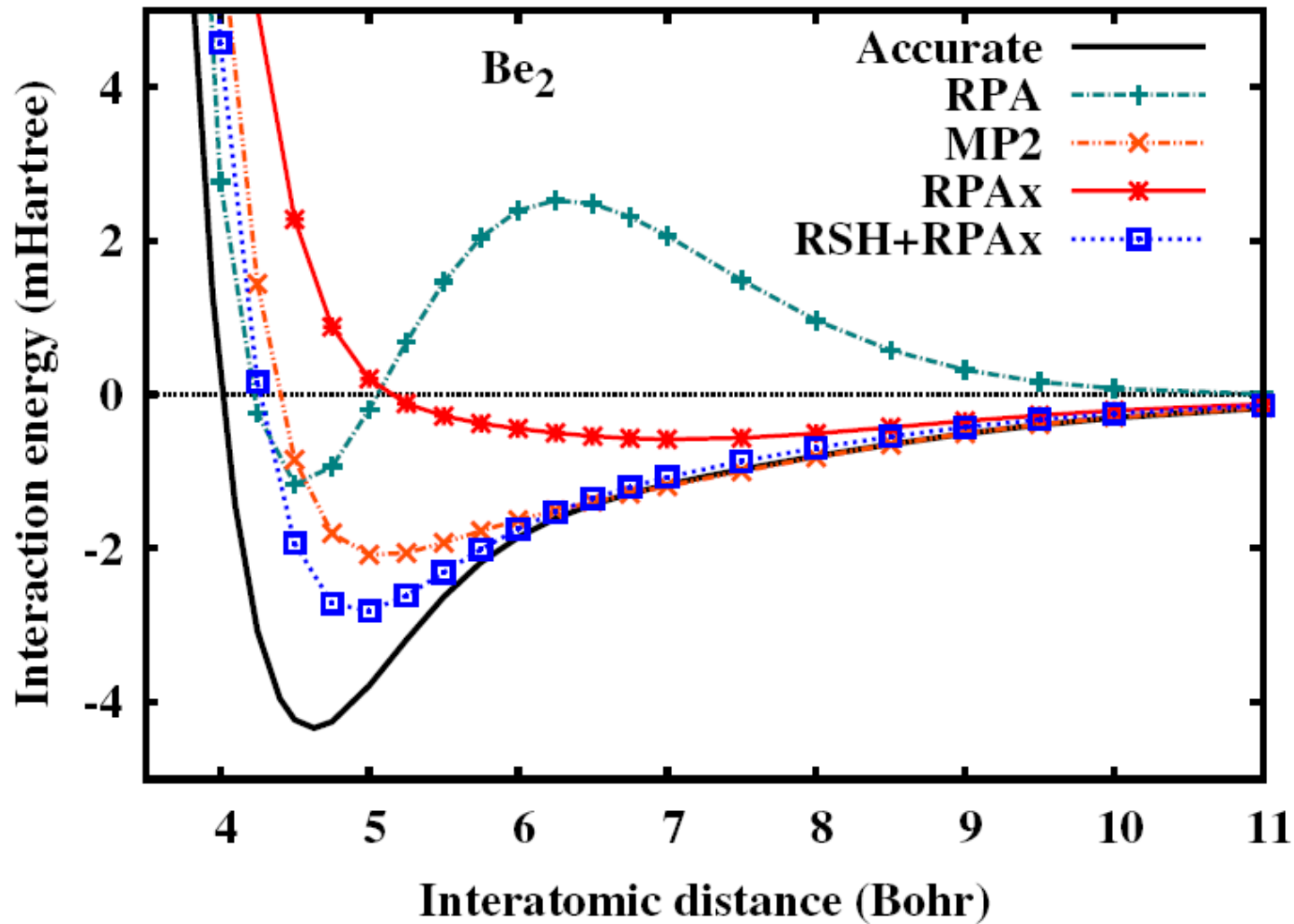
E.g. Homogeneous electron gas, $r_s = 10$,: $e^c = -22$ mH/e. $e^{cRPA} = -30$ mH/e

