Van der Waals forces in graphitic nanostructures

Norbert Nemec

QMC in the Apuan Alps IV
Vallico Sotto, 28th July 2008

History

Johannes Diderik van der Waals (1837-1923):
→ Postulation of intermolecular attraction in gases and liquids

Fritz London:
→ Unified treatment of "dispersion forces" in noble gases

[Eisenschitz und London, Z. Physik 60, 491 (1930)]

Henk Casimir and Dirk Polder
→ Proposed force between metal plates in vacuum

"The Influence of Retardation on the London-van der Waals Forces"

[Phys. Rev. **73**, 360 (1948)]

Definitions of terms

Inter-molecular forces: anything **except** covalent or ionic bonds

A) dipole-dipole force (two permanent dipoles)
[more general: multipole forces]

B) hydrogen bond

C) induced dipole force (permanent dipole/induced dipole)

D) dispersion forces (instantaneous dipole-dipole force)

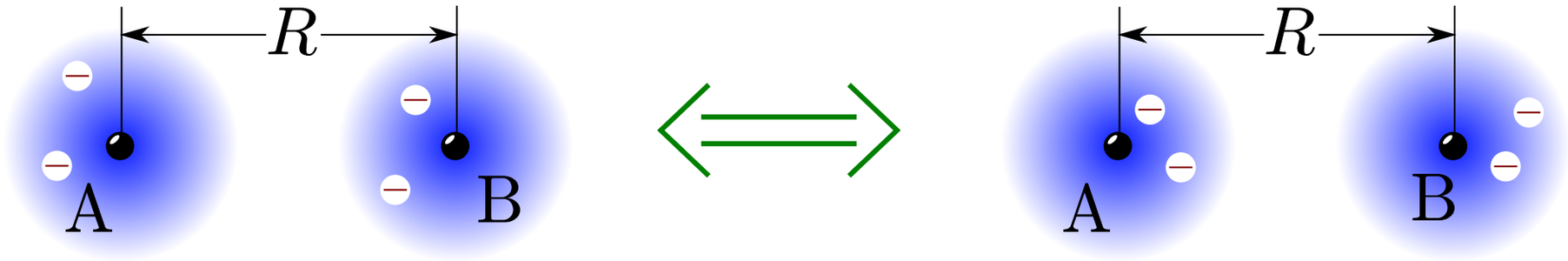
London force
→ synonym for "dispersion force" (sometimes including induced dipole force)

van der Waals force
→ synonym for "intermolecular force"
(sometimes synonym for dispersion force)

Casimir force
→ dispersion force between solids (continuum theory)

Dispersion force between atoms

$\Rightarrow$ long-distance correlations between electron positions within unpolar atom



$$E_{\mathrm{AB}}^{\mathrm{disp}} \approx -\frac{3\alpha^A \alpha^B I_A I_B}{4(I_A + I_B)} R^{-6}$$

