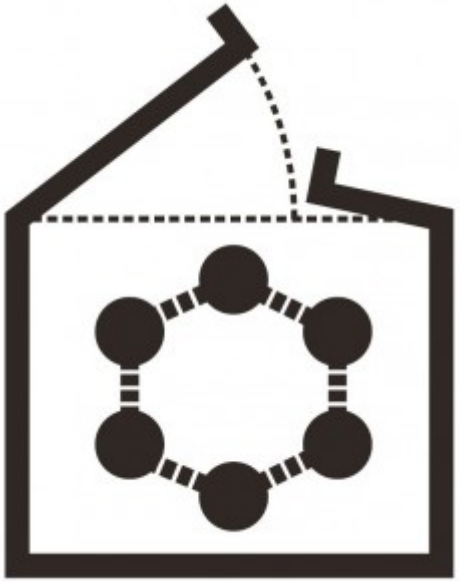
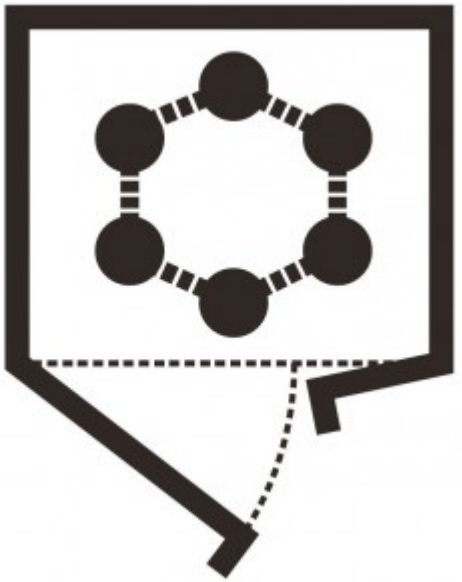


Many Particles, Collective Variables, and Machine Learning



Alexandre Tkatchenko

Fritz-Haber-Institut der Max-Planck-Gesellschaft,

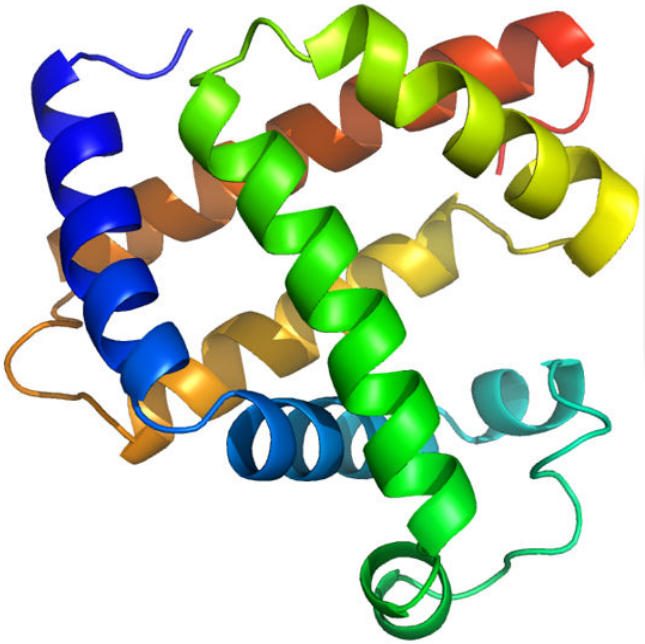
Berlin, Germany

www.fhi-berlin.mpg.de/~tkatchen

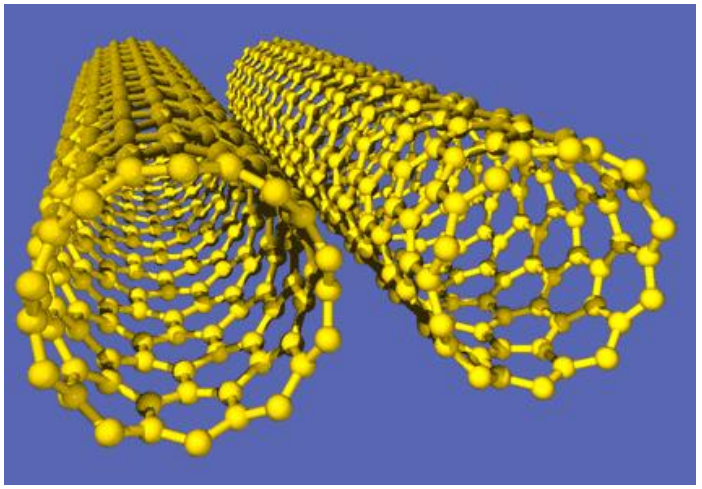
"Machine Learning for Many Particle Systems"

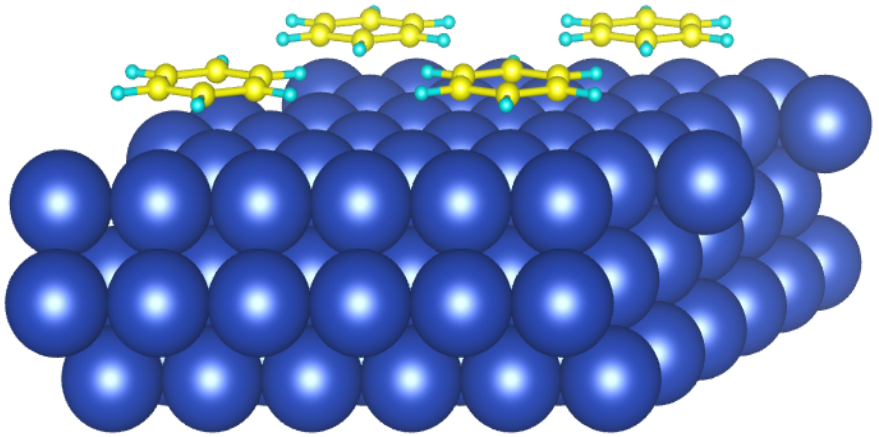
Institute for Pure and Applied Mathematics @ UCLA

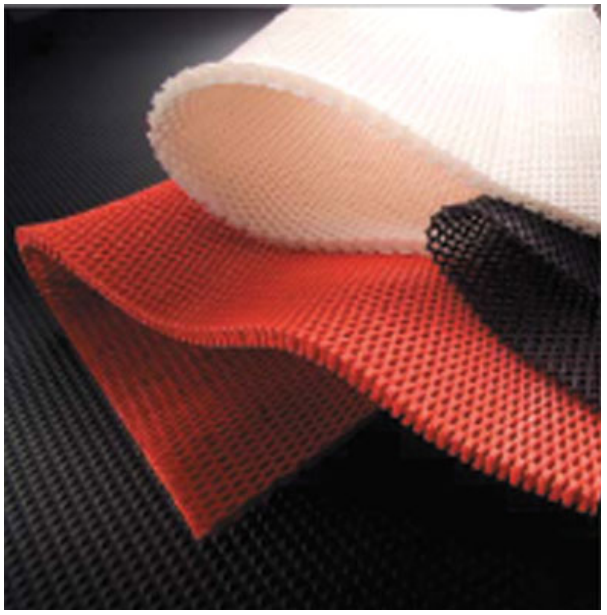
Many-Particle Systems in Physics, Chemistry, Biology, and Materials Science



