Nanoscale π–π stacked complexes bound by collective charge fluctuations

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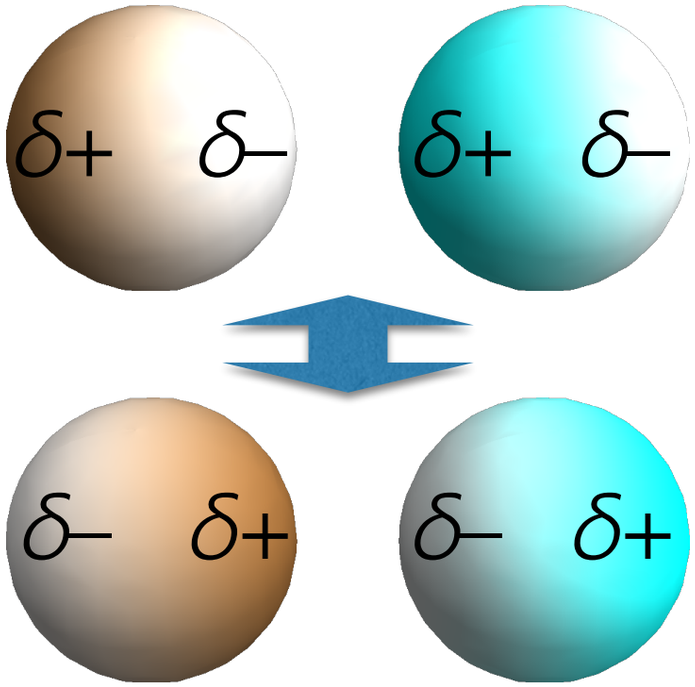
van der Waals dispersion – two atoms

- Correlation of charge fluctuations in atoms causes attraction

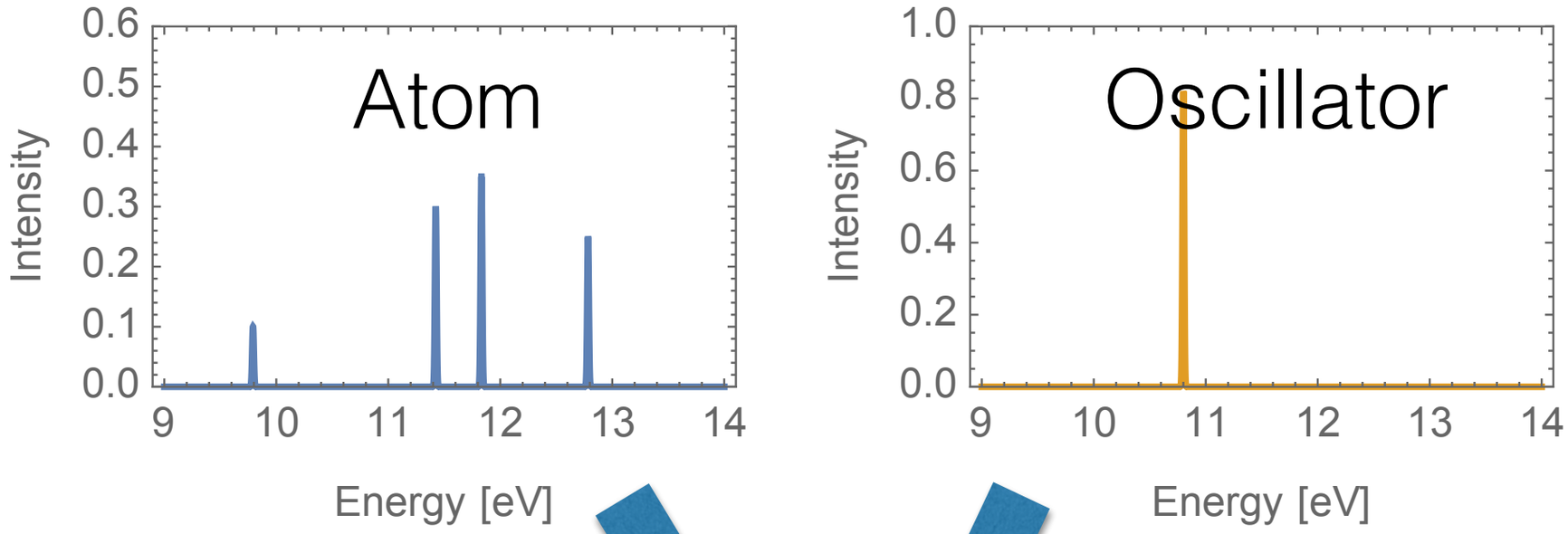


$$E \sim \frac{C_6}{R^6}$$

$$-E^{(2)}_{\text{disp}} = \sum_{mn} \frac{|\langle 00|V|mn\rangle|^2}{\omega_m + \omega_n} \approx \sum_{mn} \frac{2}{\pi} \int_0^\infty \mathrm{d}u \, \frac{\omega_m |\langle 0|\boldsymbol{\mu}|m\rangle|^2}{\omega_m^2 + u^2} \langle \mathsf{T}^2 \rangle \frac{\omega_n |\langle 0|\boldsymbol{\mu}|n\rangle|^2}{\omega_n^2 + u^2}$$

Electronic excitations ⟷ Harmonic oscillators

Real atoms as single oscillators



- van der Waals dispersion depends on the averaged effect of all charge fluctuations

