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Bringing Atomistic Modeling in <u>Chemistry and Physics</u> and <u>Machine Learning</u> Together

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Cargese, August 22, 2018

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BBDC BERLIN BIG DATA CENTER

Useful text books

- Szabo and Ostlund, *Modern Quantum Chemistry*, Dover 1996

- Parr and Yang, *Density-Functional Theory of Atoms and Molecules*, 1994

- Koch and Holthausen, *A Chemist's Guide to Density Functional Theory*, 2001

- A. J. Stone, *The Theory of Intermolecular Forces*, 1997, 2016

- Wikipedia and Google

CFM 56-7 airplane engine

Final goal: Predict properties and functions of useful molecules and materials

(Atomistic)
Computational Scientist's
Dream ...
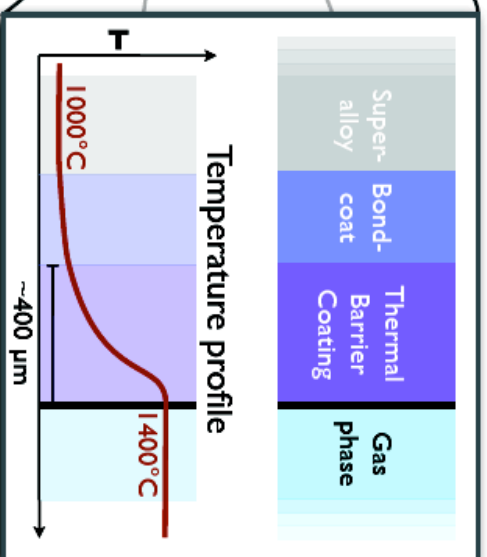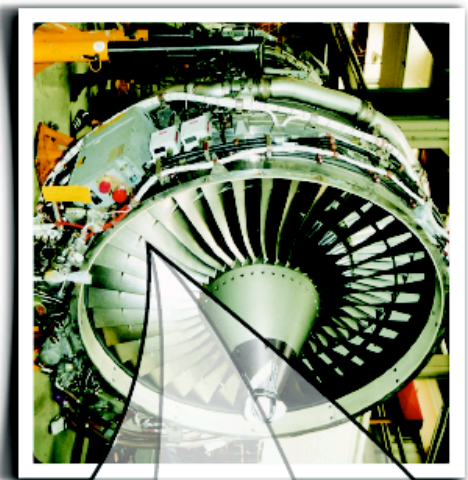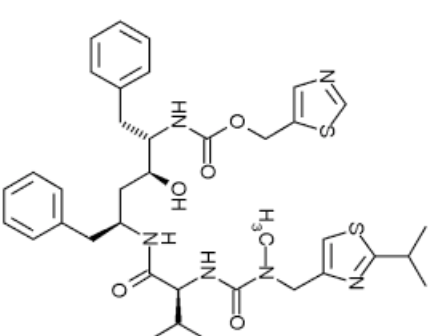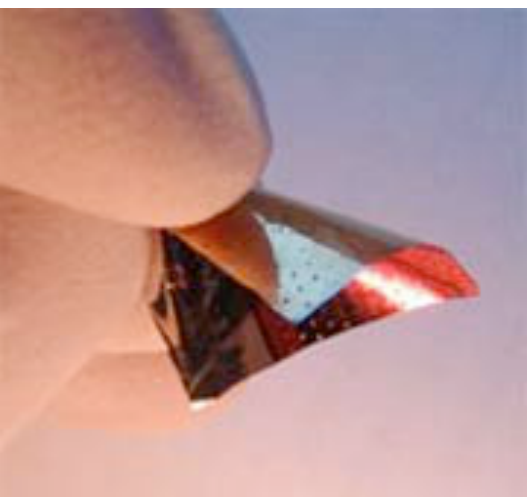
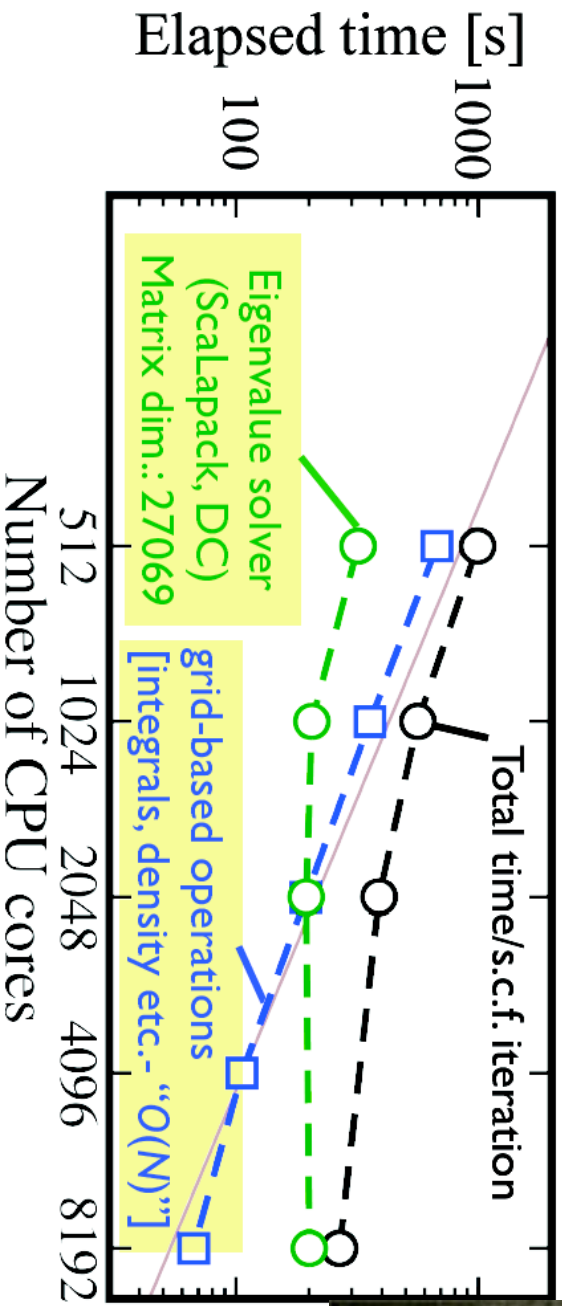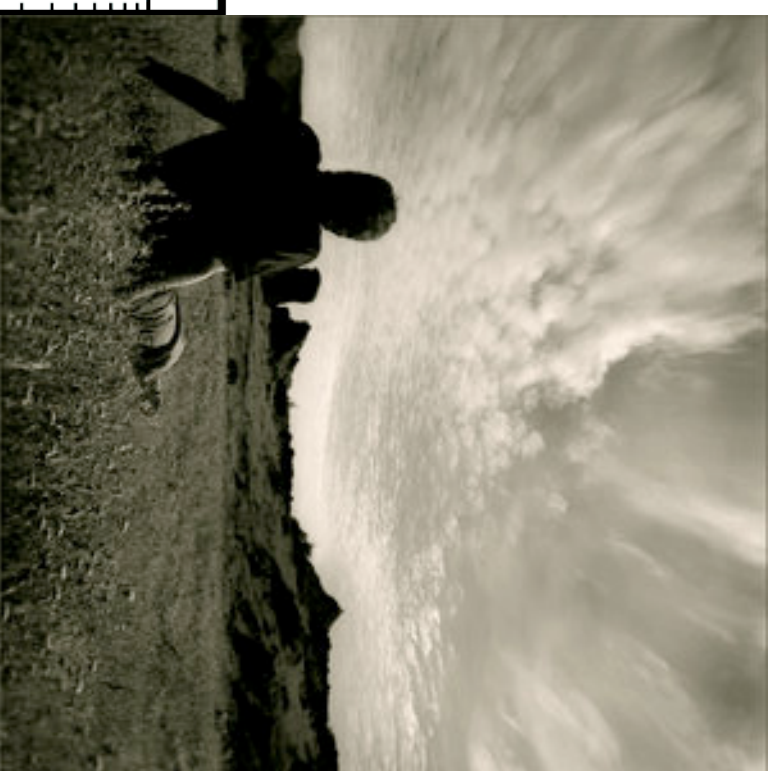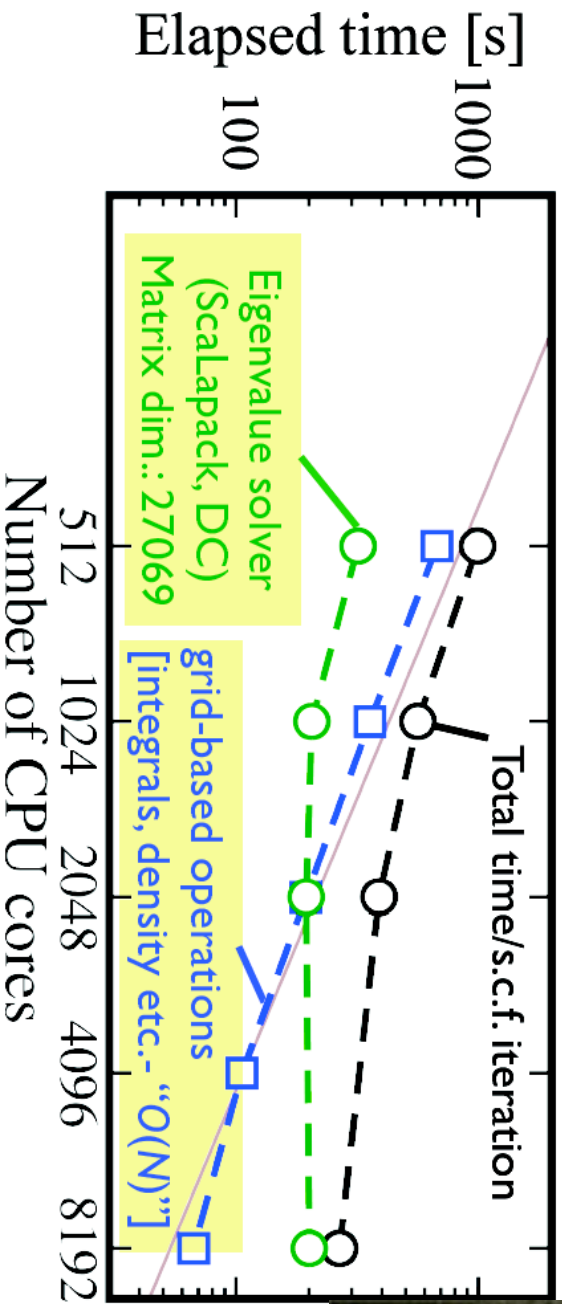# (Atomistic) Computational Scientist's Dream ...

