

Electron response in the Rutgers-Chalmers van der Waals Density Functionals

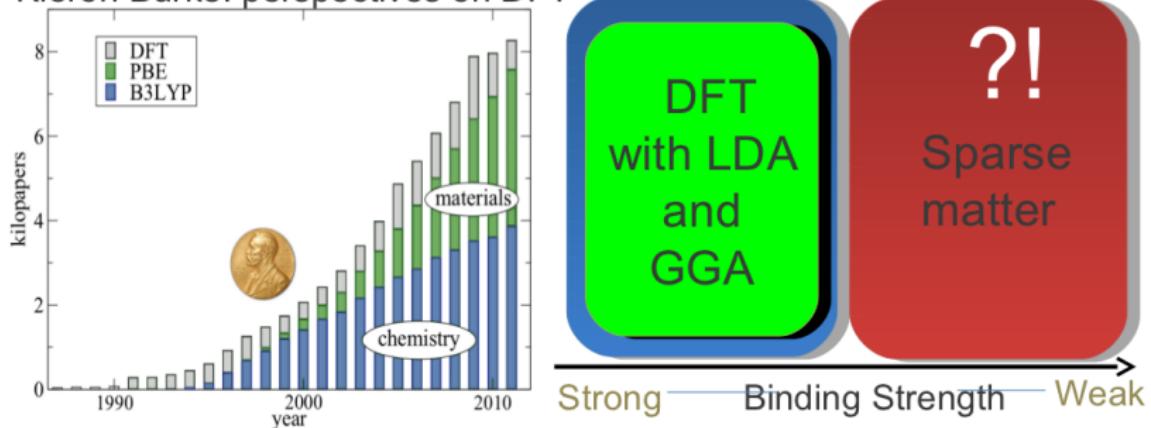
Per Hyldgaard,
Kristian Berland, Elisa Londero, Elsebeth Schröder

Microtechnology and Nanoscience, MC2,
Chalmers University of Technology, Göteborg, Sweden

GPAW workshop, Lyngby, May 21-22, 2013

Density Functional Theory (DFT)

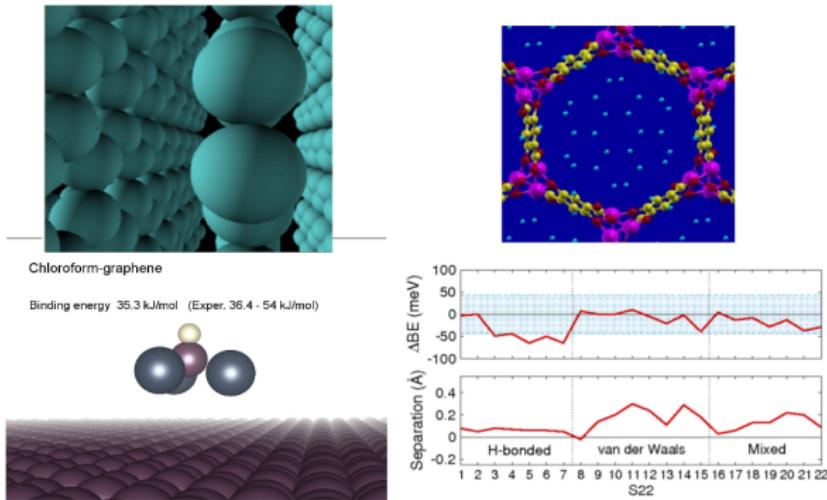
Kieron Burke: perspectives on DFT



Must we really stop DFT before looking at broadly relevant sparse matter, molecular recognition, and life processes?

On the van der Waals density functional (vdW-DF) method

Gets van der Waals (vdW) binding, sparse matter, seamless extension w. nonlocal correlations
 Non-empirical, physics-based constraints, close relative of LDA/GGA, enhance transferability



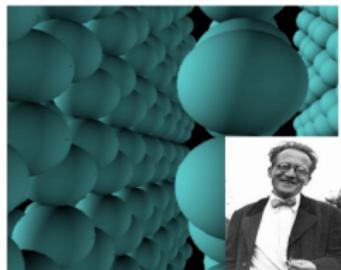
[“vdW-DF”: Surf. Sci. **493**, 253 (01); PRL **91**, 126402 (03); ‘general’ PRL **92**, 246491 (04), vdW-DF2]

Key vdW-DF works at Rutgers/WFU/ORNL and Chalmers [<http://fy.chalmers.se/~schroder/vdWDF>]

Challenges in van der Waals (vdW) bonding, sparse matter

Typical matter is sparse, combines:

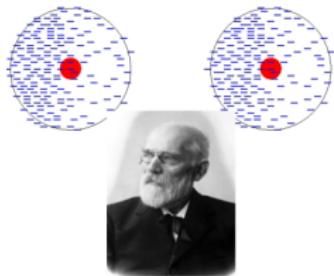
- ▶ Strong short-ranged bonds.
- ▶ Weaker van der Waals (vdW) forces acting via electrodynamics coupling across low-density voids.



Mostly a dynamics view of vdW:

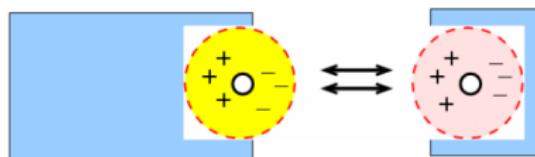
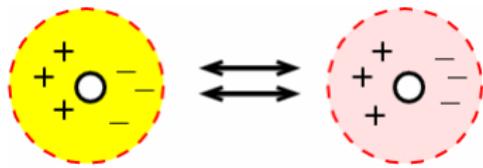
- ▶ van der Waals, London: atom focus
- ▶ Casimir: zero-point energy shifts

[Equivalence, proven for excitons, Mahan, JPC (65)]



vdW interactions from quantum-physical correlations of spontaneous and induced dynamical charge fluctuations ... in ground-state DFT?

