Dispersion-corrected mean field electronic structure methods

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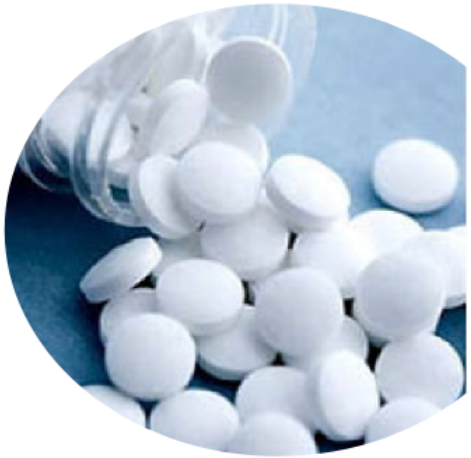
MSSC2017: Ab initio Modelling in Solid State Chemistry - Imperial College London

Outline of talk

Understanding phenomena in nature



How can a Gecko stick to a glass wall?

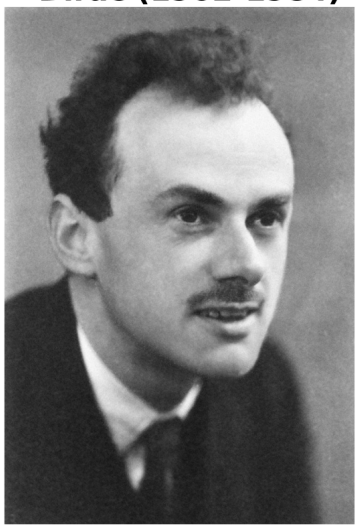
- cannot be explained by classical mechanics
- London dispersion (C_6)

Why does a tablet change its properties?

- van der Waals interaction stabilizes tablet dependent on its form
- relevant for production process and dosage

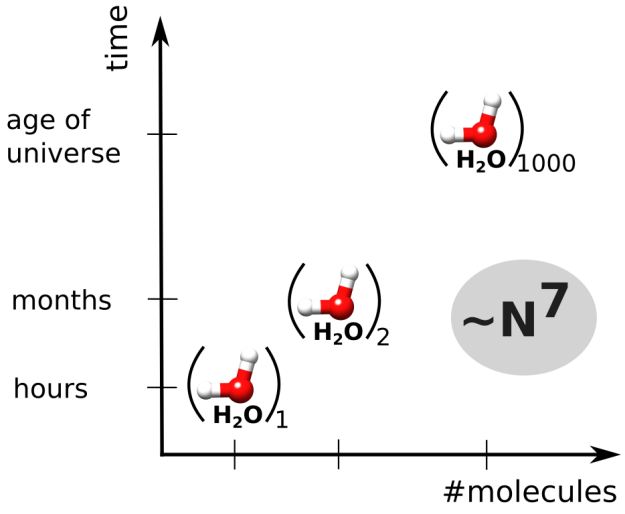
Exact simulation of extended systems computationally too demanding

Paul Adrian Maurice Dirac (1902-1984)



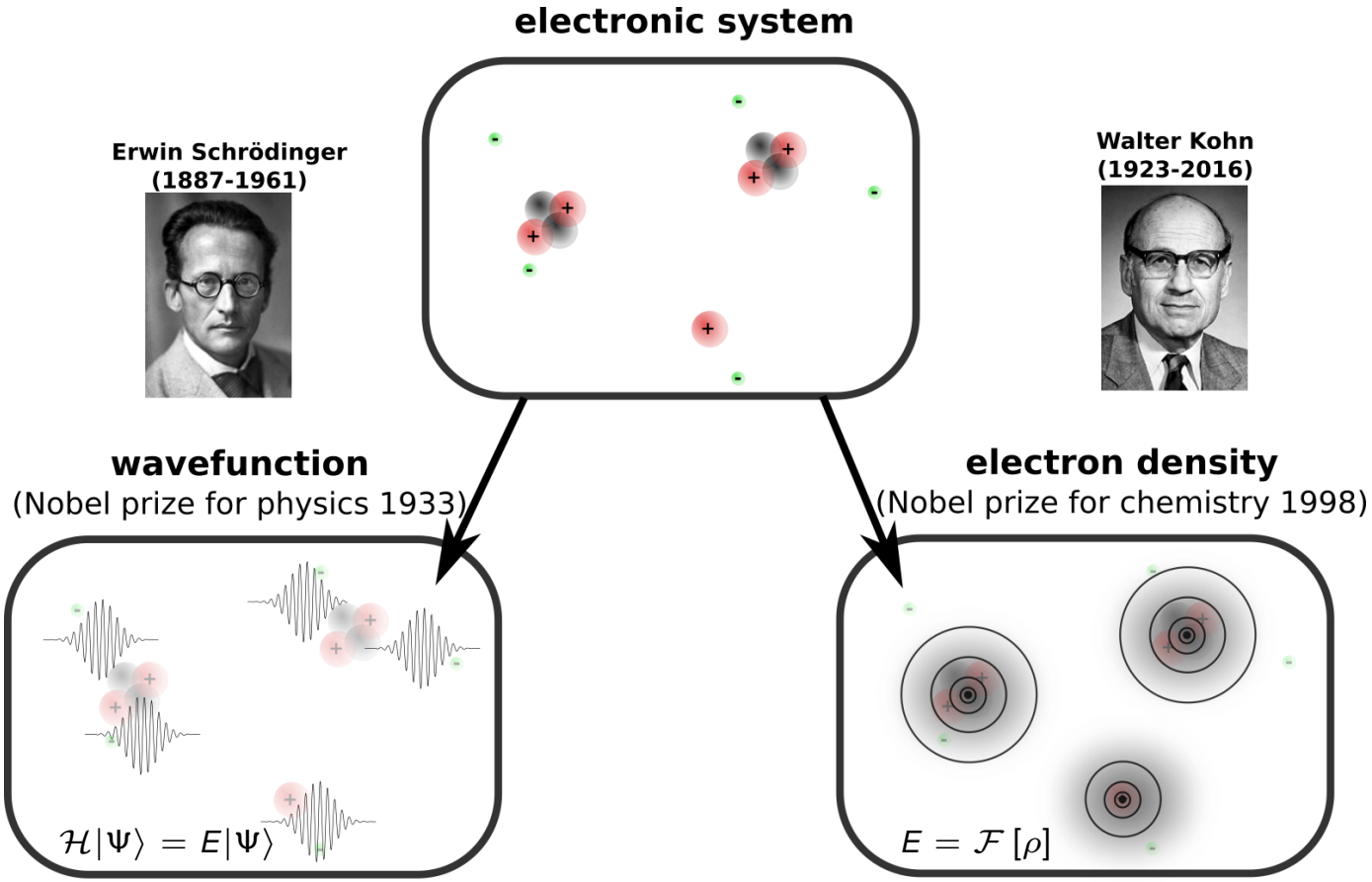
"The underlying physical laws (...) of a large part of physics and the ***whole of chemistry*** *are thus completely known,*

and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble"[1]