- Polarizability at imaginary frequencies

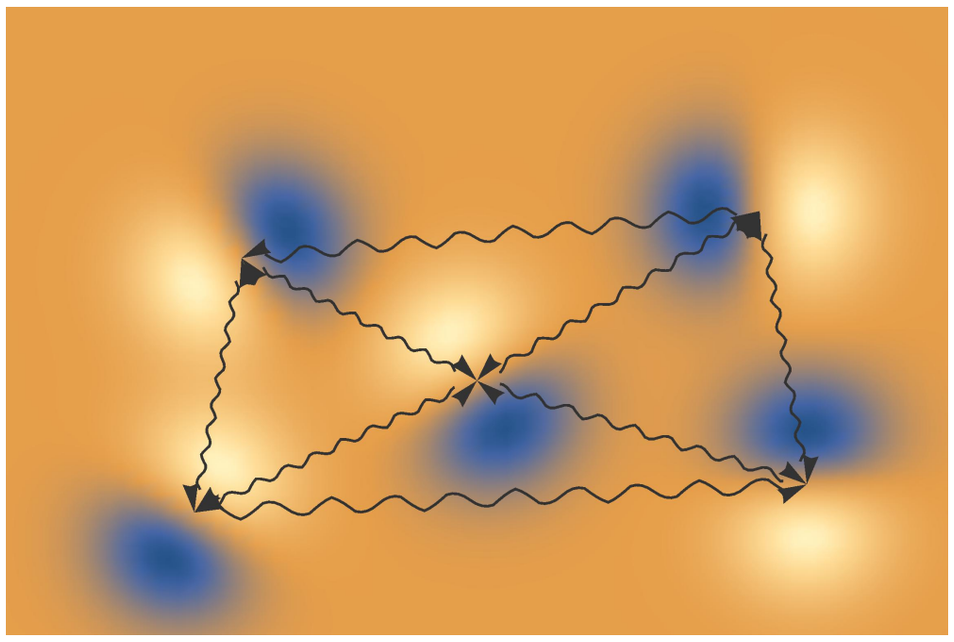
- Parametrize oscillator to match static polarizability and integral over imaginary frequency—C_6 coefficient

Many-body dispersion (MBD)

$$H = \sum_{i=1}^{3N} \left(-\frac{1}{2}\frac{\partial^2}{\partial \xi_i^2} + \frac{1}{2}\omega_i^2 \xi_i^2 \right) + \frac{1}{2} \sum_{ij} T_{ij} \omega_i \omega_j \sqrt{a_i(0) a_j(0)}\, \xi_i \xi_j$$

- Parametrize oscillators —$\alpha(0)$, ω—from a DFT calculation

- Transform to coupled coordinates with no interaction

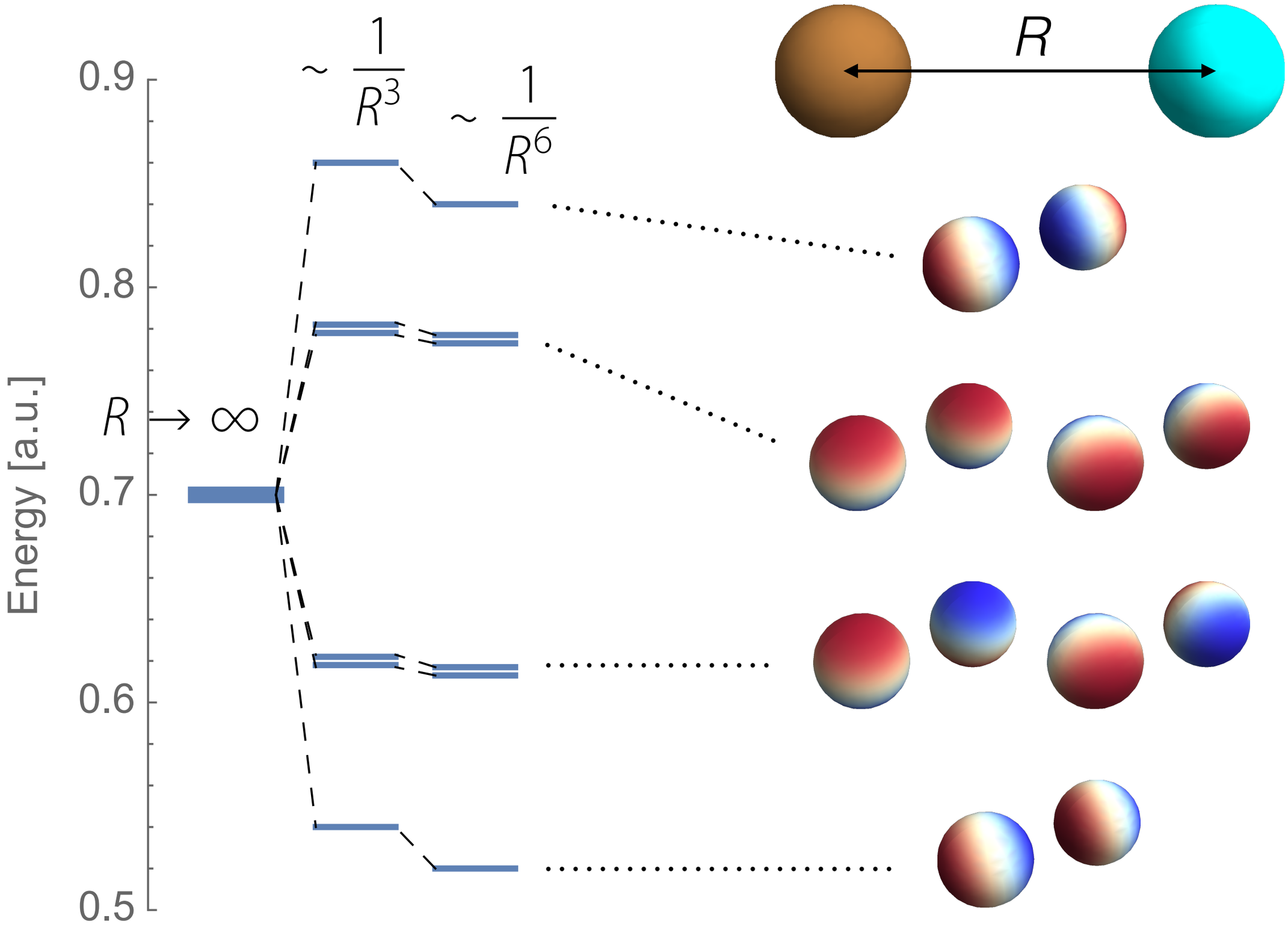


$$H = \sum_{i=1}^{3N} \left(-\frac{1}{2}\frac{\partial^2}{\partial \tilde{\xi}_i^2} + \frac{1}{2}\tilde{\omega}_i^2 \tilde{\xi}_i^2 \right)$$