van der Waals forces: nonlocal correlations, from plasmons



London++: atom oscillator coupling

Rapcewicz and Ashcroft, PRB **44**, 4032 (91):

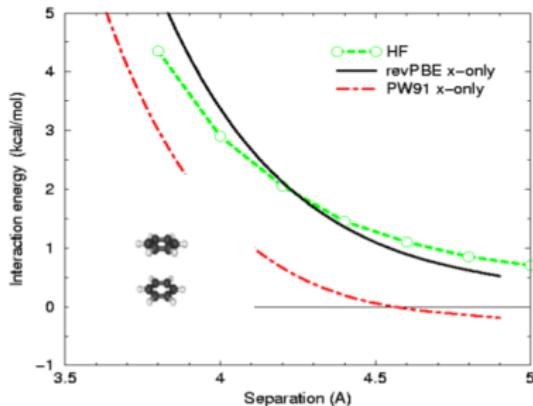
- ▶ xc-hole n_{xc}^0 [LDA/GGA-type plasmons] oscillates relative to electron; supplements Hopfield/Anderson/Mahan exciton view, links with density.
- ▶ Relevant: the plasmon coupling is dynamically screened.
- ▶ Physics picture also in Andersson/Langreth/Lundqvist+DCL/Vosko works
- ▶ **Adiabatic connection formula (ACF)** [DCL/Perdew/Gunnarsson/BIL 1975-77]
Plasmons \leftrightarrow LSDA; lower- q plasmon shifts \rightarrow surface energy.

Set to follow plasmon zero-point energy shifts Plasmons $\omega_q^{\lambda c}$ incomplete correlation.
vdW-DF builds nonlocal correlation energy from inside out, $n_{xc}^0 \leftarrow \omega_q^{\lambda c}$.

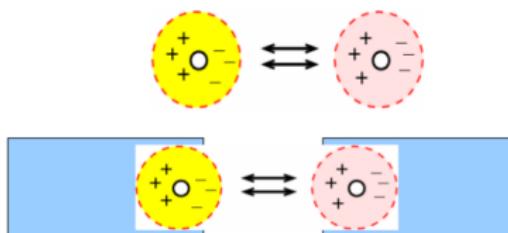
Density functional construction in vdW-DF

$$E_{xc} = E_x^{GGA} + E_c^{new}$$

An appropriately selected GGA exchange functional



Plasmon picture for both local and nonlocal parts



"Layered" PRL **91**, 126402 (03),
"General-Geometry", M. Dion et al.,
Phys. Rev. Lett. **92**, 246401 (04)

vdW-DF2 [PRB **82**, 081101R (10)] picked PW86r exchange [E. Murray/KL/DCL, JCTC **5**, 2754 (09)], following study of exchange-energy variation in vdW-bonded molecules.

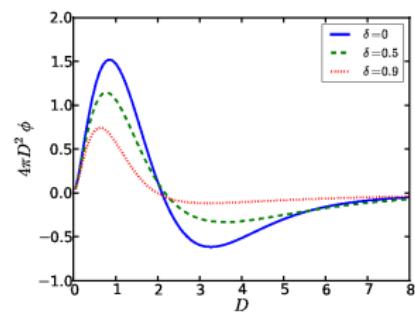
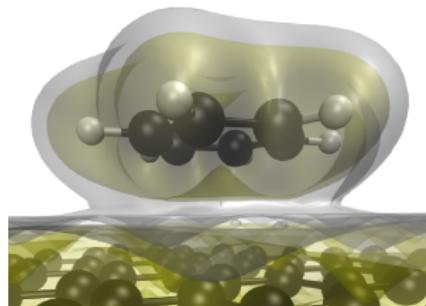
Screening and plasmon response in the vdW-DF method

With $V = -4\pi G = |\mathbf{r}_1 - \mathbf{r}_2|^{-1}$, no retardation, longitudinal response:

$$\begin{aligned} E_{xc} &= E_{xc}^{\text{ACF}} \equiv - \int_0^1 d\lambda \int_0^\infty \frac{du}{2\pi} \text{Tr}\{\chi[n](\lambda, iu) V\} \\ &\equiv \int_0^\infty \frac{du}{2\pi} \ln|\det(\nabla \cdot \epsilon[n](iu) \cdot \nabla G)| \end{aligned}$$

- ▶ $\chi[n](\lambda, iu) = \delta n / \delta \Phi_{\text{ext}}$: density response at $\lambda = (q/e)^2$,
- ▶ ACF gives vdW-DF dielectrics: $\epsilon[n](iu) \equiv 1 + 4\pi\alpha[n](iu)$
 λ -averaged response $\tilde{\chi}^{\text{ACF}}[n] \equiv \nabla \cdot \alpha[n] \cdot \nabla$, $\chi^{\text{ACF}}[n]$.
- ▶ $\kappa_r[n](iu) \equiv (1 + \chi^{\text{ACF}} V)^{-1}$ full ACF; For components,
 $[\ln(\kappa_r[n])]_{A,B} \approx [\ln(\epsilon[n])]_{A,B} \leftrightarrow$ GGA-type E_{xc}^0 , plasmons poles.
- ▶ Expand $E_c^{\text{nl}} \equiv E_{xc} - E_{xc}^0$ in fluctuation propagator $S = 1 - \epsilon^{-1}$.

vdW-DF nonlocal correlations \leftrightarrow plasmon shifts



Expansion for two fragments A and B:

$$E_c^{\text{nl}} = \text{Tr}\{\ln(1 - [\chi^{\text{ACF}} V]_{AB}[\chi^{\text{ACF}} V]_{BA})\}$$

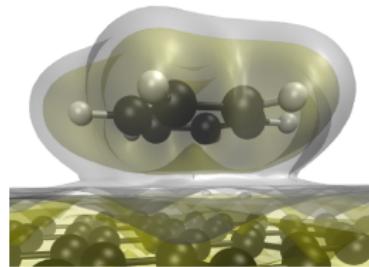
When χ^{ACF} is intra-fragment and V_{AB} mediates $\omega_q^{\lambda c}$ coupling:
vdW-DF counts zero-point energy shifts. [from exciton argument, Mahan, JCP **43**, 1569 (65)].