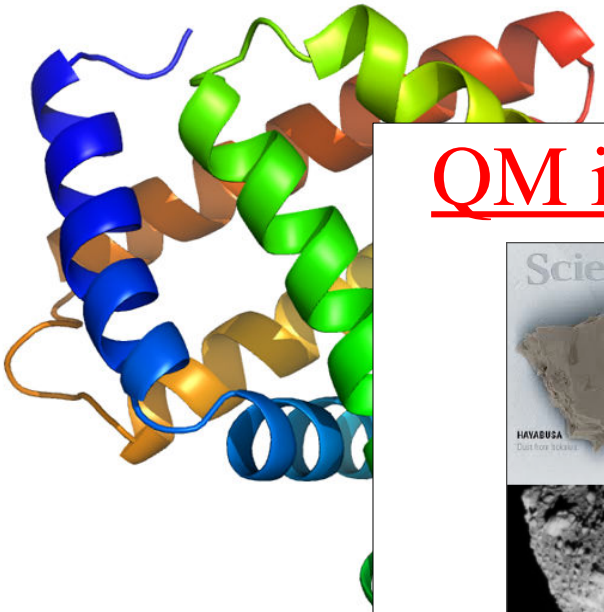
$$\hat{\mathcal{H}}\Psi = E\Psi$$

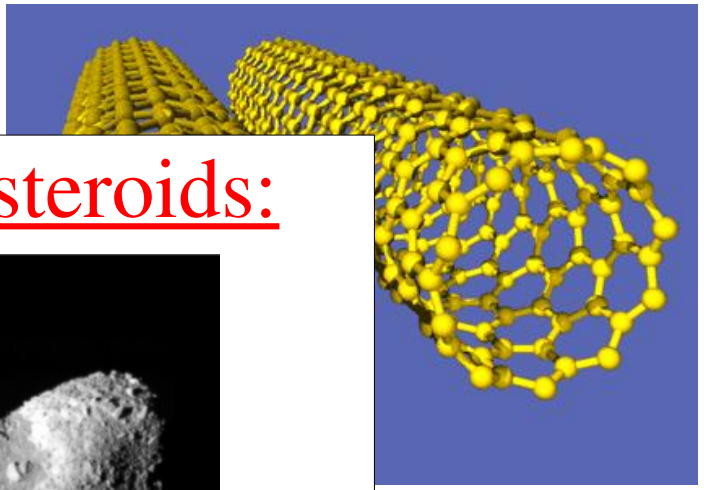




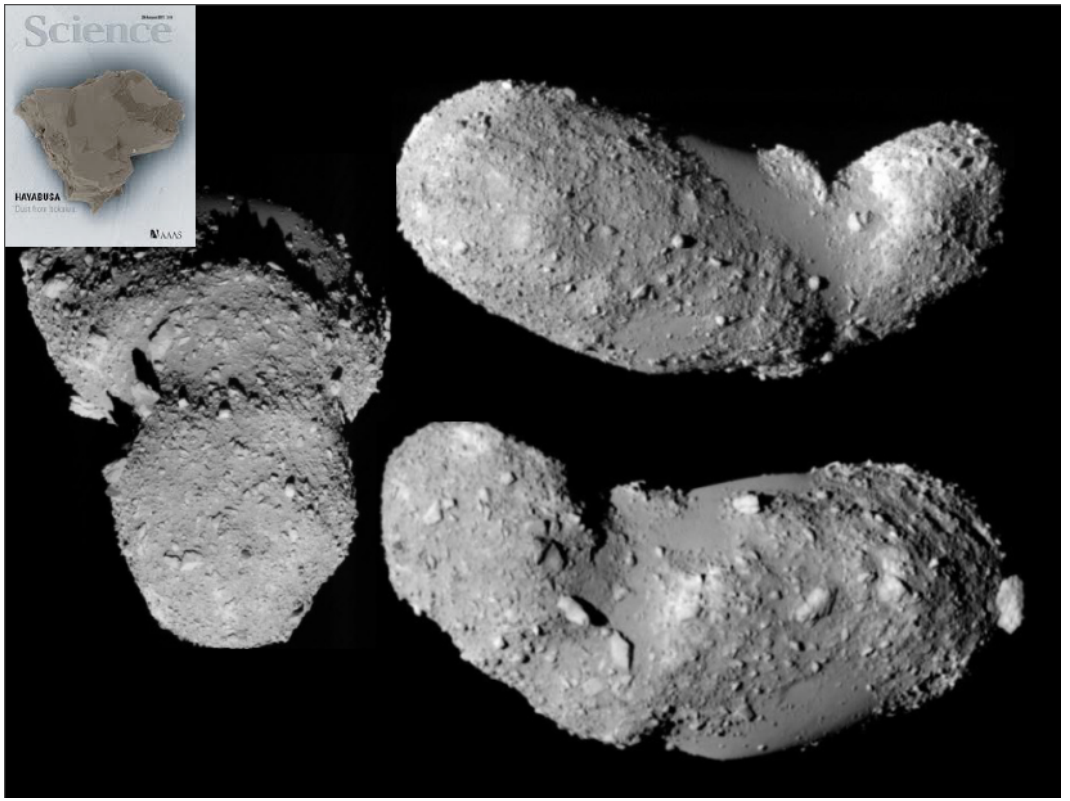


Many-Particle Systems in Physics, Chemistry, Biology, and Materials Science

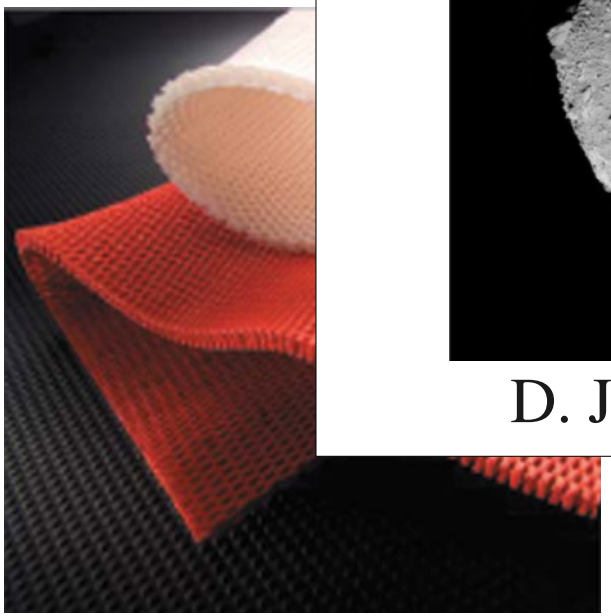




QM is important even in asteroids:

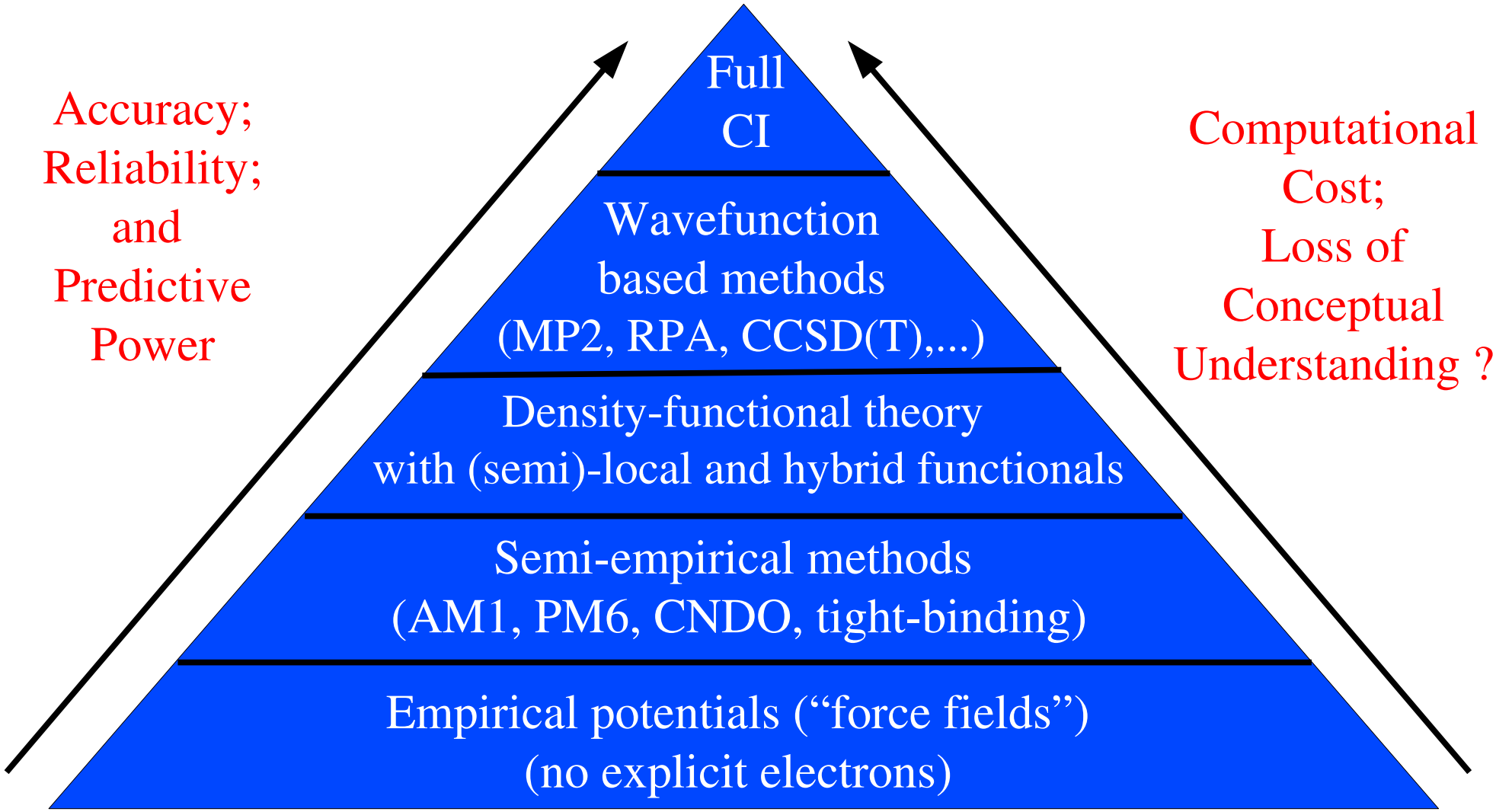


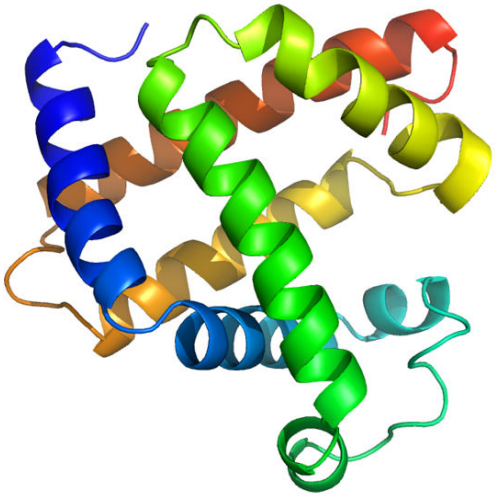
D. J. Scheeres *et al.*, ***Icarus*** (2010).