α^A, α^B	polarizability
I_A, I_B	ionization potential
R	interatomic distance

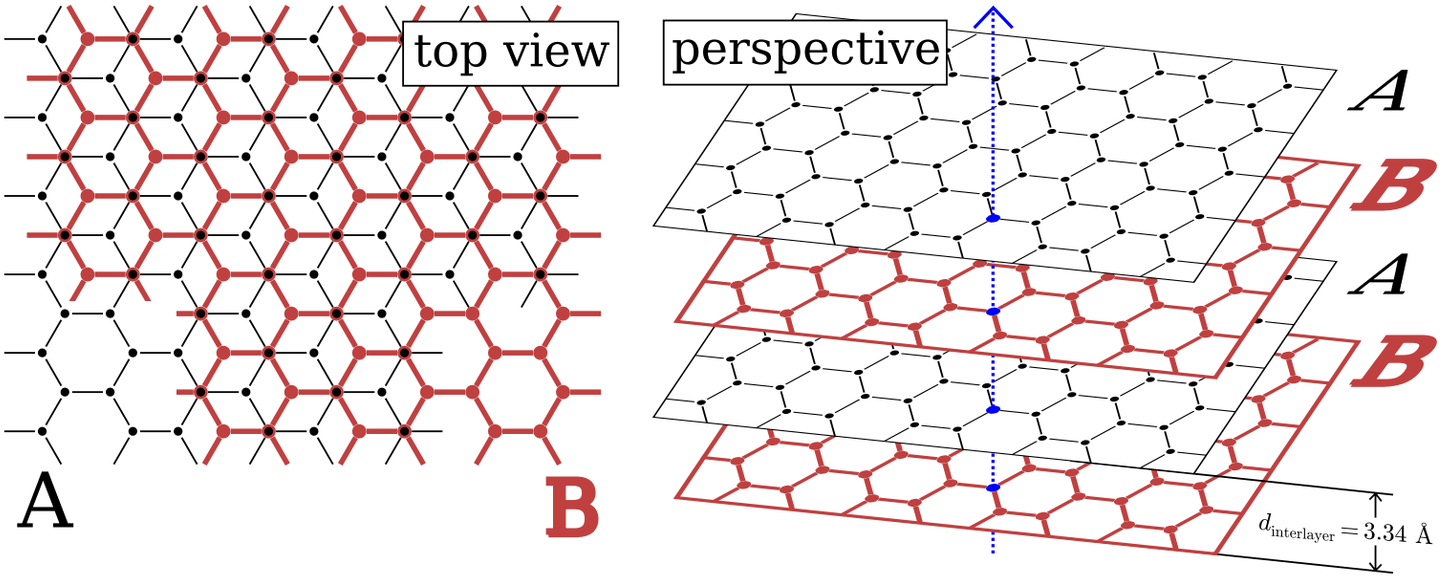
obtained via QM-multipole expansion [Eisenschitz und London, Z. Phys. 60, 491 (1930)]

Casimir force

Macroscopic bulk description of force between polarizable media.

- depends on *dynamic polarizability* and *geometry* of media
- not additive (!)
- in case of metal bodies in vacuum
  $\Rightarrow$ elegant computation via *vacuum energy* of intermediate space
- always attractive for symmetric combination of media
  (e.g. metal-vacuum-metal, air-liquid-air, etc.)
- reduced with increasing temperature
- reduced by relativistic retardation important for longer distances

