HOW RELIABLE IS THE RPA FOR VAN DER WAALS (DISPERSION) INTERACTIONS?

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FAST collaboration: Janos Angyan, Sebastien Lebegue,, Tim Gould, Andreas Savin, Julien Toulouse, Ian Snook : also Judith Harl, Georg Kresse for graphite

Simple view of van der Waals forces

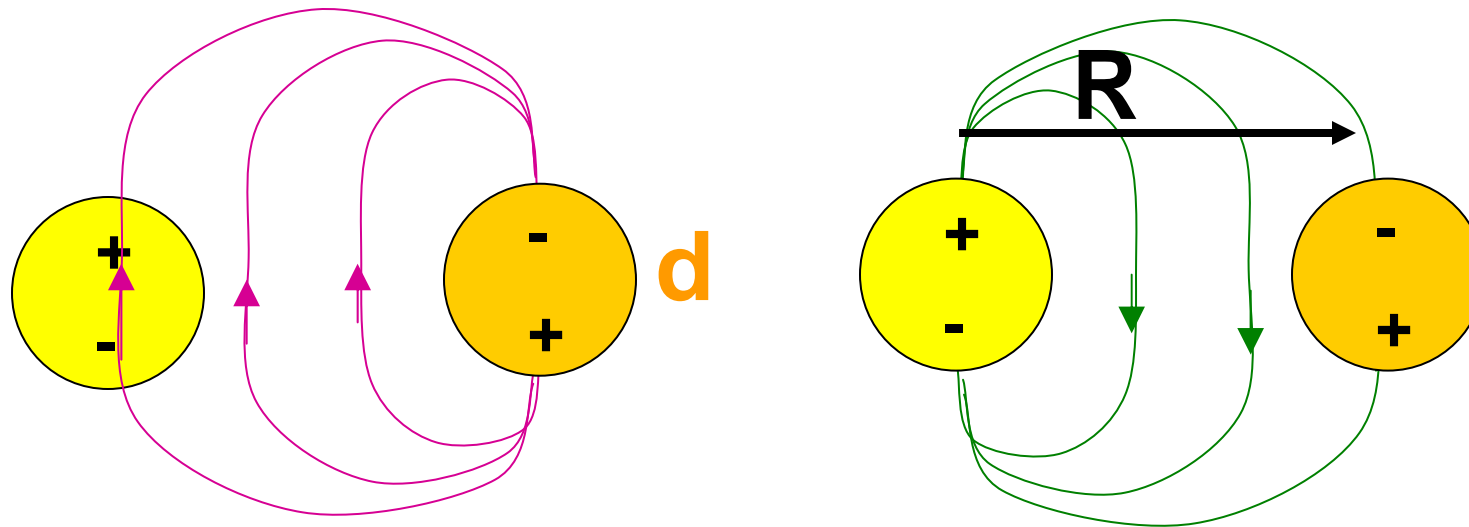**Formal expressions for vdW energy of separated and joined systems.**

Why ΔE [d-RPA] is often good enough. E_c (dRPA) results for cohesion of layered vdW xtals

Some cases where dRPA is not good enough

What are the fxc effects beyond RPA in ACFDT?

Various f_{xc} s and starting $\{ \varepsilon_I, \phi_i \}$, and their effect on vdW C_6 coefficients

ORIGIN OF VDW (DISPERSION, RESIDUAL COULOMB) FORCE

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

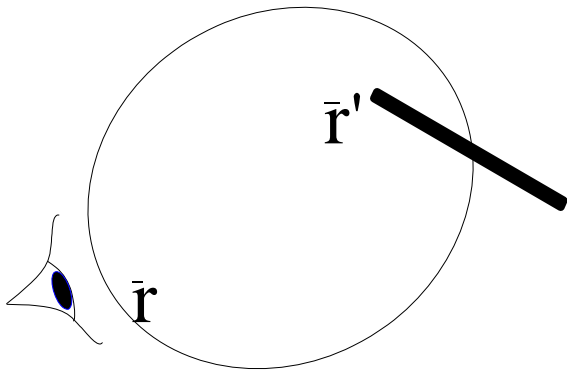A **correlation** effect, highly **nonlocal** so <u>LDA & GGA FAIL</u>

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

Electronic response functions in TDDFT
(exact but looks like mean-field theory)

Density-density response function χ_λ

$$\delta n(\vec{r})\exp(-i\omega t)$$
$$= \int \chi_\lambda(\vec{r},\vec{r}',\omega)\,\delta V(\vec{r}')\exp(-i\omega t)\,d\vec{r}'$$

Bare Resp $\chi_{KS} \equiv \chi_{\lambda=0}$ **to ext field (one-body physics)**

Bare Response to int field

$$\chi_\lambda(\vec{r},\vec{r}',\omega) = \chi_{KS}(\vec{r},\vec{r}',\omega) + \int \chi_{KS}(\vec{r},\vec{r}'',\omega)$$

$$\chi_\lambda \equiv \chi_0 + \chi_0 \, U_\lambda \, \chi_\lambda$$

$$\times \int \left(\frac{\lambda e^2}{|\vec{r}''-\vec{r}'''|} + f_{xc\lambda}(\vec{r},\vec{r}',\omega) \right) \chi_\lambda(\vec{r}''',\vec{r}',\omega)\,d\vec{r}'''\,d\vec{r}''.$$
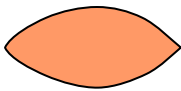
$$\Rightarrow \mathbf{dRPA,TDH}$$

Eff. Internal field **(beyond-RPA MB physics)**

Interacting(λ) and KS (λ=0) dens response

Operator for dens at <u>r</u> :
$$\hat{n}(\vec{r}) = \sum_{particles\ a} \delta(\vec{r} - \hat{\vec{r}}_a) = n(\hat{r}) + \delta\hat{n}(\vec{r})$$
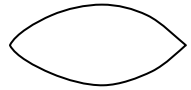
Fully interacting M-B eigenstate

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

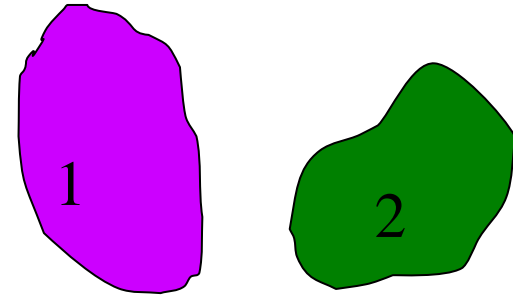Fully interacting M-B energy

Fermi factor   Kohn-Sham orbital

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

Kohn-Sham eigenvalue

W_{12} perturbation theory and vdW:

Bare inter-system Coulomb e^2/r_{12}

$$E^{(2)} = \sum_{a,b} \frac{\left|\langle ab|W_{12}|00\rangle\right|^2}{E_0^{(1)} + E_0^{(2)} - E_a^{(1)} - E_b^{(2)}}$$
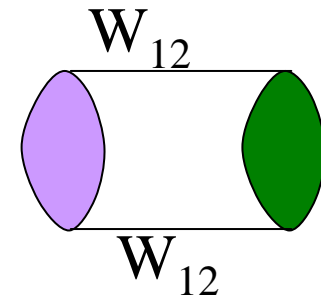
$$E_{12}^{(2)} = -\frac{\hbar}{2\pi} \int d^3r_1 d^3r_{1'} d^3r_2 d^3r_{2'} \frac{e^2}{r_{12}} \frac{e^2}{r'_{12}}$$

$$\times \int_0^\infty \chi_2(\vec{r}_1, \vec{r}_{1'}, iu)\chi_2(\vec{r}_2, \vec{r}_{2'}, iu)du$$

1

2

Gen. <u>nonoverlapping</u>

finite systems

nonlocal dens-dens resp of isolated
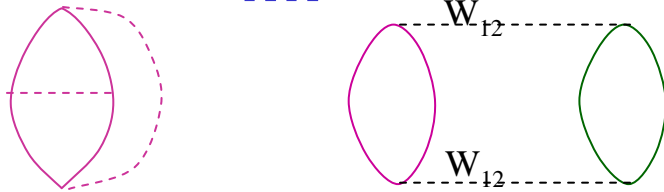system 2 (incl W_{11} to all orders)

H.C. Longuet-Higgins, Disc. Faraday Soc. 40, 7 (1965).
E. Zaremba and W. Kohn, P.R.B 13 2270 (1976).