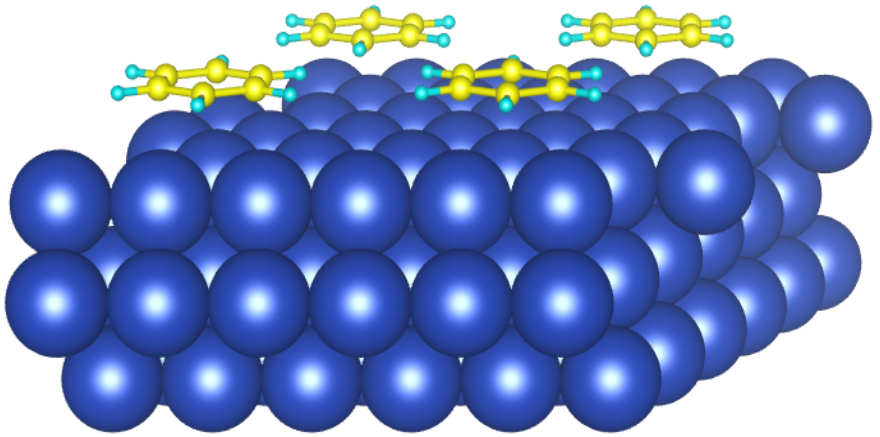


Current state-of-the-art of atomistic modeling

$$\hat{\mathcal{H}}\Psi = E\Psi$$



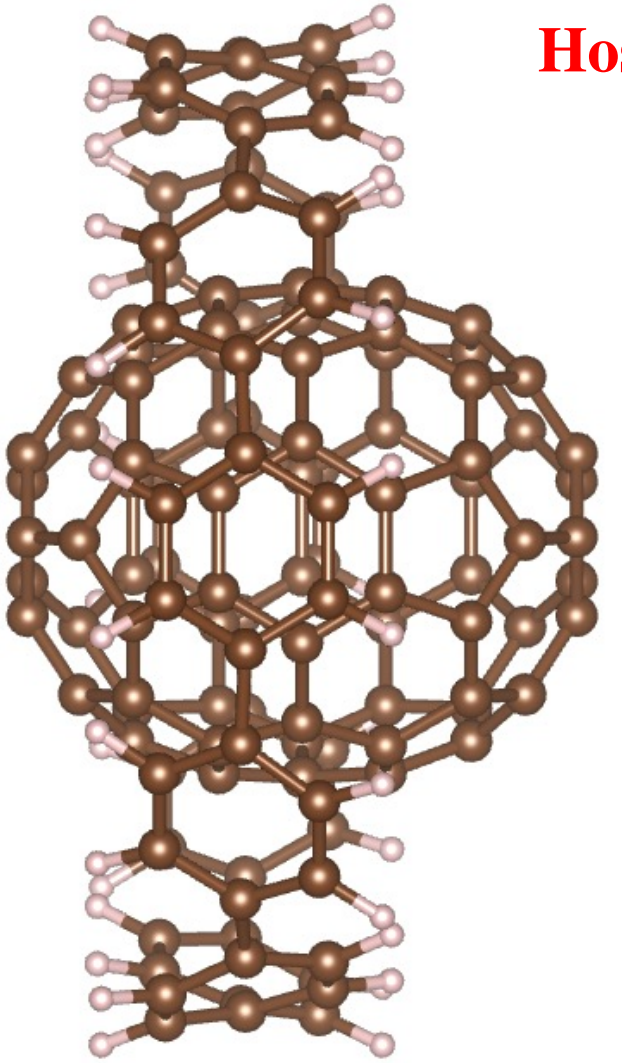




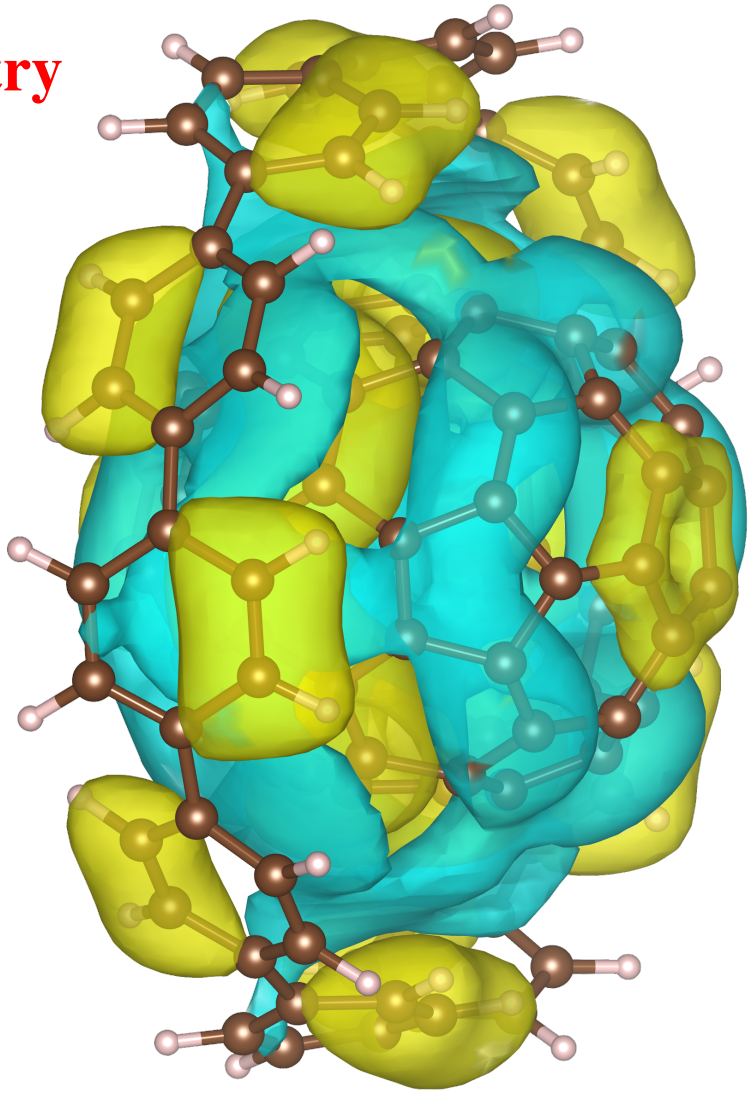
$$\hat{\mathcal{H}}\Psi = E\Psi$$

$$\Psi(\vec{r}_1, \vec{r}_2, \vec{r}_3, \ldots, \vec{R}_1, \vec{R}_2, \vec{R}_3, \ldots)$$

Why is $\hat{\mathcal{H}}\Psi = E\Psi$ complex? – Collective many-particle states



Host-guest chemistry

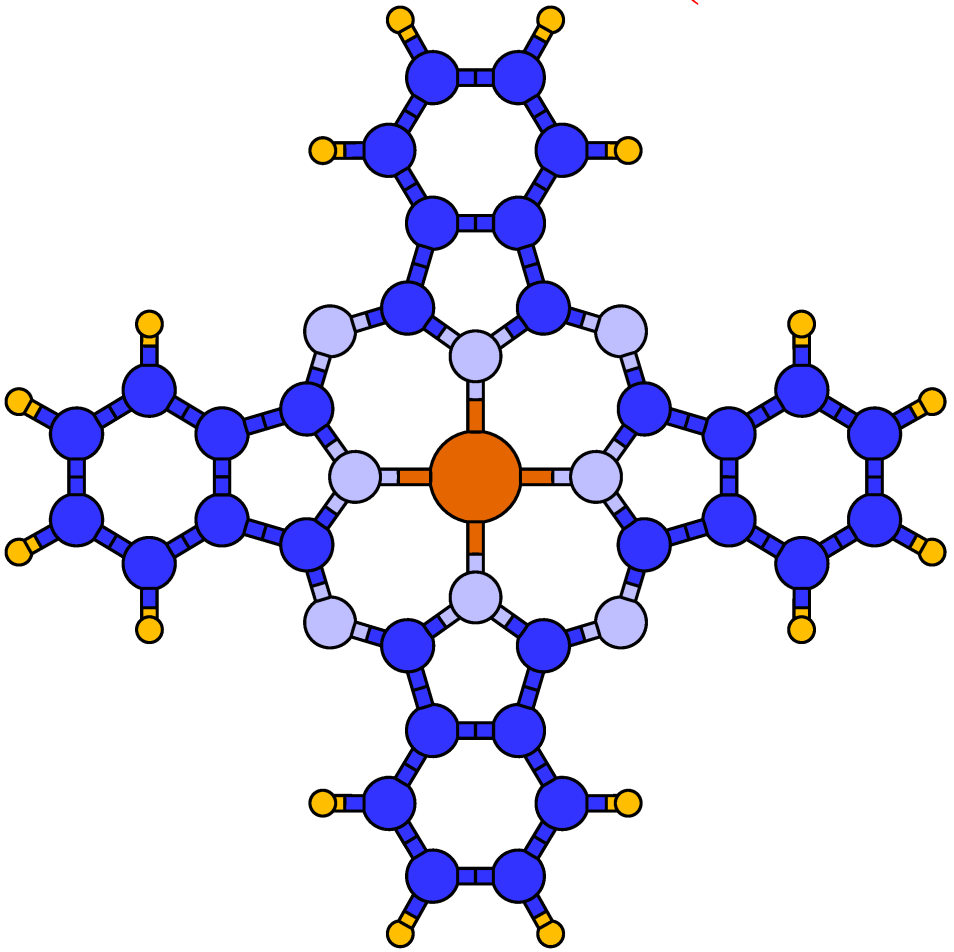


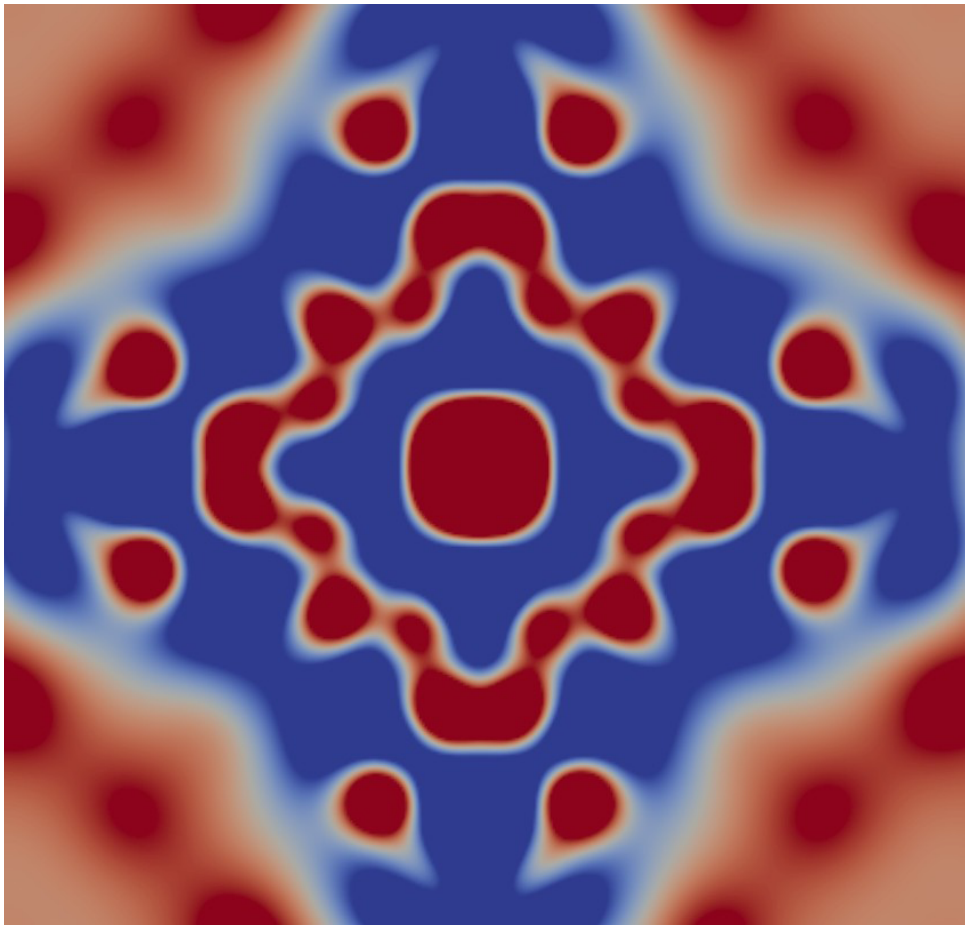
$$\Psi(\vec{r}_1, \vec{r}_2, \vec{r}_3, \ldots, \vec{R}_1, \vec{R}_2, \vec{R}_3, \ldots)$$

Why is $\hat{\mathcal{H}}\Psi = E\Psi$ complex? – Collective many-particle states

Hybrid organic/inorganic systems

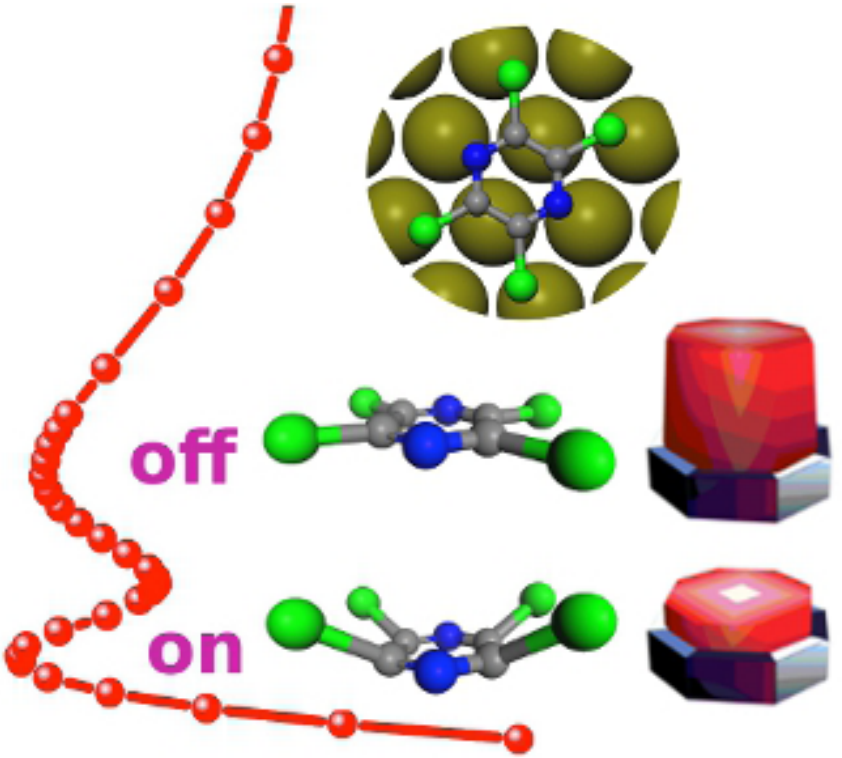
(CuPc on Ag(100) surface)