Also, vdW-DF second-order expansion

$$\begin{aligned} E_c^{\text{nl}} &= \int_{\mathbf{r}} \int_{\mathbf{r}'} n(\mathbf{r}) \phi[n, \nabla](\mathbf{r}, \mathbf{r}') n(\mathbf{r}') \\ \phi[n, \nabla n] &: \quad \{D, \delta\} \leftrightarrow \{q_0[n](\mathbf{r}), q_0[n](\mathbf{r}')\} \end{aligned}$$

permits *nontrivial universal-kernel evaluation*.

vdW-DF reflects binding regions and electron tails

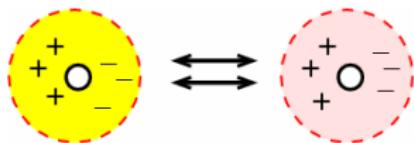


Low-density-points cut	2%	8%	50%
Trivial $n(r)\bar{\Phi}n(r')$ loss	4%	15%	75%
$\Delta E_c^{\text{nl}} \sim n(r)\phi[n]n(r')$ loss	15%	65%	97%

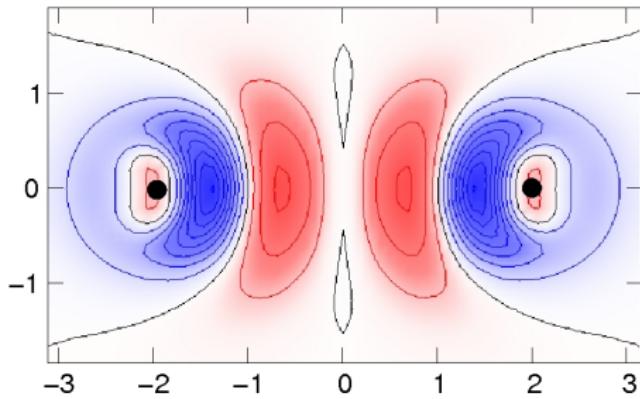
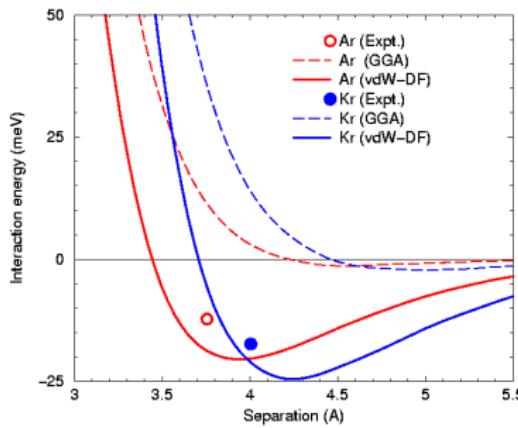
Variation demonstratively different from a simple pair-summation of densities.

[KB/PH arXiv:1303.0389, PRB in press.]

Nature, electrostatic signature of dispersive interactions

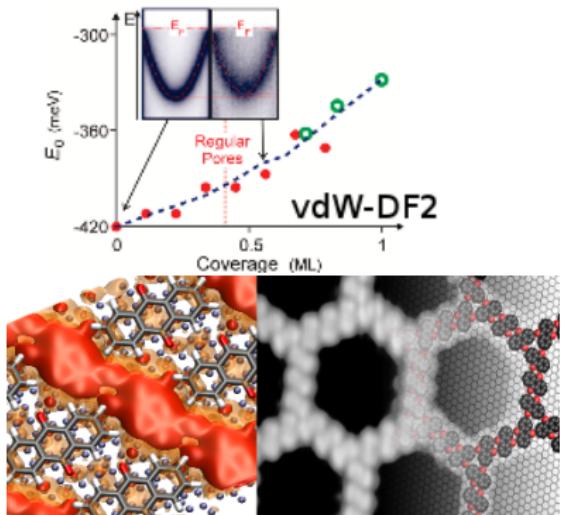


Born-Oppenheimer, equilibrium:
forces are electrostatic → vdW
attraction must have steady-state
density signature like all bonds

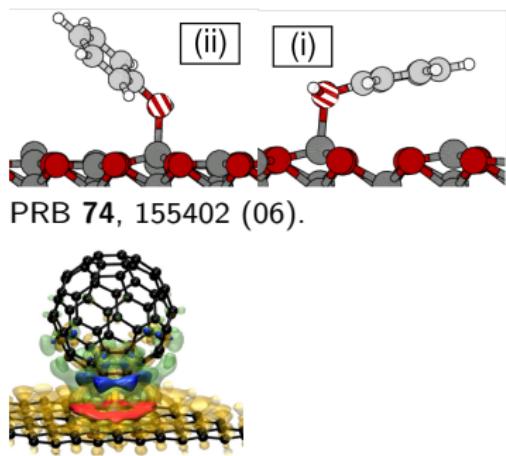


Nature + V_{xc} [PRB 76 (2007) 125112]

Spectroscopy, weak chemisorption, head/tail frustration



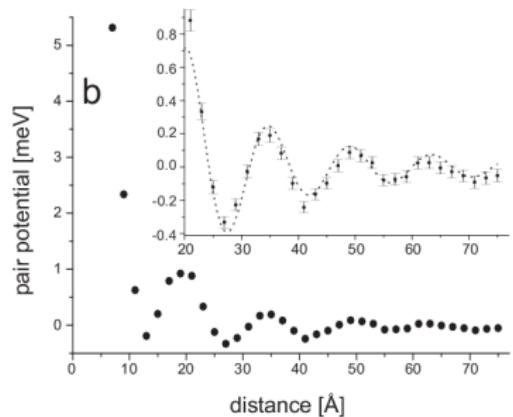
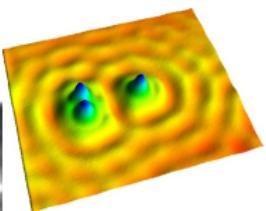
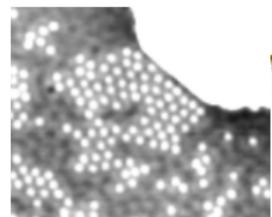
With Bartels... , vdW-DF in
co-spectroscopy/model-refinement role:
Nano Lett. **11**, 2944 (11).