W_{12}

W_{12}

"ZK formula, Generalised Casimir Polder formula"

MPx, ZK, SA perturbation theory

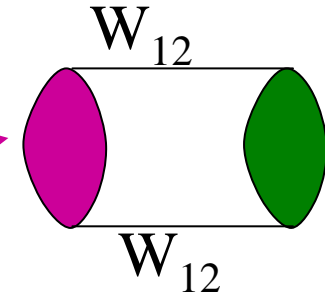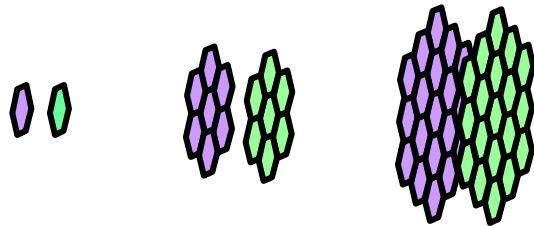| **MP**	**Gen Casimir Polder**
MPx includes all e-e interactions w, not just w_{12}. MP**2** vdW only includes *bare* responses – OK for many small weakly polarizable systems eg Ar-Ar, not v. good for (e.g.) Be-Be, wrong for extended metals. (JFD, J. Comp Th NanoSc 09)	Response includes internal interaction W_{11} to all orders
MPx OK for overlapped systems, ("seamless") but can require higher and higher order as systems become larger	ZK Not valid for overlapped systems – cannot deal with indistinguishability, exchange: <u>symmetry adapted pert. th</u>. is better See Jeziorski, Moszinski, Szalewicz et al

vdW energy: well separated systems

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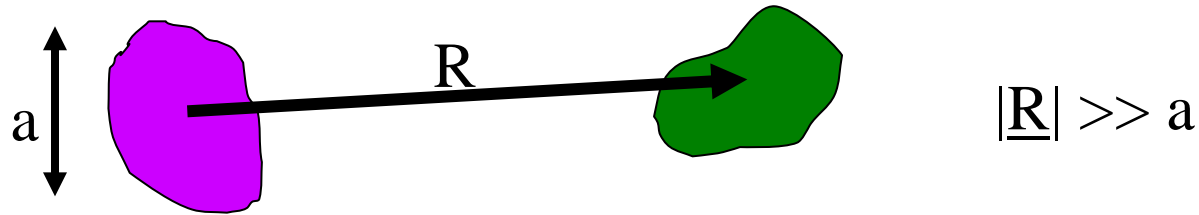
Make multipolar expansion of $\quad e^2 / |\vec{r}_1 - \vec{r}_2| \quad$ and $\quad e^2 / |\vec{r}_1{}' - \vec{r}_2{}'|$

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

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

isotropic case

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

Dipole resp of 2

EXACT ADIABATIC CONNECTION-FDT APPROACH FOR CORRELATION ENERGY (INCL VDW <u>AT ALL SEPARATIONS</u>)

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

$\downarrow$

Zero-tempFluct-dissipation thm

$\downarrow$

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

ACF-FDT (exact)

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

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

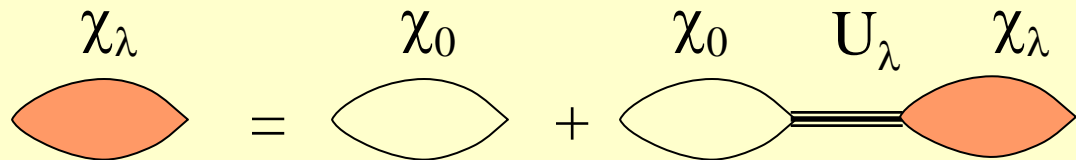**Our E_{xc} contains EXACT DFT EXCHANGE**

Can show χ_{RPA} gives asy $-C_6 R^{-6}$ result for vdW betw small systs.
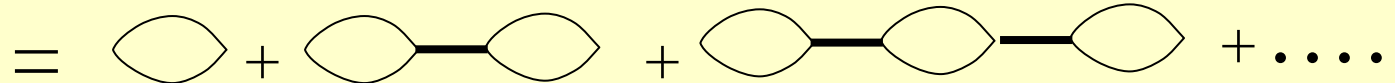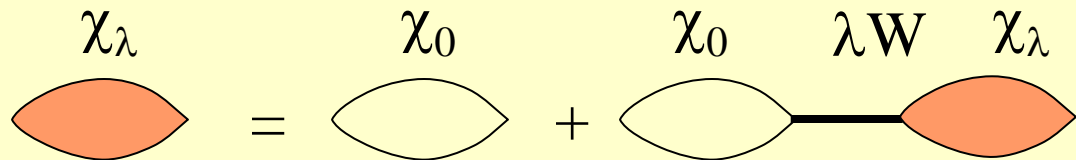
Diagrams and RPA

Bare coulomb

$$\chi_\lambda = \chi_0 + \chi_0 * U_\lambda * \chi_\lambda, \qquad U_\lambda = \lambda W + f_{xc\lambda}$$
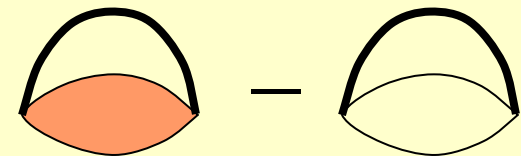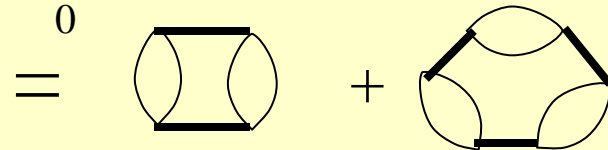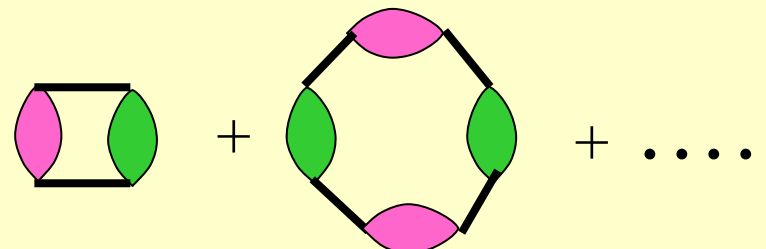
TDLDA Screening equ.

RPA Screening equ.

$$E_c = \frac{1}{2}\int_0^1 d\lambda \int_0^\infty du \, Tr(W * (\chi_\lambda - \chi_0))$$

Sum of rings

Intersystem E^{12}_c at large separation:

$$E_c^{12,RPA} = \frac{1}{2}\int_0^\infty du \, Tr\left[\ln(1 - W_{12} * \chi_2 * W_{21} * \chi_1)\right]$$

See also Lifshitz, Dzyaloshinsky

ACF/FDT STARTING WITH χ_{KS} CONTAIN ALL THE BASIC CHEMICAL AND PHYSICAL FORCES - II

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

RPA $\Rightarrow$ vdW (Casimir-Polder):
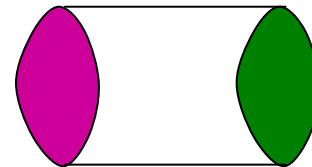
E.g. for isolated spherical systems in the dipolar approx,

$$\chi_\lambda = \chi_\lambda{}^{RPA} \Rightarrow E^{(2)} = -\frac{3\hbar}{\pi R^6}\int_0^\infty A_a{}^{RPA}(iu)\, A_b{}^{RPA}(iu)du$$

This is the exact result from perturbation theory except $A \to A^{RPA}$

Result does not appear to be true for RPA+<u>approx </u>f_{xc}!