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

(Atomistic) Computational Scientist's Dream ...

Elapsed time [s]
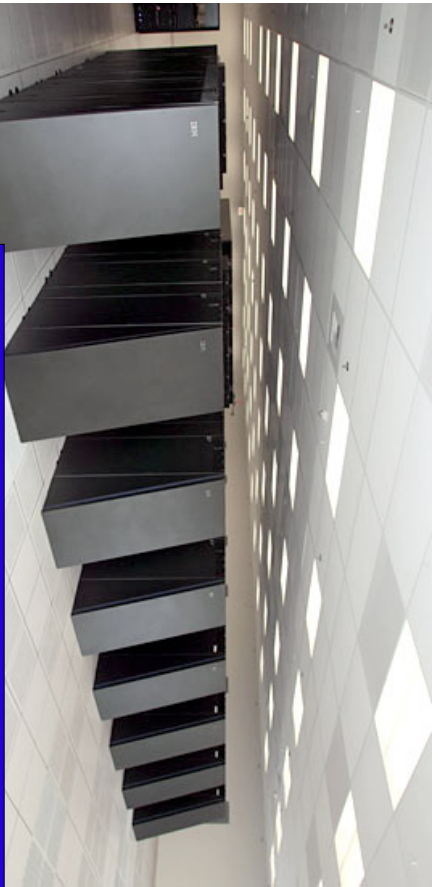
Number of CPU cores

Eigenvalue solver
(ScaLapack, DC)
Matrix dim.: 27069

grid-based operations
[integrals, density etc.- "O(N)"]

Total time/s.c.f. iteration

1000
100

512 1024 2048 4096 8192

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

(Atomistic) Computational Scientist's Dream ...

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

Elapsed time [s] vs **Number of CPU cores**

- Eigenvalue solver (ScaLapack, DC) Matrix dim.: 27069
- grid-based operations [integrals, density etc.- "O(N)"]
- Total time/s.c.f. iteration

Can we be accurate *and* efficient (fast) at the same time ?

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

Elapsed time [s]

Number of CPU cores

1000

100

512   1024   2048   4096   8192

Eigenvalue solver
(ScaLapack, DC)
Matrix dim.: 27069

grid-based operations
[integrals, density etc.- "O(N)"]

(Atom
Comp
Dream

CFM 56-7 airplane engine

Temperature profile

1000°C

~400 µm

1400°C

Super-alloy
Bond-coat
Thermal Barrier Coating
Gas phase
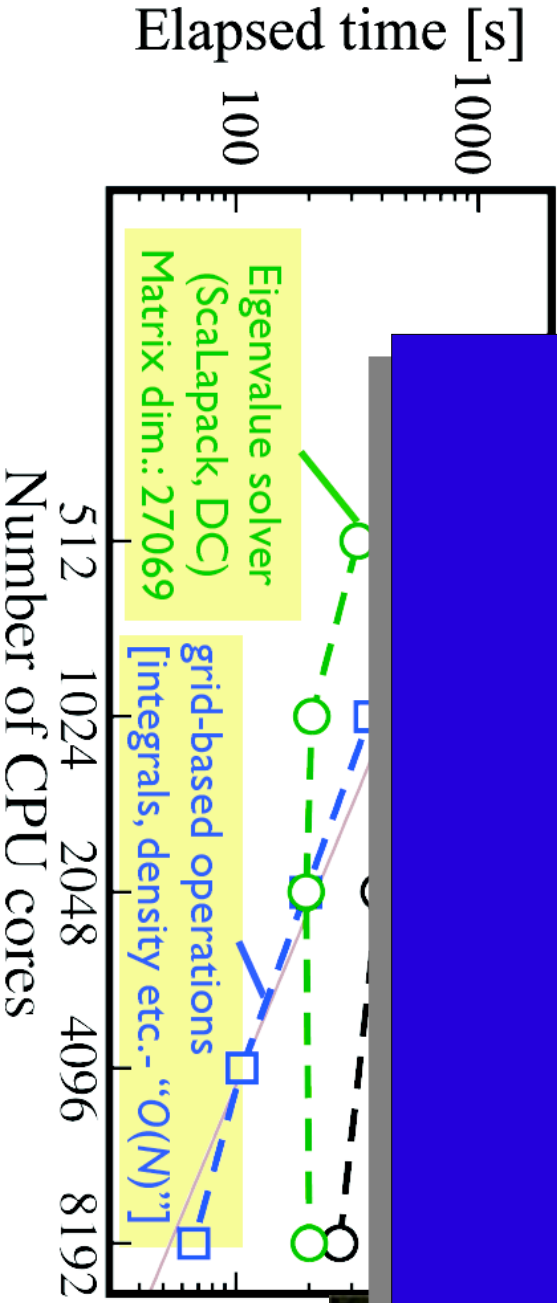
Why we care about