[1] P. A. M. Dirac, *Proc. Roy. Soc.Ser. A* **123**, 714 (1929)

Possible theoretical ansatz



- exact in principle
- complicated to solve

- semi-local, easier to solve
- **no London dispersion**

Outline of talk

Assumption and general strategy

Separated fragments A and B with non-overlapping densities

- Hamiltonian $H = H_0^A + H_0^B + V'$
- perturbation $V' = \int \mathrm{d}r\,\mathrm{d}r'\,\frac{\hat{\rho}^A(r)\hat{\rho}^B(r')}{|r - r'|}$
- eigenfunctions of fragments Ψ_n^A, Ψ_m^B
- eigenfunctions of unperturbed system direct product $\Psi_m^A \times \Psi_n^B$
- no antisymmetrization required, write as ket $|mn\rangle$

(1) perform perturbation theory to second (or higher) order

(2) expand perturbation V' in multipoles

[2] A. Stone *The Theory of Intermolecular Forces, 2nd ed.*; Oxford University Press, Oxford (2013)

Rayleigh-Schrödinger PT2

(1) Rayleigh-Schrödinger perturbation to second order

$$W^{AB} = W_0^{AB} + W_1^{AB} + W_2^{AB} + \mathcal{O}(3) \tag{1}$$

$$W_0^{AB} = W_0^A + W_0^B \tag{2}$$

$$W_1^{AB} = \langle 00|V'|00\rangle \tag{3}$$

$$\begin{aligned} W_2^{AB} &= -\sum_{mn}{}' \frac{\langle 00|V'|mn\rangle\langle mn|V'|00\rangle}{W_0^A - W_m^A + W_0^B - W_n^B} \\ &= -\sum_{m}{}' \frac{\langle 00|V'|m0\rangle\langle m0|V'|00\rangle}{W_0^A - W_m^A} - \sum_{n}{}' \frac{\langle 00|V'|0n\rangle\langle 0n|V'|00\rangle}{W_0^B - W_n^B} \\ &\quad - \sum_{mn}{}'' \frac{\langle 00|V'|mn\rangle\langle mn|V'|00\rangle}{W_0^A - W_m^A + W_0^B - W_n^B} \end{aligned} \tag{4}$$

Rayleigh-Schrödinger PT2

(1) Rayleigh-Schrödinger perturbation to second order

(a) Electrostatic in first order

$$
\begin{aligned}
U_{es}^{AB} =& \langle 00 | V' | 00 \rangle \\
=& \left\langle 00 \left| \int \mathrm{d}r\, \mathrm{d}r' \, \frac{\hat{\rho}^A(r)\hat{\rho}^B(r')}{|r-r'|} \right| 00 \right\rangle = \int \mathrm{d}r\, \mathrm{d}r' \, \frac{\rho^A(r)\rho^B(r')}{|r-r'|}
\end{aligned}
\tag{5}
$$

(b) Induction in second order

$$
\begin{aligned}
U_{ind}^{A} &= -\sum_{m}{}' \frac{\langle 00 | V' | m0 \rangle \langle m0 | V' | 00 \rangle}{W_0^A - W_m^A} \\
U_{ind}^{B} &= -\sum_{n}{}' \frac{\langle 00 | V' | 0n \rangle \langle 0n | V' | 00 \rangle}{W_0^B - W_n^B}
\end{aligned}
\tag{6}
$$

Rayleigh-Schrödinger PT2

(1) Rayleigh-Schrödinger perturbation to second oder

(c) Dispersion in second order

$$U_{disp}^{AB} = -\sum_{mn}{}'' \frac{\langle 00|V'|mn\rangle\langle mn|V'|00\rangle}{W_0^A - W_m^A + W_0^B - W_n^B} \tag{7}$$

Multipole expansion

(2) Expand V' in Cartesian multipoles

$$\begin{aligned} V' = \; & \mathcal{T} q^A q^B + \mathcal{T}_\alpha \left(q^A \mu^B_\alpha - \mu^A_\alpha q^B \right) \\ & + \mathcal{T}_{\alpha\beta} \left(\frac{1}{3} q^A \Theta^B_{\alpha\beta} - \mu^A_\alpha \mu^B_\beta + \frac{1}{3} \Theta^A_{\alpha\beta} q^B \right) + \mathcal{O}(n^3) \end{aligned} \tag{8}$$

$$\mathcal{T}^n_{\alpha\beta\ldots\nu} = \nabla_\alpha \nabla_\beta \ldots \nabla_\nu \left(\frac{1}{R} \right) \tag{9}$$

more compact in spherical harmonics

$$V' = \; \mathcal{Q}^A_{l_1 m_1} \mathcal{T}_{l_1 m_1, l_2 m_2} \mathcal{Q}^B_{l_2 m_2} \tag{10}$$