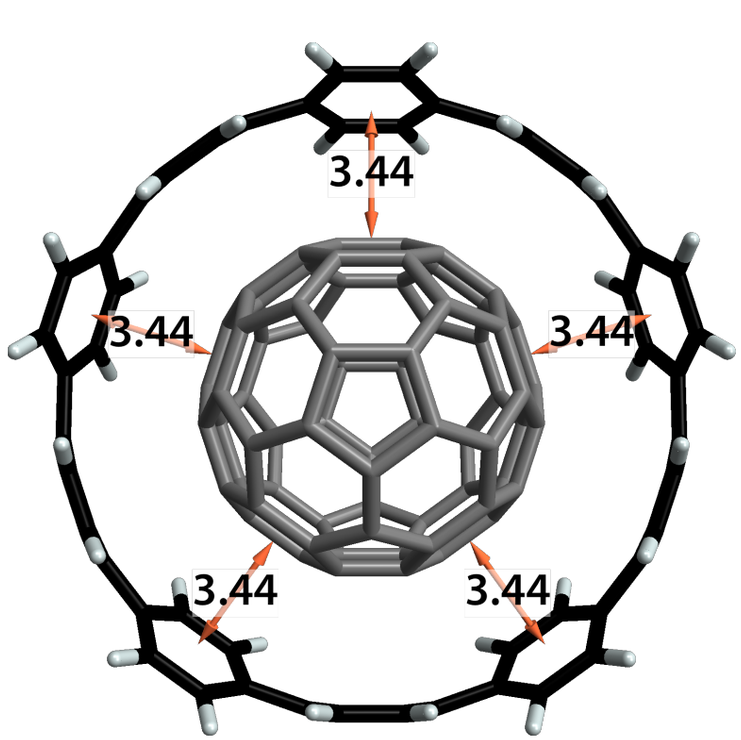
Quantum mechanics

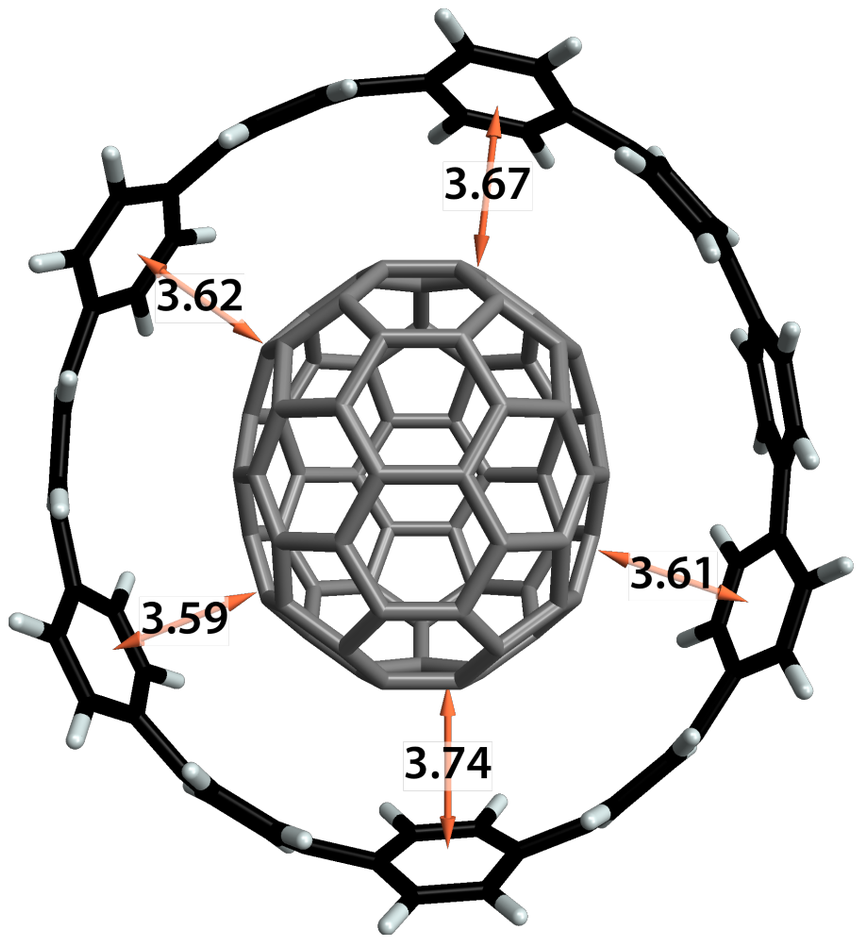
$$E = \sum_{i=1}^{3N} \frac{\tilde{\omega}_i}{2}$$