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

?
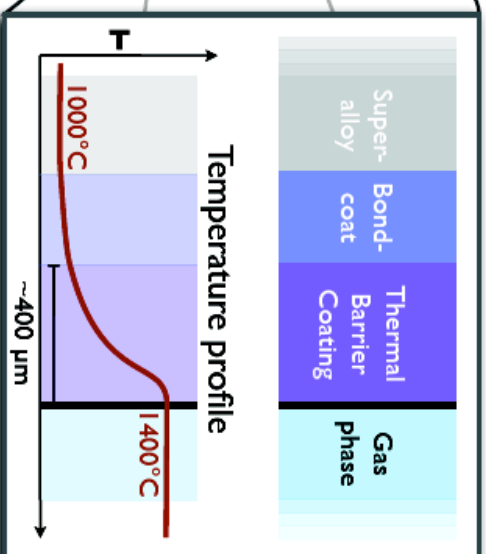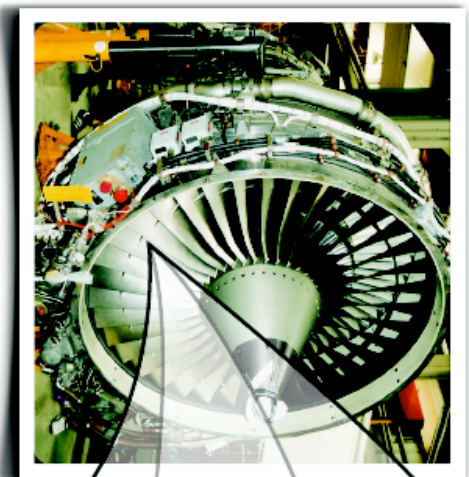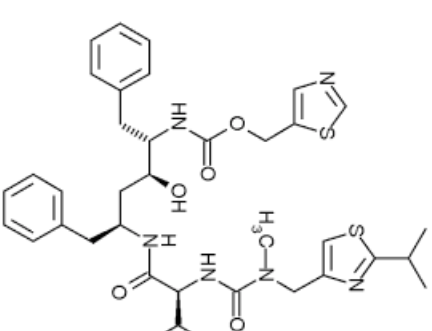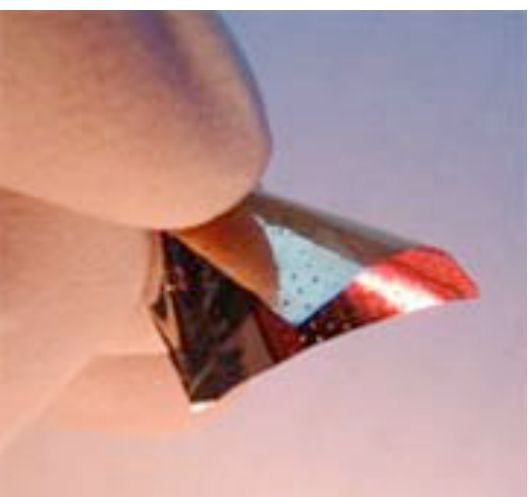
Quantum Atomistic Modeling:
"The Base" of a Multiscale Hierarchy
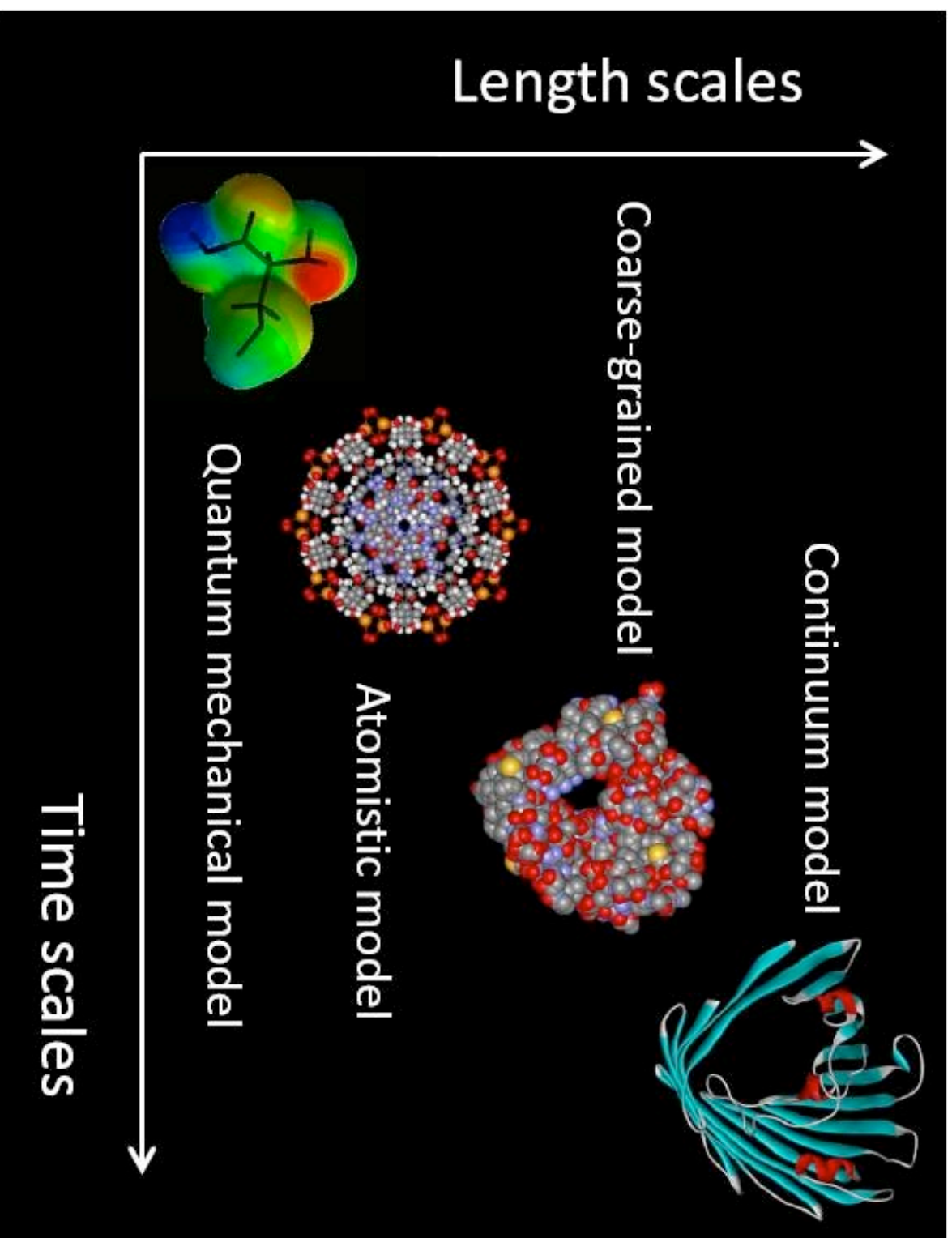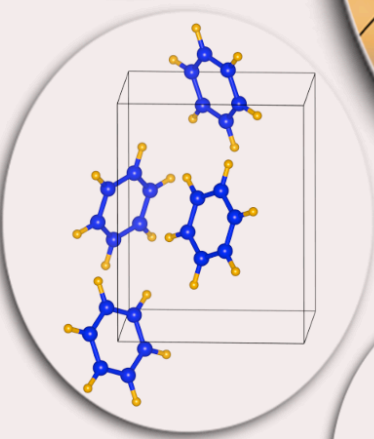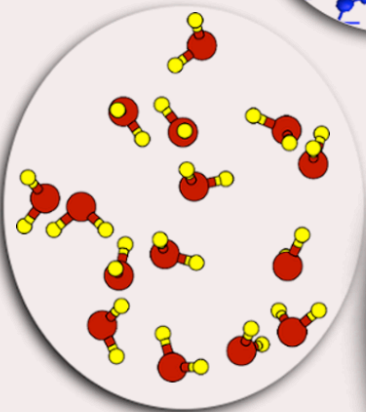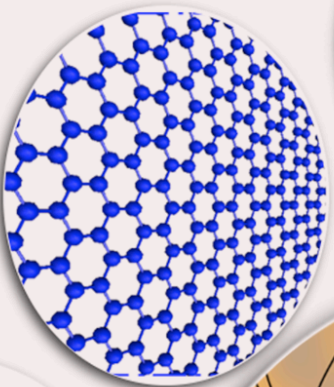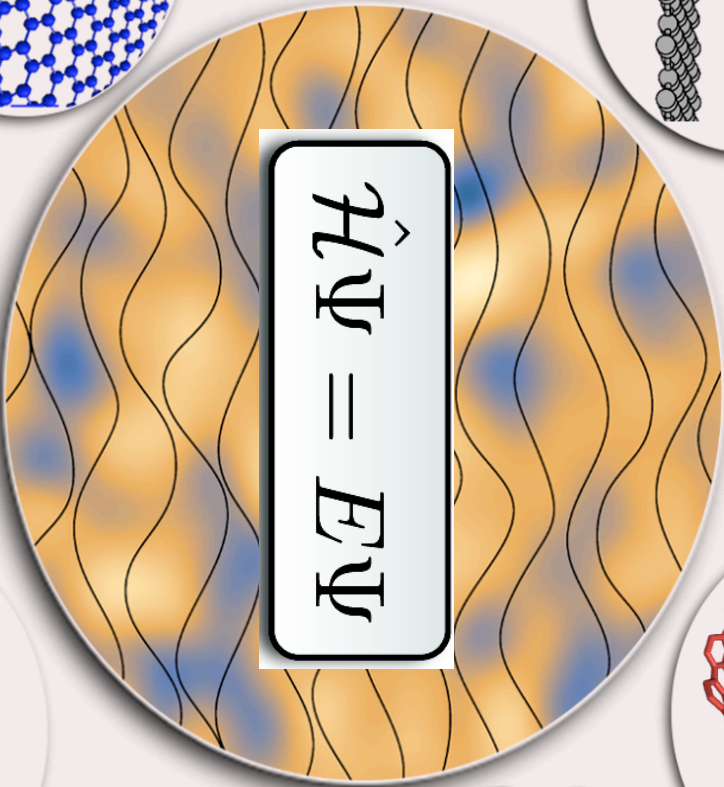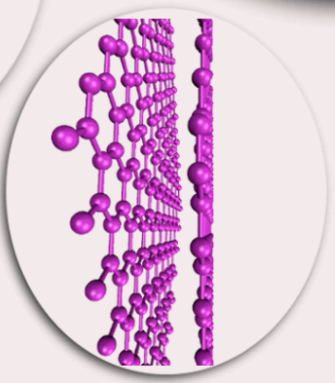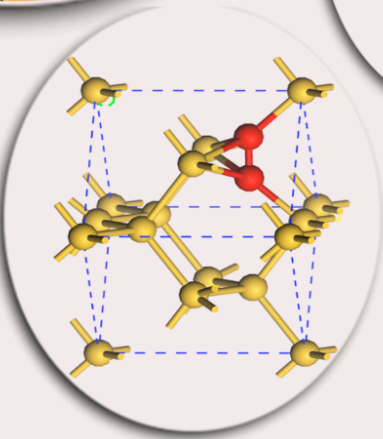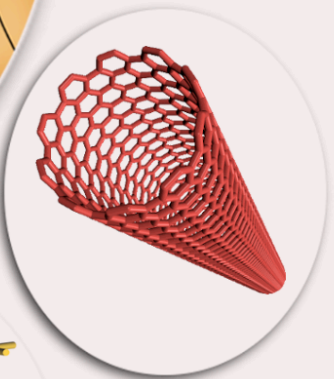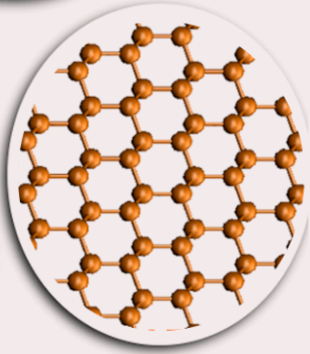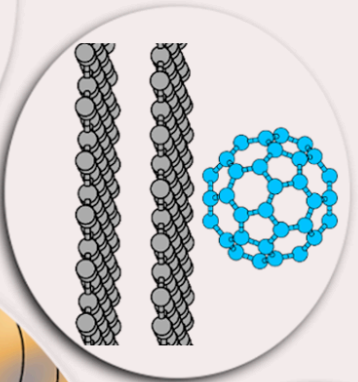
Length scales

Coarse-grained model

Continuum model

Quantum mechanical model

Atomistic model

Time scales

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

Ambrosetti, Ferri, DiStasio Jr., and Tkatchenko, *Science* (2016).

van der Waals power law exponent

Wire - protein separation (D/nm)

Nanotube separation (D/nm)

△ nanotube - nanotube
▢ wire - protein

5.21
6.05
7.07

1.17
1.30
1.44

D
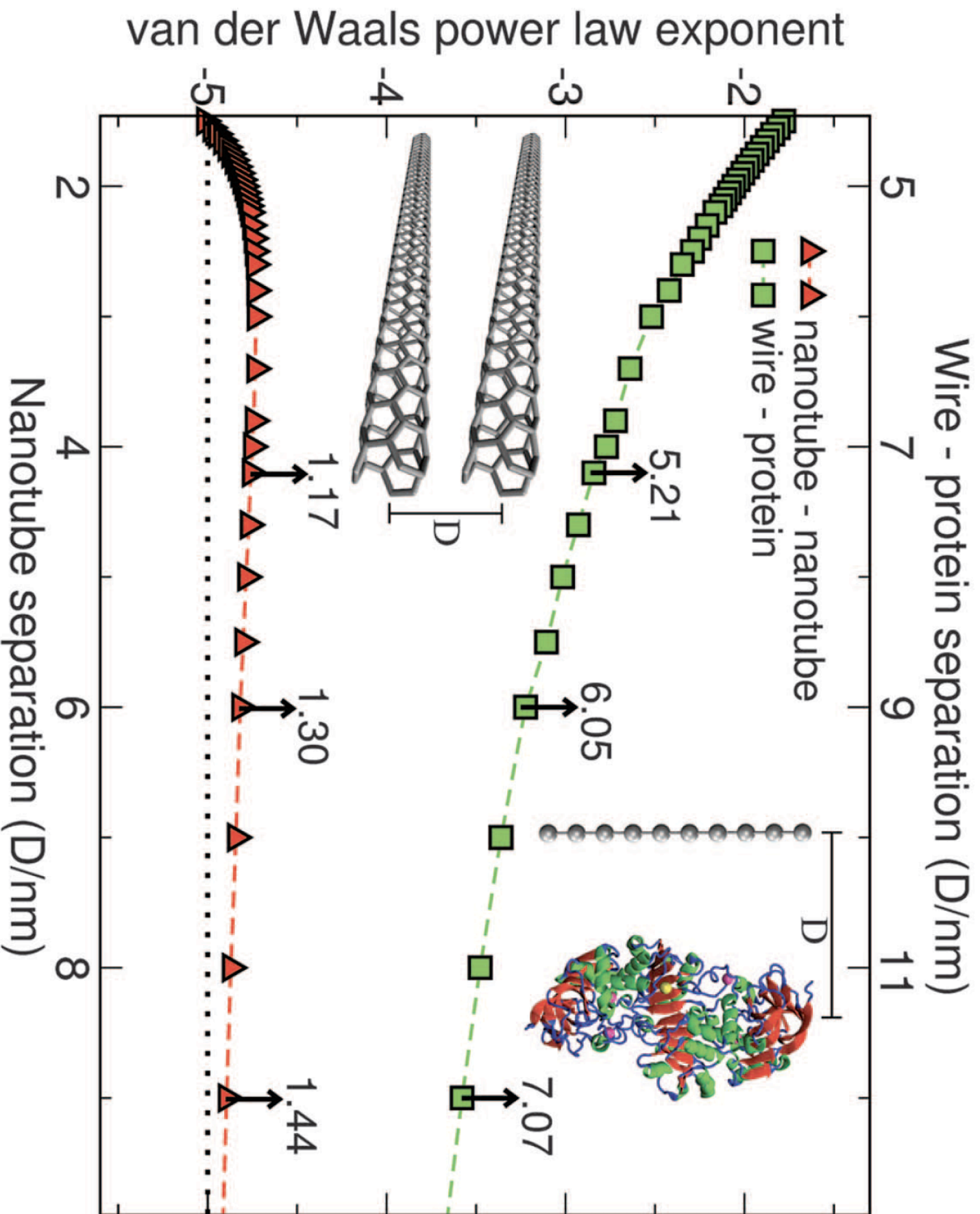
Ambrosetti, Ferri, DiStasio Jr., and Tkatchenko, *Science* (2016).