As pointed out by John Perdew et al, the RPA error in E^c often largely cancels out in forming isoelectronic energy differences – e.g. change in correlation energy when one moves two nanostructures apart, as in binding energy curve calculations. This is especially true where the orbital symmetry and degree of localization are not changing. Example: graphite layer binding. This **sr corr hole problem** can also be addressed by (e.g.) **RPAx**, **SOSEX**, **RPA+f_{xcr}** or range separation methods. Num. application to layer binding of graphitics in ACFDT is rather good (Seb Lebegue has prelim results).

3. RPA as usually implemented may strongly depend on input orbitals

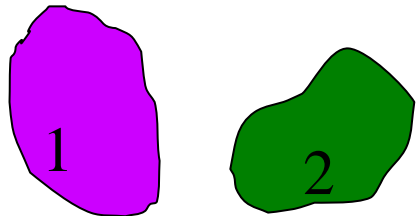
and self-interaction effects are very important here (ideally need SC RPA???)

Severe failure of RPA in Be₂ binding curve:
related to SIC and/or degeneracy effects?

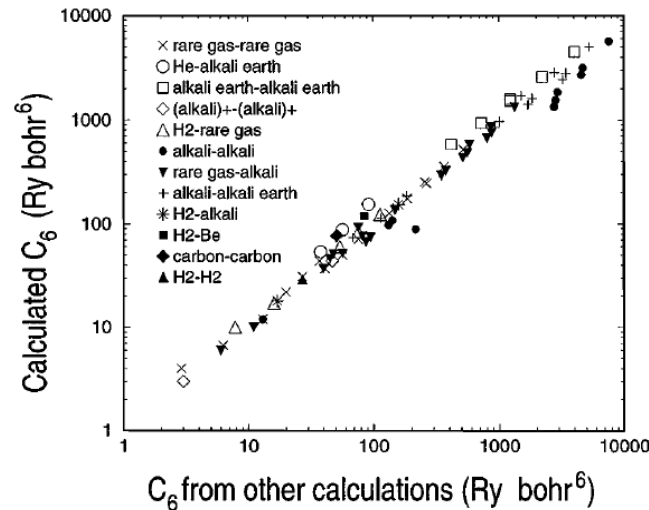


J. Toulouse et al, PRL 102, 096404 (2009)

DENSITY FUNCTIONALS FOR VDW ENERGY I



Nonoverlapping
finite systems



Andersson et al PRL **76**, 102 (1996): (indirect, based on Rapcewicz+Ashcroft)

$$E^{vdW} = -C \int_{V_1} d^3 r_1 \int_{V_2} d^3 r_2 \frac{\sqrt{n(\vec{r}_1)n(\vec{r}_2)}}{\sqrt{n(\vec{r}_1) + n(\vec{r}_2)}} \frac{1}{|\vec{r}_1 - \vec{r}_2|^6} \quad \text{Needs spatial cutoffs}$$

Dobson/Dinte PRL **76**, 1780 (1996): direct derivation from local polarizability

$$\chi_{\text{local}}^{\text{inhom}}(\mathbf{r}, \mathbf{r}', \omega) = \nabla_{\mathbf{r}} \cdot \nabla_{\mathbf{r}'} \left[\frac{1}{m} \frac{n(\mathbf{r}) \delta^3(\mathbf{r} - \mathbf{r}')}{\omega^2 - \omega_P^2[n(\mathbf{r})]} \right] \quad \text{+ used 2}^{\text{nd}} \text{ order pert}^{\text{n}} \text{ th in } V_{12}^{\text{coulomb}}$$

Sato & Nakai JCP **131**, 224104 2009 (atoms, molecules)

133, 194101 2010 Incl some triplets etc.