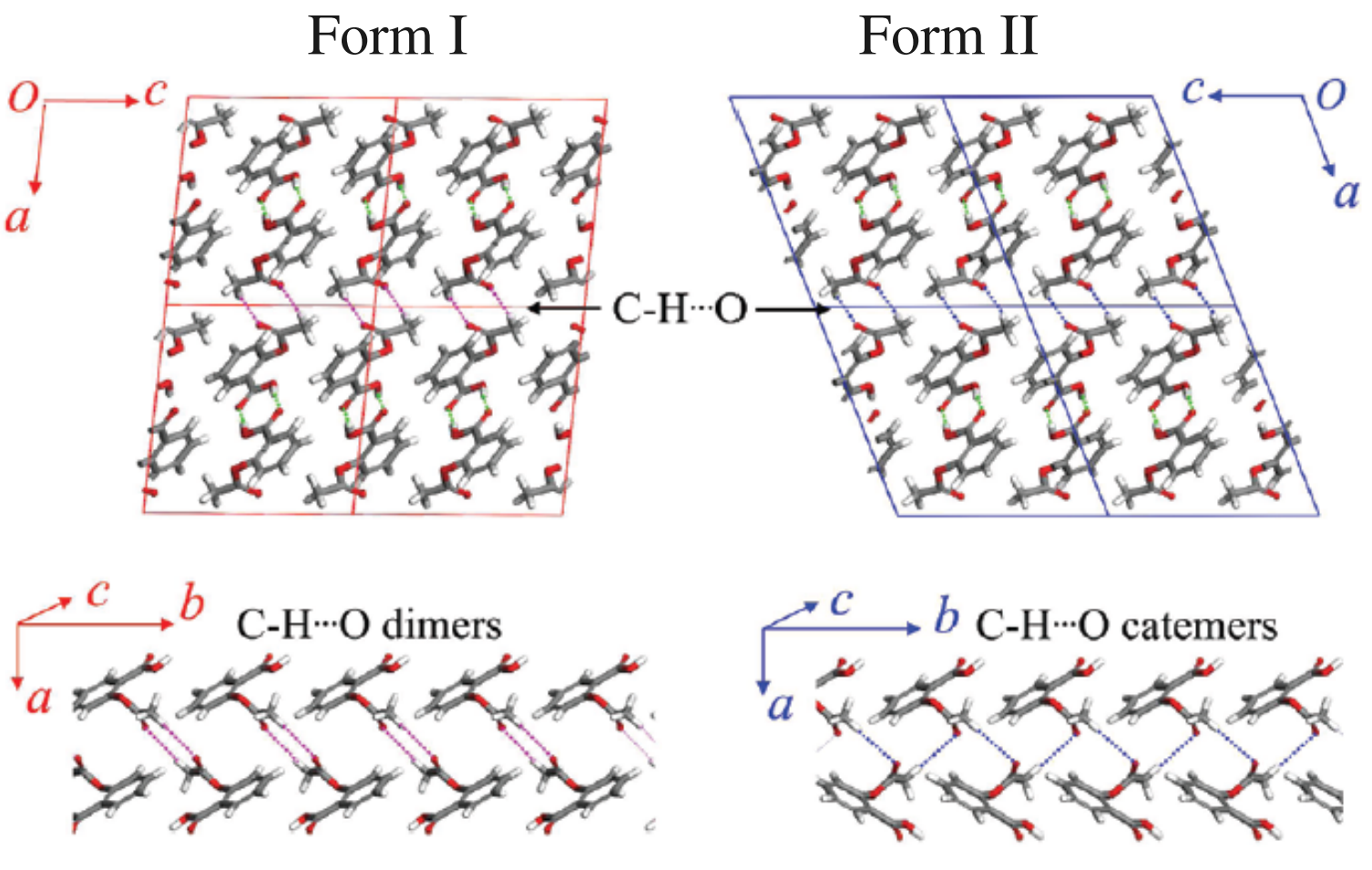
$$\Psi(\vec{r}_1, \vec{r}_2, \vec{r}_3, \ldots, \vec{R}_1, \vec{R}_2, \vec{R}_3, \ldots)$$

Predictive power of current many-particle methods



Predictive power of current many-particle methods: Aspirin "Headache"

Aspirin crystal



Anthony Reilly

C. Ouvrard and S. L. Price, ***Cryst. Growth Des.*** (2004).

A. D. Bond, R. Boese, G. R. Desiraju, ***Angew. Chem. Int. Ed.*** (2007).

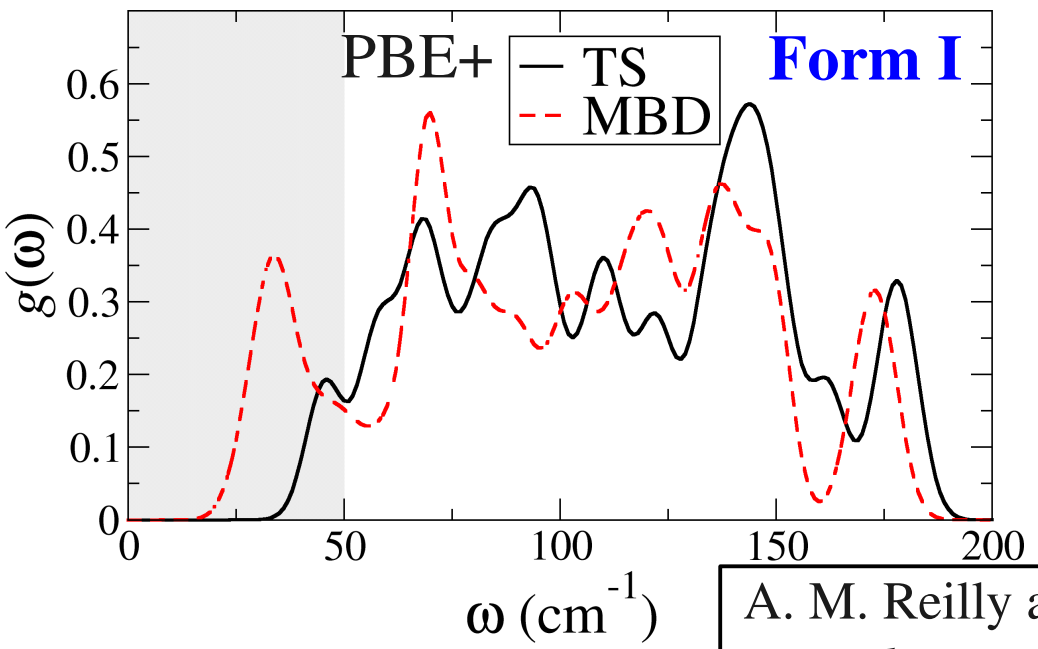
Solution of Aspirin Headache: Dynamic plasmon-phonon coupling

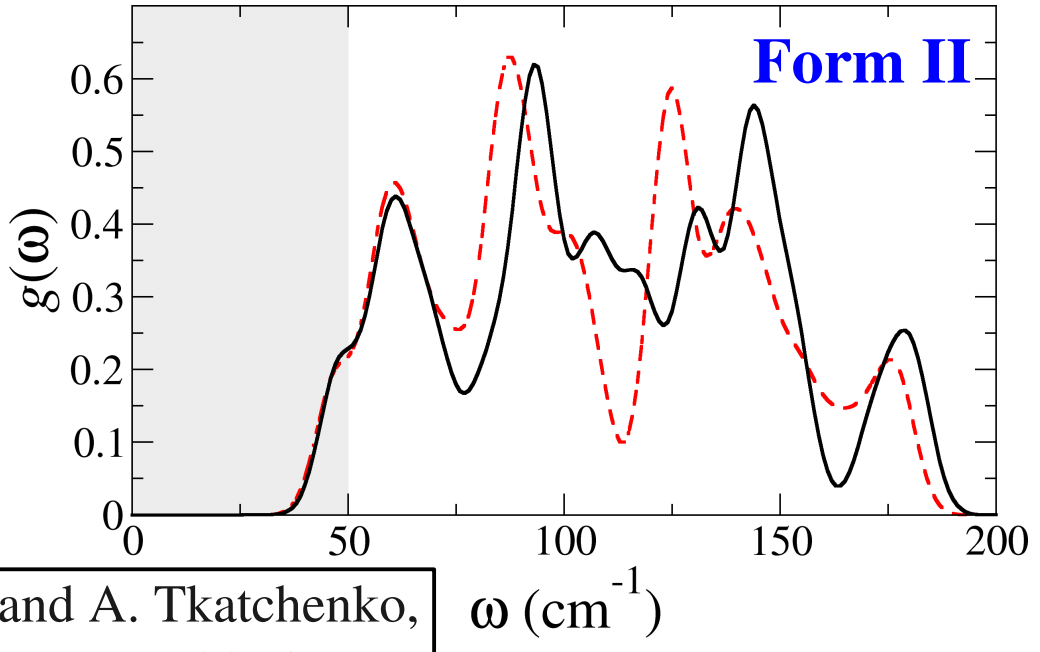
Free energy difference at room temperature between form I and II

(positive means form I is more stable, in kJ/mol)