Relativistic Quantum Effects at Mesoscopic Scales
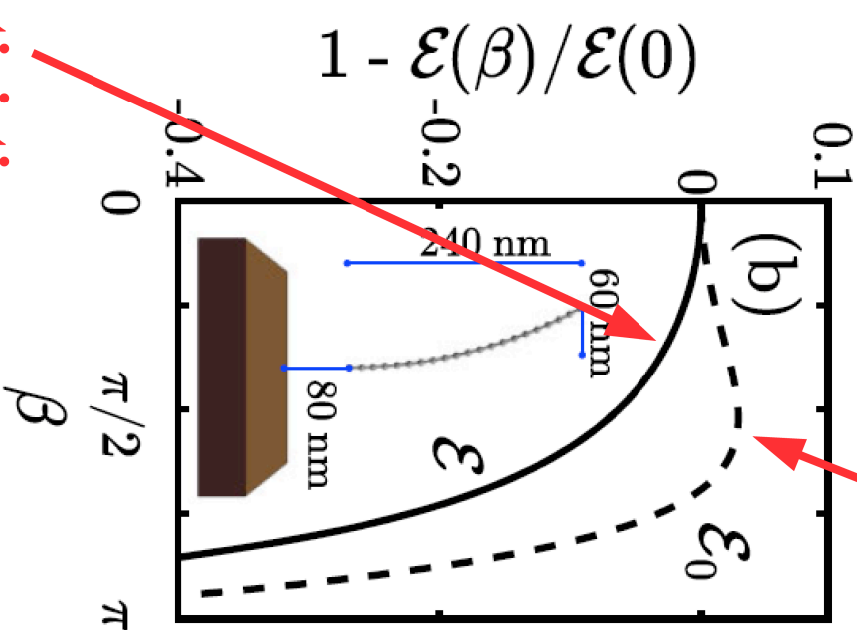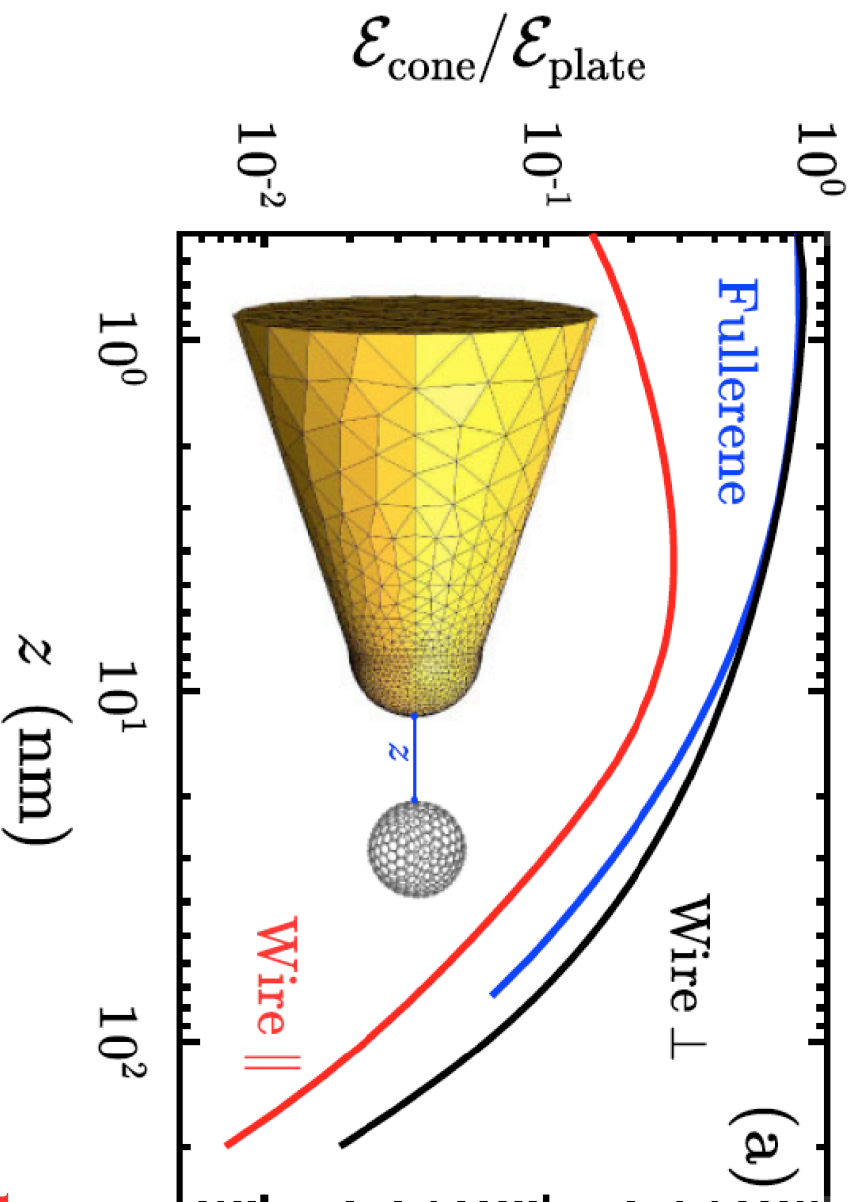
P. S. Venkataram, J. Hermann, A. Tkatchenko, and A. W. Rodriguez, *Phys. Rev. Lett.* 118, 266802 (2017).

QM effects at macroscopic scales:
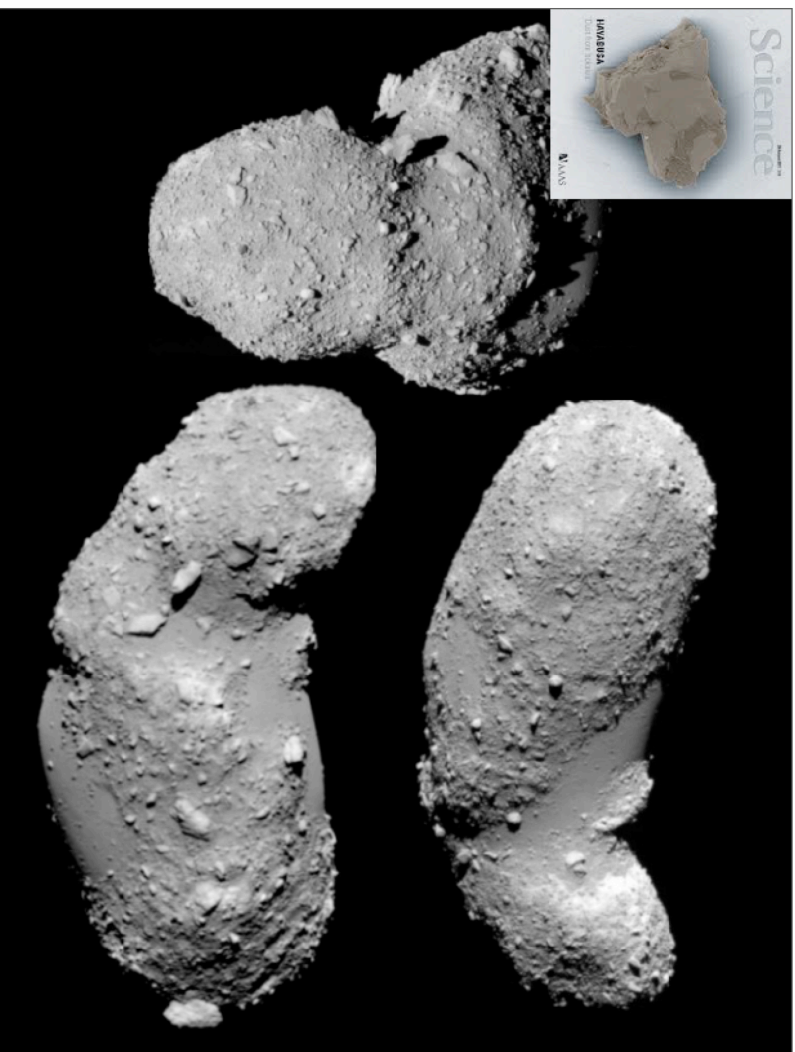
B. Rozitis *et al.*, *Nature* 512, 174 (2014).

For a free particle in free space (vacuum):

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}) \right) |\psi(\mathbf{r}, t)\rangle = i\hbar \frac{d}{dt} |\psi(\mathbf{r}, t)\rangle$$

The Schrödinger Equation

For a free particle in free space (vacuum):

$$\left(-\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) \right) |\psi(\mathbf{r}, t)\rangle = i\hbar \frac{d}{dt} |\psi(\mathbf{r}, t)\rangle$$

Caution: no spin, no relativity, no field-matter interaction (QED), ...

However, for most molecules and materials, this is a VERY good approximation.