summation over identical indices always implied

Multipole expansion in PT2

(1+2) For simplicity start with dipole-dipole term

$$
\begin{aligned}
U^{AB}_{disp} &= -\sum_{m_A\neq 0}\sum_{n_B\neq 0}\frac{\langle 0_A 0_B|\mu^A_\alpha \mathcal{T}_{\alpha\beta}\mu^B_\beta|m_A n_B\rangle\langle m_A n_B|\mu^A_\gamma \mathcal{T}_{\gamma\delta}\mu^B_\delta|0_A 0_B\rangle}{W^A_0 - W^A_m + W^B_0 - W^B_n} \\
&= -\mathcal{T}_{\alpha\beta}\mathcal{T}_{\gamma\delta}\sum_{m_A\neq 0}\sum_{n_B\neq 0}\frac{\langle 0_A|\mu^A_\alpha|m_A\rangle\langle m_A|\mu^A_\gamma|0_A\rangle\langle 0_B|\mu^B_\beta|n_B\rangle\langle n_B|\mu^B_\delta|0_B\rangle}{W^A_0 - W^A_m + W^B_0 - W^B_n} \\
&= -\frac{2}{\pi}\mathcal{T}_{\alpha\beta}\mathcal{T}_{\gamma\delta}\int \mathrm{d}\omega \left[\sum_m{}' \frac{\omega^A_m \langle 0_A|\mu^A_\alpha|m_A\rangle\langle m_A|\mu^A_\gamma|0_A\rangle}{{\omega^A_m}^2+\omega^2}\right. \\
&\qquad \left.\times \sum_n{}' \frac{\omega^B_n \langle 0_B|\mu^B_\beta|n_B\rangle\langle n_B|\mu^B_\delta|0_B\rangle}{{\omega^B_n}^2+\omega^2}\right]
\end{aligned}
\tag{11}
$$

Use McLachlan integral identity to factorize energy denominator

$$
\frac{1}{A+B} = \frac{2}{\pi}\int \mathrm{d}\omega\, \frac{AB}{(A^2+\omega^2)(B^2+\omega^2)} \tag{12}
$$

Multipole expansion in PT2

(1+2) Identify dynamic polarizability

$$U_{disp}^{AB} = -\frac{2}{\pi}\mathcal{T}_{\alpha\beta}\mathcal{T}_{\gamma\delta}\int \mathrm{d}\omega\, \alpha_{\alpha\gamma}^{A}(i\omega)\,\alpha_{\beta\delta}^{B}(i\omega) \tag{13}$$

Spherical averaging (exact for atoms)

$$U_{disp}^{AB} = -\frac{3}{\pi}\int \mathrm{d}\omega\, \overline{\alpha}^{A}(i\omega)\,\overline{\alpha}^{B}(i\omega) \times \frac{1}{R^6} = -\frac{C_6^{AB}}{R^6} \tag{14}$$

Analogue for higher order terms, short-range damping

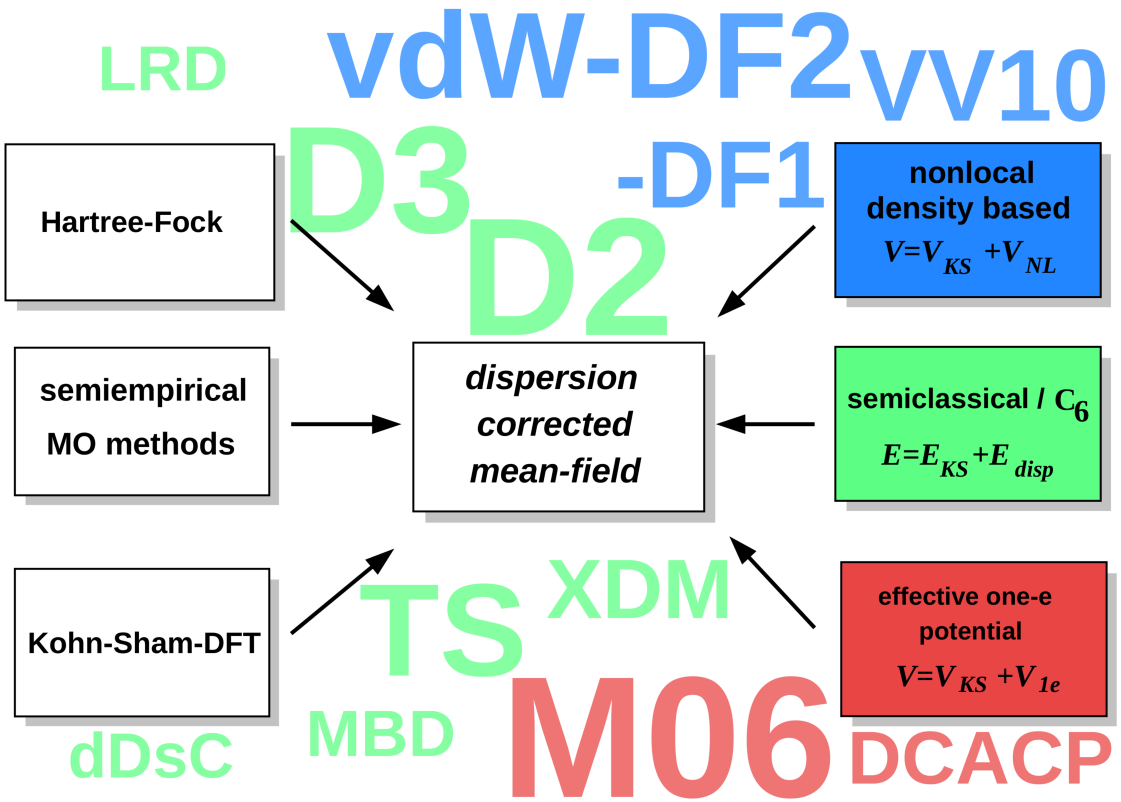
$$U_{disp}^{AB} = = \sum_{n=6,8,10,\ldots} \frac{C_n^{AB}}{R^n} f_{damp}^{(n)} \tag{15}$$

More general via charge density susceptibility

$$U_{disp}^{AB} = -\frac{1}{2\pi}\int \mathrm{d}\omega \int \mathrm{d}r_a\,\mathrm{d}r_a'\,\mathrm{d}r_b\,\mathrm{d}r_b'\,\frac{\chi(r_a, r_a', i\omega)\chi(r_b, r_b', i\omega)}{|r_a - r_b||r_a' - r_b'|} \tag{16}$$

Outline of talk

Many good dispersion corrections exist



- focus on D3 scheme as it can be used at all computational levels
- own work started with extension of D3 type corrections

[3] S. Grimme, A. Hansen, JGB, C. Bannwarth, *Chem. Rev.* **116**, 5105 (2016)