PBE+TS	-0.18
PBE+TS+ZPE	-0.42
PBE+TS+F_{vib}(298K)	-0.68

PBE+MBD	0.04
PBE+MBD+ZPE	0.35
PBE+MBD+F_{vib}(298K)	**2.56**



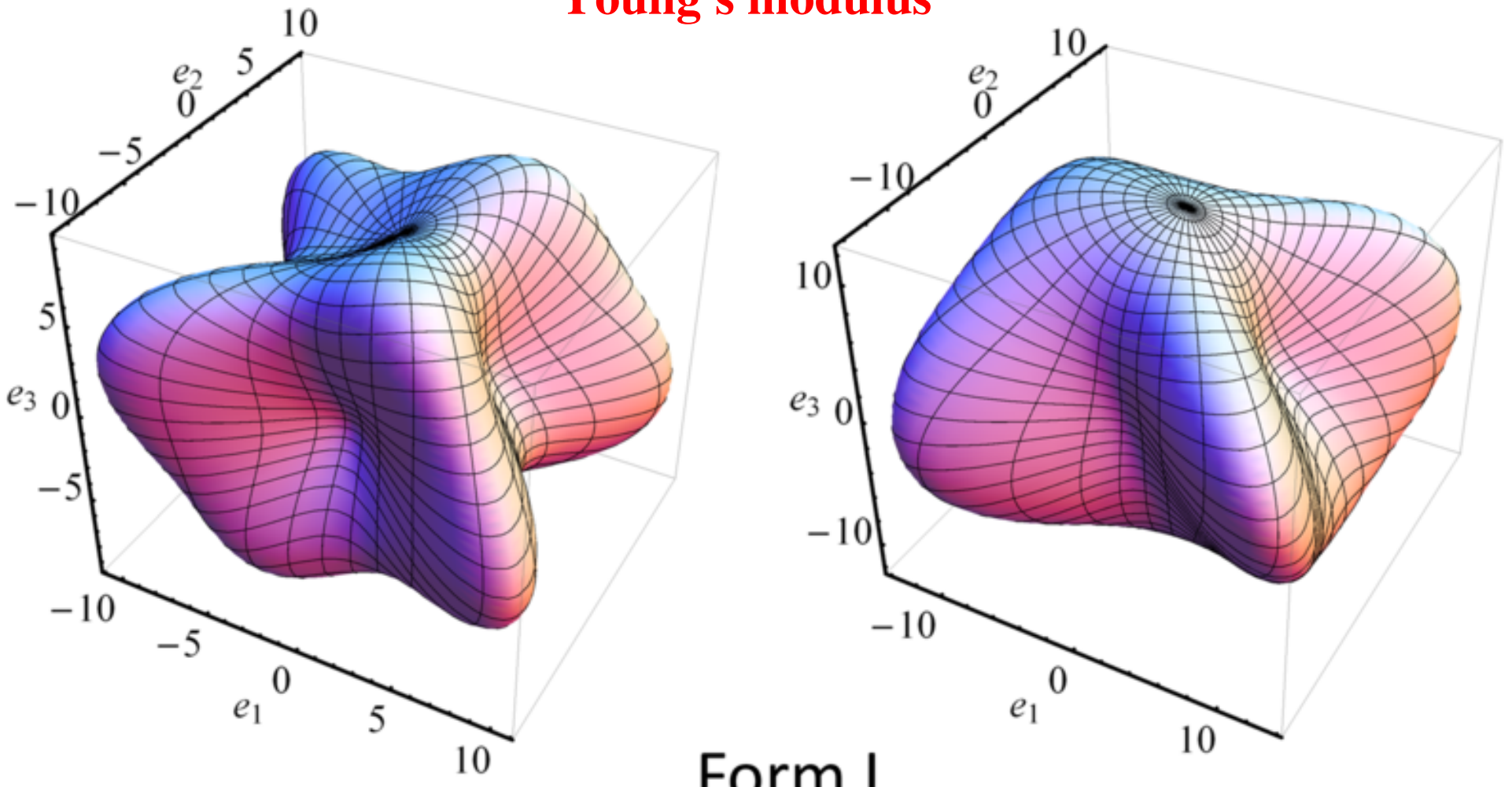


A. M. Reilly and A. Tkatchenko, ***Phys. Rev. Lett.*** (2014).

“Many-Particle Elasticity” in Aspirin

A. M. Reilly and A. Tkatchenko,
Phys. Rev. Lett. (2014).

Young's modulus

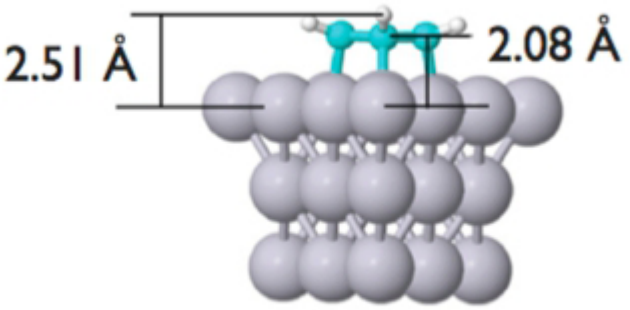


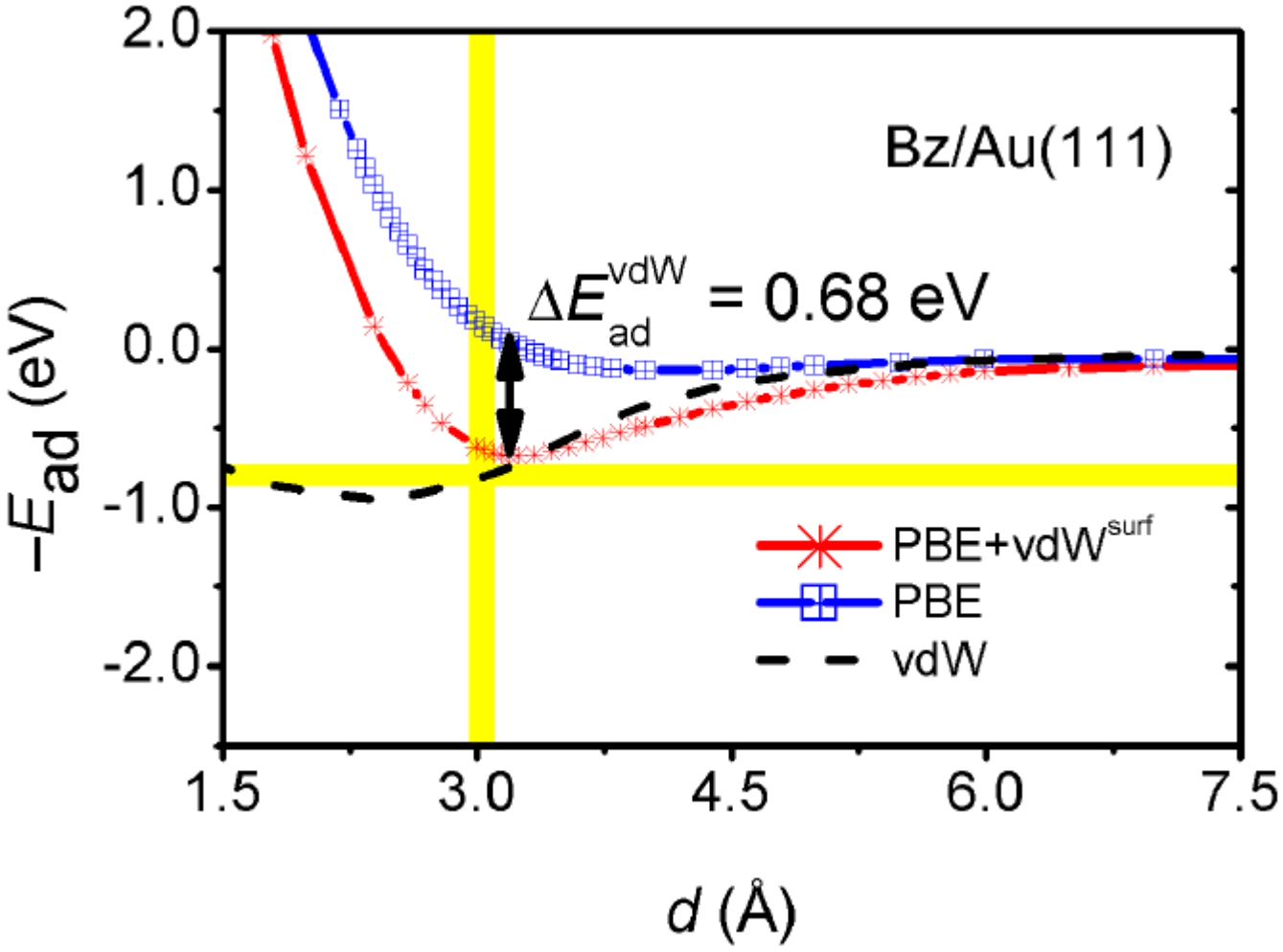
Form I

PBE+MBD

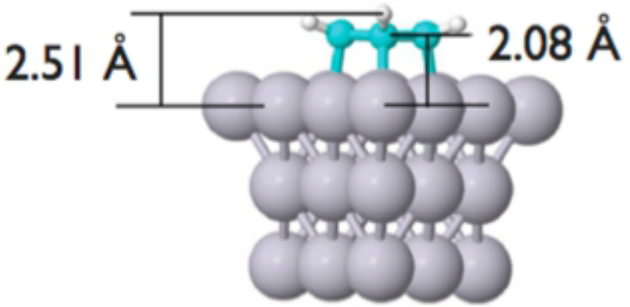
PBE+TS

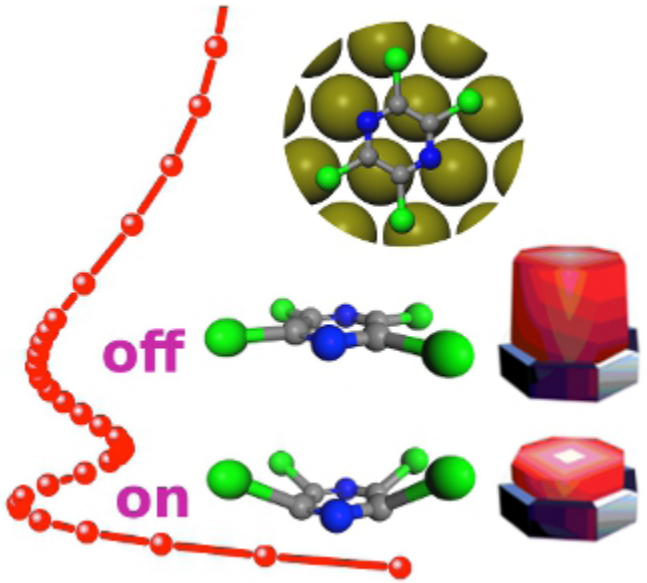
Predictive power of current many-particle methods: Designing a molecular switch