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})\right)|\psi(\mathbf{r},t)\rangle = i\hbar\frac{d}{dt}|\psi(\mathbf{r},t)\rangle$$

The Schrödinger Equation

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V(\boldsymbol{r}) \right)|\psi(\boldsymbol{r},t)\rangle = i\hbar\frac{d}{dt}|\psi(\boldsymbol{r},t)\rangle$$

Separation of variables:

$$\frac{1}{f(t)}\frac{df(t)}{dt} = -\frac{iE}{\hbar} \qquad -\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r}) + V(\mathbf{r})\psi(\mathbf{r}) = E\psi(\mathbf{r})$$

The Schrödinger Equation

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}) \right)|\psi(\mathbf{r},t)\rangle = i\hbar\frac{d}{dt}|\psi(\mathbf{r},t)\rangle$$

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$$\psi(\mathbf{r},t) = \psi(\mathbf{r})e^{-iEt/\hbar}$$

The Schrödinger Equation

$$\left(-\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) \right) |\psi(\mathbf{r}, t)\rangle = i\hbar \frac{d}{dt} |\psi(\mathbf{r}, t)\rangle$$

Separation of variables:

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The density $|\psi(\mathbf{r}, t)|^2$ (in this case) is time-independent and such solution is called a **stationary state**
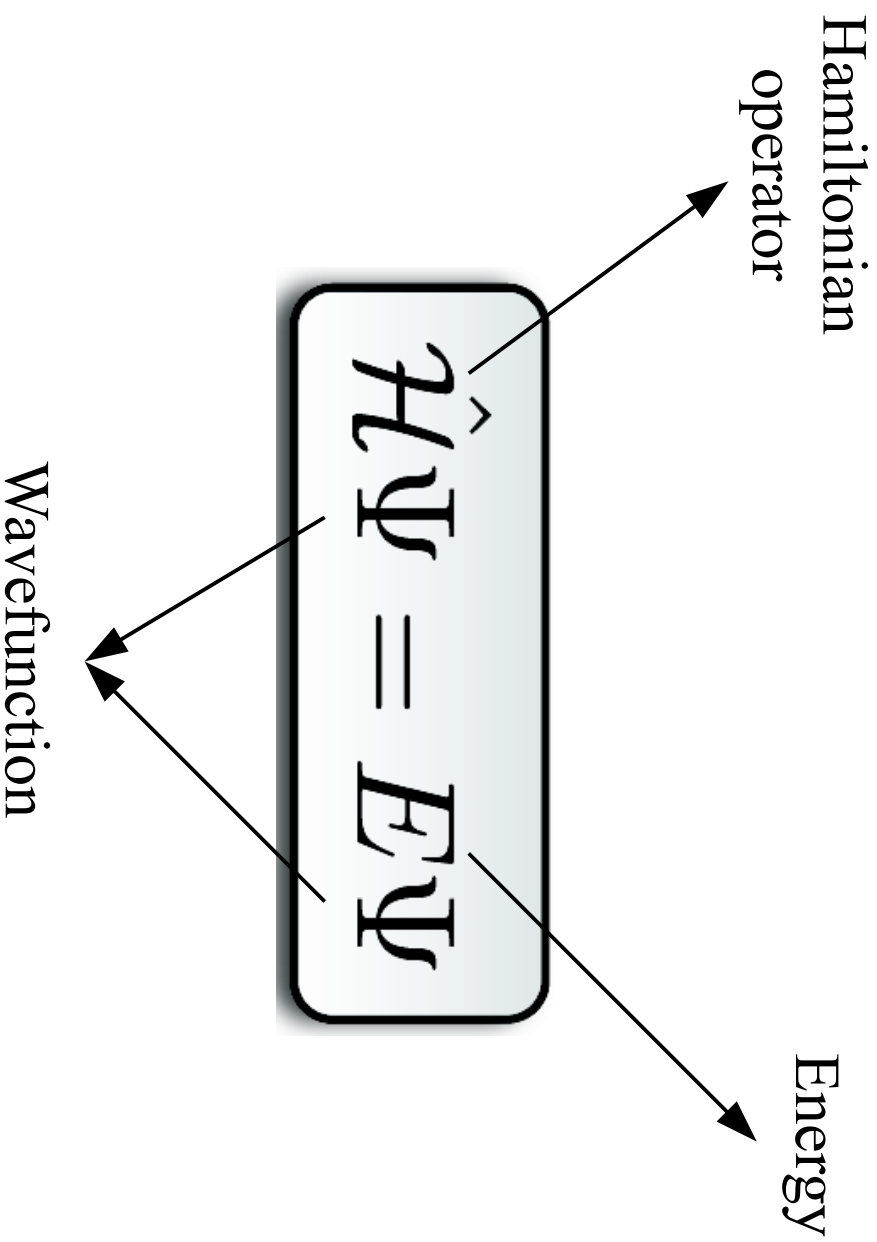
$$\psi(\mathbf{r}, t) = \psi(\mathbf{r}) e^{-iEt/\hbar}$$

The time-independent Schrödinger equation

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

Hamiltonian operator

Wavefunction

Energy

The time-independent Schrödinger equation

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

Hamiltonian operator

Wavefunction

Energy

$$\hat{H} = T + V$$

$$\hat{H} = \sum_i^N -\frac{\hbar^2}{2m}\nabla_{\mathbf{r}_i}^2 + V(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$$

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

$$\hat{H} = T + V$$

$$\hat{H} = \sum_i^N -\frac{\hbar^2}{2m}\nabla_{r_i}^2 + V(r_1, r_2, \ldots, r_N)$$

Hamiltonian operator

Wavefunction

Energy

E_2
E_1
E_0

$\cdots$

$$\Psi_k(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \ldots, \mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3, \ldots)$$

The time-independent Schrödinger equation

Few remarks:

• Wavefunction can be an immensely complex object for N particles

• Wavefunctions are difficult to interpret. Densities (square of the wavefunction) and other expectations values are typically used for conceptual insights.

• In classical mechanics: $[T,V] = 0$. Particle kinetic energies are additive.

• In quantum mechanics: $[T,V] \neq 0$. Kinetic energy is non-additive, i.e. has a many-body nature. Energy can be generally expressed as an infinite power series in terms of distances (angles, ...) between particles.

The time-independent Schrödinger equation

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

• One particle: free particle, particle in a box, harmonic (and some anharmonic) oscillators, Dirac delta potential, hydrogen atom, H_2^+, …

• Two particles: two non-interacting particles, "harmonium" atom, …

• Three and more particles: non-interacting particles, effective 1D Hamiltonians (Hubbard model), N harmonic oscillators coupled with dipole potential, …

• Most realistic Hamiltonians have no known analytic (or exact numerical) solution. This leads to a zoo of approximations.

Molecular and solid-state Hamiltonians

$$\hat{\mathcal{H}} = -\underbrace{\frac{1}{2}\sum_{i=1}^{P}\nabla_{r_i}^2}_{\text{Electronic KE}} - \underbrace{\frac{1}{2M_I}\sum_{I=1}^{Q}\nabla_{R_I}^2}_{\text{Nuclear KE}} - \underbrace{\sum_{i=1}^{P}\sum_{I=1}^{Q}\frac{Z_I}{|r_i - R_I|}}_{\text{Electron-Nuclear attraction energy}}$$

$$+ \underbrace{\sum_{i=1}^{P}\sum_{j>i}^{P}\frac{1}{|r_i - r_j|}}_{\text{Electron-Electron repulsion energy}} + \underbrace{\sum_{I=1}^{Q}\sum_{J>I}^{Q}\frac{Z_I Z_J}{|R_I - R_J|}}_{\text{Nucleus-Nucleus repulsion energy}}$$

Nuclei are much heavier than electrons:

H nucleus is ~1800 times heavier than an electron

$$\hat{\mathcal{H}} = -\frac{1}{2}\sum_{i=1}^{P}\nabla_{r_i}^2 - \sum_{I=1}^{Q}\frac{1}{2M_I}\nabla_{R_I}^2 - \sum_{i=1}^{P}\sum_{I=1}^{Q}\frac{Z_I}{|r_i - R_I|}$$

$$\underbrace{\qquad}_{\text{Electronic KE}} \qquad \underbrace{\qquad}_{\text{Nuclear KE}} \qquad \underbrace{\qquad}_{\text{Electron-Nuclear attraction energy}}$$

$$+ \sum_{i=1}^{P}\sum_{j>i}^{P}\frac{1}{|r_i - r_j|} + \sum_{I=1}^{Q}\sum_{J>I}^{Q}\frac{Z_I Z_J}{|R_I - R_J|}$$

$$\underbrace{\qquad}_{\text{Electron-Electron repulsion energy}} \qquad \underbrace{\qquad}_{\text{Nucleus-Nucleus repulsion energy}}$$

Separating nuclei and electrons: Born-Oppenheimer approximation

Nuclei are much heavier than electrons:
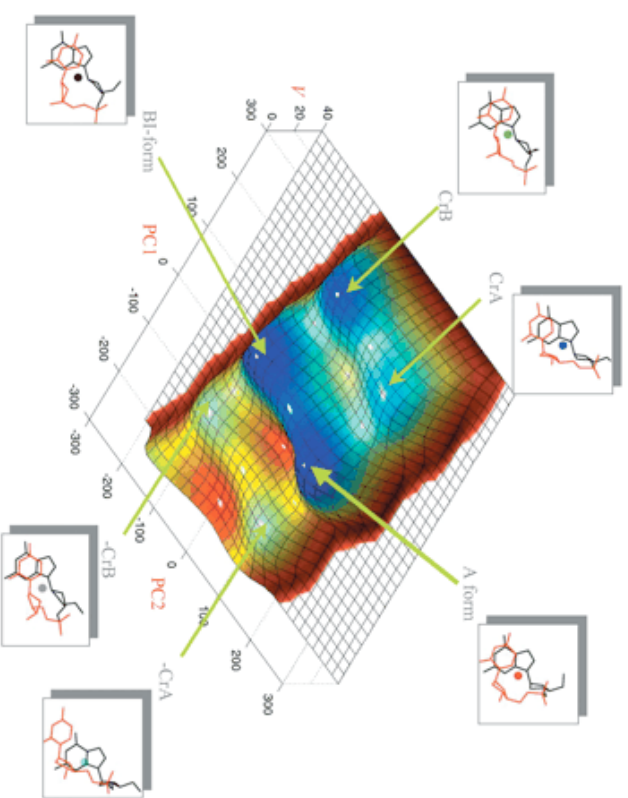H nuclei is ~1800 times heavier than an electron

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

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

The wavefunction in $3(N+M)$ dimensions is split in two wavefunctions with $3N$ and $3M$ dimensions.