“VDW-DF” Dion et al PRL 04 FROM PRESENT POINT OF VIEW

Starting point : exact ACFD

$$E_{xc} \propto \int_0^1 Tr \left([1 - \tilde{\chi}_\lambda * \lambda V]^{-1} \tilde{\chi}_\lambda V \right) d\lambda - SI = \int_0^1 d\lambda Tr \left(\epsilon^{scr}_\lambda^{-1} \tilde{\chi}_\lambda V \right) - SI$$

Assumption 1: “Full potential approximation”: $\tilde{\chi}_\lambda$ assumed indep of λ so

$$E_{xc} \approx Tr \left(\ln [1 - \tilde{\chi}_{\lambda=1} * V] \right) - SI = Tr \ln \left(\epsilon^{scr}_{\lambda=1} \right) - SI \quad (RPA-like)$$

Assumption 2: “Reference approximation” The theory is obtained as a correction to the following reference energy

$$E^{ref}_{xc} = Tr \left(\ln [\epsilon] \right) - SI : RPA-like, \text{ but with } \epsilon \text{ instead of } \epsilon^{scr}$$

The assumption is (?) then that this is something like the LDA energy, since it becomes correct for a 3DEG? Then it is assumed that $E^{ref}_{xc} \sim E^{LDA} + E_{nl}$

Assumption 3: “Perturbative screening” $f \propto |\vec{r} - \vec{r}'|^{-6}, |\vec{r} - \vec{r}'| \rightarrow \infty$

$$E_{nl} \propto Tr \{ \ln [\epsilon^{-1} (1 - V * \tilde{\chi})] \}, \quad \tilde{\chi} = \nabla \tilde{\alpha} \nabla = (4\pi e^2)^{-1} \nabla (\epsilon - 1) \nabla$$

Treat only to second order in $S \equiv 1 - \epsilon^{-1} \Rightarrow$ pairwise additive for multimers.

Assumption 4: “Separable Plasmon Pole Approx”.

$S(q, q', \omega)$ approximated in a separable way with semilocal behavior (dep $n(r), \partial n.$)

$$E^{nl} = \frac{1}{2} \int d^3r d^3r' n(\underline{r}) n(\underline{r}') f(\underline{r}, n(\underline{r}), \nabla n(\underline{r}); \underline{r}', n(\underline{r}'), \nabla n(\underline{r}'))$$