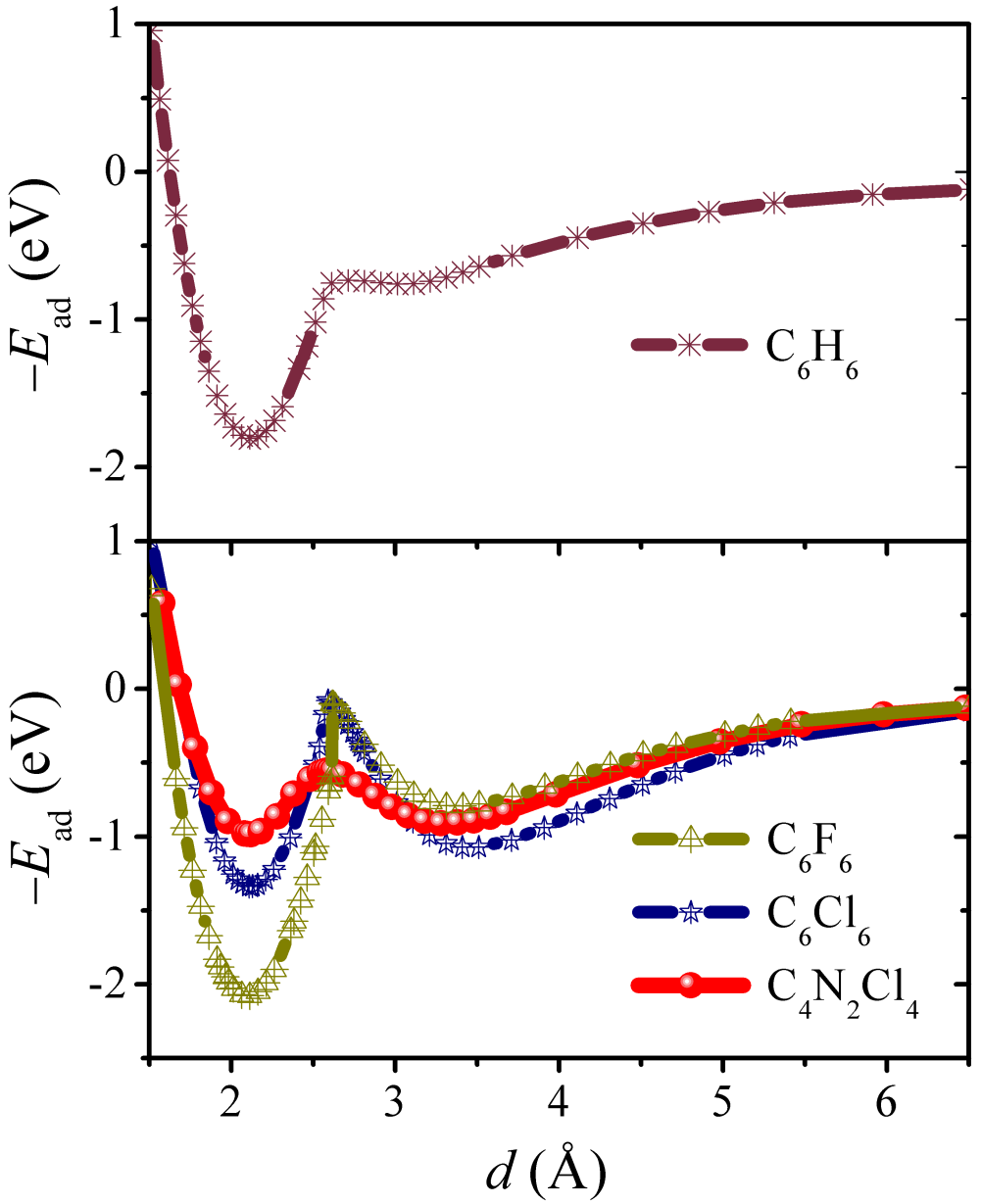




Predictive power of current many-particle methods: Designing a molecular switch







W. Liu, S. Filimonov, J. Carrasco, A. Tkatchenko, ***Nature Comm.*** (2013)

How physicists approach

$$\hat{\mathcal{H}}\Psi = E\Psi$$

How physicists approach

$$\hat{\mathcal{H}}\Psi = E\Psi$$

$$(\hat{T}^e + \hat{T}^{ion} + \hat{V}^{e-e} + \hat{V}^{e-ion} + \hat{V}^{ion-ion})\Psi = E\Psi$$

With: $\Psi(\mathbf{r_1}, \cdots \mathbf{r_N}; \mathbf{R}_1, \cdots \mathbf{R_M})$

$$\hat{T}^e = \sum_{k=1}^{N} \frac{\mathbf{p}_k^2}{2m} \qquad \hat{T}^{ion} = \sum_{I=1}^{M} \frac{\mathbf{P}_I^2}{2M_I}$$

$$\hat{V}^{e-e} = \frac{1}{2}\frac{1}{4\pi\epsilon_0}\sum_{k\neq k'}^{N,N} \frac{e^2}{|\mathbf{r_k} - \mathbf{r_{k'}}|}$$

$$\hat{V}^{ion-ion} = \frac{1}{2}\frac{1}{4\pi\epsilon_0}\sum_{I\neq I'}^{M,M} \frac{Z_I Z_{I'}}{|\mathbf{R_I} - \mathbf{R_{I'}}|}$$

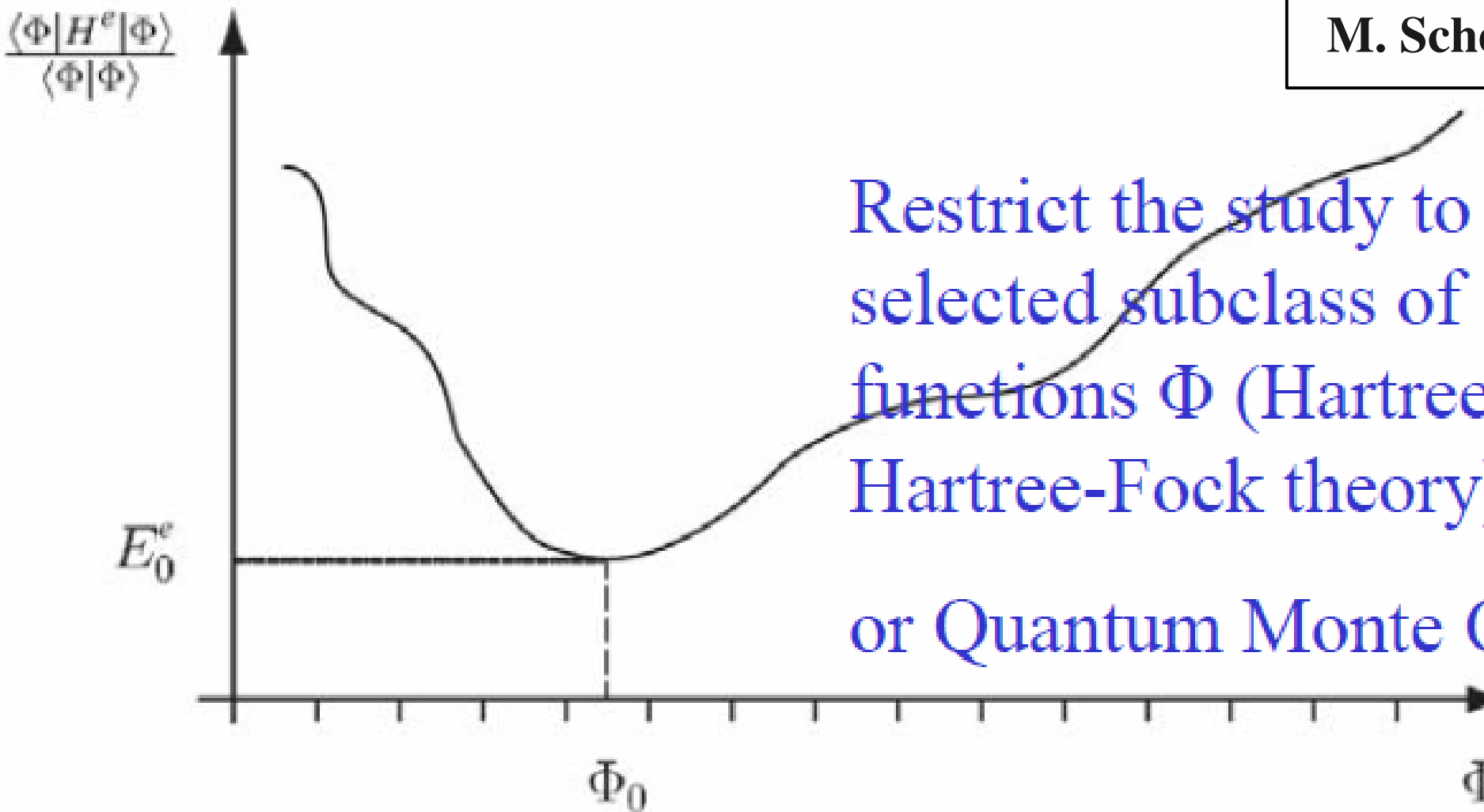
$$\hat{V}^{e-ion}(\mathbf{r_k}, \mathbf{R_I}) = \sum_{\mathbf{k}=1}^{\mathbf{N}}\sum_{\mathbf{I}=1}^{\mathbf{M}} \mathbf{v_I^{ion}}(|\mathbf{R_I} - \mathbf{r_k}|)$$

Slide from
M. Scheffler

Wave-function theories

$$H^e = \sum_{k=1}^{N} -\frac{\hbar^2}{2m}\nabla^2_{\mathbf{r}_k} + \sum_{k=1}^{N} v(\mathbf{r}_k) + \frac{1}{2}\frac{1}{4\pi\varepsilon_0}\sum_{\substack{k,k' \\ k\neq k'}}^{N,N} \frac{e^2}{|\mathbf{r}_k - \mathbf{r}_{k'}|}$$

Slide from
M. Scheffler

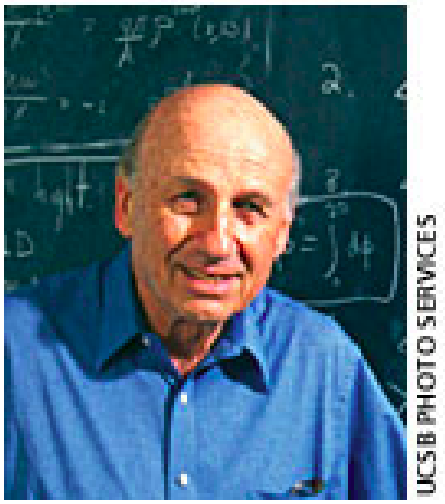


Restrict the study to a selected subclass of functions Φ (Hartree and Hartree-Fock theory);

or Quantum Monte Carlo.

Density-functional theory (DFT): Solid starting point

$$\Psi(\vec{r}_1, \vec{r}_2, \vec{r}_3, \ldots, \vec{r}_n)$$



$$n(\vec{r}) \quad \textbf{or} \quad \rho(\vec{r})$$

Density-functional theory (DFT): Solid starting point

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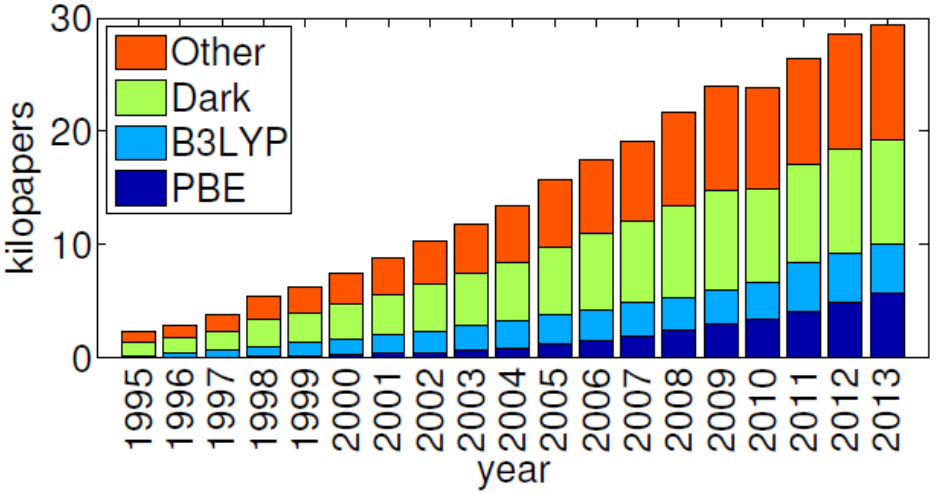
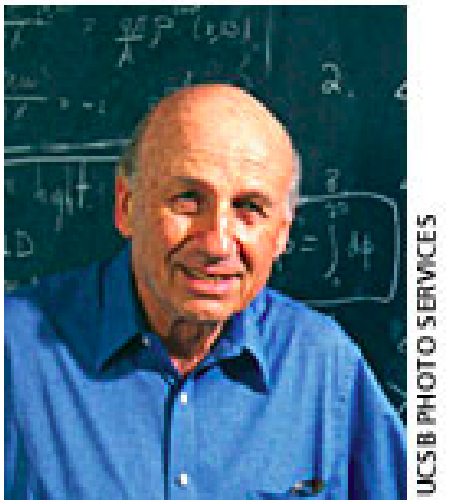