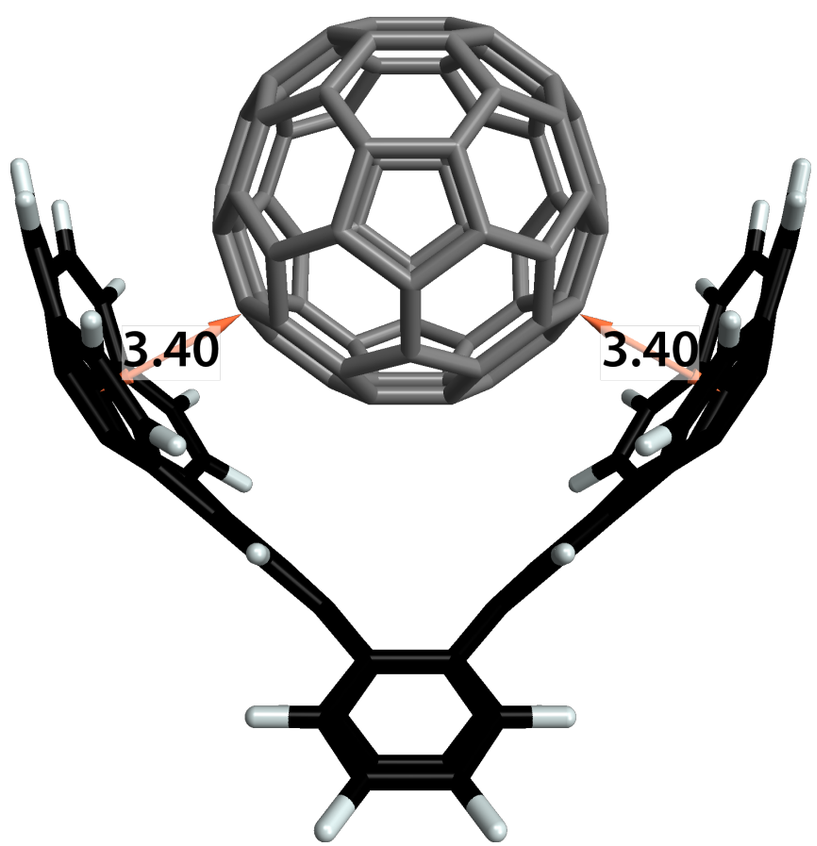
Two atoms in MBD



Supramolecular complexes







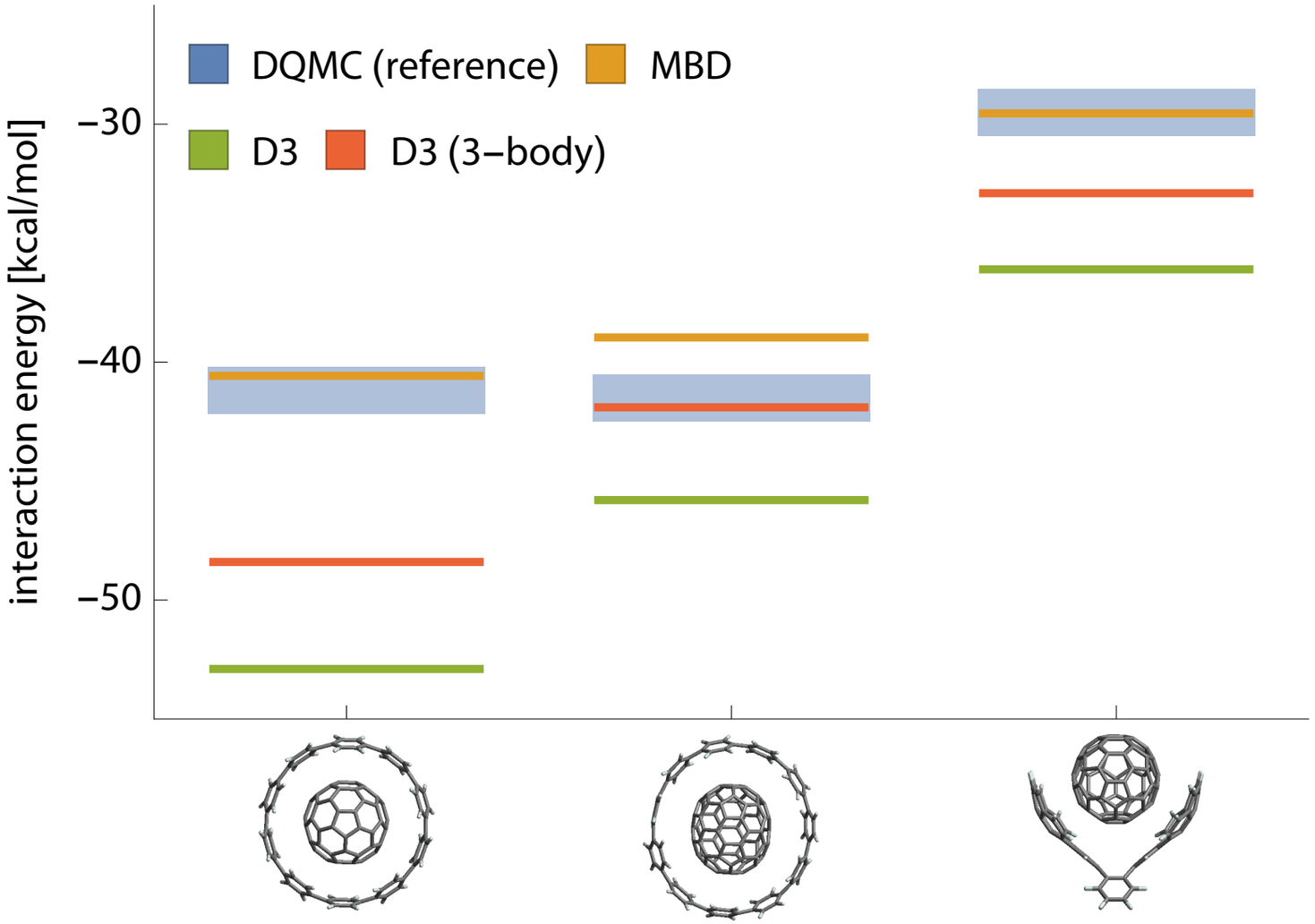
- C_{70} fullerene in cycloparaphenylenes & buckyball catcher

- Synthesized and characterized in solution

Methods

Diffusion quantum Monte Carlo (DQMC)	many-body “exact”, expensive
Many-body dispersion (D3)	many-body approximate, cheap
D3: dispersion correction	2-body/3-body approximate, cheap