Refinements by Vydrov+. Efficient implementations: Soler, Klimes,

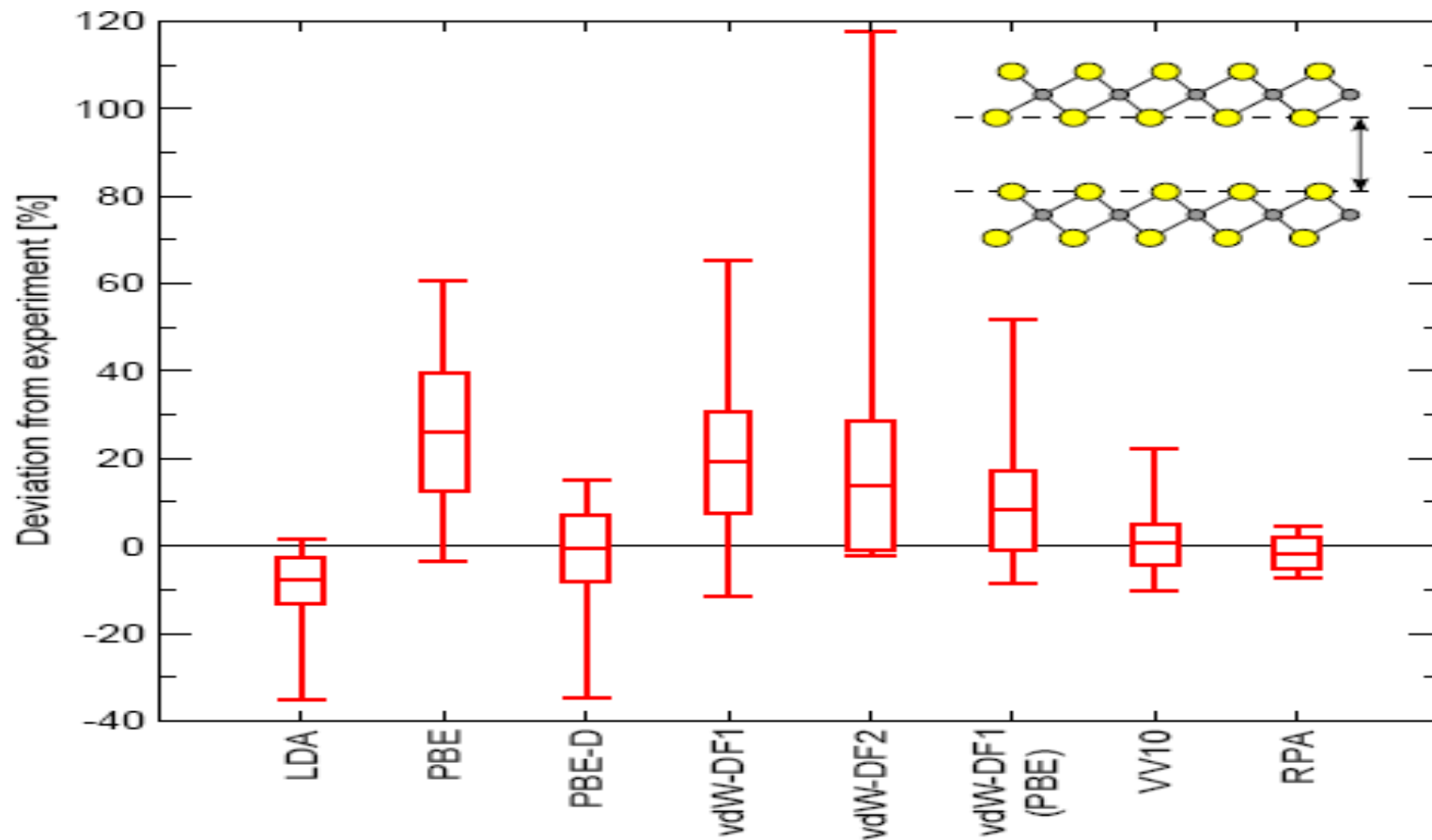
CAN COMMON NANOSTRUCTURE vdW METHODS HANDLE NONADDITIVITY?

Method	Gets Type A nonadd. ?	Gets Type B nonadd.?	Gets Type C nonadd.?	COMMENTS
Grimme, Yang $\Sigma C_6^{(ij)} R^{-6}$	Y	N	N	Gets type A by adopting diff C_6 for atom in molec.
Tkatchenko + I Tkatchenko + II	Y Y	N Y	N N	I Gets type A via volume compression in molecule II uses dynamic RPA
vdW DF	Y	N	N	Loses type B because of pert. Coulomb screening
Lifshitz	N/A	Y	N/A	Takes dielectric fn from experiment
RPA	Y	Y	Y	Right answers for right reasons
DMC	Y	Y	Y	Right answers for right reasons (converged??)

CAN COMMON vdW METHODS HANDLE LAYERED vdW SOLIDS?

Bjorkman et al, PRL 108, 235502 (2012) & [arXiv:1206.3542v1](https://arxiv.org/abs/1206.3542v1)