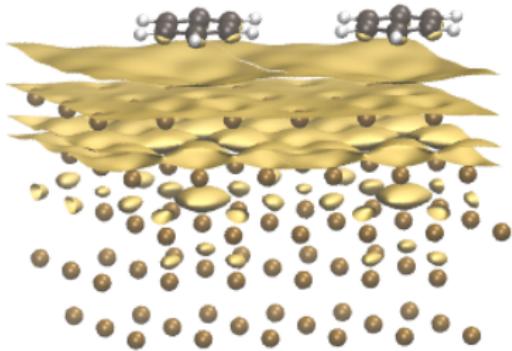
Molecular electronic contacts →
adsorbate in dopant role.

PRB **84**, 155451 (11).

Interference coupling by metallic surface state propagation



w. Repp/Moresco/Meyer/Rieder/Persson,
PRL **85**, 2981 (00), Focus story, [& Repp]



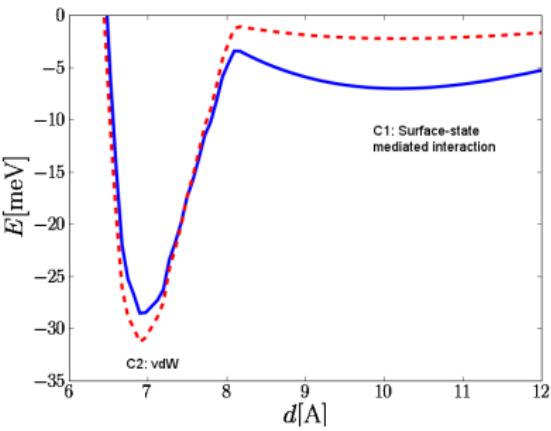
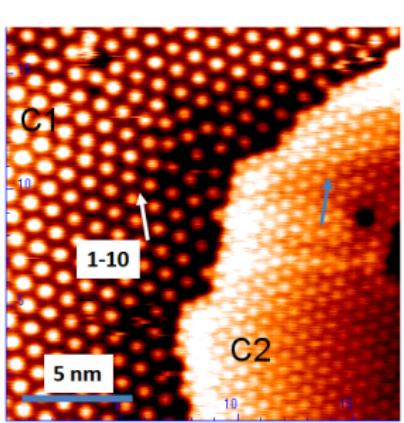
Surface-state signature, Bz/Cu, PRB **80** (09) 155431;

KS decoupling, PRB **85**, 035427 (12).

Asymptotically exact thermodynamics DFT evaluation of
thermodynamics DFT calculations: JPCM **24**, 424219
(12), EPL **59**, 265 (02), JPCM **12**, L13 (00).

Benzene/Cu(111): co-existing adsorbate condensations

- Experiments: two dense phases, $a \approx 6.8 \text{ \AA}$ and $a \approx 10.2 \text{ \AA}$:

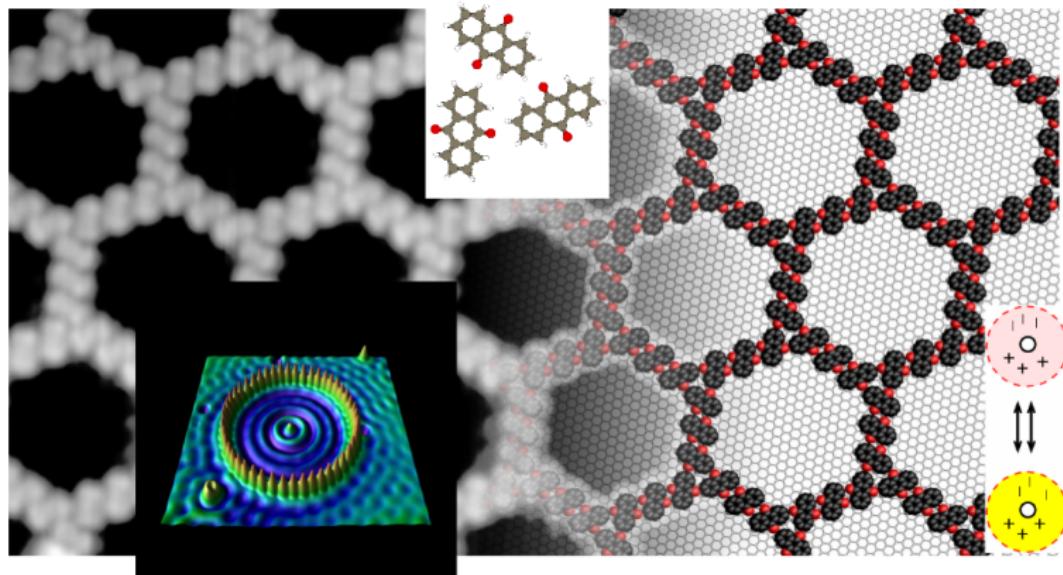


- With vdW-DF, we interpret C2 phase as vdW-bound overlayer.
- C1 phase as organized by interference of Friedel oscillations

Friedel-interference force relevant when mediated by metallic surface state (MSS) as on Cu(111).