Graphite

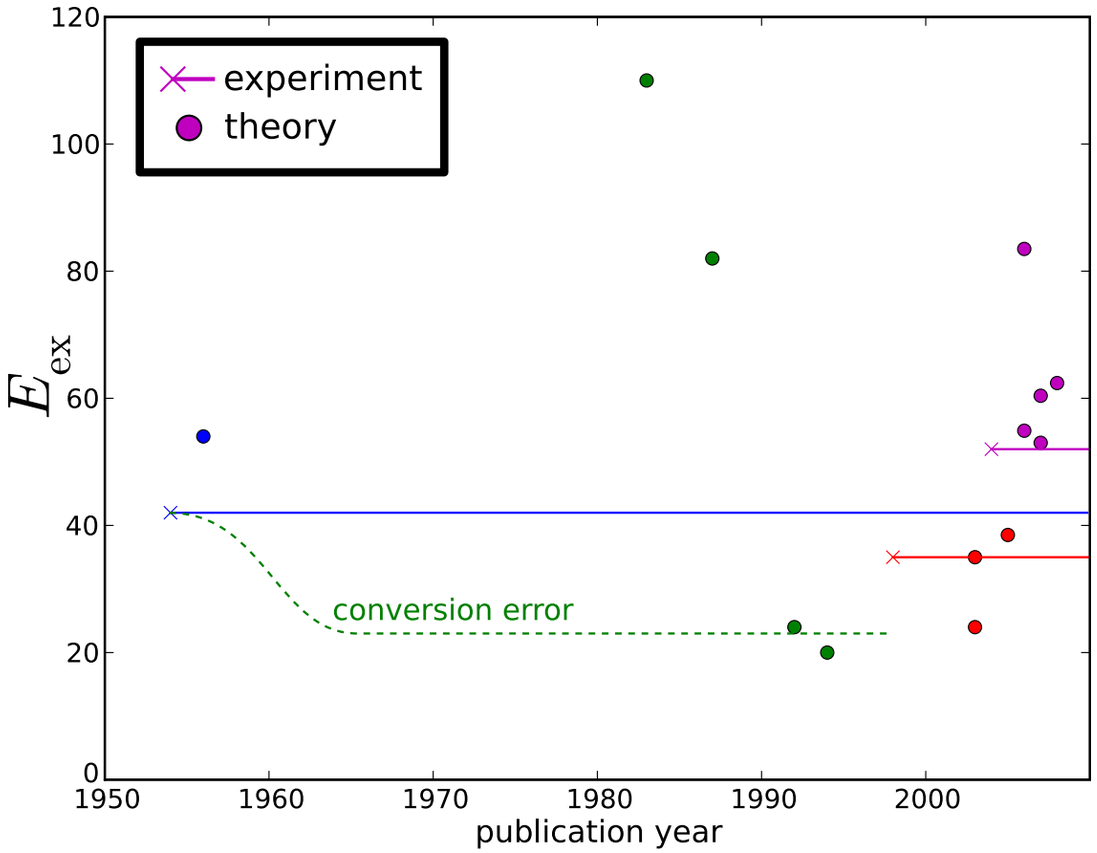


intralayer bond length:	$d_{CC} = 1.4196\,\text{Å}$
atomization energy	$E_{\mathrm{at}} = 7.374\,\mathrm{eV/atom}$
intralayer isotrop. elastic constant:	$C_{11} + C_{22} = 1240\,\mathrm{GPa}$
interlayer distance:	$d_{\mathrm{interlayer}} = 3.335\,\text{Å}$
exfoliation energy:	$E_{\mathrm{ex}} = 35...52\,\mathrm{meV/atom}$
interlayer elastic constant:	$C_{33} = 36.5\,\mathrm{GPa}$

Theoretical attempts on interlayer energetics

	Method	$d_{\mathrm{interlayer}}$ (Å)	$E_{\mathrm{ex}}\left(\frac{\mathrm{meV}}{\mathrm{atom}}\right)$	$C_{33}\,(\mathrm{GPa})$
Brennan (1952)	LCAO + vdW	exp. input	11 / 172	39 / 11
Girifalco (1956)	lattice summation		54	
DiVincenzo (1983)	DFT + Thomas Fermi	5.6	110	
Yin (1984)	DFT-LDA	7.05 ± 0.7	~ 13.6	54 ± 20
Jansen (1987)	all elec. augmented PW	6.83 ± 0.06		56 ± 9
Schabel (1992)	DFT-LDA	6.72	24	24.3
Charlier (1994)	DFT-LDA	6.60	20	
Telling (2003)	DFT-LDA	6.70	35	
Rydberg (2003)	layered DFT-vdW	7.52	24	13
Zhechkov (2005)	DFTB + a posteriori vdW	6.76	38.5	
Mounet (2005)	GGA (at exp. lattice const.)	exp. input		45
Donchev (2006)	QMPFF	6.972	54.9	40.6
Ortmann (2006)	GGA + semiemp. vdW	6.69	83.5	41.7
Ziambaras (2007)	general DFT-vdW	7.18	53	27
Hasegawa (2007)	DFT + semiemp. corr.	exp. input	60.4	exp. input
Gould (2008)	LDA/GGA + semiemp. corr.	exp. input	62.4 / 59.7	exp. input

Correlation between experiment and theory



exfoliation energy:

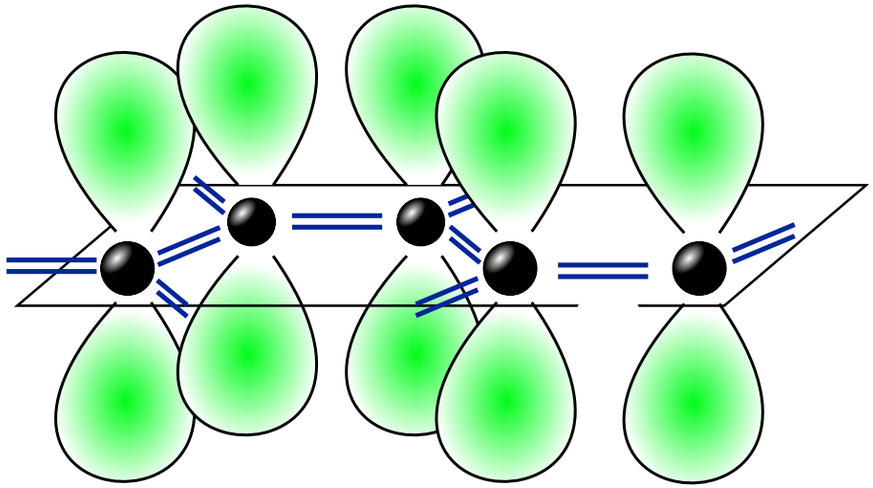
42 meV/atom [Girifalco 1952: wetting by organic liquids]