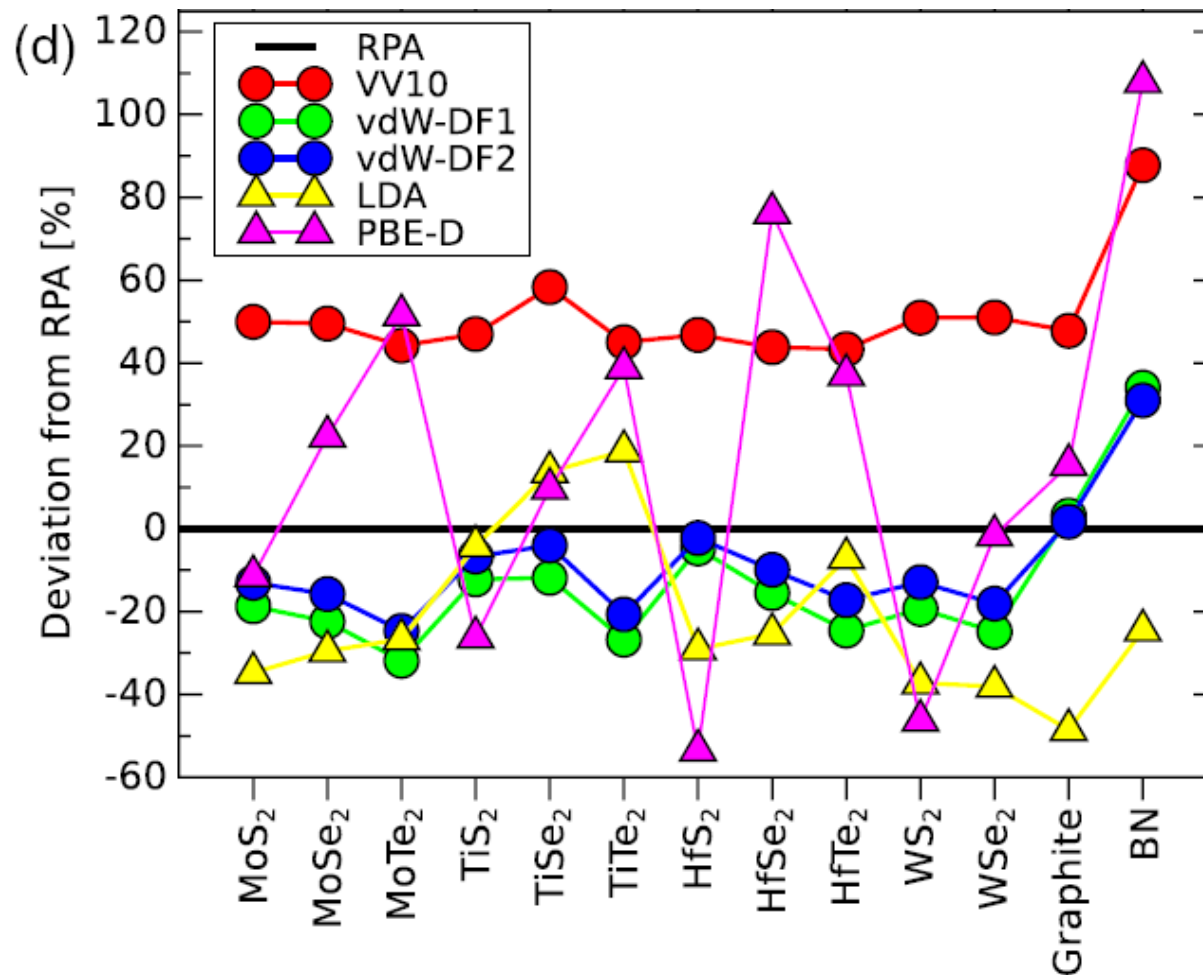
ΔD = Predicted Interlayer spacing - experiment



CAN COMMON vdW METHODS HANDLE LAYERED vdW SOLIDS?

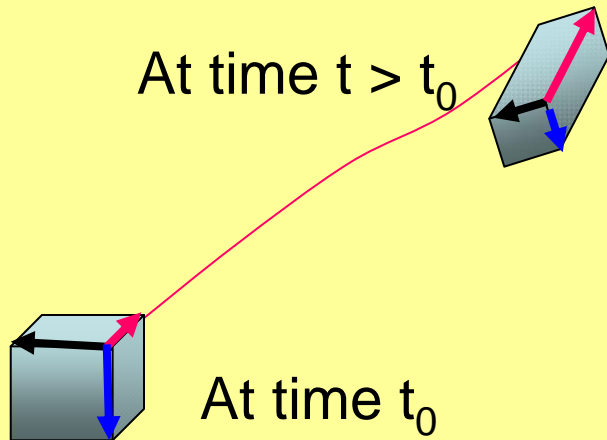
Bjorkman et al, PRL 108, 235502 (2012) & [arXiv:1206.3542v1](https://arxiv.org/abs/1206.3542v1)