Exp.: PRL 97 (06) 236806; KB/TLE/PH, PRB 80 (09) 155431 [EPL 59, 265 (02), PRL 85, 2981 (00)]

Organic-molecular assembly: excitement at surfaces



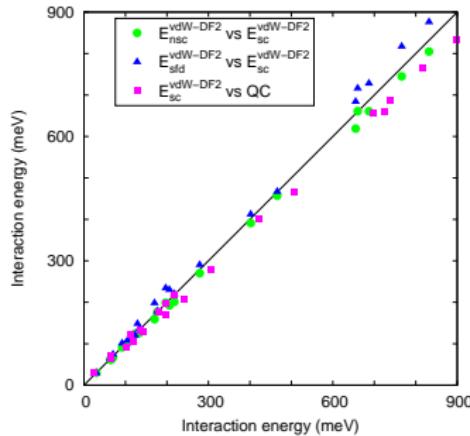
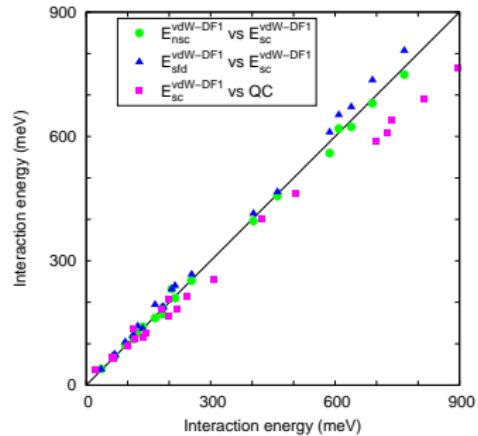
van der Waals and Friedel play with molecules in the surface lab.

Grateful for surface-science collaborations, e.g., w. Bartels/Einstein/Rahman.

<http://fy.chalmers.se/~hyldgaard/FirstPrincipleNobleSurfaces>

<http://fy.chalmers.se/~hyldgaard/FirstPrincipleCarbonHill>

Ideas for vdW-DF study of large (biomolecular) systems

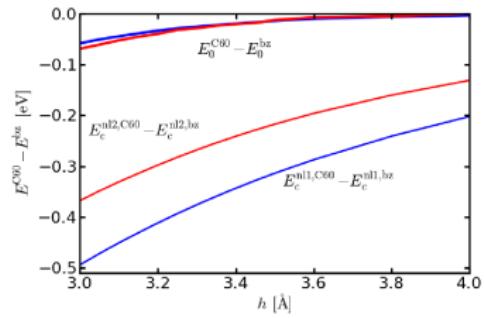
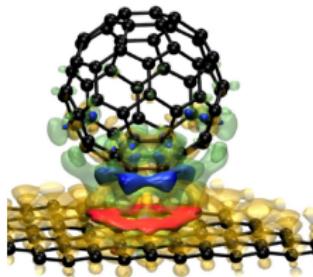
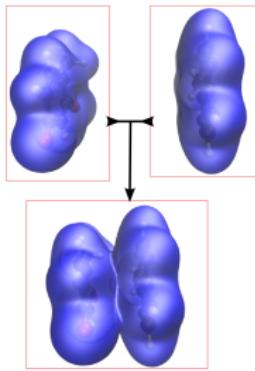


Until 2007– we had no V_{xc} and used a non-selfconsistent (nsc-)vdW-DF [in (03)/(04) vdW-DF papers]

- ▶ Real-space evaluation of E_c^{nl} is essentially *cost free* [for biomolecules at 1000+ cores].
- ▶ Biomolecular vdW-DF promising yet all DFT suffer: **kinetic-energy bottleneck**.
- ▶ Superposition-of-fragment-density “ E_{sfd}^{vdW-DF} ” nsc* vdW-DF w. acceleration, for analysis

KB, EL, ES, PH arXiv:1303.3762; *unpubl.*

A superposition-of-fragment-density vdW-DF scheme?



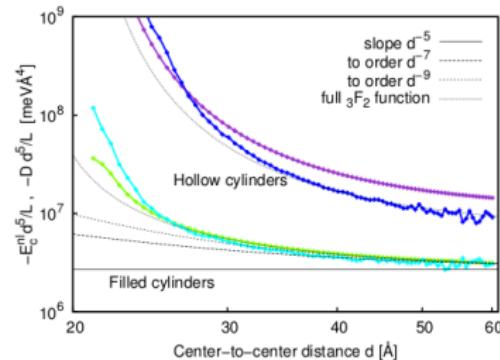
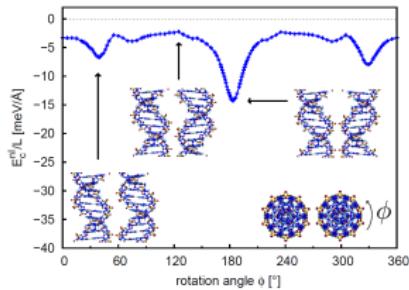
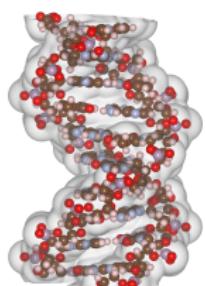
Harris-type philosophy and scheme 'sfd-vdW-DF'; Limited effects of Coulomb, Kinetic energy — E_c^{nl} is key, naturally handles charging, *can be cost free w. real space code.*

- Classical-MD plus E_c^{nl} for Molecular recognition ??? No, lacks $n(\mathbf{r})$
- EMT* plus E_c^{nl} for Molecular recognition ? ...
- or at least a *Harris-type scheme plus start with E_c^{nl} mapping.*

sfd-vdW-DF: KB/EL/ES/PH, arXiv:1303.3762; B-DNA-dimer vdW-DF mapping arXiv:1304.yyyy.