$\sim$20 meV/atom $\longrightarrow$ various incorrect conversions

35 meV/atom [Benedict 1998: collapse of nanotubes]

52 meV/atom [Zacharia 2004: polyaromatic hydrocarbons]

π-conjugated electronic structure of graphene



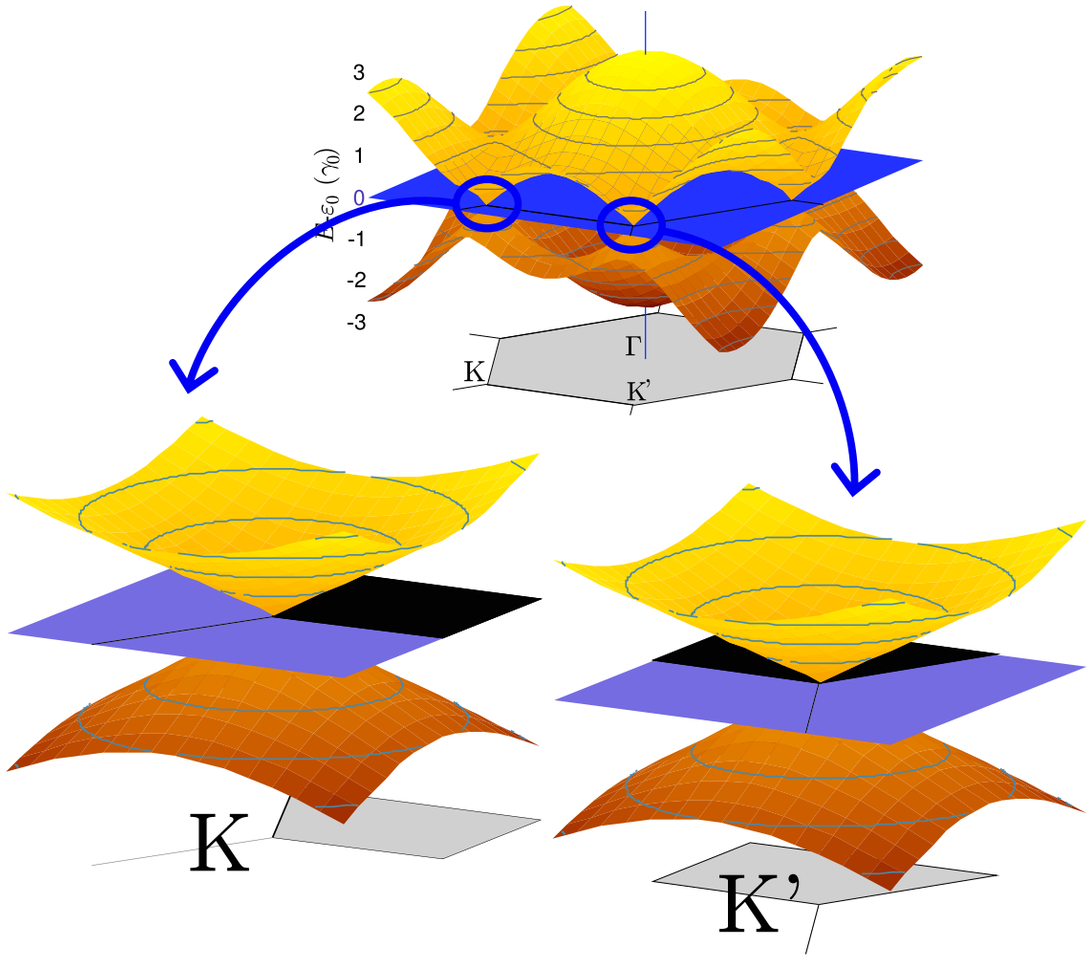
in-plane sp^2-orbitals

$\longrightarrow$ strong σ-bonds

remaining p_z-orbitals

$\longrightarrow$ semi-metallic π-bands

π-band structure of graphene:



Dispersion forces for thin layers

TABLE I. Asymptotic vdW energy of parallel structures. K and D_0 are constants.