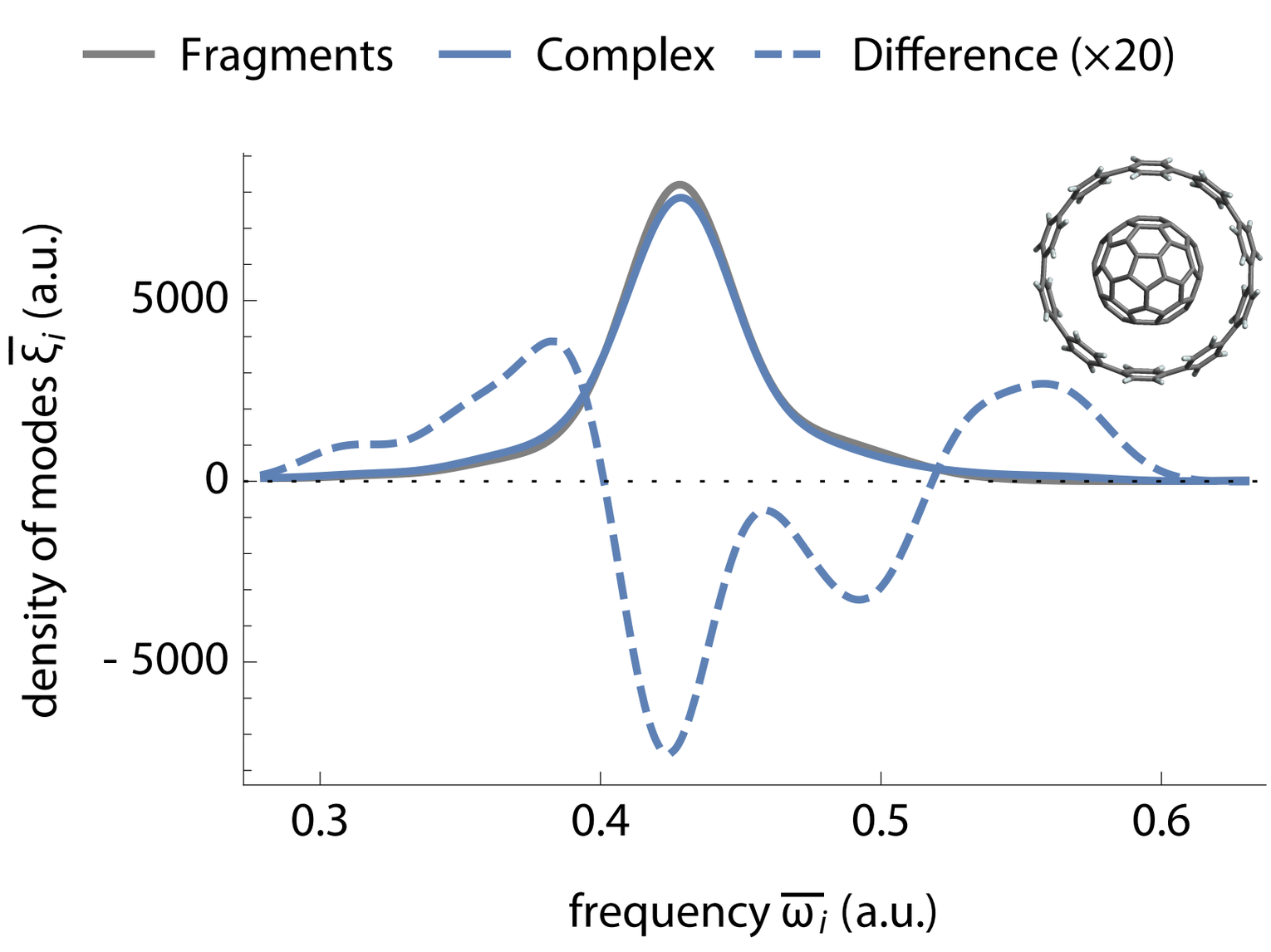
Interaction energies



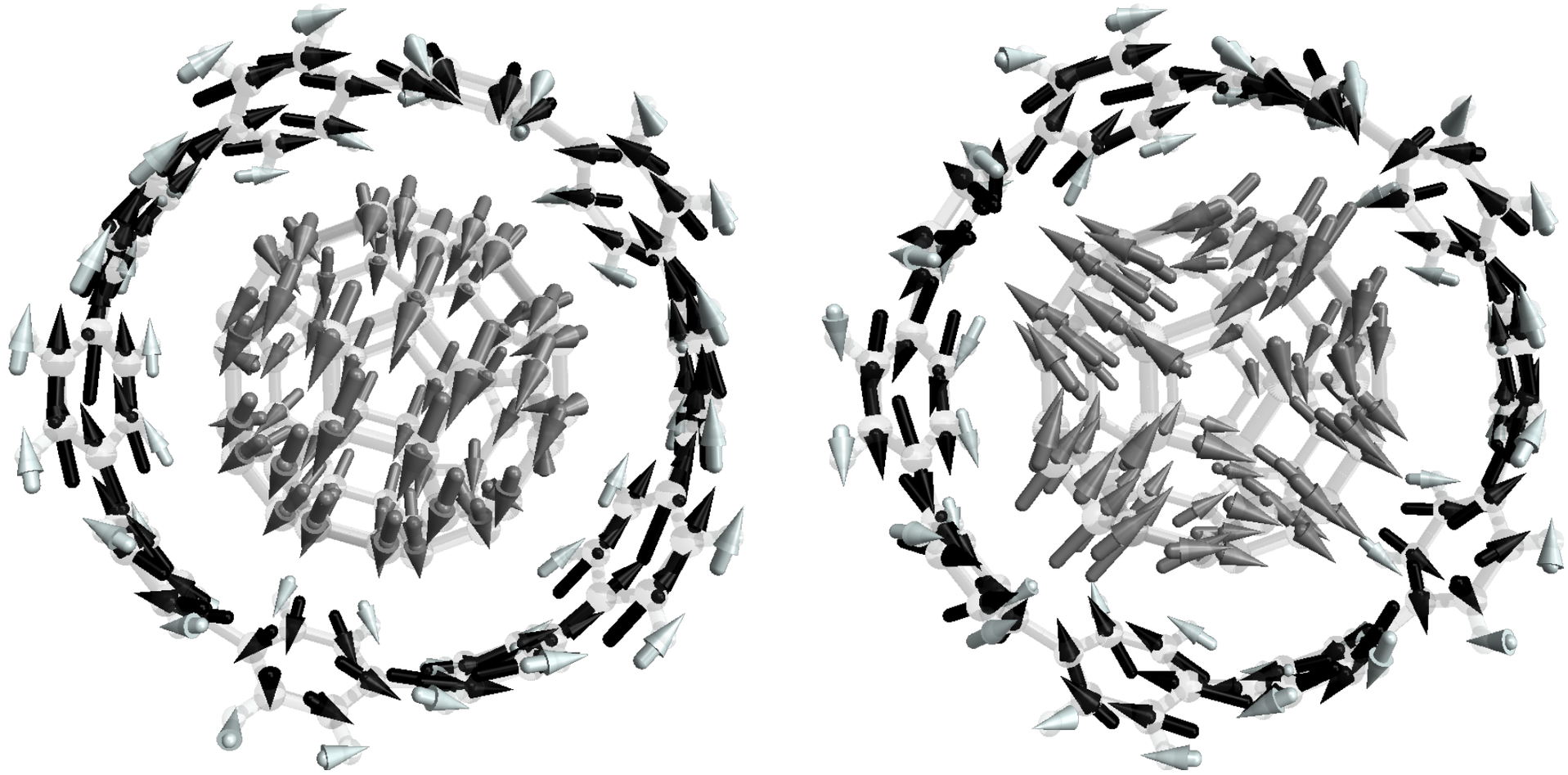
- MBD within 5% of reference Monte Carlo
- 3-body correction improves overall but misses specificity