Exact expression for correlation energy cannot be solved for many systems

$$E_c = -\frac{1}{2\pi}\int_0^1 \mathrm{d}\lambda \int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' \frac{1}{|\mathbf{r}-\mathbf{r}'|} \times \int_0^\infty \mathrm{d}\omega \left[\chi_\lambda(\mathbf{r},\mathbf{r}',i\omega) - \chi_0(\mathbf{r},\mathbf{r}',i\omega)\right]$$

- from adiabatic connection fluctuation dissipation theorem[4]
- Coulomb interaction scaled by λ
- dynamical charge density susceptibility

$$\chi_0(\mathbf{r},\mathbf{r}',i\omega) = -4\sum_i\sum_a \frac{\omega_{ai}}{\omega_{ai}^2+\omega^2}\varphi_i(\mathbf{r})\varphi_a(\mathbf{r})\varphi_a(\mathbf{r}')\varphi_i(\mathbf{r}')\,,$$

$\rightarrow$ approximation needed

[4] A. Zangwill, P. Soven, *Phys. Rev. A* **21**, 1561 (1980)

Coarse-graining to atomic contributions leads to significant simplifications

- coarse-grain to atomic contributions

$$\alpha_{ij}(i\omega) = \int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'\, \mathbf{r}_i \mathbf{r}'_j \chi(\mathbf{r}, \mathbf{r}', i\omega)$$

- expansion of Coulomb operator in multipoles[5]

$$E^{AB}_{\text{disp}} = -\underbrace{\frac{3}{\pi}\int \mathrm{d}\omega\, \alpha_A(i\omega)\alpha_B(i\omega)}_{C_6^{AB}} \times \frac{1}{R^6_{AB}}$$

- C_8^{AB} and C_9^{AB} from recursion relations and averages[6]

$$E^{(\text{D3})}_{\text{disp}} = -\frac{1}{2}\sum_{n=6,8}\sum_{A,B}^{\text{atoms}} \frac{C_n^{AB}}{R^n_{AB}} \cdot f_n^d(R_{AB}) - \frac{1}{6}\sum_{A,B,C}^{\text{atoms}} \frac{C_9^{ABC}}{R^9_{ABC}} \cdot f_9^d(R_{ABC}, \theta_{ABC})$$

[5] H. B. G. Casimir. D. Polder, *Phys. Rev.* **73**, 360 (1948)

[6] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **132**, 154104 (2010)

Dynamic polarizability via linear response DFT

- use frequency domain formalism to get excitation frequencies[7]

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{A}^* & \mathbf{B}^* \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} = \omega \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix}$$

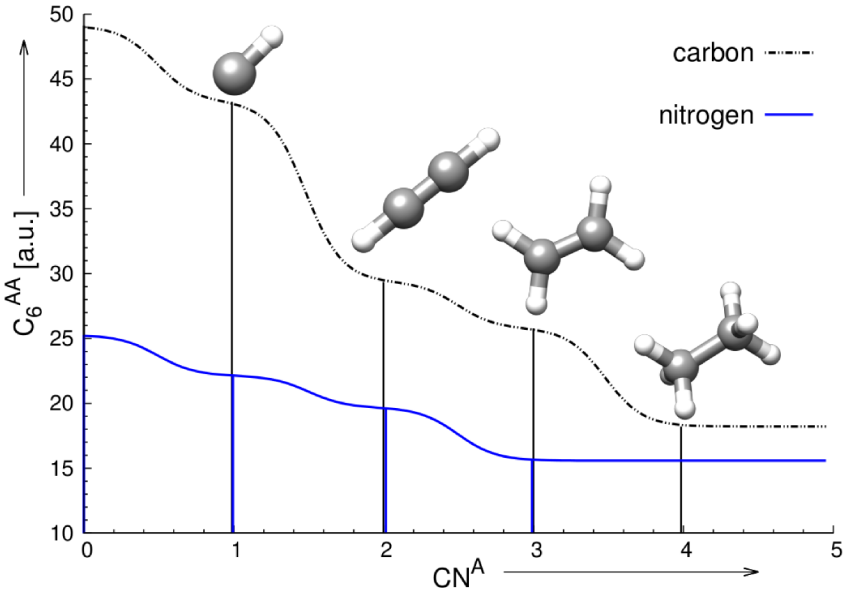
- orbital rotation matrices

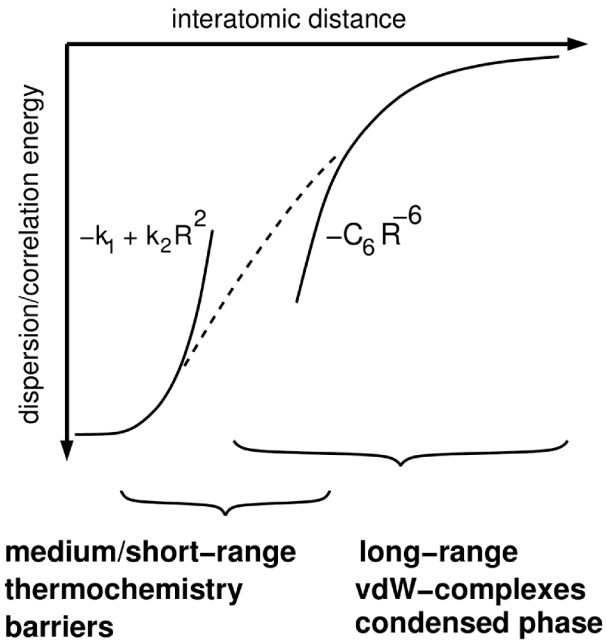
$$A_{ia.jb} = \delta_{ij}\delta_{ab}(\epsilon_a - \epsilon_i) + \langle ab|1/r|ij\rangle + \langle ab|f_{xc}|ij\rangle$$
$$B_{ia.jb} = \langle aj|1/r|ib\rangle + \langle aj|f_{xc}|ib\rangle$$

- approximation: neglect frequency dependence of f_{xc} and use ground state functional (PBE38)
- similar to random phase approximation with exchange

[7] M. E. Casida, *Recent Advances in Density Functional Methods*, D. P. Chong (World Scientific, Singapore), 155 (1995)