System	Present	Standard
1D metals[a]	$-\mathbf{D^{-2}(\ln(KD))^{-3/2}}$	$-D^{-5}$
1D insulators [9]	$-D^{-5}$	$-D^{-5}$
2D metals [10,11]	$-\mathbf{D^{-5/2}}$	$-D^{-4}$
π-conjugated layers[a]	$-\mathbf{D^{-3}}$	$-D^{-4}$
1 metallic, 1 π layer[a]	$-\mathbf{D^{-3}\ln(D/D_0)}$	$-D^{-4}$
2D insulators [6]	$-D^{-4}$	$-D^{-4}$
Thick metals or ins. [11]	$-D^{-2}$	$-D^{-2}$

[a]* Denotes new derivations given here.

[from Dobson, White and Rubio, Phys. Rev. Lett. **96**, 073201 (2006)]

Graphite and QMC

[Fahy et al., Phys. Rev. B **42**, 3503 (1990)]

- VMC with nonlocal pseudopotential

$\longrightarrow$ precision insufficient for vdW interactions

[Prendergast et al., Phys. Rev. B **66**, 155104 (2002)]

- VMC with inhomogeneous e-e-Jastrow term

$\longrightarrow$ no binding energy extracted

$\longrightarrow$ large number of parameters (3000 for 3x3x3 super cell)

Our approaches (work in progress!!)

↙ ↘

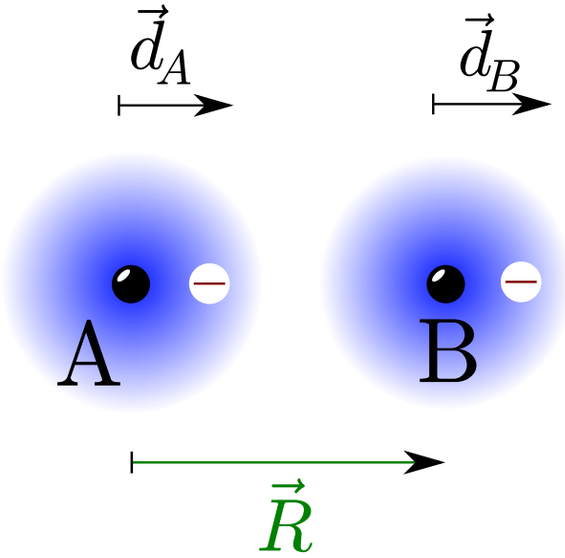
vdW-tailored Jastrow term **DMC with finite-size corrections**

The Jastrow-D-term

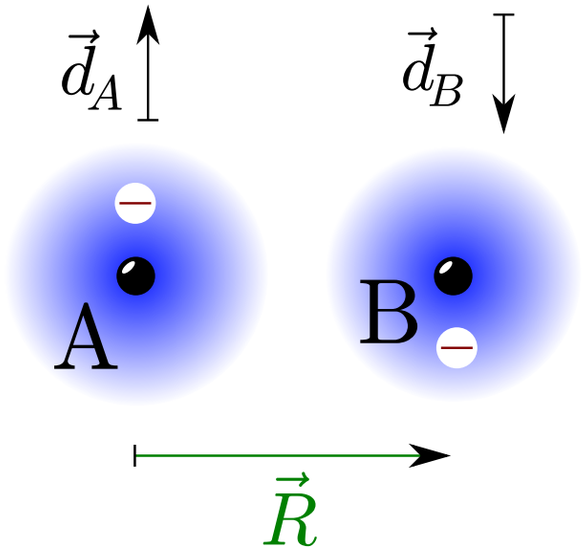
Inspired by classical dipole-dipole interaction:

$$E = \frac{1}{4\pi\epsilon_0 R^3}(\boldsymbol{d}_A \cdot \boldsymbol{d}_B - 3(\boldsymbol{d}_A \cdot \boldsymbol{R})(\boldsymbol{d}_B \cdot \boldsymbol{R}))$$

longitudial dipoles



attractive transverse dipoles



The Jastrow-D-term

Inspired by classical dipole-dipole interaction:

$$E = \frac{1}{4\pi\epsilon_0 R^3}(\boldsymbol{d}_A \cdot \boldsymbol{d}_B - 3(\boldsymbol{d}_A \cdot \boldsymbol{R})(\boldsymbol{d}_B \cdot \boldsymbol{R}))$$