Conventional view:
"universality" of asymptotic vdW
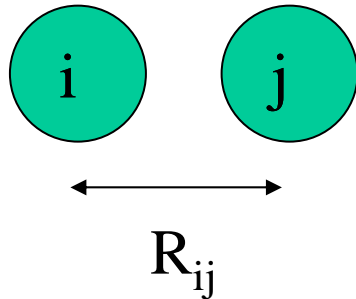
"Take vdW as given between atoms or sub-units: $E_{ij} \approx -C_6^{(ij)} R_{ij}^{-6}$, $R_{ij} \to \infty$."

R_{ij}
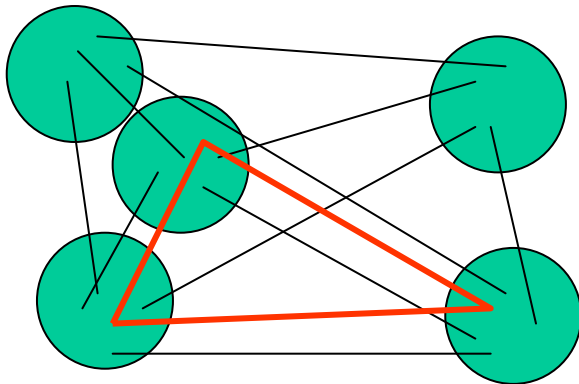
"Then total E_{vdW} is the sum of pairwise contributions

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

"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."

Distant vdW interaction from coupled-plasmon ZPE / RPA - preview

$L \ll D$

$W \gg D$

D

$L \gg D$

$W \gg D$

W

D

$$\Delta E_c \sim \text{const } D^{-2}$$

(metallic or insulating)

$2A \ll D$

$L \gg D$

D

$$\Delta E_c \sim \begin{array}{ll} AD^{-5/2} & \text{conducting} \\ BD^{-4} & \text{insulating} \\ CD^{-3} & pi-conj \text{ (graphene)} \end{array}$$

$$\Delta E_c \sim \begin{array}{ll} KD^{-2}[\ln(D/A)]^{-3/2} & \text{conducting} \\ CD^{-5} & \text{insulating} \end{array}$$
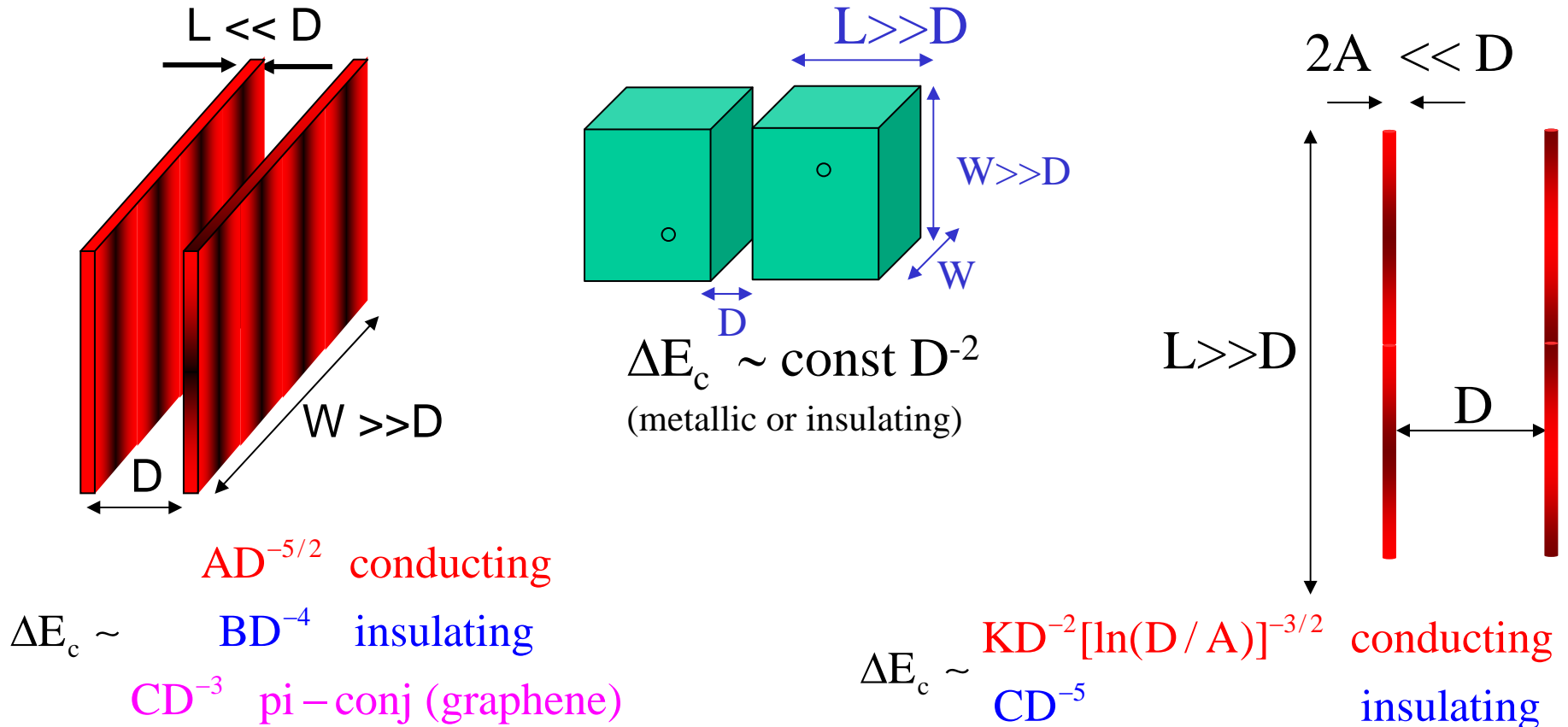
- Insulators, **3D** metals: $\Sigma C_6 R^{-6}$ gives <u>qualitatively</u> OK results, but

- $\Sigma C_6 R^{-6}$ can be very wrong for <u>anisotropic</u> **nano**conductors where electrons can move large distances leading to large **poorly screened** polarizations

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, 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. See example next slide.
This sr corr hole problem can also be addressed by (e.g.) RPAx, RPA+f_{xcr} or range separation methods or ISTLS. Num. application to layer binding of graphitics in ACFDT is not complete (Seb Lebegue has preliminary results).

3. **RPA as usually implemented may strongly depend on input orbitals**
and self-interaction effects are very important here (ideally need SC RPA????)