A contrast of vdW attraction: DNA and CNT dimers

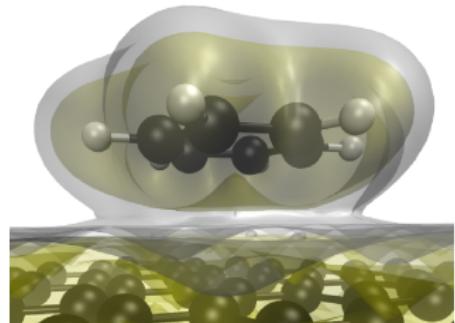
With sfD-vdW-DF strategy, we *begin* by evaluating the variation in E_c^{nl} ; DFT-D vs. vdW-DF characterization:



- ▶ DFT-D-type/electron functional for *charged* biomolecules?
- ▶ Beyond-morphology enhancements extend *longer* in CNT.
- ▶ vdW-DF is electron based, conserving; ready for next E_c^{nl} exploration of the attraction effects of counter ions.

vdW-DF builds on conservation, aware of global density

- ▶ vdW-DF exploits conservation, for example, of the exchange correlation hole,



$$n_{xc} = n_{xc}^0 + n_c^{nl} \leftrightarrow \chi^{\text{ACF}} + \dots \leftrightarrow \nabla \cdot \{S + \dots\}.$$

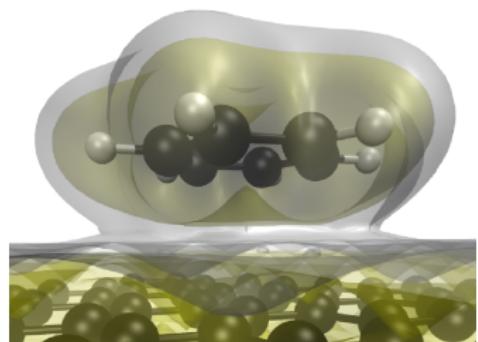
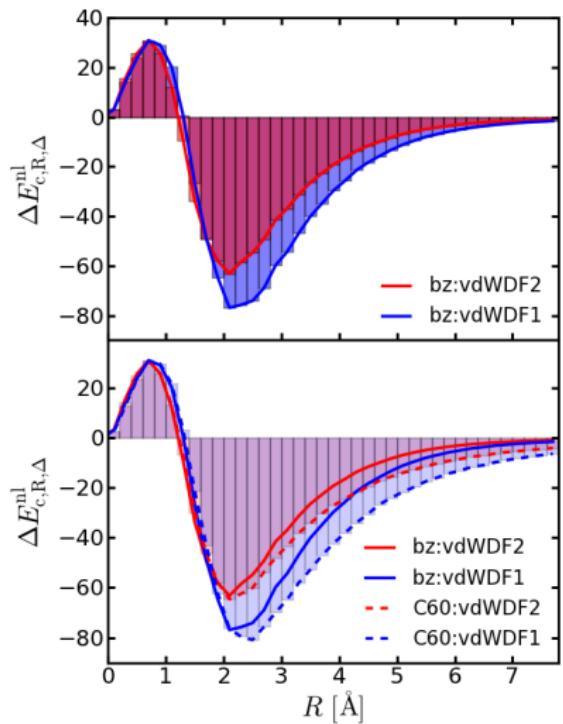
- ▶ Plasmon are collective excitations,

$$E_c^{nl} = \int_{\mathbf{r}} \int_{\mathbf{r}'} n(\mathbf{r}) \phi[n, \nabla n](\mathbf{r}, \mathbf{r}') n(\mathbf{r}')$$

has a GGA-type ability to reflect the global density variation inside components
 $q_0[n, \nabla n] \leftrightarrow \epsilon_{xc}^0 \leftrightarrow n_{xc}^0$.

ACF-based reformulation of vdW-DF, exchange-correlation hole analysis, PH/KB/ES, in preparation.

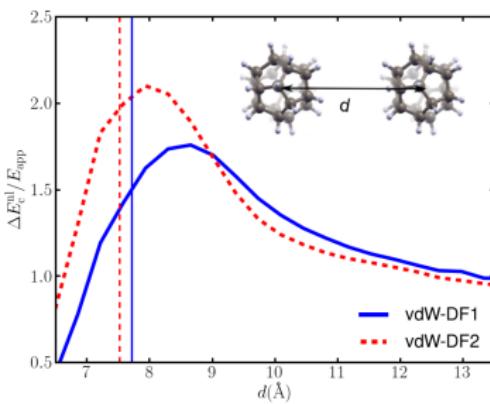
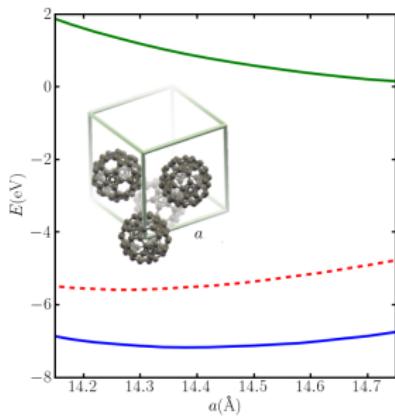
vdW-DF reflects electron distribution, needs $q \neq 0$



Most E_{nl} contributions inside d_{bind} ,
(unlike pair-potential descriptions).

[KB/PH arXiv:1303.0389, PRB in press.]