ΔE_L = Predicted Interlayer binding energy - RPA



QUANTUM CONTINUUM MECHANICS (pseudo-hydrodynamics)

I.V. Tokatly, Phys. Rev. B 71, 165105 (2005); 75, 125105 (2007).



Tokatly looked at the Schrodinger equation in the co-moving (rotating and translating) reference frame that moves with the fluid \Rightarrow General-relativity style theory with metric tensor g

LINEARIZED QUANTUM CONTINUUM MECHANICS “CM”

J. Tao, X. Gao, G. Vignale, and I. V. Tokatly, Phys. Rev. Lett. 103, 086401 (2009);
X. Gao, J. Tao, G. Vignale, and I. V. Tokatly, Phys. Rev. B 81, 195106 (2010).

Assumed the MB wavefunction is stationary in the co-moving frame – means this is a short-time or high- ω theory – response correct to $O(\omega^{-2})$, $O(\omega^{-4})$.

No longer contains g tensors explicitly, but the evolution equations for $u(r,t)$ involve a the groundstate number density $n_0(\underline{r})$, the groundstate KS potential $V_{KS}(\underline{r})$ and a “new density”, the groundstate KS stress tensor $\underline{T}_0(\underline{r})$

Exact linear response of 1- e^- quantum system

NEW QCM/RPA SCHEME FOR NONPAIRWISE e⁻ CORR^{ln} ENERGY

(Gould&Dobson PRB **84**, 241108(R) (2011))

Calculate bare density response $\chi_0(r,r')$ from occ & unocc KS orbitals

$$\chi_0(\vec{r}, \vec{r}', \omega) = \sum_{i,j} (f_i - f_j) \frac{\phi_i^*(\vec{r}) \phi_j^*(\vec{r}') \phi_j(r) \phi_i(r')}{\epsilon_i - \epsilon_j - \hbar\omega}$$

Or solve time-dep. equ. for perturbation to each occupied orbital $\delta\psi_i(t)$

Approximate χ_0 from CM (Continuum mechanics). 3 coupled DEs

Do TDH selfconsistency, RPA screening, Dyson-like equation

$$\chi_\lambda = \chi_0 + \chi_0 \lambda V \chi_\lambda \quad \rightarrow \quad \chi_\lambda = (1 - \lambda \chi_0 V)^{-1} \chi_0$$

Use Fluct Diss Thm ($\int \chi du$) and Adiabatic Connection ($\int d\lambda$) to get E_c

$$E^c = \frac{\hbar}{\pi} \int_0^\infty du \int_0^1 d\lambda \int d\vec{r} [(\chi_\lambda - \chi_0)V]_{rr}$$

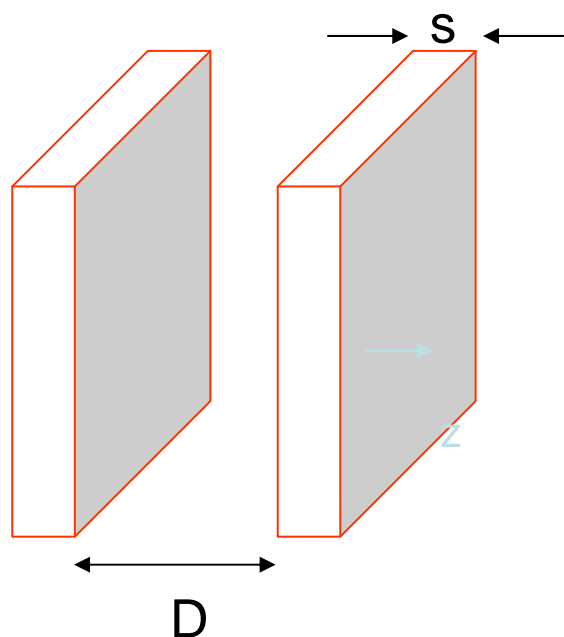
$$= \frac{\hbar}{\pi} \int_0^\infty du \text{Tr}_r [\ln(1 - \chi_0 V) + \chi_0 V]$$