Short ranged correlation from Energy Optimized f_xc : little effect on jellium slab binding cw RPA
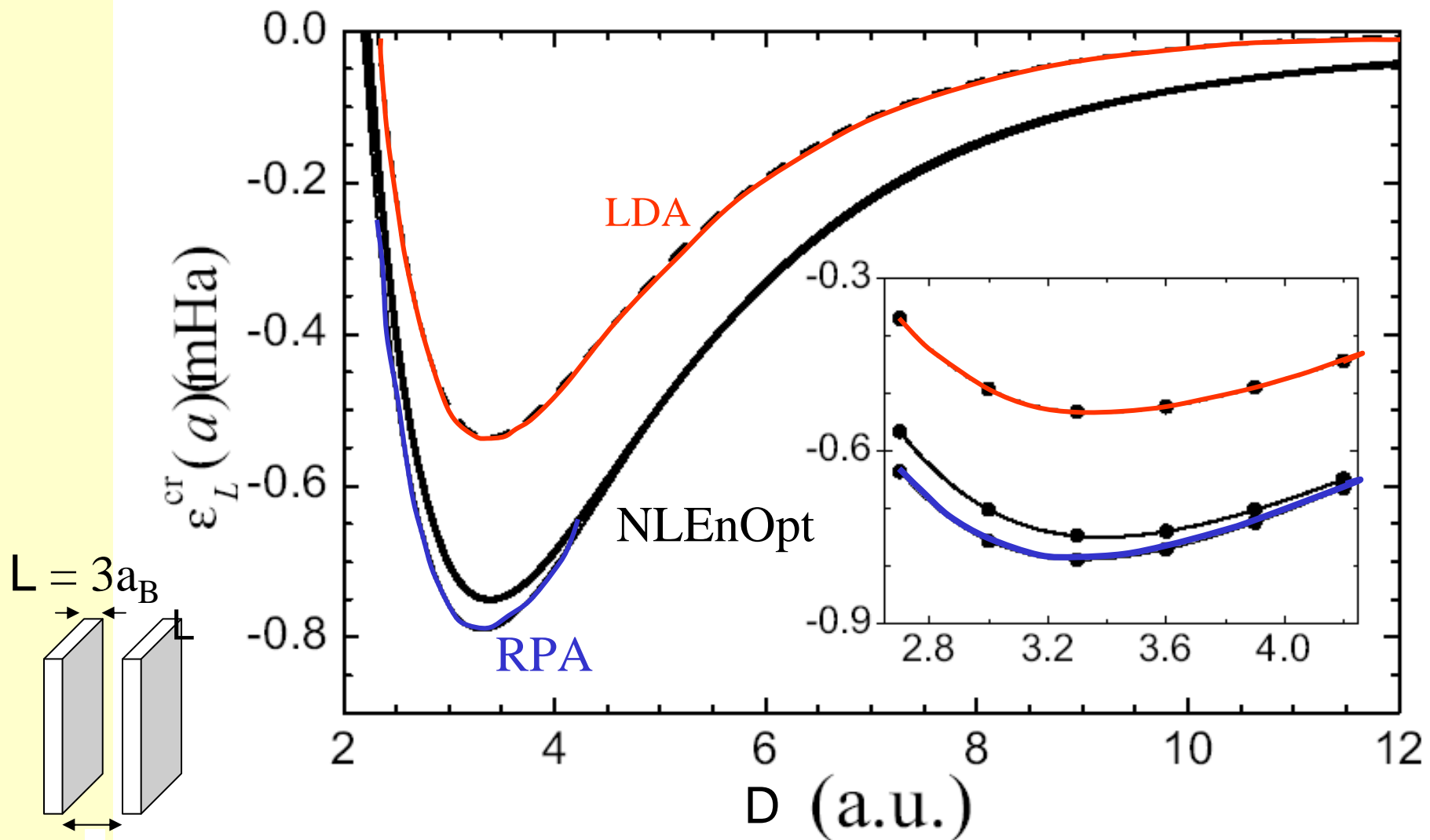
J. Jeil, P. Garcia-Gonzalez+JFD+, PRB **70**, 205107 (2004)

NANOSCIENCE: 2D BLOCH BANDSTRUCTURE OF ISOLATED 2D GRAPHENE

$E(\underline{k})$

Γ

E [eV]

15.0
10.0
5.0
0.0
-5.0
-10.0

$\pi*$

π

K $\quad$ Γ $\quad$ M $\quad$ K

k_y

k_x

M

K $\quad$ K
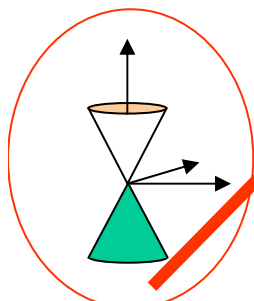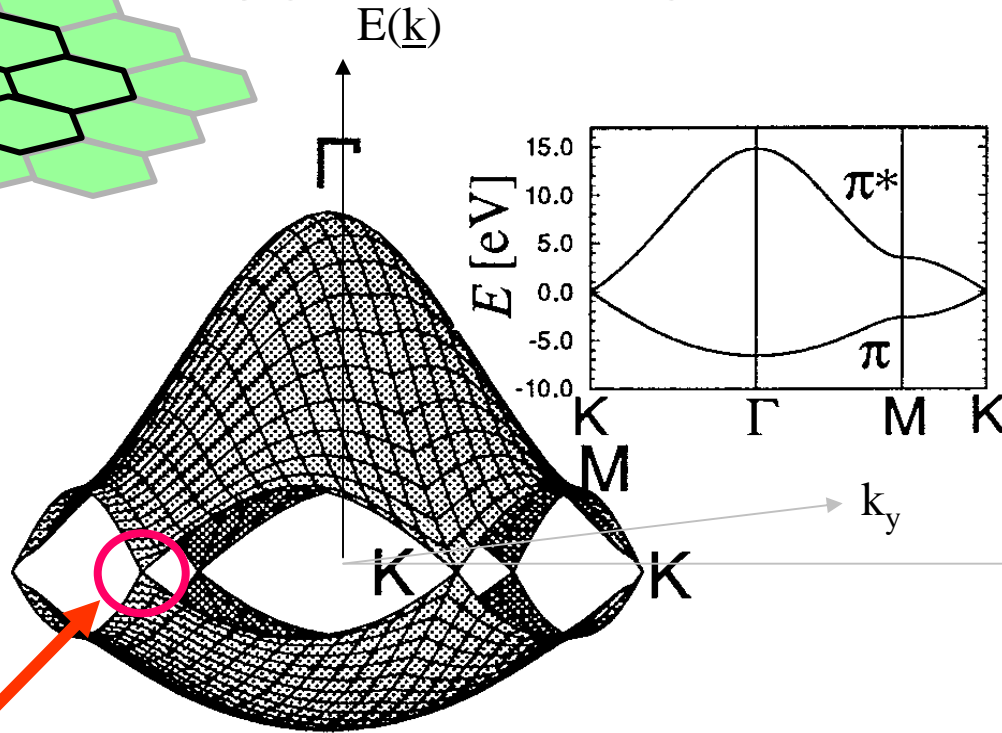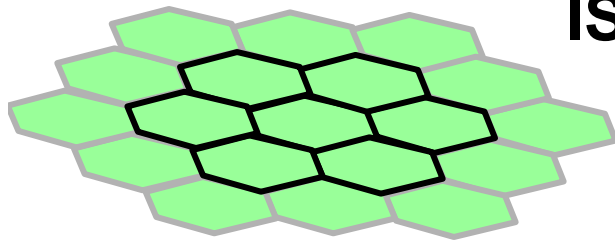
Bandstructure near "Dirac" K-points in Brillioun Zone is crucial for density response at low frequency and wavenumber: see next slide.

k_y

K_2 $(0, 4\pi/(3a))$

K_1 $(2\pi/(\sqrt{3}a), 2\pi/(3a))$

Γ $(0, 0)$

M

k_x

K_2''

K_2'

K_1'
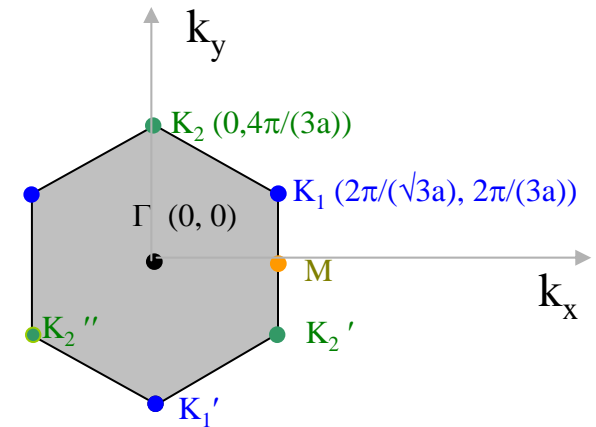
1st Brillouin Zone (k space)

B ●
N ○
C ●

$E(k_x,k_y)$

k_y

k_x

$E(k_x,k_y)$

k_y

k_x

$E(k_x,k_y)$

k_y

k_x

Bandstructure of metal
(e.g. e$^-$ doped BN
plane)

Bandstructure of
single graphene plane
(semimetal)