Geometric coordination number for interpolations of reference C_6

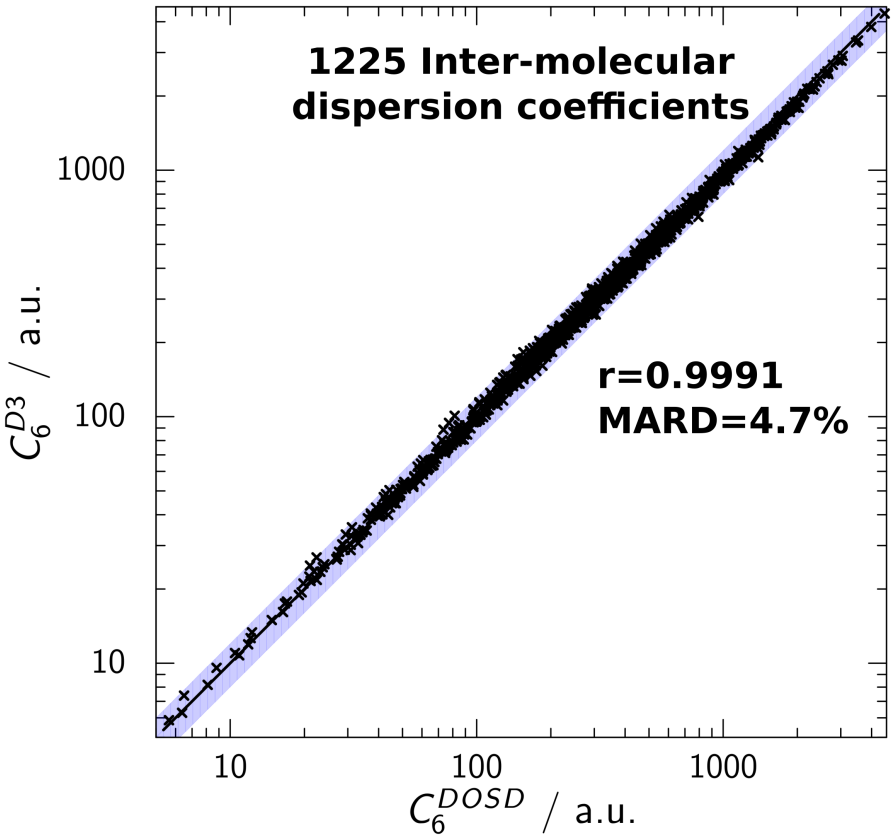




- atoms-in-molecules C_6 by TD-DFT of $\alpha(i\omega)$ on model hydrides
- reference C_6 are mapped to real system via geometrical coordination
- short-range damping avoids double counting[8]

[8] S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem.*, **32**, 1456 (2011)

Semi-classical scheme yields highly accurate dispersion coefficients



D3 correction

- dipole oscillator strength distribution (DOSD) yield $C_6^{\text{exptl.}}$ (compiled by A. Tkatchenko)
- residual long-range mean absolute relative deviation (MARD) of D3 $<$ 5% [9]
- deviations are close to intrinsic TD-DFT errors of $\alpha(i\omega)$

[9] S. Grimme, *WIREs Comput. Mol. Sci.* **1**, 211-228 (2011)

D3 in a nutshell: High accuracy at force field speed

Advantages of D3 model

- intermolecular C_6 coefficients are very accurate
- no electronic structure input needed
- computation is extremely fast D3(two-body) $\sim$ FF speed
- analytical first (and second) derivatives

Possible shortcomings

- no automatic adjustment to unusual electronic structures[*]
- missing anisotropy of dispersion interaction
- no many-body contributions beyond Axilrod-Teller-Muto term
- high empiricism in short-range damping

Multilevel methodologies: finding the right compromise

	task/property	example method
accurate QM	single-point energy	DLPNO-CCSD(T) DMC[10], FCIQMC
cheap QM	optimization	metaGGA (SCAN-D3[11]) HSE-3c[12]
very cheap QM	optimization/Hessians conformations	semi-empirical HF-3c[13,14], DFTB3-D3[15]
force field	dynamics conformational sampling	transferable or molecule specific (QM derived) FF

[10] A. Zen, JGB, J. KlimesJ. Klimeš, A. Tkatchenko, D. Alfè, A. Michaelides, *submitted*

[11] JGB, J. E. Bates, J. Sun, J. P. Perdew *Phys. Rev. B*, **94**, 115144 (2016)

[12] JGB, E. Caldeweyher, S. Grimme, *Phys. Chem. Chem. Phys.*, **18**, 15519 (2016)

[13] R. Sure, S. Grimme, *J. Comput. Chem.*, **34**, 1672 (2013) [14] JGB, S. Grimme, *Top. Curr. Chem*, **345**, 1 (2014)

[15] JGB, S. Grimme,*J. Phys. Chem. Lett.* **5**, 1785 (2014)

Simple input of D3 dispersion correction in CRYSTAL17

UCL

old calculation

```
MOLECULE
40
2
6    1.209708   0.698426   0.000000
1    2.152747   1.242889   0.000000
BASISSET
def2-mTZVP
DFT
PBE
END
END
```