Cause of binding

- Asymmetry in broadening of the fluctuation frequency spectrum

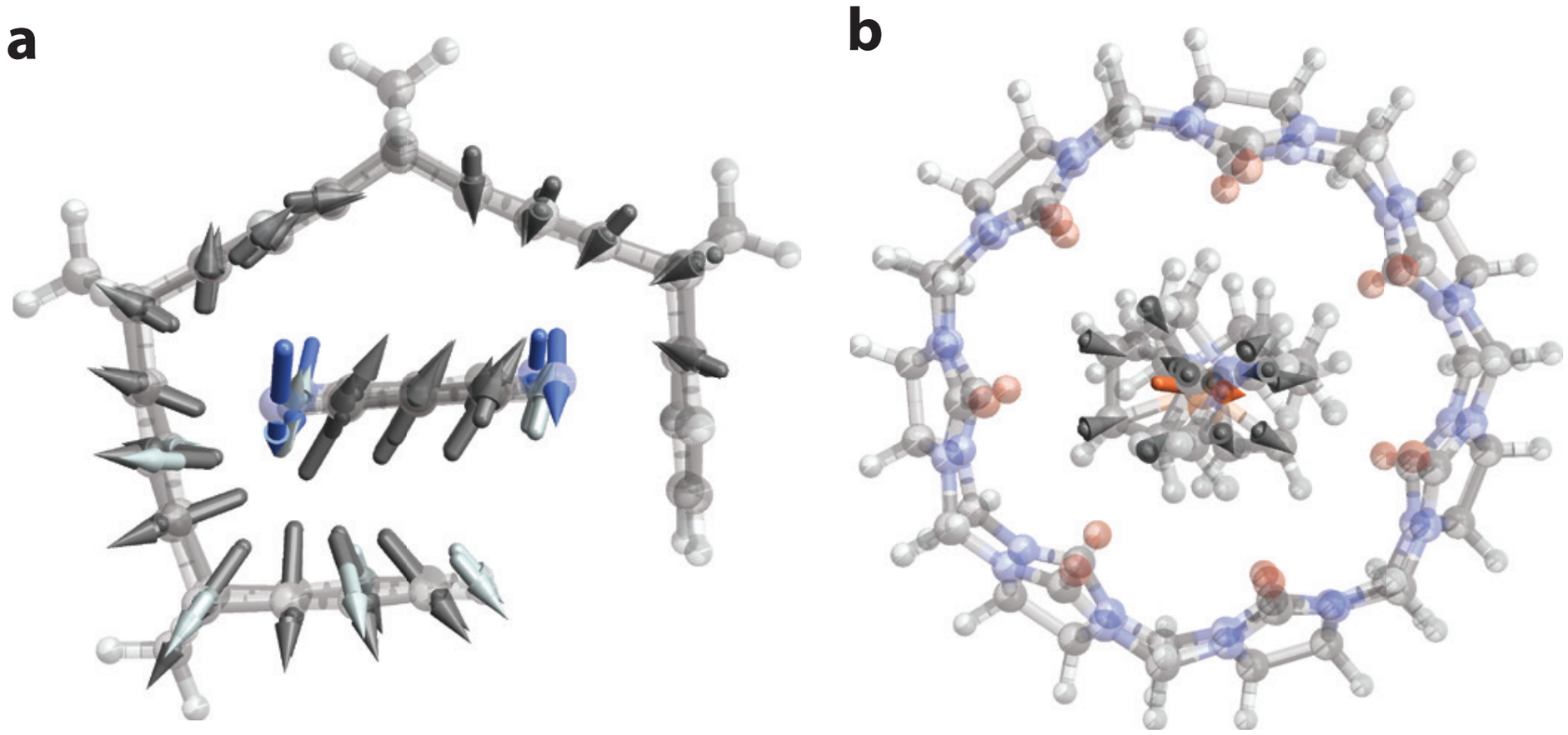


Collective fluctuations



- Dipole fluctuations of charge density (not atomic nuclei)
- Two fluctuation modes most contributing to the binding energy