Most often, the nuclear degrees of freedom $\mathbf{R}_i$ are treated classically, *via* Newton's equations of motion

For each $\{\mathbf{R}_i\}$, the solution of the electronic Schrödinger equation provides energies/forces, generating a so-called **potential-energy surface** (PES)

"Standard" electronic structure atomistic modeling procedure
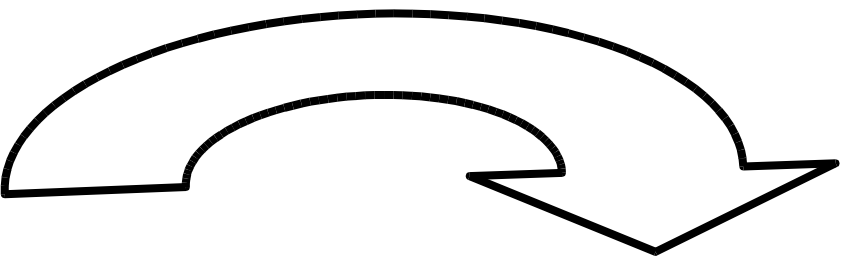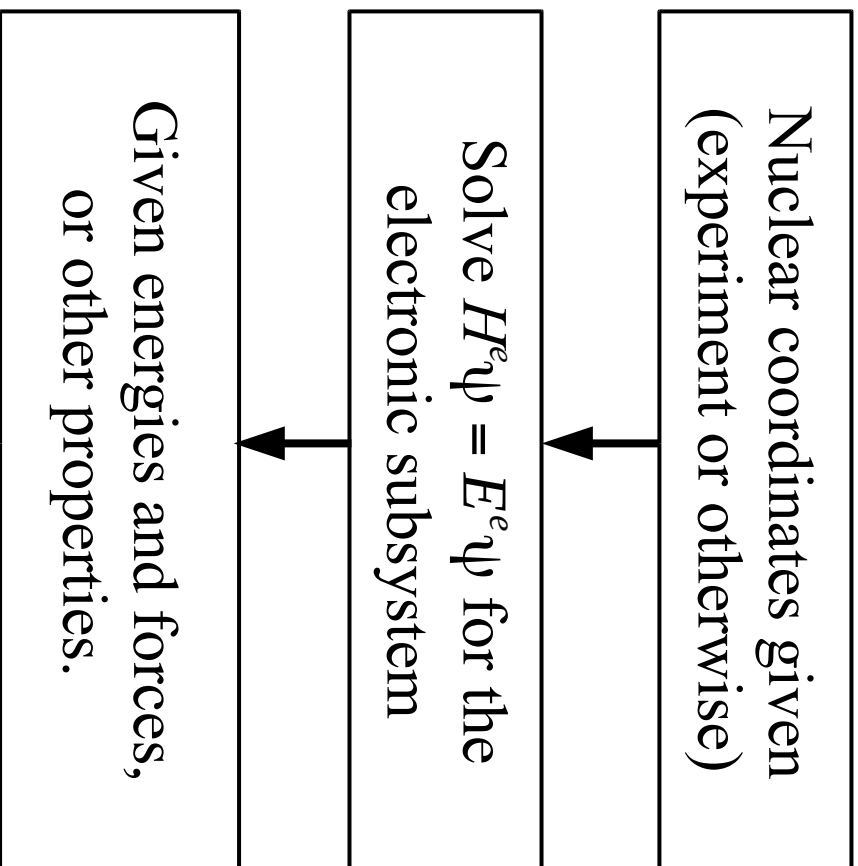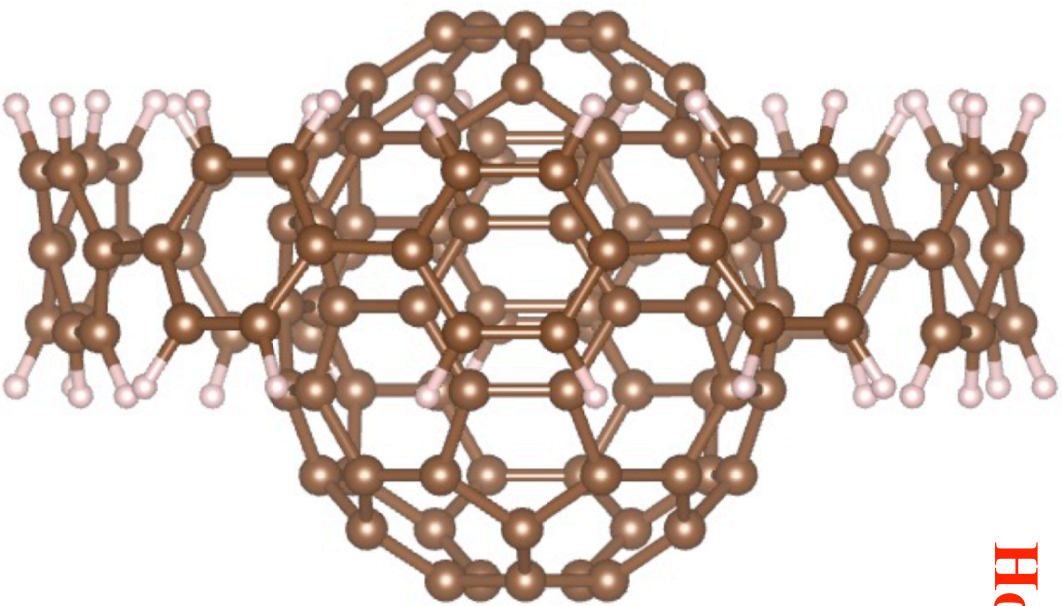
Nuclear coordinates given (experiment or otherwise)

Solve $H^e \psi = E^e \psi$ for the electronic subsystem

Given energies and forces, or other properties.

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

Host-guest chemistry

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

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

Host-guest chemistry

$$\Psi(\vec{r}_1, \vec{r}_2, \vec{r}_3, \dots, \vec{R}_1, \vec{R}_2, \vec{R}_3, \dots)$$
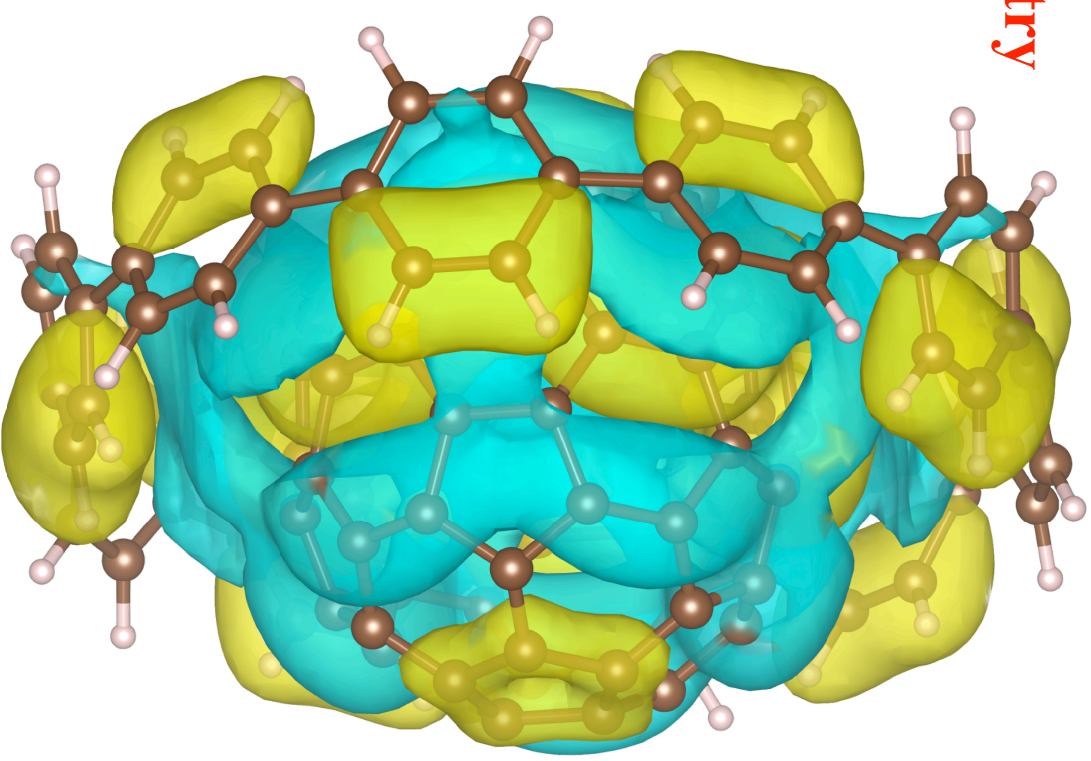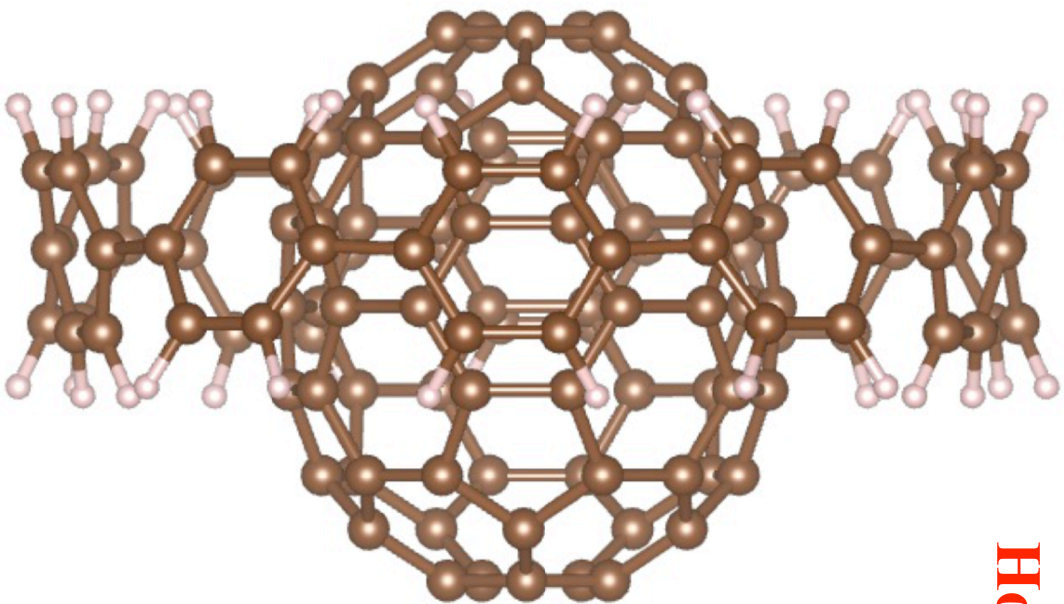
Why is $\hat{\mathcal{H}}\Psi = E\Psi$ complex? –
Collective many-particle states