Kieron Burke, 2014

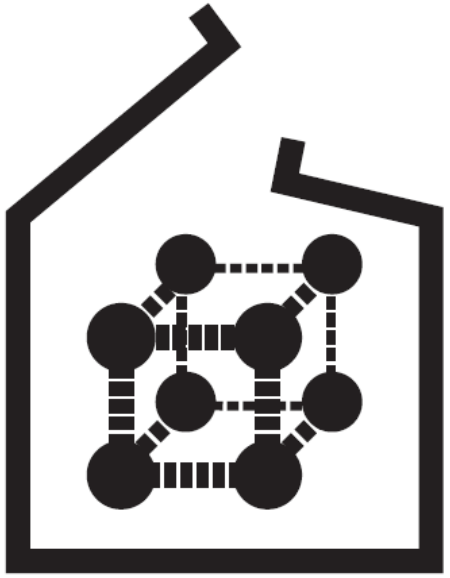


$$n(\vec{r}) \quad \textbf{or} \quad \rho(\vec{r})$$

Density-functional theory (DFT): Solid starting point

$$\Psi\left(\vec{r}_1, \vec{r}_2, \vec{r}_3, \ldots, \vec{r}_n\right)$$

Exchange and **Correlation** functionals

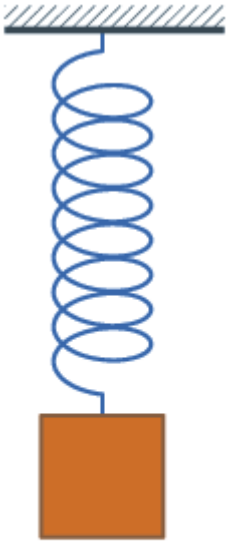


$$n(\vec{r}); \vec{\nabla} n(\vec{r}); \nabla^2 n(\vec{r}); \ldots$$

- ✗ **Self-interaction error**
- ✗ **Lack of long-range correlation (van der Waals interactions)**

$$n\left(\vec{r}\right) \quad \textbf{or} \quad \rho\left(\vec{r}\right)$$

Physicist's Dream: Mapping Electrons to Quantum Harmonic Oscillators (QHO)



Nucleus (q)

Harmonic bond (ω)

"Electron" ($-q$,m)

Model proposed by *W. L. Bade* (1957); and used by *B. J. Berne*; *A. Donchev*; *M. W. Cole*; *G. Martyna*; *K. Jordan*; and others.

Physicist's Dream: Mapping Electrons to Quantum Harmonic Oscillators (QHO)

Nucleus (***q***)

$$\hat{H}_0 = \frac{\hbar^2 \nabla_r^2}{2m} + \frac{1}{2} m\omega^2 (\mathbf{r} - \mathbf{R})^2$$

Harmonic bond ($\boldsymbol{\omega}$)

"Electron" (***-q***,***m***)

Model proposed by *W. L. Bade* (1957); and used by *B. J. Berne*; *A. Donchev*; *M. W. Cole*; *G. Martyna*; *K. Jordan*; and others.

Physicist's Dream: Mapping Electrons to Quantum Harmonic Oscillators (QHO)

Nucleus (***q***)

$$\hat{H}_0 = \frac{\hbar^2 \nabla_r^2}{2m} + \frac{1}{2} m\omega^2 (\mathbf{r} - \mathbf{R})^2$$

Harmonic bond (***ω***)

$$\hat{H} = \sum_{k=1}^{N} \hat{H}_{0k} + \frac{1}{2} \sum_{k \neq k'=1}^{N} q_k q_{k'} \left(\frac{1}{|\mathbf{R}_k - \mathbf{R}_{k'}|} \right.$$

"Electron" (***-q***,***m***)

$$\left. + \frac{1}{|\mathbf{r}_k - \mathbf{r}_{k'}|} - \frac{1}{|\mathbf{r}_k - \mathbf{R}_{k'}|} - \frac{1}{|\mathbf{R}_k - \mathbf{r}_{k'}|} \right)$$

Model proposed by *W. L. Bade* (1957); and used by *B. J. Berne*; *A. Donchev*; *M. W. Cole*; *G. Martyna*; *K. Jordan*; and others.

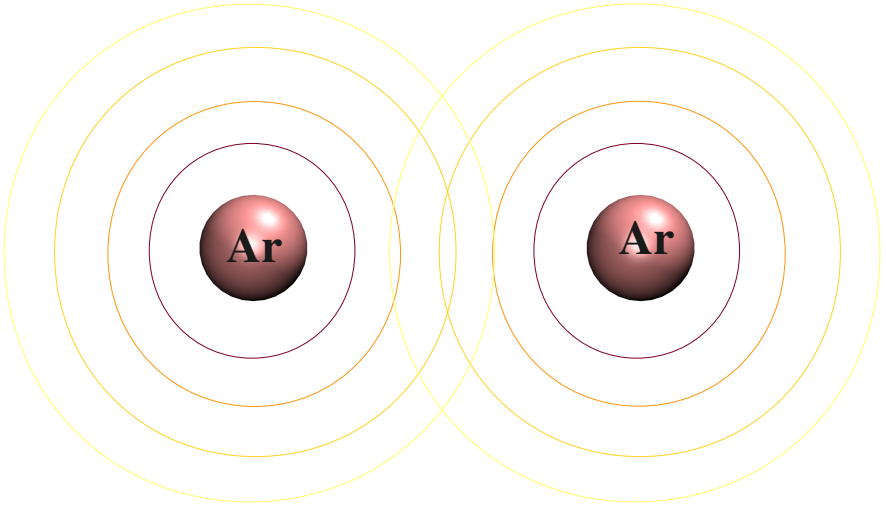
From Dream to Reality:

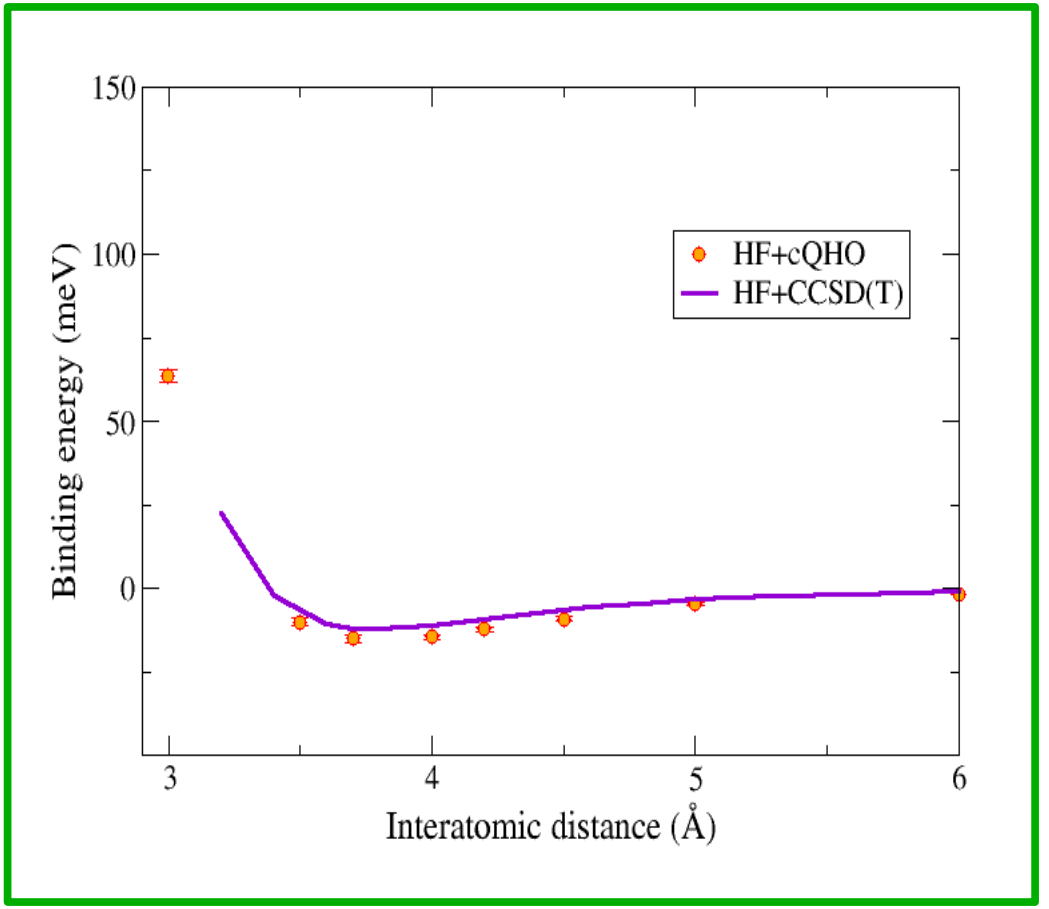
Ar dimer described by two QHOs

- **Coupled QHO correlation energy** computed through **Diffusion Monte Carlo** (exact for bosons)

$$\{\alpha(0), C_6, C_8\} \rightarrow \{m, q, \omega\}$$

- Exchange and electrostatic energy from **Hartree-Fock** (HF)



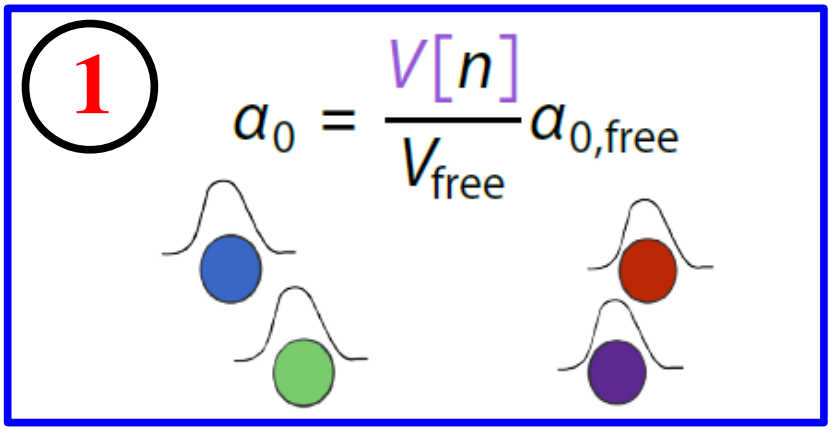


HF+cQHO: almost exact binding energy curve (within 3 meV at minimum) without any specific adjustments.

Fermionic effects in correlation energy kick in only at very short distances.