Bandstructure of
single BN plane
(semiconductor)

$$\overline{\chi}_0(\vec{q},iu) \approx \frac{-q^2 n_0}{m^* u^2}$$
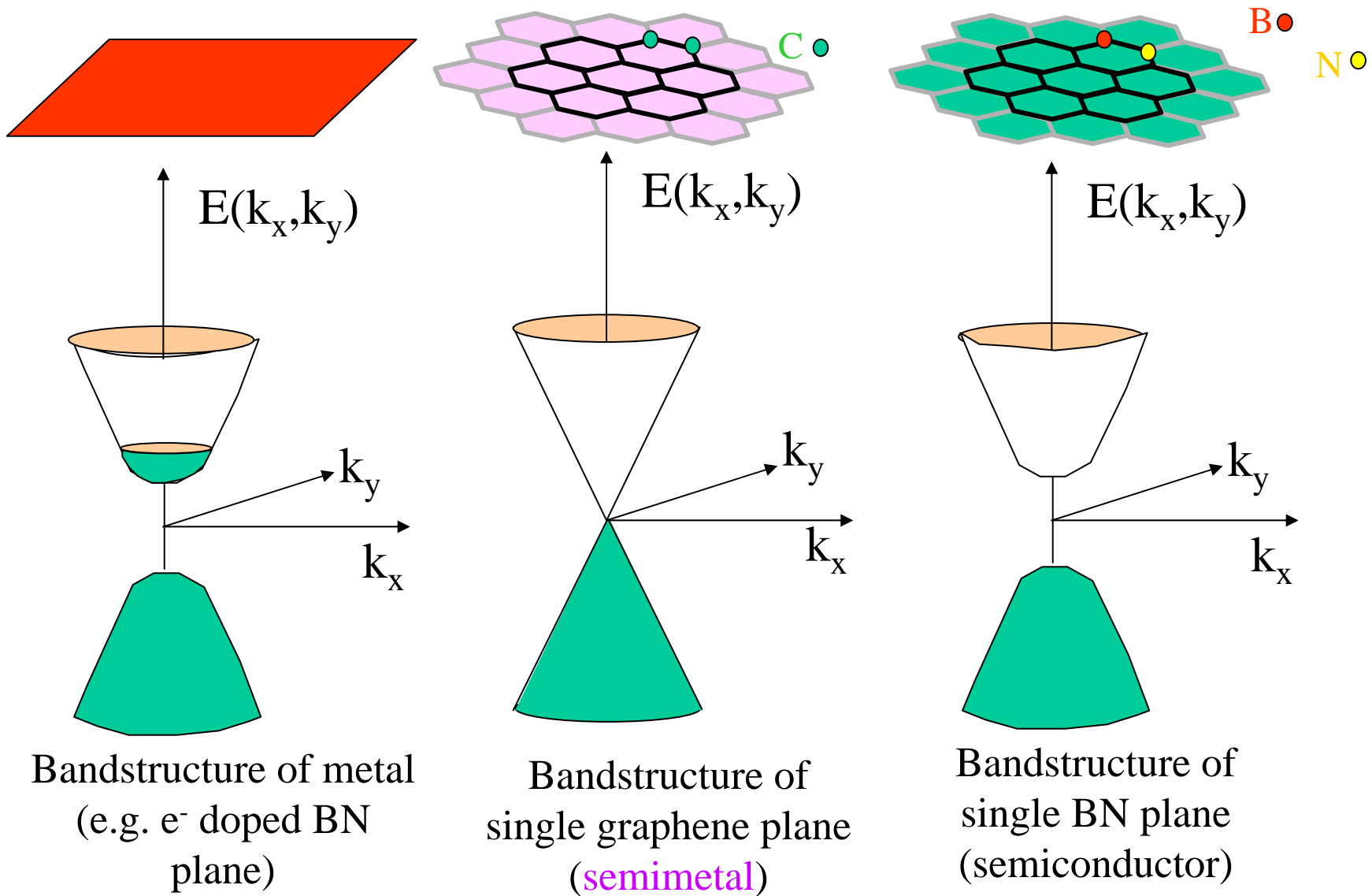
$$\overline{\chi}_0(\vec{q},iu) \approx \frac{-q^2}{2\hbar\sqrt{v_0^2 q^2 + u^2}}$$

$$\overline{\chi}_0(\vec{q},iu) \approx \frac{-q^2}{m^*(u^2 + \omega_0^2)}$$

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

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

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

Lattice and bandstructure of graphite

(a)

(b)

$E(k_x, k_y)$

k_y

k_x

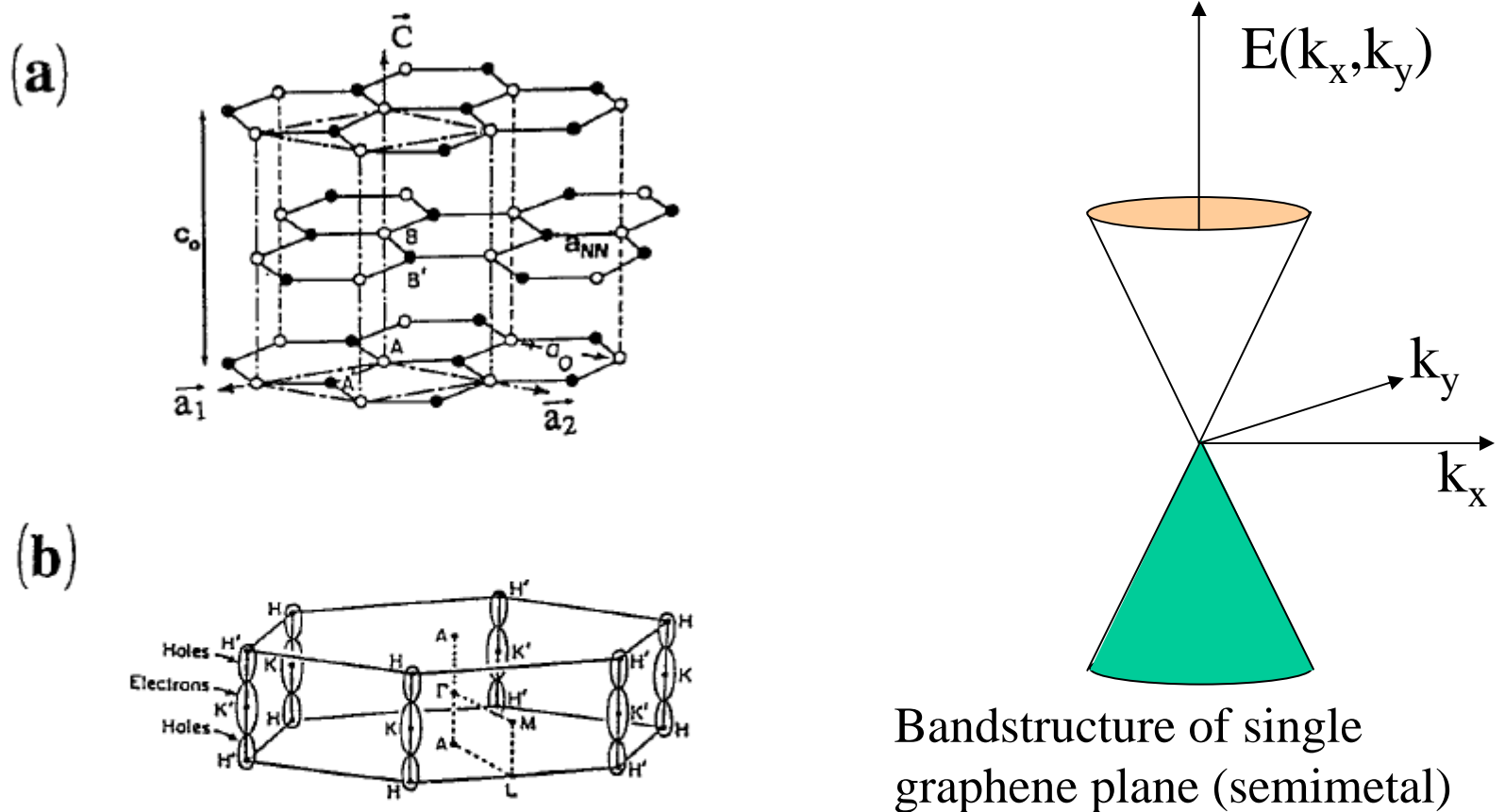Bandstructure of single graphene plane (semimetal)

FIG. 1. (a) Crystalline structure of hexagonal graphite (Ref. 1). The dimensions of the unit cell, which is represented by dotted-dashed lines, are a_0 and c_0. a_{NN} is the distance between nearest neighbors. (b) Graphite Brillouin zone showing several high-symmetry points and a schematic version of the graphite electron and hole Fermi surfaces located along the H-K axes (Ref. 24). Each symmetric point is labeled with the usual Bouckaert-Smoluchowski-Wigner notation (Γ, A, H, K, L, M).