new D3 inclusive calculation

```
MOLECULE
40
2
6    1.209708   0.698426   0.000000
1    2.152747   1.242889   0.000000
BASISSET
def2-mTZVP
DFT
PBE-D3
END
END
```

```
*******************************************************************************

 DFT-D3 DISPERSION ENERGY CORRECTION

 D3 DISPERSION ENERGY (AU)          -1.0948042757474E-02
 TOTAL ENERGY + DISP (AU)           -2.3201130812713E+02

*******************************************************************************
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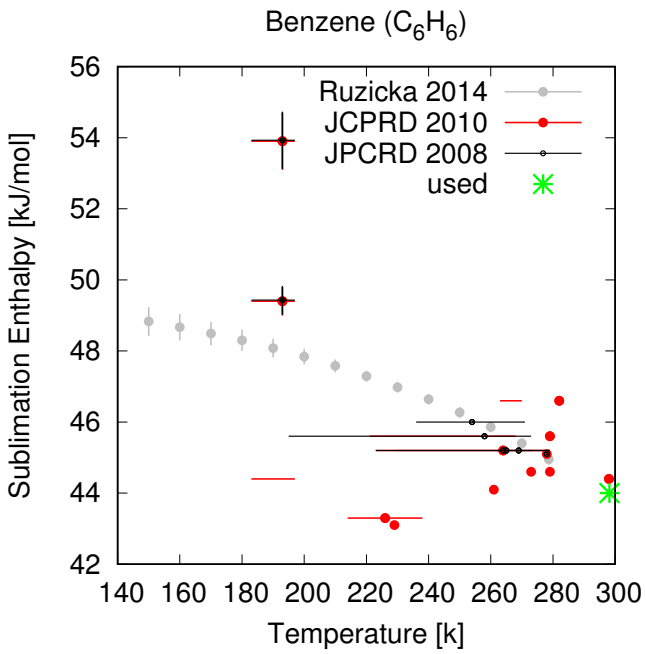
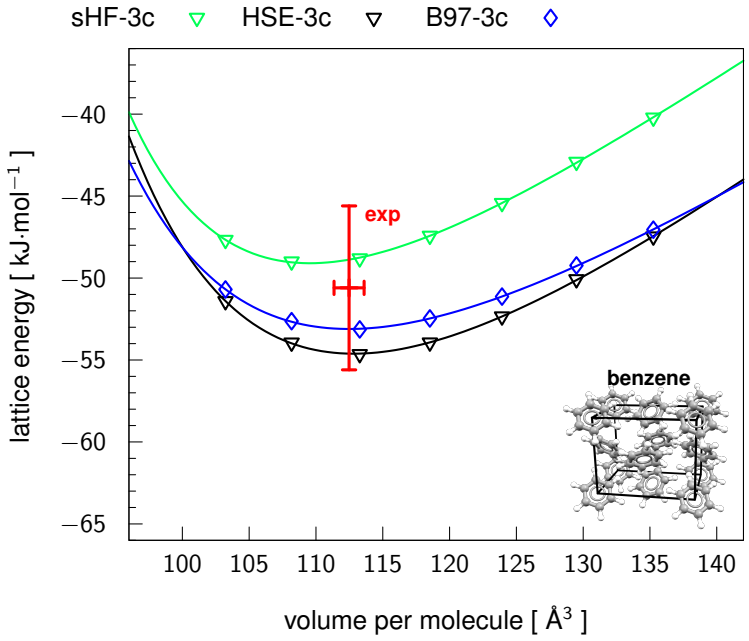
- combinable with geometry optimization, frequencies, QHA, etc.
- impact of D3 should be tested for all DFT applications

Outline of talk

High-level QM data needed to test DFT for organic solids

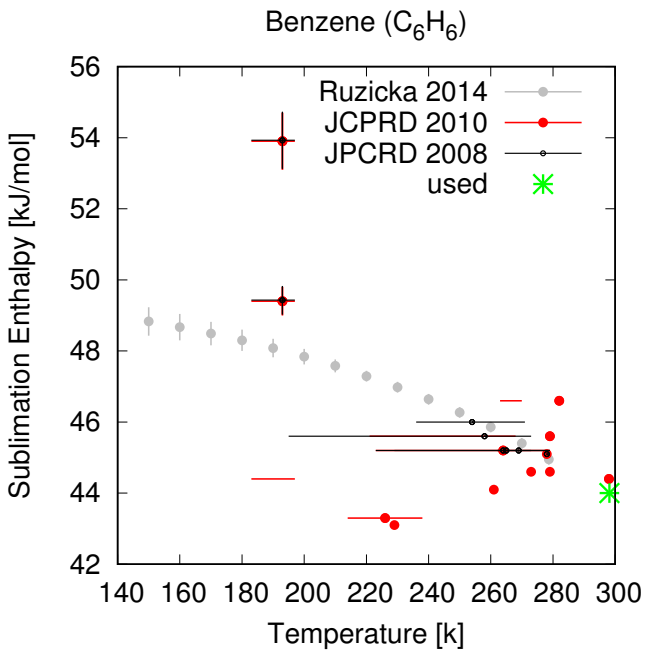




- substantial uncertainties in $H_{\text{sub}}^{\text{exp}}$ and thermodynamic corrections [16]
- high-level data needed to judge approximate methods

[16] W. Acree, J. S. Chickos, *J. Phys. Chem. Ref. Data* **39**, 043101 (2010).

High-level QM data needed to test DFT for organic solids



{non-published data}

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- high-level data needed to judge approximate methods

[16] W. Acree, J. S. Chickos, *J. Phys. Chem. Ref. Data* **39**, 043101 (2010).

Modern DFT-D methods have excellent accuracy

{non-published data}

- benzene crystal purely vdW bonded
- significant effect of many-body dispersion

Choosing the right functional and basis set combination

{non-published data}

- effect of semi-local functional as important as many-body dispersion
- significant BSSE up to triple-ζ basis sets