Comparison to other bond types

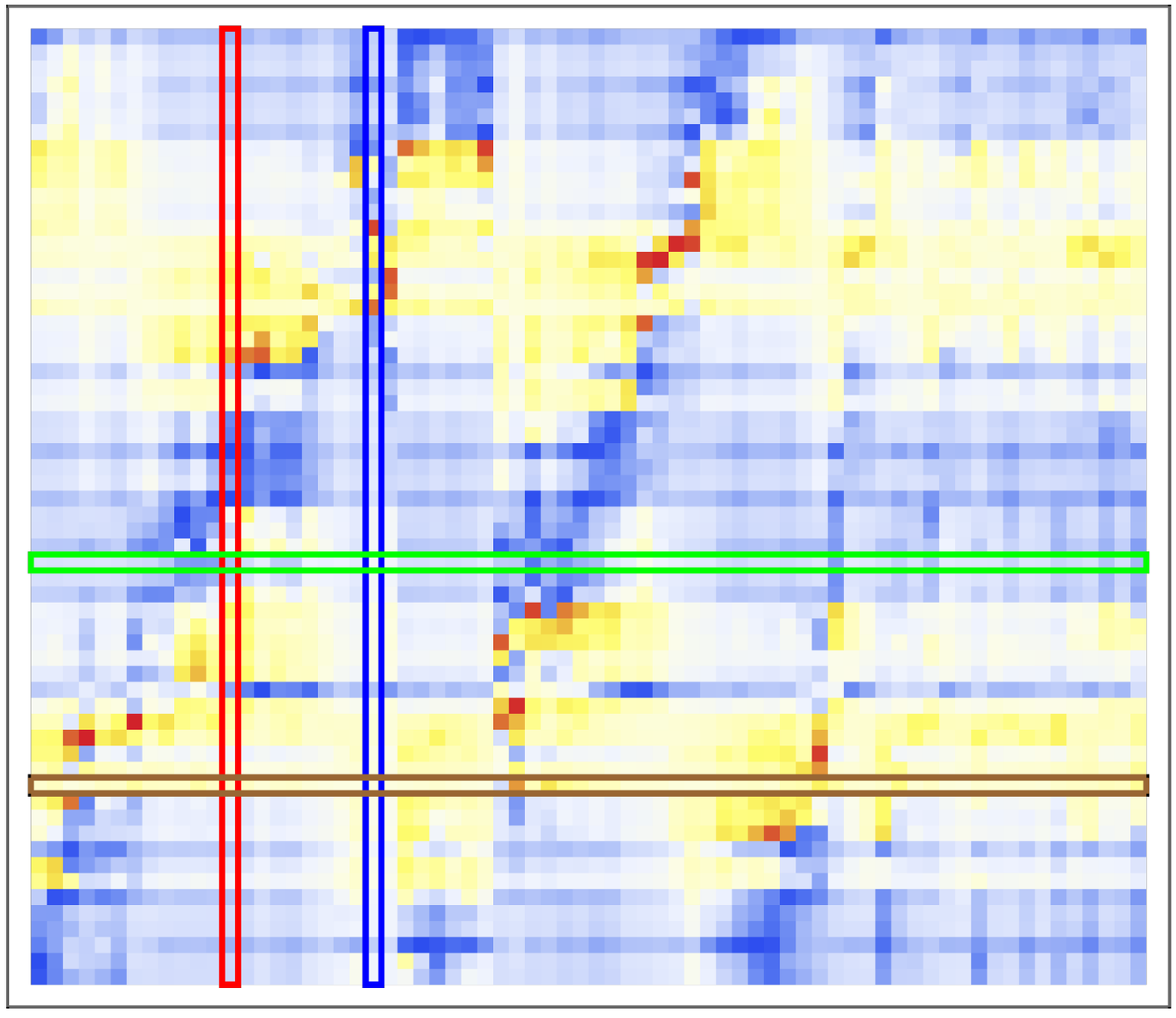


- π–π complexes: the most binding fluctuations are collective

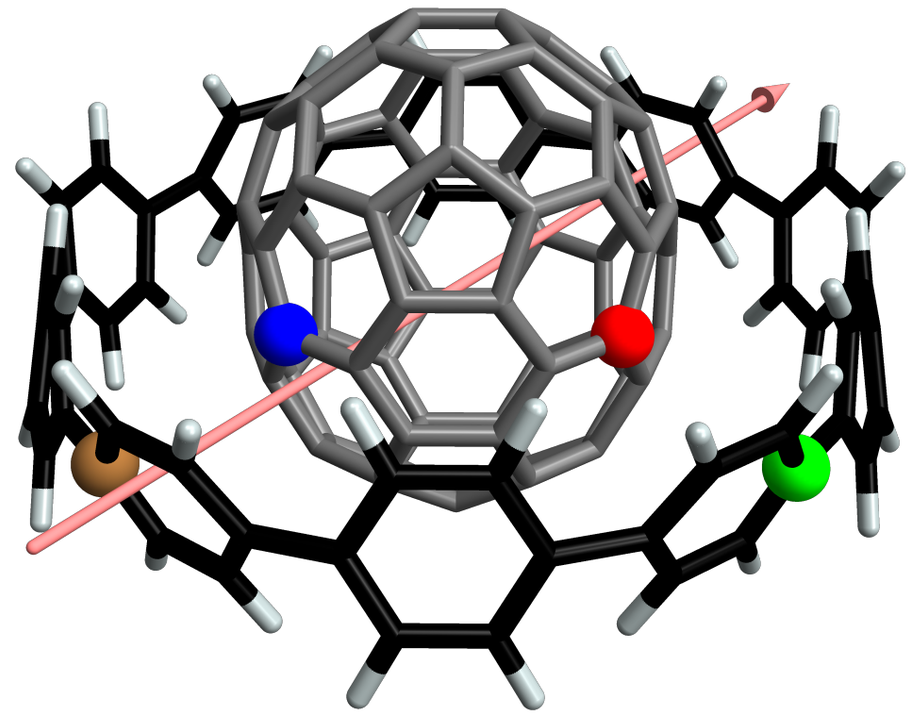
- Electrostatically bound complexes: disordered fluctuations

Nonlocal polarizability

- What dipole at point **r** is induced by field at point **r**'?