From J. C. Charlier, X. Gonze and J.-P. Michenaud,

PRA 43, 4579 (1991)

RPA CALCULATION OF CRYSTALS: GRAPHITE LAYER BINDING ENERGY

Previous full RPA calculations for crystals: Si, Na, boron nitride, rare gases..

Miyake, Aryasetiawan, et al: Marini, Rubio et al: Harl et al

Graphite, Sebastien Lebegue et al (VASP) unpublished 2009

AB graphite geometry with in-plane lattice parameter fixed at exptal value 2.46 A.

**Computations done for various values of layer stacking parameter D.**

Plane wave cut-offs: 800 eV for the correlation part and 700 eV for the Hartree Fock part.

k-points used: Up to $14 \times 14 \times 6$ for correlation part, $26 \times 26 \times 8$ for HF part

This fine $\underline{k}$ subdivision was needed to sample reasonably finely the regions round the Dirac points K, K' in the 2D graphene Brillouin zone, where the gapless feature of the graphene electronic bandstructure occurs. leading to small pockets of electrons and holes. This affects E_x and also unusual causes singularities in response functions at long wavelength and low frequency, affecting E_c
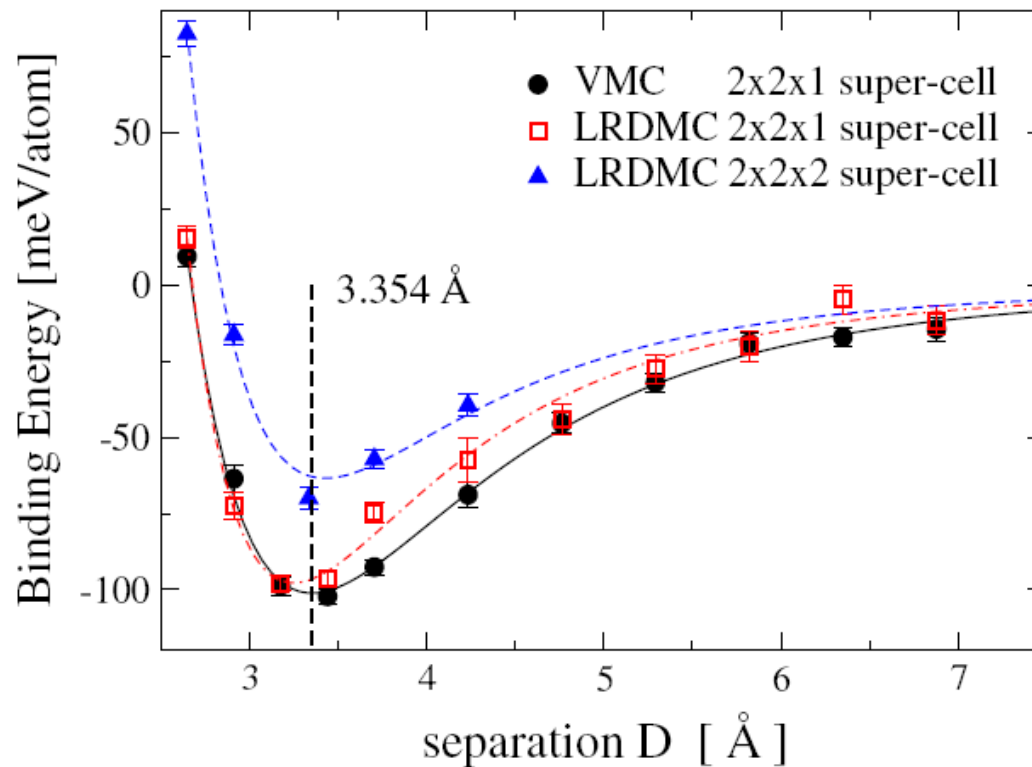
LAYER BINDING ENERGY GURVE OF AB GRAPHITE:
Lebegue et al, unpub 2009

Best lattice spacing and layer-stretching elastic constant, and benchmark layer binding
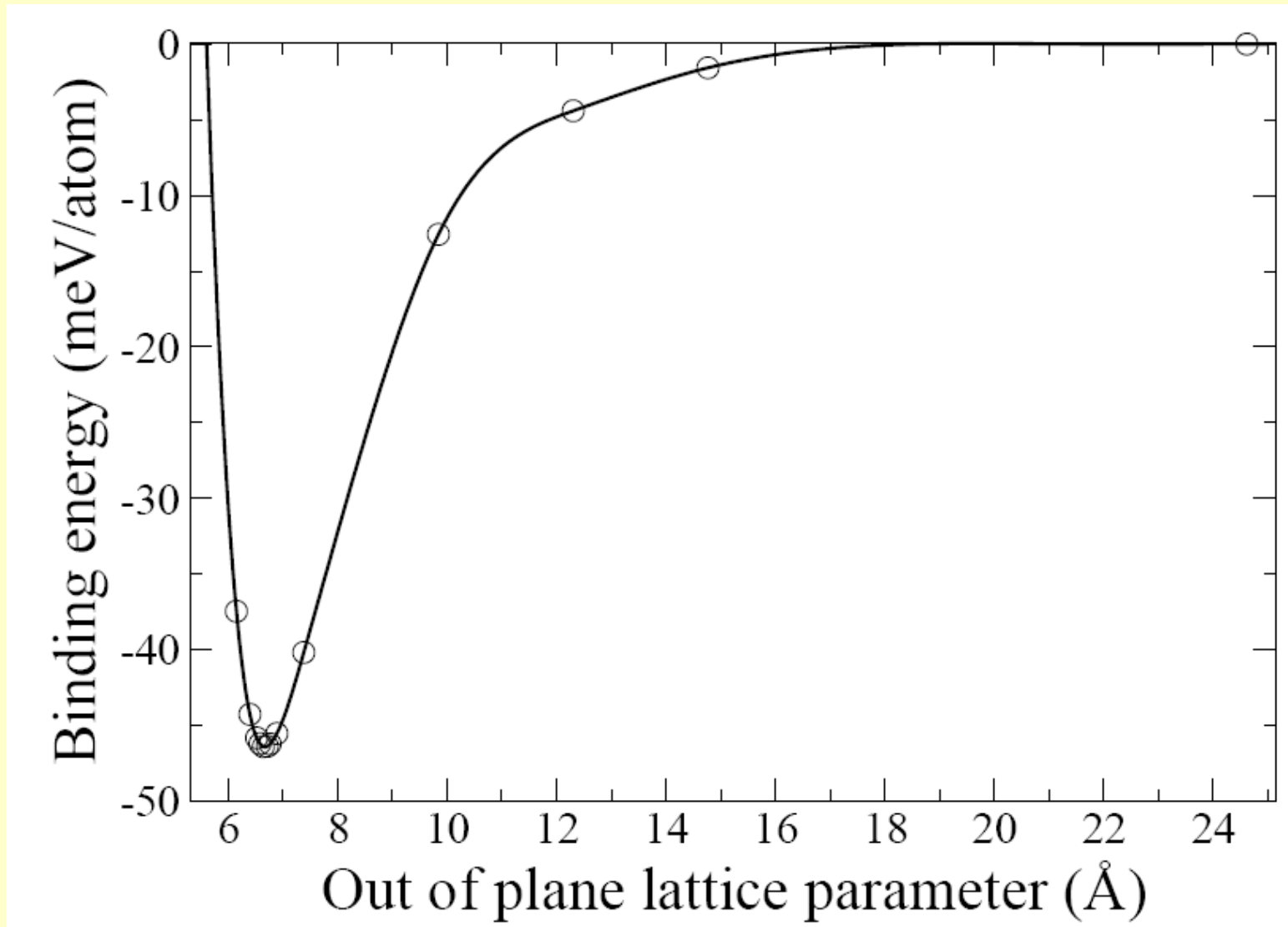
LAYER BINDING PROPERTIES OF GRAPHITE
IN QUANTUM MONTE CARLO (VMC, DMC)