Hybrid organic/inorganic systems
(CuPc on Ag(100) surface)
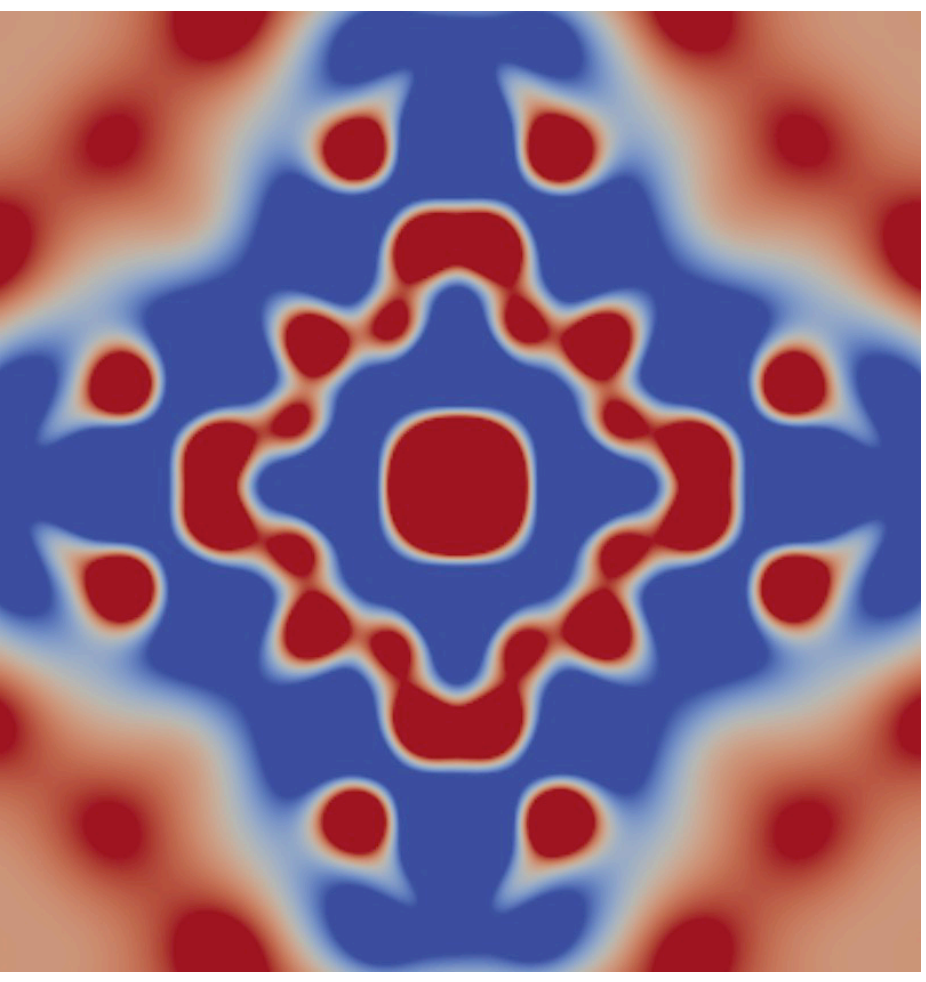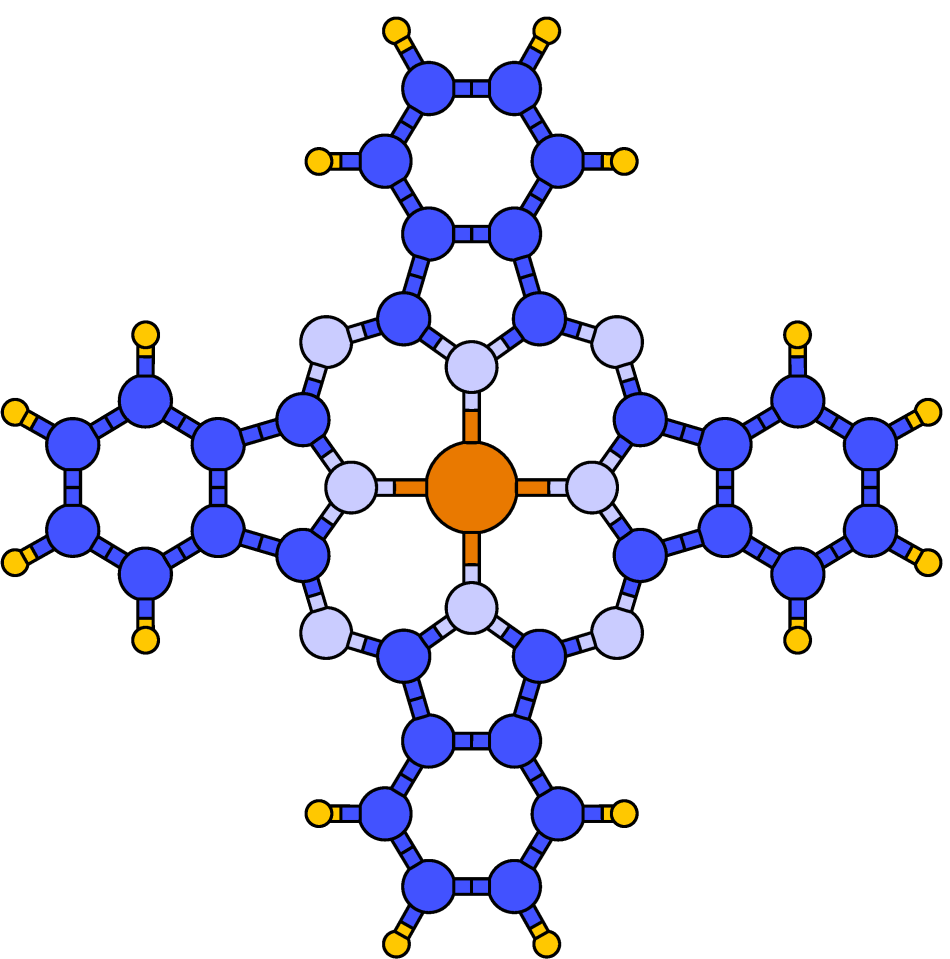
$\Psi(\vec{r}_1, \vec{r}_2, \vec{r}_3, \ldots, \vec{R}_1, \vec{R}_2, \vec{R}_3, \ldots)$

Current state-of-the-art of atomistic modeling

$$H\Psi = E\Psi$$

Accuracy,
Reliability,
and
Predictive
Power

Full
CI

Wavefunction
based methods
(MP2, RPA, CCSD(T),....)

Density-functional theory
with (semi)-local and hybrid functionals

Semi-empirical methods
(AM1, PM6, CNDO, tight-binding)

Empirical potentials ("force fields")
(no explicit electrons)
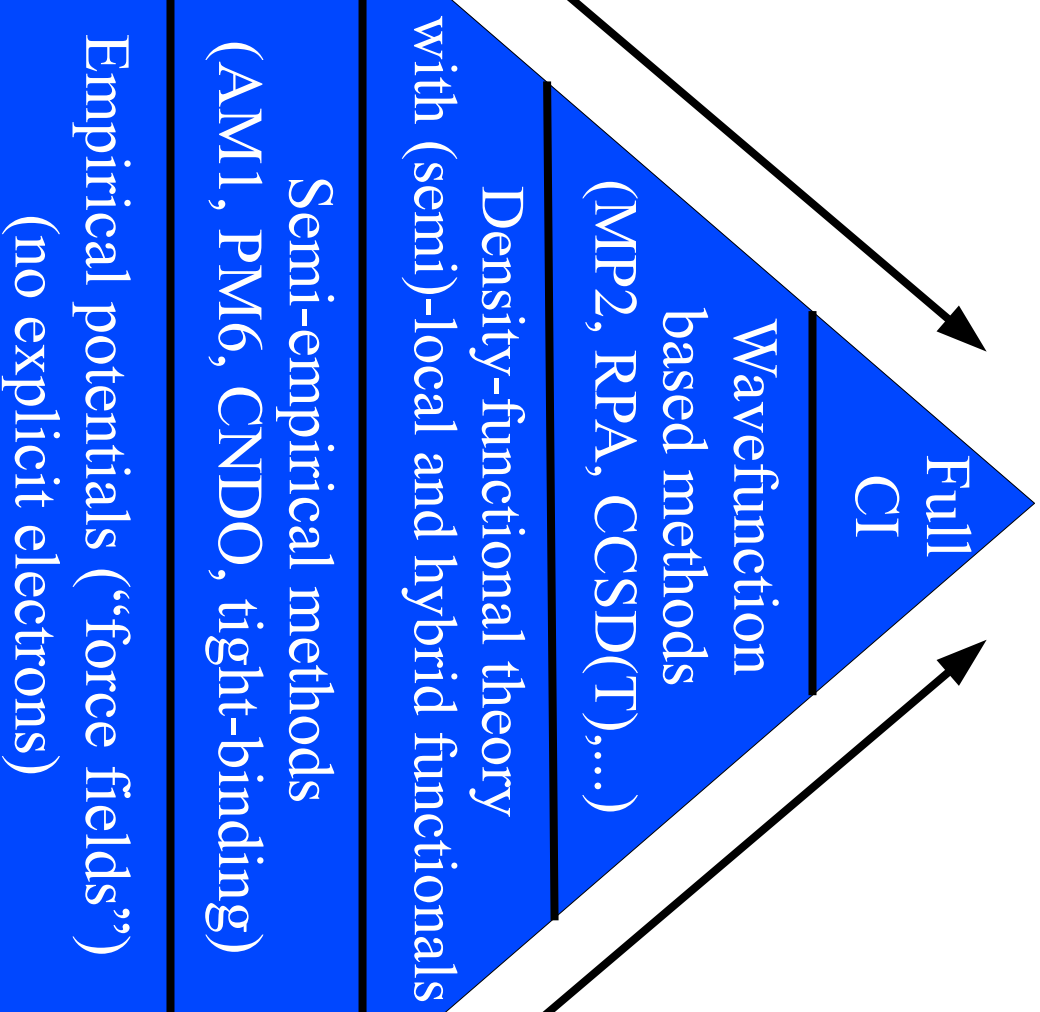
Computational
Cost;
Loss of
Conceptual
Understanding ?