Plasmons → collective/nonlocal S : binding ≠ asymptotics

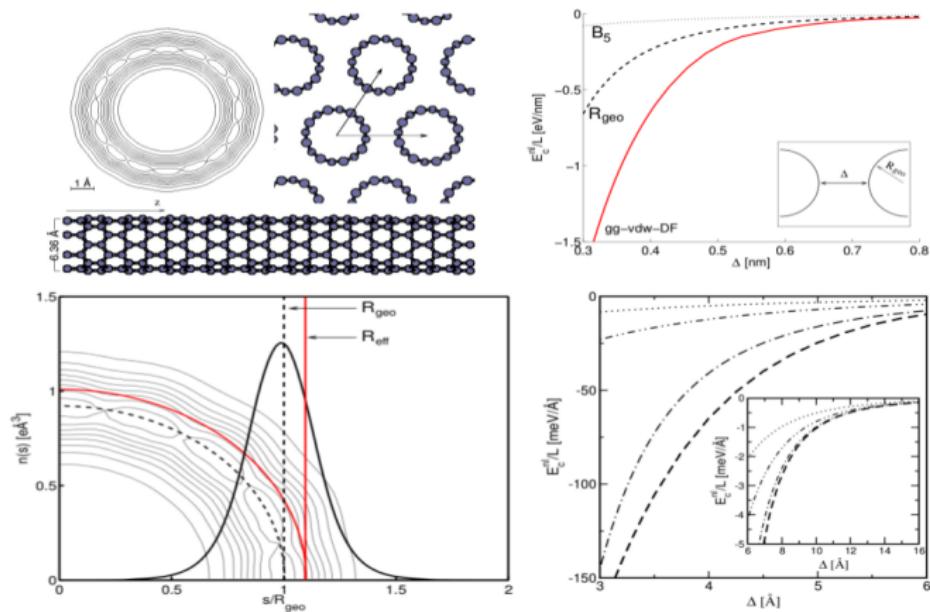


vdW-DF enhancements over its asymptotics (i.e., over the vdW-DF atom-based pair-potential limit)
 [JCP **132**, 134705 (10); Comp. Phys. Commun. **182**, 1800 (11)].

For example, C₆₀ has an enhanced far-regime interactions [e.g., Surf. Sci. **605**, 1621 (11); PRL **109**, 233203 (12)] due to formation of $\omega_{q=0,l=0} \rightarrow 0$ excitation. Collective effects in present vdW-DFs are limited to shorter ranges.

Surface nature & collectivity, by plasmons response: CNTs

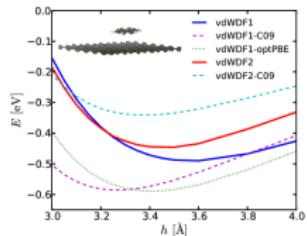
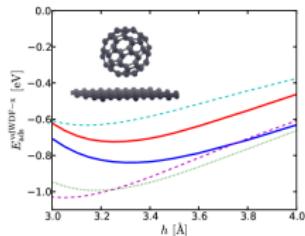
Morphology+image-plane formation+nonlocal plasmon form in S:



Contrasting nsc-vdW-DF1 [PRB 77, 205422 (08)] and

analytic evaluations [Comput. Mat. Sci. 33, 195 (05); Mater. Sci. Eng. C 73, 721 (03)]

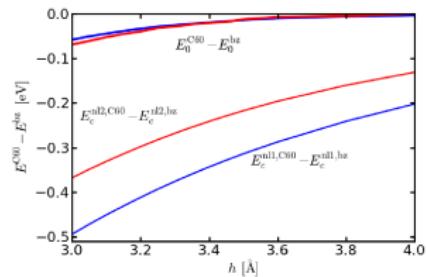
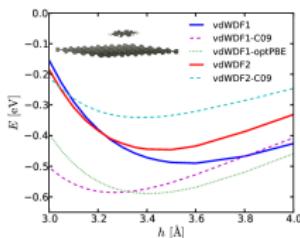
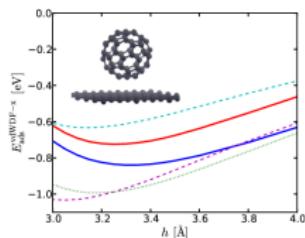
Same-interface/different-volume (physi-)sorption



Functional	Bz/G h [\AA]	Bz/G E_a [eV]	C60/G h	C60/G E_a
vdW-DF1	3.6	0.49	3.3	0.85
vdW-DF1(C09)	3.25	0.59	3.0	1.06
vdW-DF1(optPBE)	3.4	0.59	3.15	1.01
vdW-DF1(PW86r)	3.35	0.66	3.15	1.10
vdW-DF2	3.5	0.43	3.25	0.72
vdW-DF2(C09)	3.4	0.34	3.1	0.65
Exp.	—	0.50 ± 0.08	—	0.85

Exp.: Hertel; Bz/Graphene: PRB **89**, 155406 (04); C60/Graphene: PRL **90**, 095501 (03).

Same-interface/different-volume (physi-)sorption

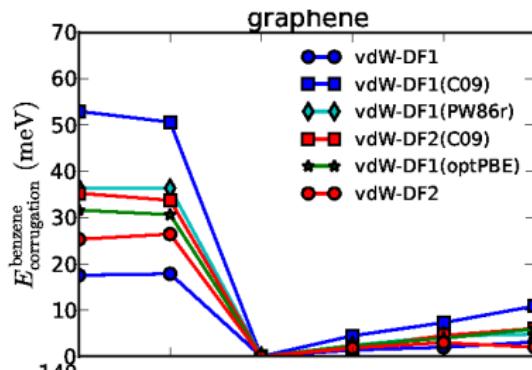


- ▶ Benzene vs. C60 different volume/same interface.
- ▶ *Similar interface reflected in E_0 , semilocal parts of total energy.*
- ▶ *Different volume expressed in E_c^{n1} .*
- ▶ **Complicated to fit exchange choice** Balance may be offset by volume increase.

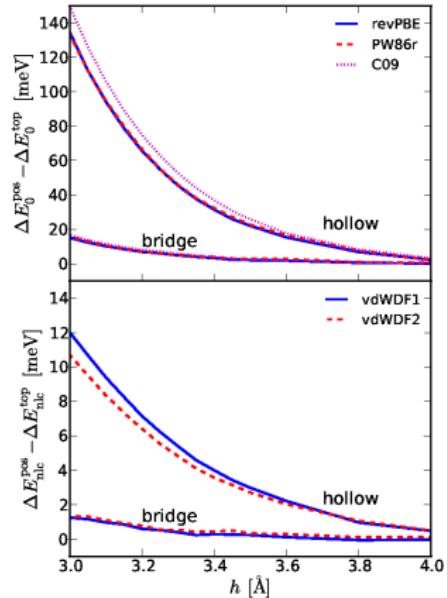
Also: complex-data-set benchmarking of vdW-DF exchange and vdW attraction

H₂/Cu, PRB **84**, 193408 (11); JPCM , **24**, 424213 (12); *vdW-DF2 exchange good.*

Functional components in benzene on graphene adsorption



- ▶ Corrugation is sensitive to choice of exchange in vdW-DF version or variant
- ▶ Corrugation is *insensitive* to exchange choice when viewed at given separation $\langle h \rangle$.
- ▶ Corrugation reflects exchange choice — because $(\Delta E_{x1} - \Delta E_{x2})$ acts as load line and therefore changes $\langle h \rangle$.