Two independent D-terms:

$$D_\parallel = \sum_{I<J} \sum_{i,j} (\boldsymbol{r}_{Ii} \cdot \boldsymbol{R}_{IJ})(\boldsymbol{r}_{Jj} \cdot \boldsymbol{R}_{IJ}) f_\parallel^{IJ}(r_{Ii}, r_{Jj})$$

$$D_\perp = \sum_{I<J} \sum_{i,j} \left[(\boldsymbol{r}_{Ii} \cdot \boldsymbol{r}_{Jj}) R_{IJ}^2 - (\boldsymbol{r}_{Ii} \cdot \boldsymbol{R}_{IJ})(\boldsymbol{r}_{Jj} \cdot \boldsymbol{R}_{IJ})\right] f_\perp^{IJ}(r_{Ii}, r_{Jj})$$

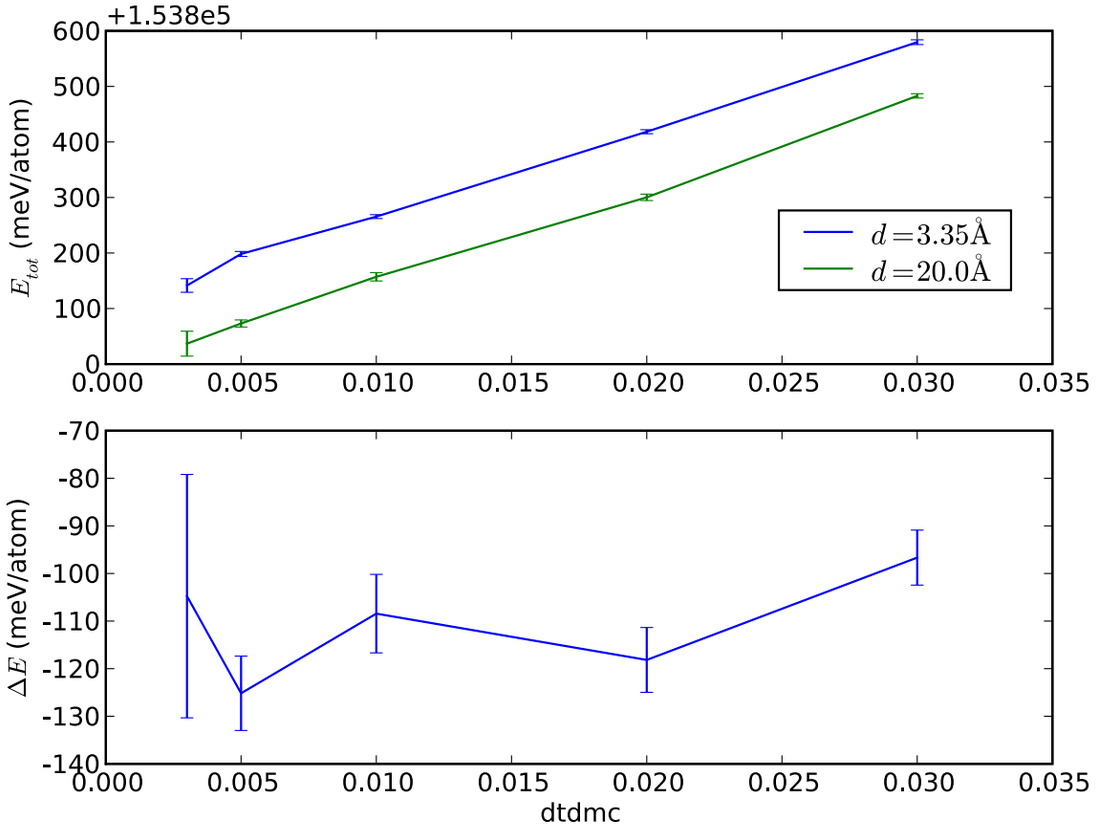
$f_\parallel^{IJ}$ and $f_\perp^{IJ}$: scalar functions with cutoff, analogous to U term
$\longrightarrow$ optimized independently for each pair of atoms (reduced by symmetry)

$\Rightarrow$ implemented, but yet to be tested ...