First num. test of CM-RPA on vdW system: parallel jellium slabs

Auxiliary basis:

$$\phi_{k_n, q_{||}} = \exp(iq_{||} \cdot \underline{r}) \exp(ikz),$$

$$\exp(iq_{||} \cdot \underline{r}) \exp(ikz) \tanh(k_t z), \quad k_t \text{ opt for convergence}$$



Positive background

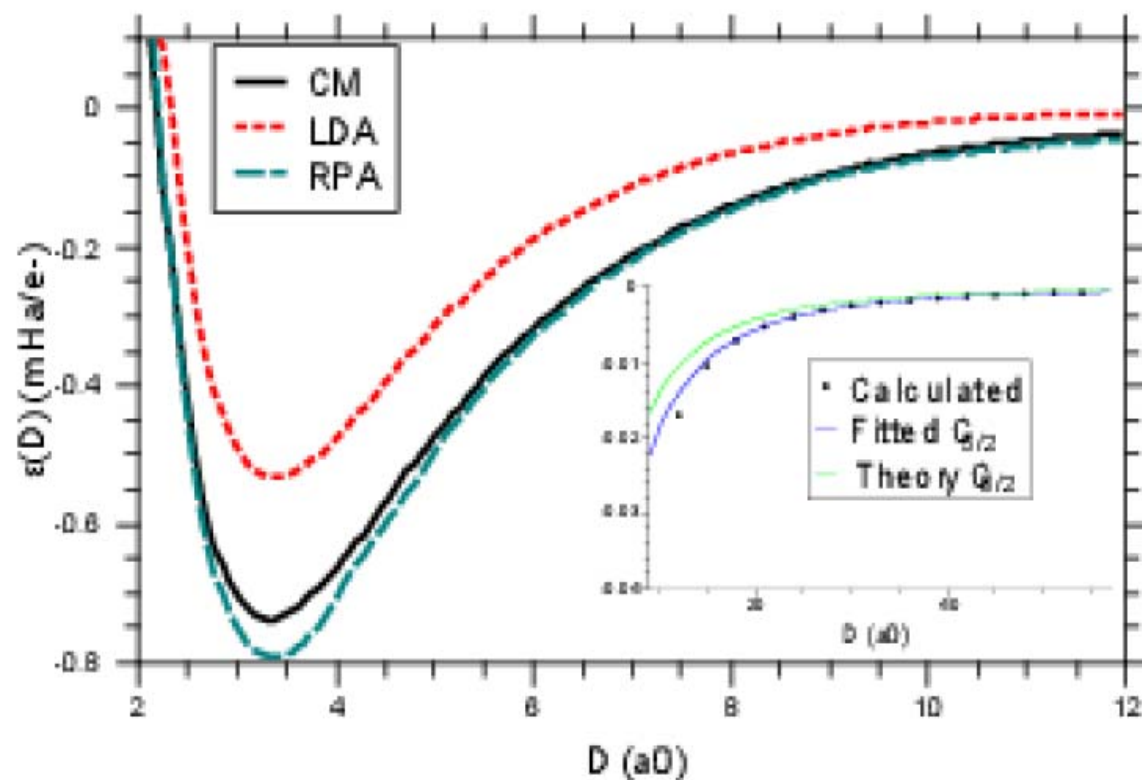


FIG. 1. $\epsilon(D)$ graph for $r_s = 1.25$, $s = 3$. RPA data from [23]. Inset data shows the vdW dominated region.

TEST OF QCM-dRPA FOR SOLID NA