Choosing the right functional and basis set combination

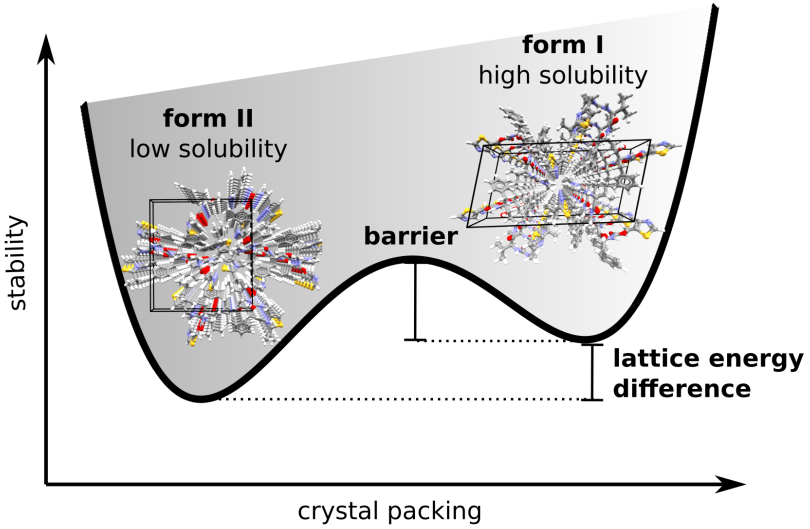
{non-published data}

- ice VIII: high-density phase
- BSSE even stronger in H-bonded systems

Many properties depend on the polymorphic form of a crystal

Polymorphism

- ability of a molecule to crystallize in more than one structure[17]
- properties change with crystal packing, e.g. solubility, color, etc.[18]



- late appearing polymorph disrupted supply of antiviral drug ritonavir[19]

→ Tools to predict possible polymorphs would be valuable

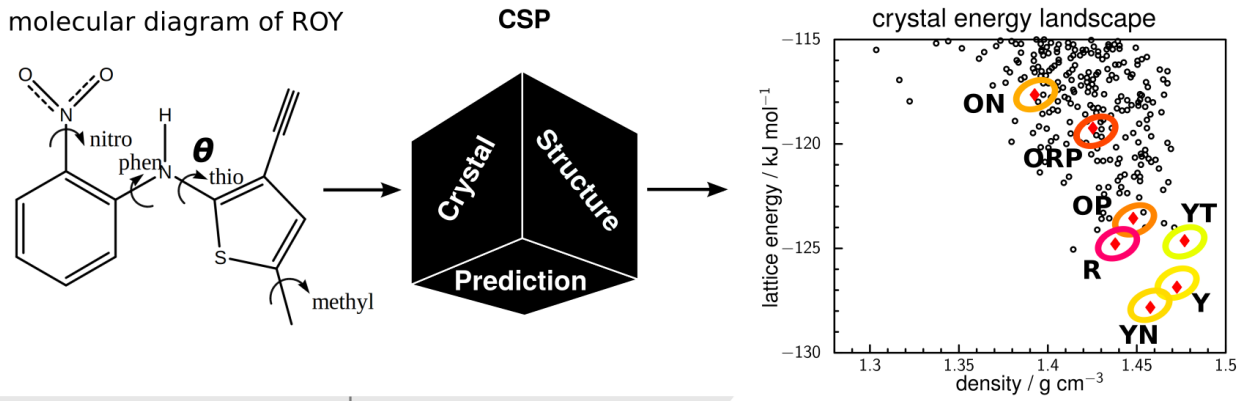
→ High accuracy ∼1 kJ/mol needed

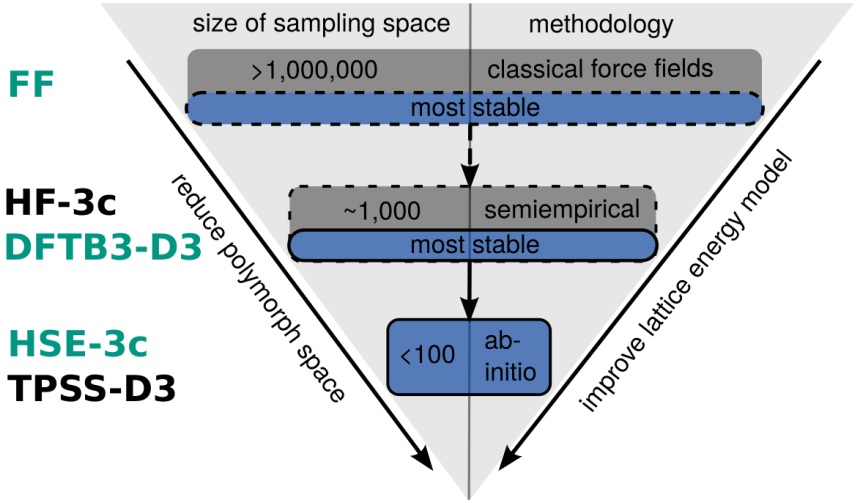
[17] A. J. Cruz-Cabeza, S. M. Reutzel-Edens, J. Bernstein, *Chem. Soc. Rev.* **44**, 8619-8635 (2015).

[18] S. L. Price, JGB, *Molecular Crystal Structure Prediction; Non-covalent interactions in Quantum Chemistry and Physics*, G. DiLabio, A. Otero-de-la-Roza, Eds., Elsevier Australia, Melbourne, ISBN: 9780128098356 (2017).

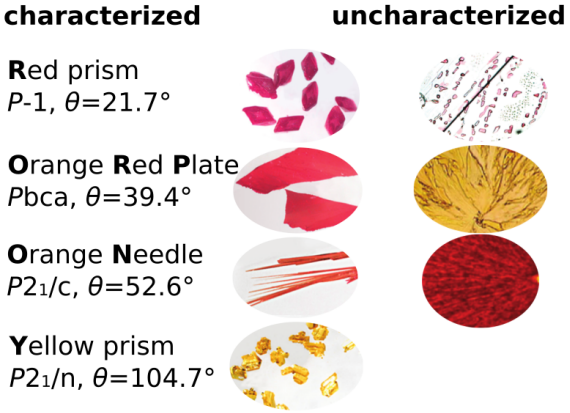
[19] J. Bauer, et al., *J. Pharm. Res.* **18**, 859-866 (2001).

Sampling and energetic ranking for crystal structure prediction





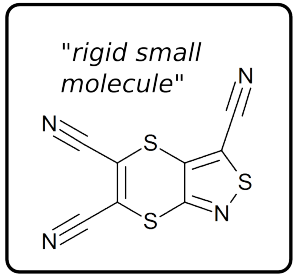
Properties
of ROY polymorphs

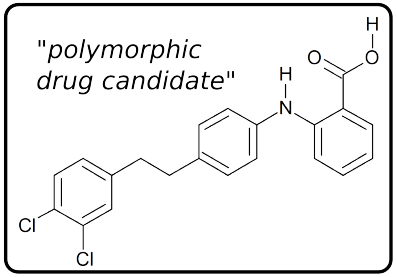


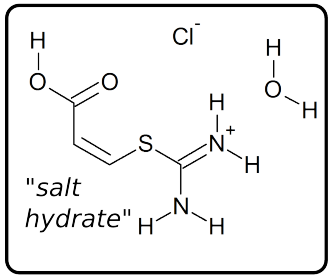
[20] S. Price, *Chem. Soc. Rev.* **43**, 2098 (2014)

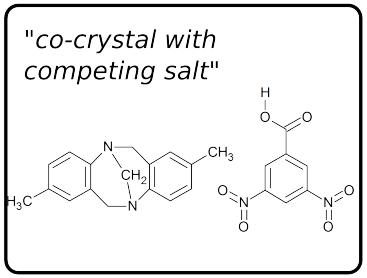
[21] M. Vasileiadis, A. V. Kazantsev, P. G. Karamertzanis, C. S. Adjiman, C. C. Pantelides, *Acta Cryst. B* **68**, 677 (2012)

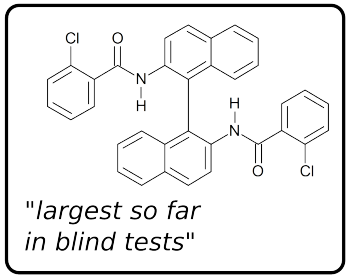
Promising results in the 6th blind test











	22	23	24	25	26
PBE	2	1-9	6	3	1