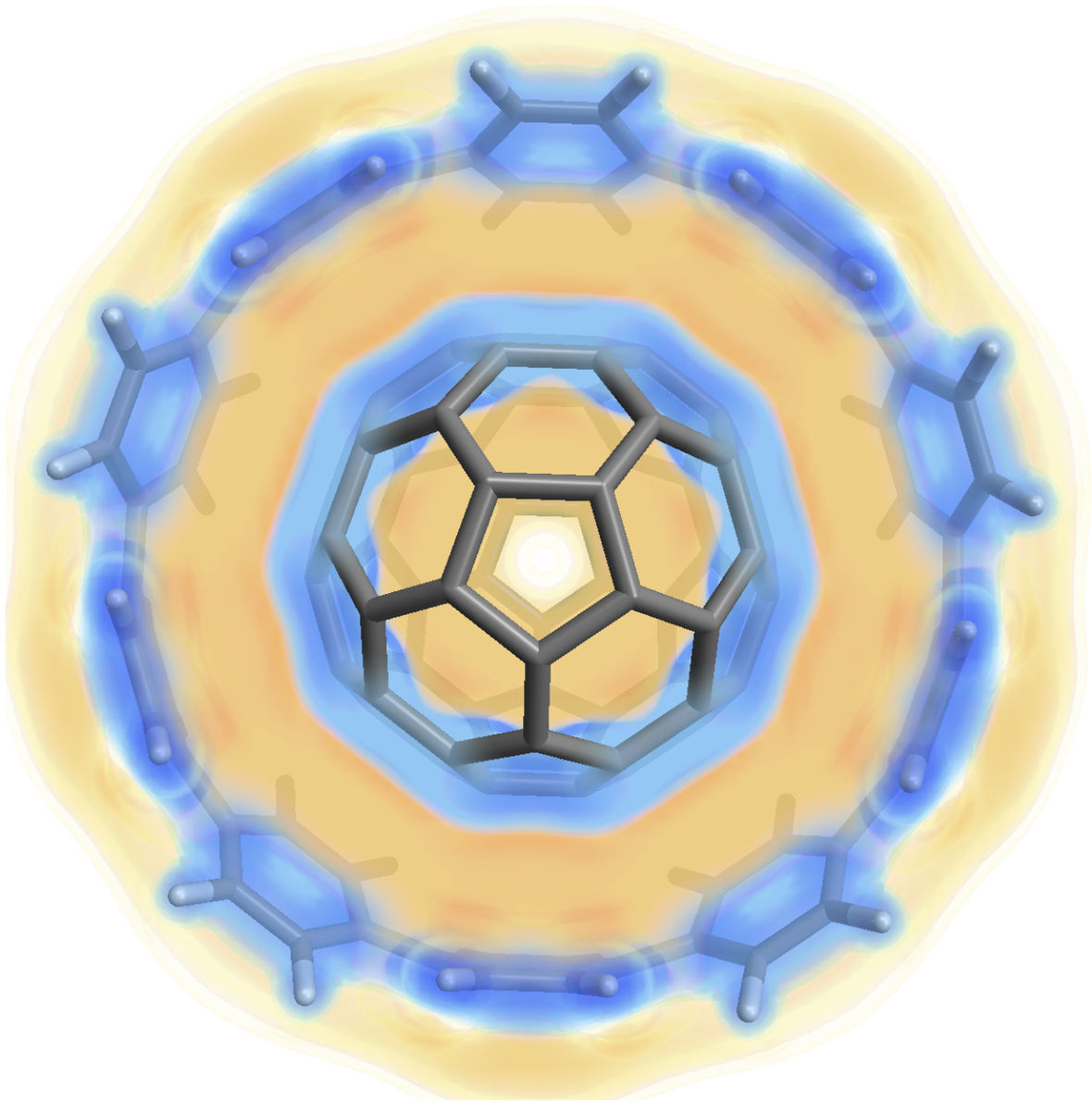


$$\alpha_{xx}(\mathbf{r}, \mathbf{r}', 0)$$



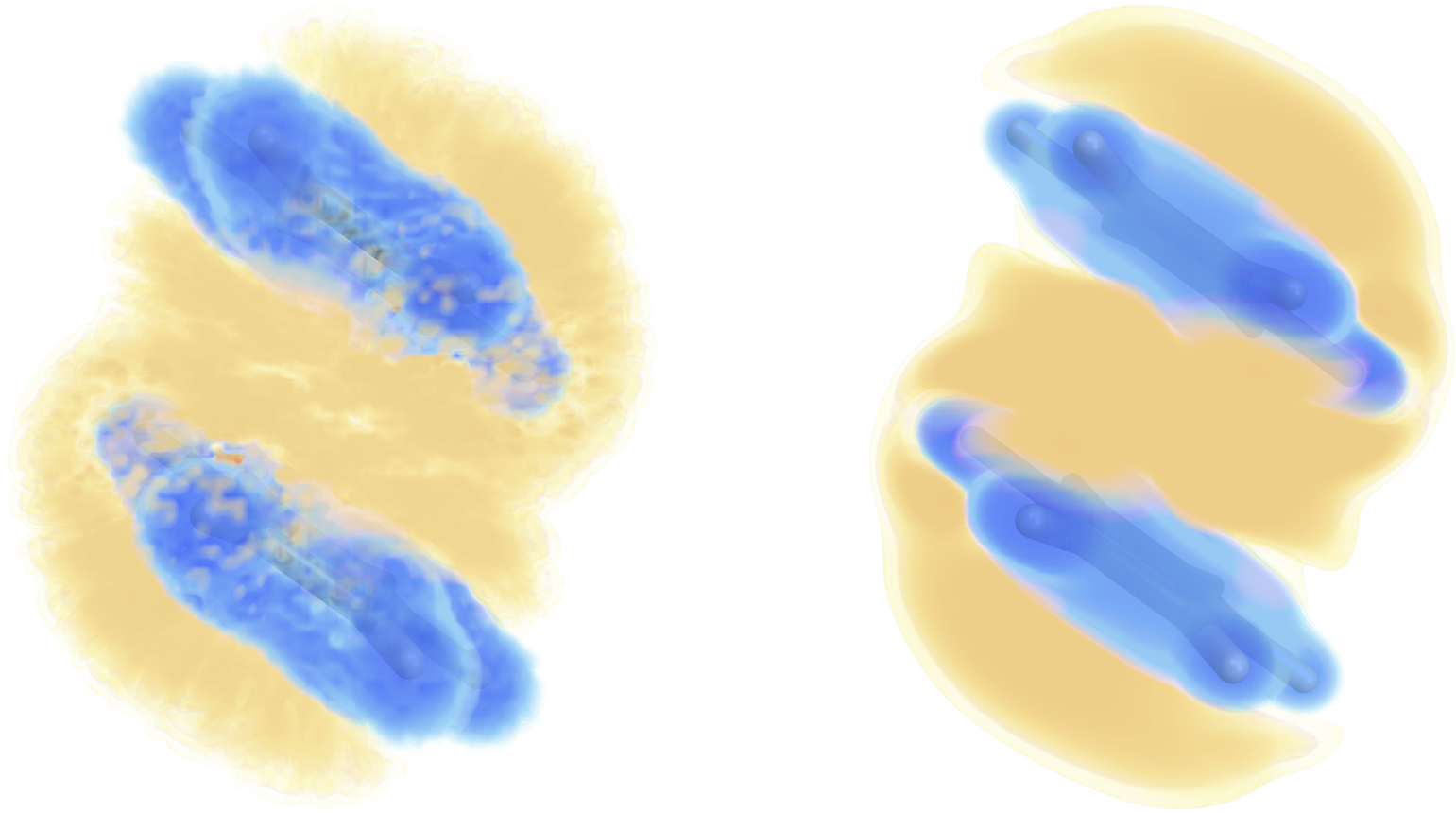
Polarization of charge density

- Lowering of fluctuation energies due to interaction leads to charge polarization (delocalization)



- Perturbation picture—virtual excited states are more delocalized

Polarization of charge density



- DFT electron density using xc functional with long-range correlation (Tkatchenko–Scheffler)
- Harmonic oscillator density with MBD

Summary

- van der Waals interactions can be efficiently and effectively described by quantum harmonic oscillators
- In nanoscale π–π complexes, the coupled charge fluctuations are highly collective (c.f. pairwise models)
- The harmonic oscillator description is not limited to binding energies

Hermann, Alfè & Tkatchenko, Nat. Commun. [accepted]