Graphite interlayer binding with CASINO

- CASTEP wave function (plane-wave $\rightarrow$ blip)
- using pseudo-potentials $\Rightarrow$ 4 electrons per C atom
- primitive cell containing two graphene layers with two atoms each
  $\Rightarrow$ 16 electrons per primitive cell
- starting out with 3x3x1 simulation cell
  $\Rightarrow$ 144 electrons in simulation cell
- Jastrow terms: U, χ, F
  $\rightarrow N_u = N_\chi = 6$, $N_{f-\mathrm{ee}} = N_{f-\mathrm{eN}} = 2$
  $\rightarrow$ fixed cutoffs $L_u = 4$ a.u., $L_\chi = 3$ a.u., $L_f = 2$ a.u.
  $\rightarrow$ varmin-linjas optimization

DMC time-step and CPU cost analysis



$\longrightarrow$ 64 nodes á 100 configs

$\longrightarrow$ 1000 time steps data collection

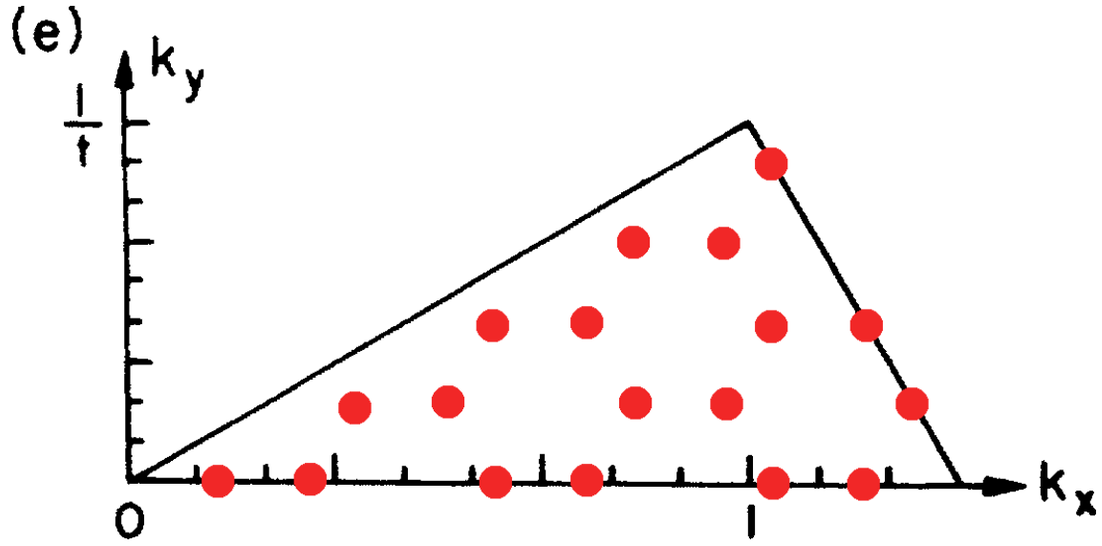
$\longrightarrow 5 \times 64 = 320$ CPU hours

$\longrightarrow$ correlation time: ~ 2 a.u.

$\longrightarrow$ using `dtdmc=0.01`

Twist averaging

18 twist angles according to special points in hexagonal 2D Brillouin zone



[Cunningham, Phys. Rev. B 10, 4988 (1974)]

Preliminary results

super cell	E_{ex} (meV/atom)	CPU hours
$3 \times 3 \times 1$	102 ± 6	2×1000
$3 \times 3 \times 2$	68 ± 5	2×5000
$4 \times 4 \times 1$	53 ± 4	2×5000
experiment	*35...52*	

Next steps

- more careful Jastrow optimization
- finite size correction for kinetic energy
- Ewald $\leftrightarrow$ MPC
- check error from finite k-grid in DFT
- localize blip wfn (not yet implemented for complex wfn)

$\rightarrow$ larger systems and more smaller and intermediate system sizes

Acknowledgements

- Richard Needs
- Neil Drummond
- everyone else in the QMC group, Cambridge
- DAAD for financing the project