PBE-D3	**1**	**1-9**	**1**	**1**	**1**
PBE-MBD	1	1-7	1	2	1
vdW-DF2	1	4-8	1	3	2
M06L	1	4-13	1	1	7

lattice energy on fixed TPSS-D3 structures

- good lattice energy based ranking of PBE-D3
- impact of free energy contributions estimated to $\sim$ 1-3 kJ/mol[24,25]

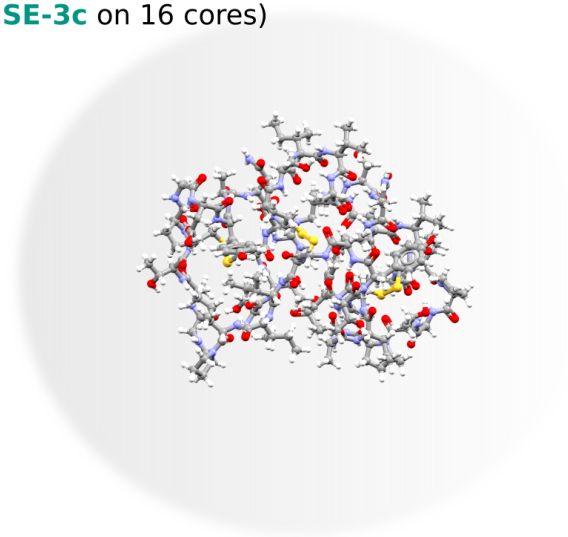
[22] A. Reilly, et al. *Acta Cryst. B*, **72**, 439 (2016)

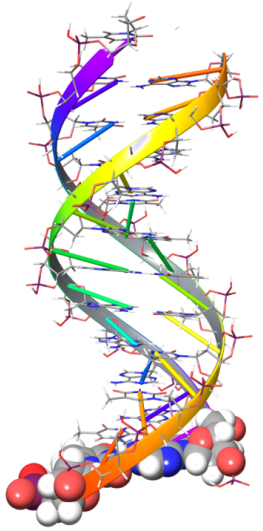
[23] JGB, S. Grimme *Acta Cryst. B*, **72**, 502 (2016)

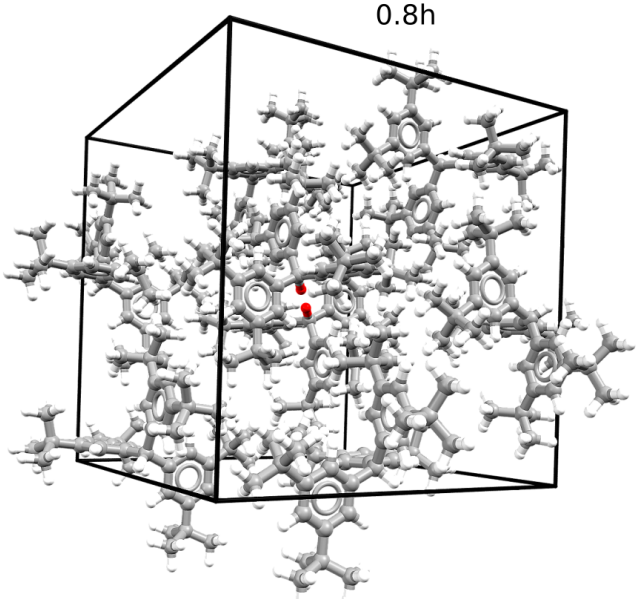
Fast electronic structure for large systems

	gas phase protein	DNA helix	molecular crystal
dim:	0D	1D	3D
#atoms/unit:	647 (647)	726 (66)	856 (37)
wall time:	5h	0.5h	0.8h

(**HSE-3c** on 16 cores)







- fast computer code CRYSTAL17[26] with cost-efficient methods[11]
- enabling routine electronic structure calculation of large systems

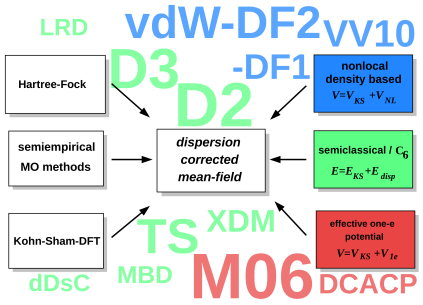
[24] R. Dovesi, et al., *Int. J. Quantum Chem.*, **114**, 1287-1317 (2014)

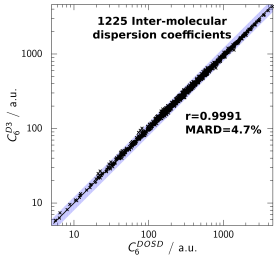
[12] JGB, E. Caldeweyher, S. Grimme, *Phys. Chem. Chem. Phys.*, **18**, 15519 (2016)

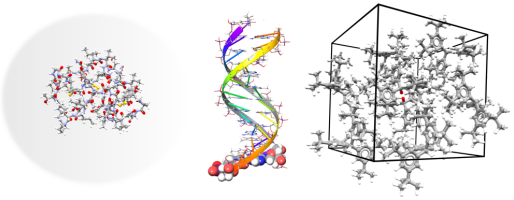
Summary

Take-home messages

- D3 London dispersion interaction arises in second order perturbation theory.
- C_6 based dispersion corrections are most efficient in DFT framework.
- DFT-D methods show excellent performance for organic crystals.
- D3, gCP, and composite methods implemented in CRYSTAL17







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  S. L. Price, JGB, *Molecular Crystal Structure Prediction*, G. DiLabio, A. Otero-de-la-Roza, Eds., Elsevier Australia, *ISBN: 9780128098356* (2017).

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