Spanu, Sorella & Galli, Phys. Rev. Lett. 103, 196401 (2009)

RPA in Ne2 binding curve

Ne$_2$

Accurate ———
RPA —·+·—
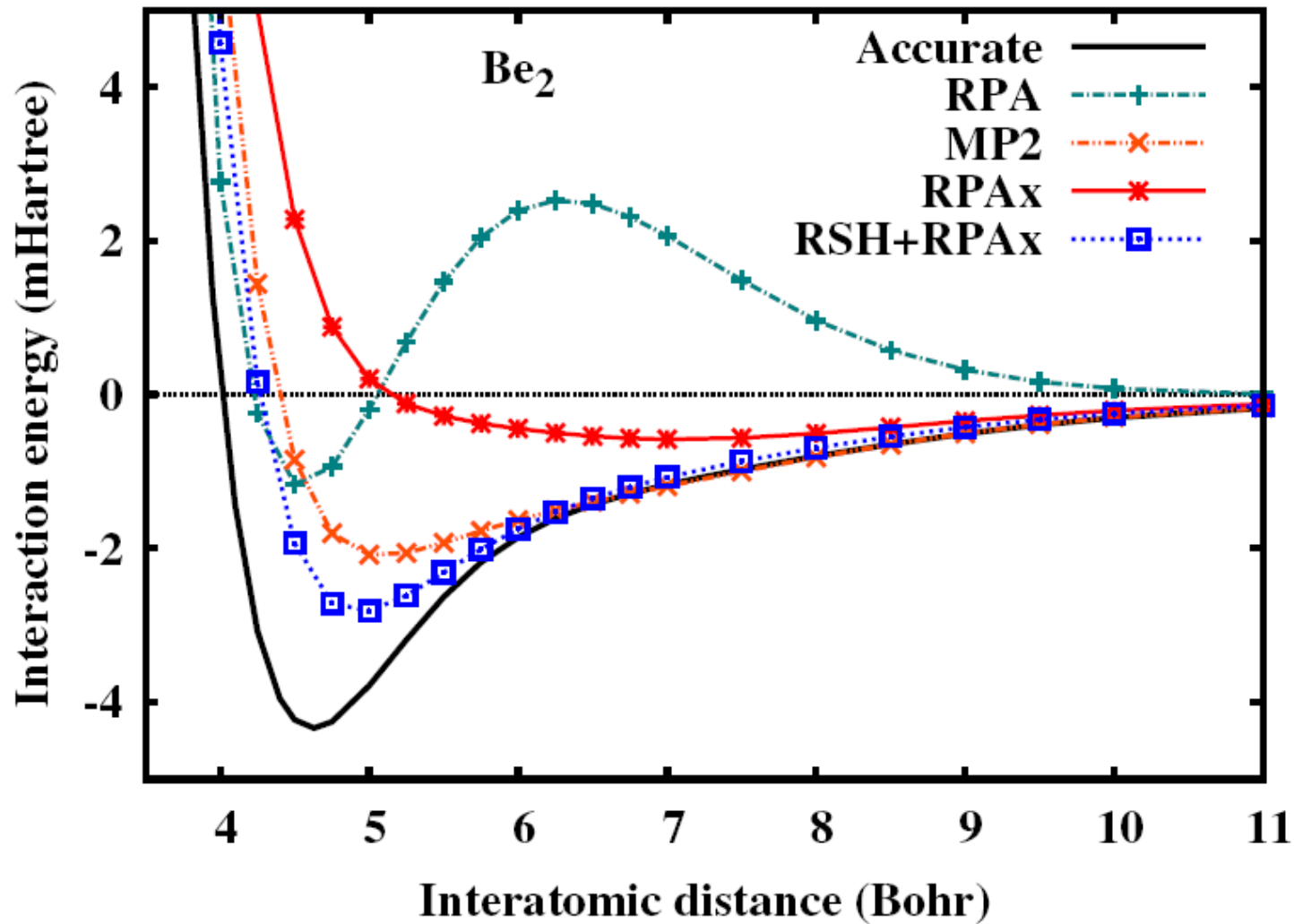MP2 —·×·—
RPAx ——*——
RSH+RPAx ·····□·····

Interatomic distance (Bohr)
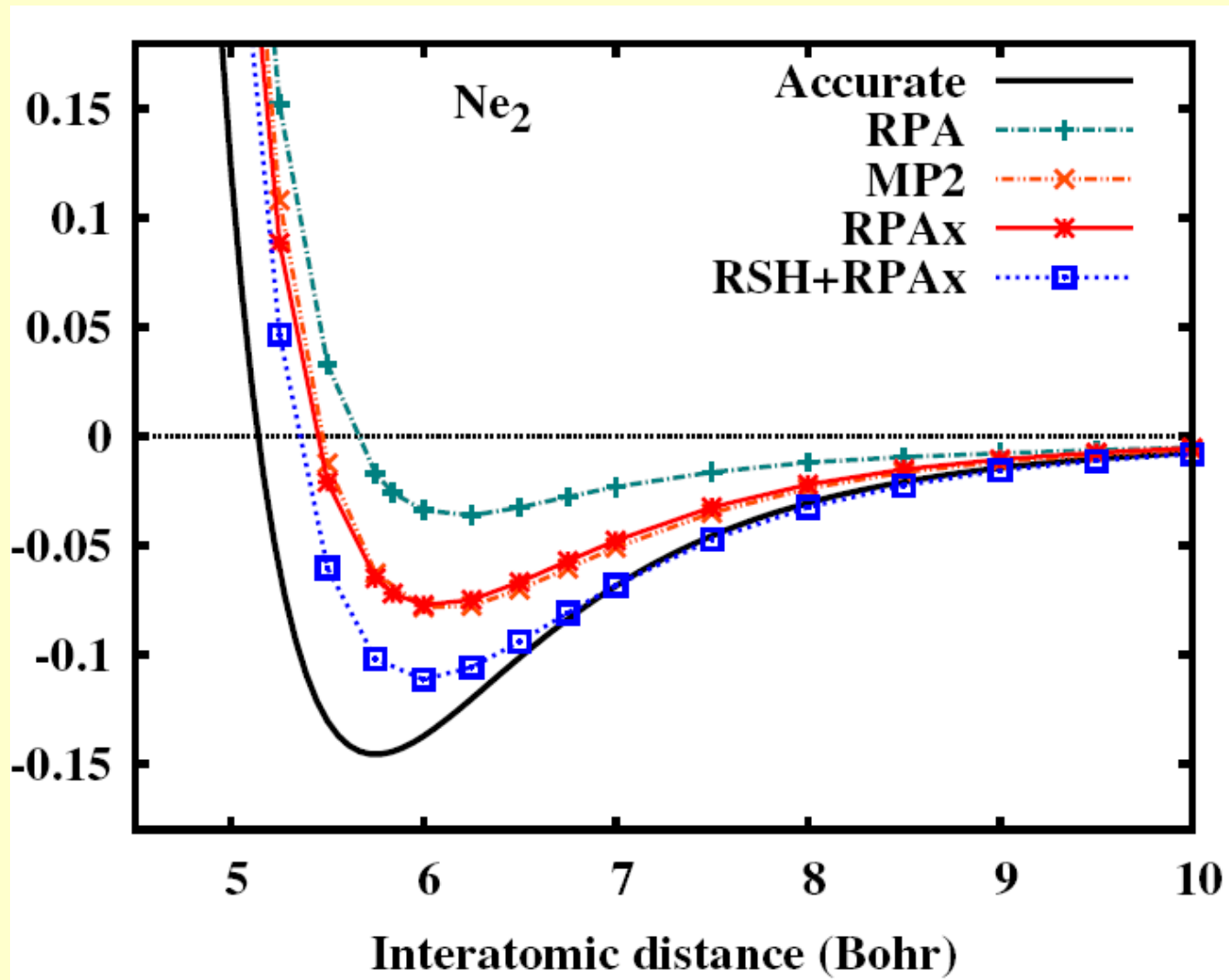
J. Toulouse et al, PRL **102,** 096404 (2009)