KB/PH, arXiv:1303.0389;
PRB in press

Functional components in benzene on graphene adsorption

- ▶ Corrugation reflects exchange choice — *because* $(\Delta E_{x1} - \Delta E_{x2})$ acts as load line and therefore changes $\langle h \rangle$.
- ▶ There exists analysis to prefer *one* exchange choice [PW86r] for molecular systems and one choice [C09] for bulk.
- ▶ Measuring corrugation might allow bootstrap specification of physisorption $\langle h \rangle$; Note physisorbed molecules is *not* ‘on site.’
- ▶ One may even obtain an extraction of $E_{xc}[\langle h \rangle]$ because nonlocal kinetic-energy effects are found small.
- ▶ Contrasting same-interface/different volume physisorption might then analyse the role of nonlocal correlations ΔE_c^{nl} .

KB/PH, arXiv:1303.0389; PRB in press

Conclusions

- ▶ Presentation of vdW-DF, a first-principle sparse-matter DFT.
- ▶ vdW-DF permits analysis of molecular-adsorption experiments.
- ▶ Physics picture: vdW-DF counts coupling-induced shifts.
- ▶ vdW-DF captures effects beyond morphology.
- ▶ System-specific mappings of details in the vdW-DF binding.

Pleasure to acknowledge our excellent Ph.D. graduates in the Rutgers-Chalmers vdW-DF program, Ylva Andersson, Erika Hult, Henrik Rydberg, Max Dion, *Svetla Chakarova-Käck*, *Øyvind Borck*, *Jesper Kleis*, *Eleni Ziambaras*, *Jochen Rohrer*, André Kelkkanen, *Kristian Berland*, *Elisa Londero*



Vetenskapsrådet



CHALMERS

SNIC



Rutgers-Chalmers vdW-DF stakeholders welcome questions



Rutgers++: Valentino R. Cooper, D.C. Langreth†, Kyuho Lee, Timo Thonhauser
Chalmers: Kristian Berland, Per Hyldgaard, B.I. Lundqvist, Elsebeth Schröder
Fellow key vdW-DF actors: Y. Andersson, M. Dion, and H. Rydberg.

CHALMERS/RUTGERS vdW-DF publications I

(Recent) Method Papers:

- ▶ K. Lee, E.D. Murray, L. Kong, B.I. Lundqvist, and D.C. Langreth, Phys. Rev. B **82** (2010) 081101(R).
- ▶ T. Thonhauser, V. R. Cooper, S. Li, A. Puzder, P. Hyldgaard, and D.C. Langreth, Phys. Rev. B, **76** (2007) 125112.
- ▶ D.C. Langreth, M. Dion, H. Rydberg, E. Schröder, P. Hyldgaard, and B.I. Lundqvist, Int. J. Quantum Chem. **101** (2005) 599.
- ▶ M. Dion, H. Rydberg, E. Schröder, D.C. Langreth, and B.I. Lundqvist, Phys. Rev. Lett. **92** (2004) 246401; **95** (2005) 109902(E).
- ▶ H. Rydberg, M. Dion, N. Jacobson, E. Schröder, P. Hyldgaard, S.I. Simak, D.C. Langreth, and B.I. Lundqvist, Phys. Rev. Lett. **91** (2003) 126402.

vdW-related Thesis at Chalmers and Rutgers:

- ▶ E. Londero, *Theory of van der Waals bonding: from bulk materials to biomolecules*, Ph.D. Thesis, MC2/Applied Physics, Chalmers, Dec. 2012.
- ▶ K. Berland, *Connected by voids: Interactions and screening in sparse matter*, Ph.D. Thesis, MC2, Chalmers, Aug. 2012.
- ▶ J. Kleis, *Van der Waals density-functional description of polymers and other sparse materials*, Ph.D. Thesis, Applied Physics, Chalmers, June 2006.
- ▶ M. Dion, *van der Waals Forces in Density Functional Theory*, Ph.D. Thesis, Physics, Rutgers, State University of New Jersey, 2004.
- ▶ H. Rydberg, *Nonlocal Correlations in Density Functional Theory*, Ph.D. Thesis, Applied Physics, Chalmers/GU, 2001.

vdW-DF publications II

A few (recent) application/analysis papers (Chalmers):

- ▶ K. Lee et al, Phys. Rev. B **84**, 193408 (2011); JPCM **24**, 424213 (2012).
- ▶ K. Berland and P. Hyldgaard, J. Chem. Phys **132** (2010) 134705.
- ▶ E. Londero and E. Schröder, Phys. Rev. B **82** (2010) 054166.
- ▶ K. Berland, T.L. Einstein, and P. Hyldgaard, Phys. Rev. B **80** (2009) 155431.
- ▶ D.C Langreth, et al, invited, J. Phys.:Condens. Matter **21** (2009) 084203.
- ▶ J. Kleis, E. Schröder, and P. Hyldgaard, Phys. Rev. B **77**, 205422 (2008).
- ▶ V.R. Cooper, T. Thonhauser, A. Puzder, E. Schröder, B.I. Lundqvist, and D.C. Langreth, JACS **130**, 1304 (2008).
- ▶ E. Ziambaras, J. Kleis, E. Schröder, and P. Hyldgaard, Phys. Rev. B **76** (2007) 155425.
- ▶ J. Kleis, B.I. Lundqvist, D.C. Langreth, and E. Schröder, Phys. Rev. B **76** (2007) 100201(R).
- ▶ S.D. Chakarova-Käck, E. Schröder, Bengt I. Lundqvist, and D.C. Langreth, Phys. Rev. Lett. **96** (2006) 146107.