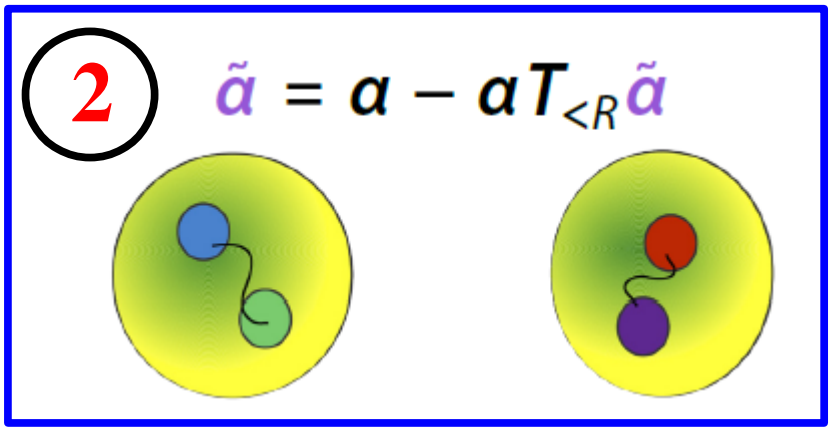
Modeling Real Materials: DFT+MBD method

A. Tkatchenko and M. Scheffler, ***Phys. Rev. Lett.*** (2009)



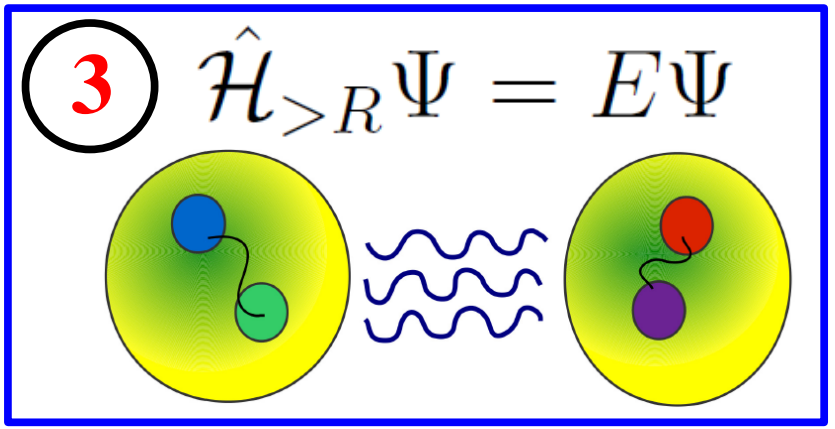
Valence electrons projected to oscillators (Tkatchenko-Scheffler)

A. Tkatchenko, R. A. DiStasio Jr., R. Car, M. Scheffler, ***Phys. Rev. Lett.*** (2012)



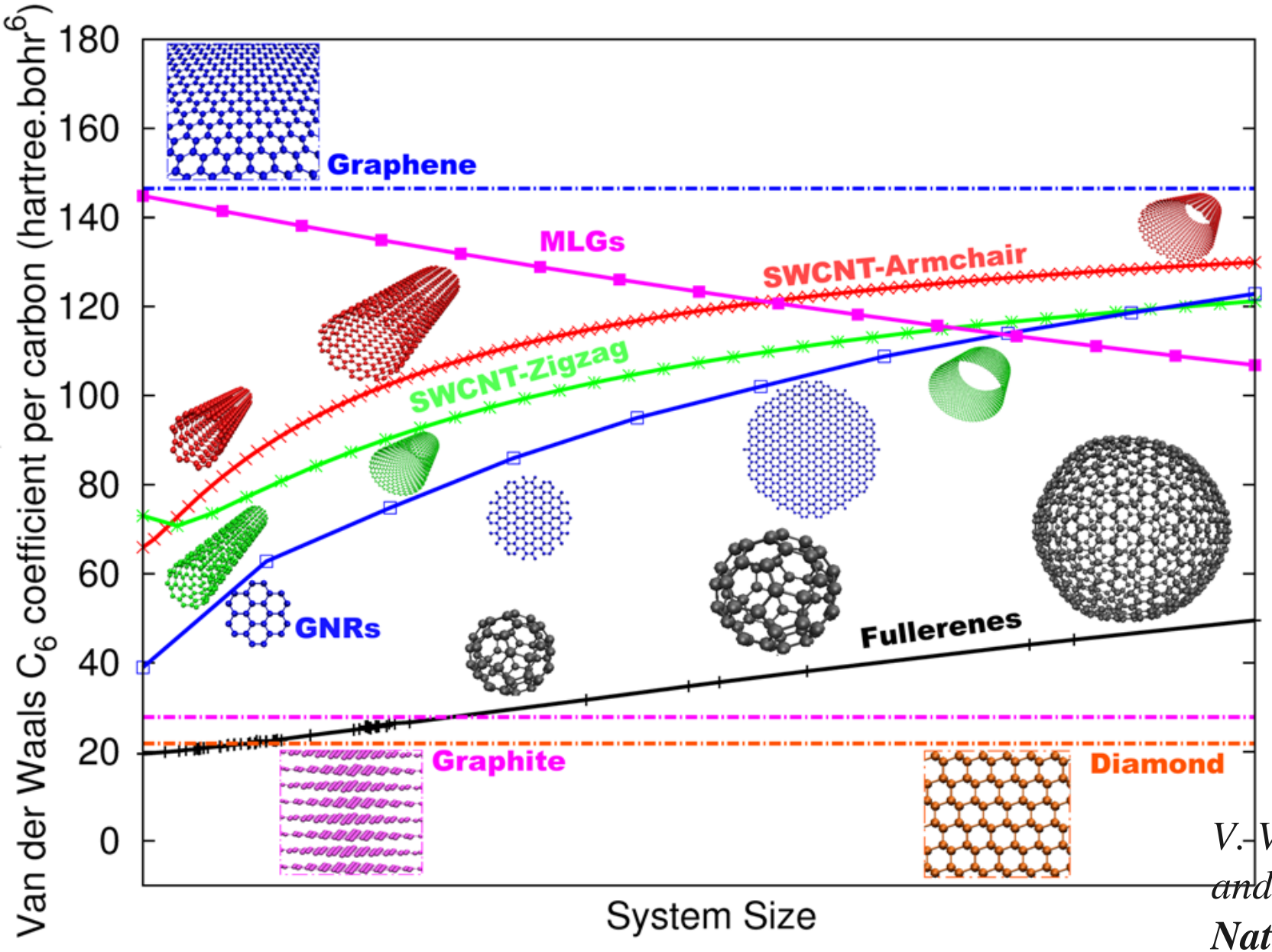
Dyson-like short-range electrodynamic screening

A. Ambrosetti, R. A. Distasio Jr., A. M. Reilly, A. Tkatchenko, ***J. Chem. Phys.*** (2014)



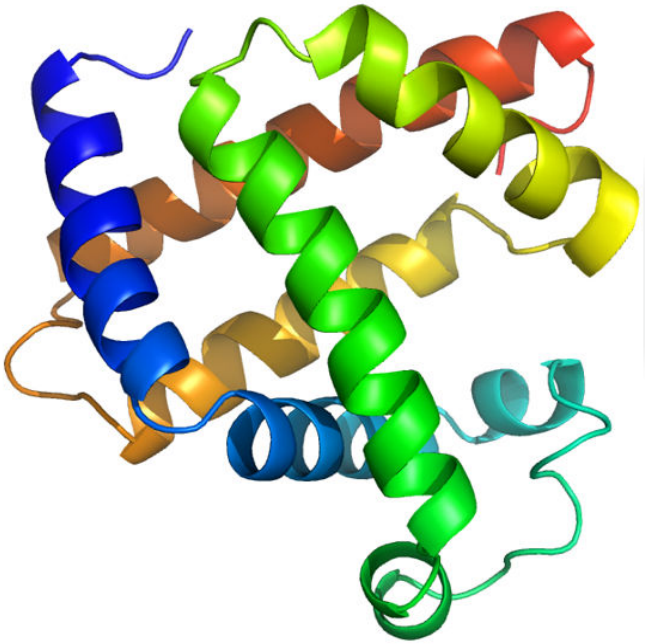
Long-range correlation energy calculated using ACFD

Application of DFT+MBD: Many-particle effects in carbon nanostructures

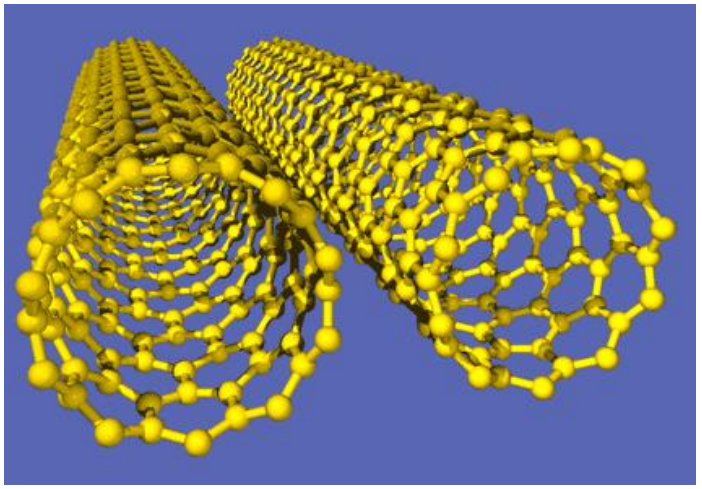


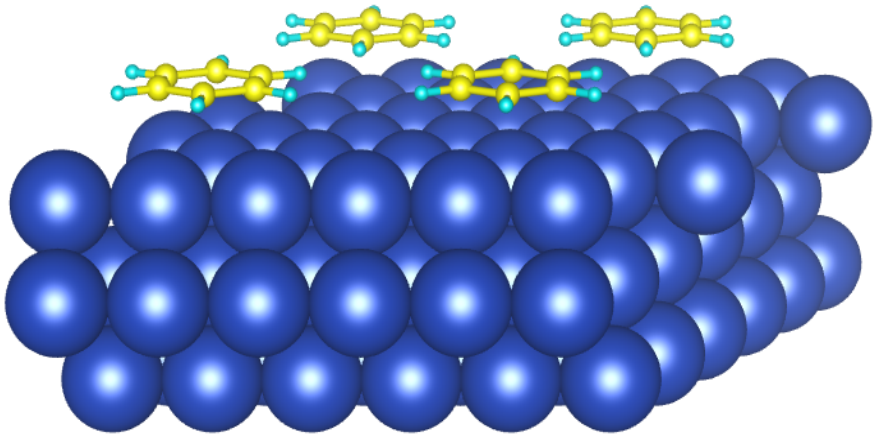
V. V. Gobre and A. Tkatchenko, ***Nature Comm.*** (2013)

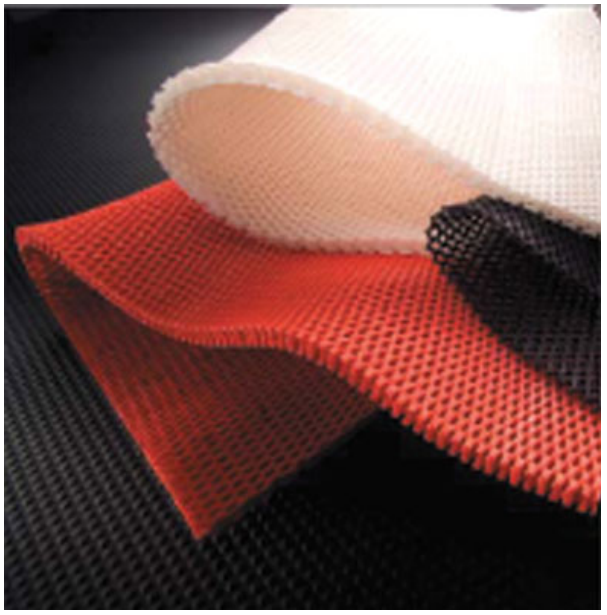
Many-Particle Systems in Physics, Chemistry, Biology, and Materials Science



$$\hat{\mathcal{H}}\Psi = E\Psi$$







Machine Learning for Many-Particle Systems

$$\hat{\mathcal{H}}\Psi = E\Psi$$