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

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

FUTURE DIRECTIONS – GRAPHITIC ENERGETICS VIA RPA

The present graphite calculation was a tour de force, made possible because VASP is efficient and a large number of k points were able to be used.

More complicated geometries – intercalates, nanotubes, etc etc – would be very difficult within RPA (even within VASP) if many need k points are needed.

A possible solution involves the use of much coarser k grids, but with analytic calculation of the response contributions from the sensitive regions near the Dirac K points.

The failure of the short-ranged correlation hole in RPA should be addressed, although experience with jellium layer problems suggests its effect on the energy <u>differences</u> of interest here is probably quite small.

One way to improve this is the <u>range-separated approach</u> in which the short-ranged correlations are treated separately.

One can hopefully also try higher theories (eg RPAx vs present d-RPA).

A quite different way to simplify the calculations is to use hydrodynamic-style approximations for χ_0 (JFD has grant for this).

SOME LESS-KNOWN WAYS TO GO BEYOND RPA IN ACFDT

Range-separated energy functionals

Started with Savin et al 1980's (short-ranged LDA with long-ranged CI)

Split bare Coulomb interaction $W = W_{short\ range} + W_{long\ range}$

Treat SR by DFT, LR by another method (perturbation, ACF/FDT….)

Kohn, Meir, Makarov PRL 1998: rigorous SR/LR separation for ACF/FDT

Angyan, Savin, Toulouse et al : another aproach, using 2nd order pert. for LR part, and recently RPA RPA/x correlation for long ranged part. Also TD.

More empirical hybrids: Goursot, Elstner

Energy optimized f_{xc}

The "Energy optimized Fxc" (Dobson, Wang PRB 2000) was designed to be local and frequency independent, but to give correct Ec via ACFDT for hom. gas.
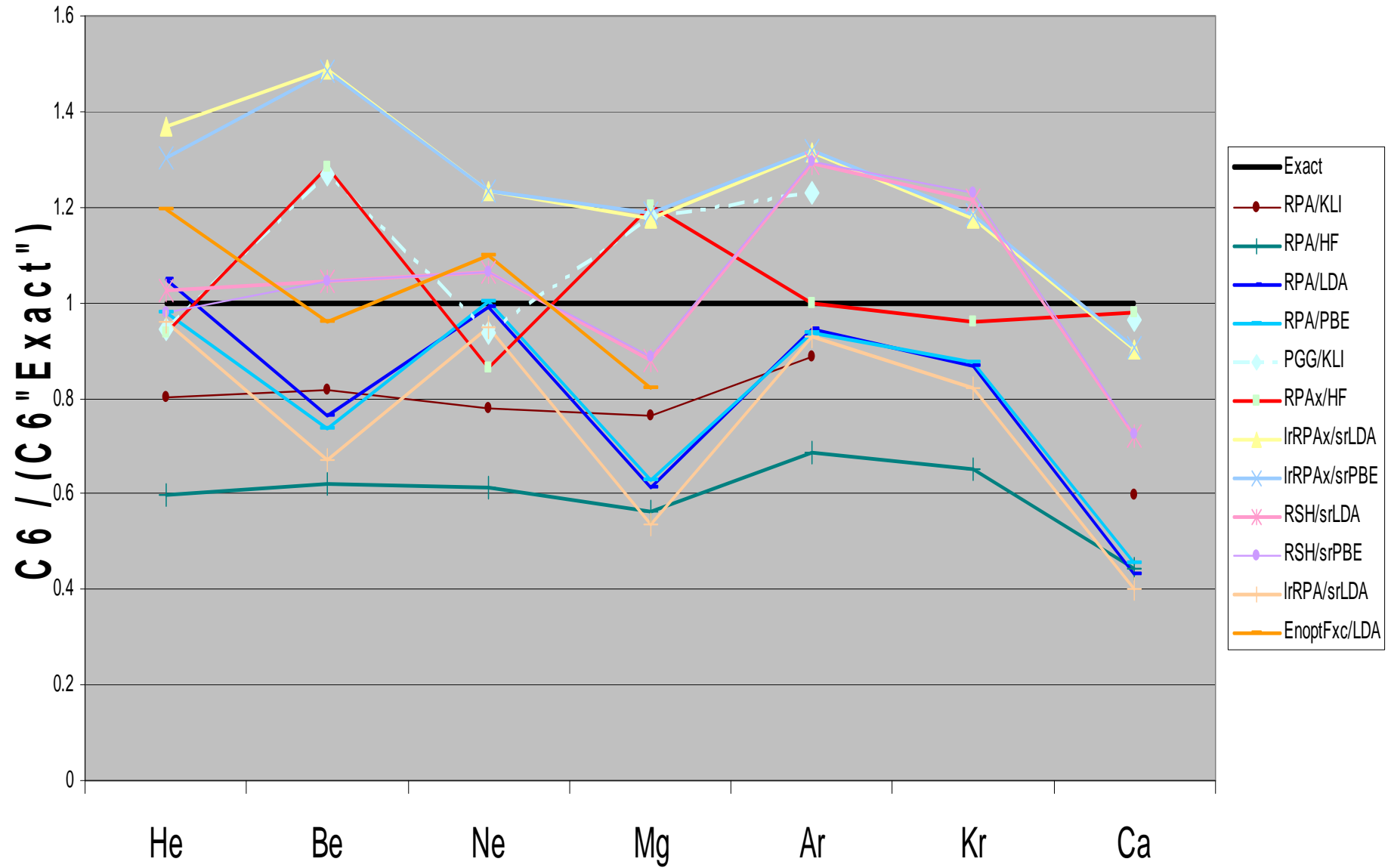
A spatially nonlocal version was given in Jung et al PRB 04

$$f_x^{PGG} = (g^{HF}(\vec{r}, \vec{r}\,') - 1)\frac{e^2}{|\vec{r} - \vec{r}\,'|}$$

Petersilka, Gossmann, Gross

$\approx$ **TD OEP**

C6 /C6 (exact) for closed shell atoms

Toulouse, Gould et al 2009 unpublished

Legend:
- Exact
- RPA/KLI
- RPA/HF
- RPA/LDA
- RPA/PBE
- PGG/KLI
- RPAx/HF
- lrRPAx/srLDA
- lrRPAx/srPBE
- RSH/srLDA
- RSH/srPBE
- lrRPA/srLDA
- EnoptFxc/LDA

Y-axis: C6 /(C6"Exact")

X-axis: He, Be, Ne, Mg, Ar, Kr, Ca

SOME RECENT VDW PAPERS

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(Effect of f^{en-opt} on vdW attraction of 2 thin jellium slabs)

JFD, J. Wang, B. P. Dinte, K. McLennan and H. M. Le. **IJQC 101, 579 (2005)** (Review)

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