Variational principle for wavefunctions

$$H^e = \sum_{k=1}^{N} -\frac{\hbar^2}{2m} \nabla^2_{\mathbf{r}_k} + \sum_{k=1}^{N} v(\mathbf{r}_k) + \frac{1}{2}\frac{1}{4\pi\epsilon_0} \sum_{\substack{k,k'\\k\neq k'}}^{N,N} \frac{e^2}{|\mathbf{r}_k - \mathbf{r}_{k'}|}$$

$$\frac{\langle\Phi|H^e|\Phi\rangle}{\langle\Phi|\Phi\rangle}$$

E_0^e

Φ_0

Φ

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

or Quantum Monte Carlo.
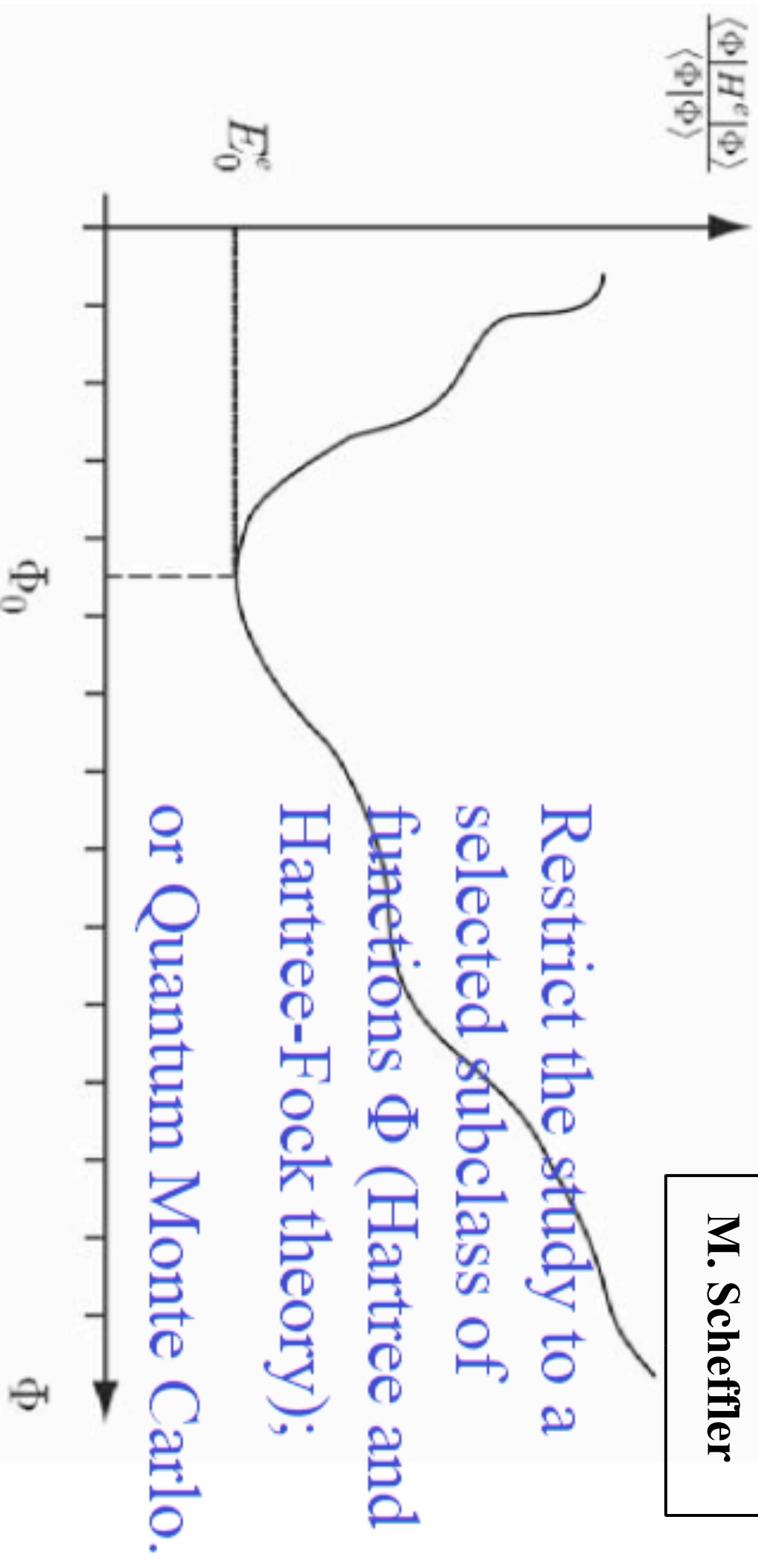
Hartree theory: product wavefunction

$$\Psi^H(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n) = \phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)\cdots\phi_n(\mathbf{r}_n)$$

In general, exact when $\hat{H} = \sum_i^n \hat{h}_i$

Some many-body problems can be reduced to a Hartree-type wavefunction by using an appropriate coordinate transformation. For example, dipole-coupled harmonic oscillators.

For electrons, Hartree wavefunction misses their correct *Fermionic* nature, i.e. the antisymmetry of the wavefunction to the exchange of two electrons.

$$\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_i, \ldots, \mathbf{r}_j, \ldots, \mathbf{r}_n) = -\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_j, \ldots, \mathbf{r}_i, \ldots, \mathbf{r}_n)$$

Hartree-Fock theory: orbital determinants

$$\psi^{\mathrm{HF}} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(\boldsymbol{r}_1) & \phi_2(\boldsymbol{r}_1) & \phi_3(\boldsymbol{r}_1) & \cdots & \phi_N(\boldsymbol{r}_1) \\ \phi_1(\boldsymbol{r}_2) & \phi_2(\boldsymbol{r}_2) & \phi_3(\boldsymbol{r}_2) & \cdots & \phi_N(\boldsymbol{r}_2) \\ \phi_1(\boldsymbol{r}_3) & \phi_2(\boldsymbol{r}_3) & \phi_3(\boldsymbol{r}_3) & \cdots & \phi_N(\boldsymbol{r}_3) \\ \cdots & \cdots & \cdots & \ddots & \cdots \\ \phi_1(\boldsymbol{r}_N) & \phi_2(\boldsymbol{r}_N) & \phi_3(\boldsymbol{r}_N) & \cdots & \phi_N(\boldsymbol{r}_N) \end{vmatrix}$$

Minimize (subject to orbital ortonormalization and constant N):

$$E_0 = \langle \psi_0^{\mathrm{HF}} | \hat{\mathcal{H}}_e | \psi_0^{\mathrm{HF}} \rangle = \langle \psi_0^{\mathrm{HF}} | \hat{T}_e + \hat{V}_{n-e} + \hat{V}_{e-e} | \psi_0^{\mathrm{HF}} \rangle$$
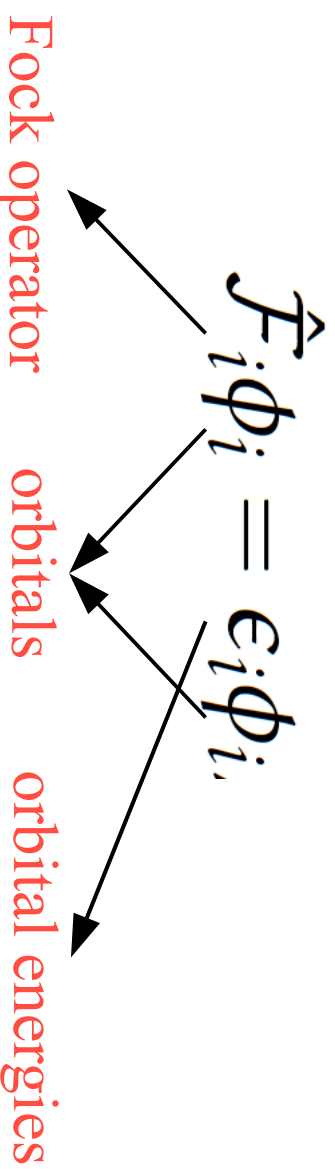
Hartree-Fock theory: Solution

$$E_0 = \langle \Psi_0^{\mathrm{HF}} | \hat{\mathcal{H}}_e | \Psi_0^{\mathrm{HF}} \rangle = \langle \Psi_0^{\mathrm{HF}} | \hat{T}_e + \hat{V}_{\mathrm{n-e}} + \hat{V}_{\mathrm{e-e}} | \Psi_0^{\mathrm{HF}} \rangle$$

$$\langle \Psi_0^{\mathrm{HF}} | \hat{\mathcal{H}}_e | \Psi_0^{\mathrm{HF}} \rangle = \sum_{i=1}^{N} \left[\int \phi_i^*(\boldsymbol{r}_i) \left(-\frac{1}{2}\nabla_i^2 + \hat{V}_{\mathrm{n-e}} \right) \phi_i(\boldsymbol{r}_i) d^3 r_i \right.$$

$$\left. + \frac{1}{2} \sum_{i=1}^{N}\sum_{i \neq j}^{N} \int\int \phi_i^*(\boldsymbol{r}_i)\phi_j^*(\boldsymbol{r}_j) \frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}_j|} \phi_i(\boldsymbol{r}_i)\phi_j(\boldsymbol{r}_j) d^3 r_i d^3 r_j \right\}_{E_{\mathrm{Hartree}}}$$

$$- \frac{1}{2} \sum_{i=1}^{N}\sum_{i \neq j}^{N} \int\int \phi_i^*(\boldsymbol{r}_j)\phi_j^*(\boldsymbol{r}_i) \frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}_j|} \phi_i(\boldsymbol{r}_i)\phi_j(\boldsymbol{r}_j) d^3 r_i d^3 r_j \right\}_{E_x}$$

Hartree-Fock theory: Remarks

- Captures > 98% of the electronic energy

- The missing energy from the Hartree-Fock solution is called the electronic *correlation energy*. The correlation energy is negative (stabilizing) by definition.

- Hartree-Fock is the base for so-called post-HF quantum-chemical approaches, including Moller-Plesset perturbation theory, coupled cluster theory, configuration interactions, random-phase approximation, HF-based quantum Monte Carlo, …

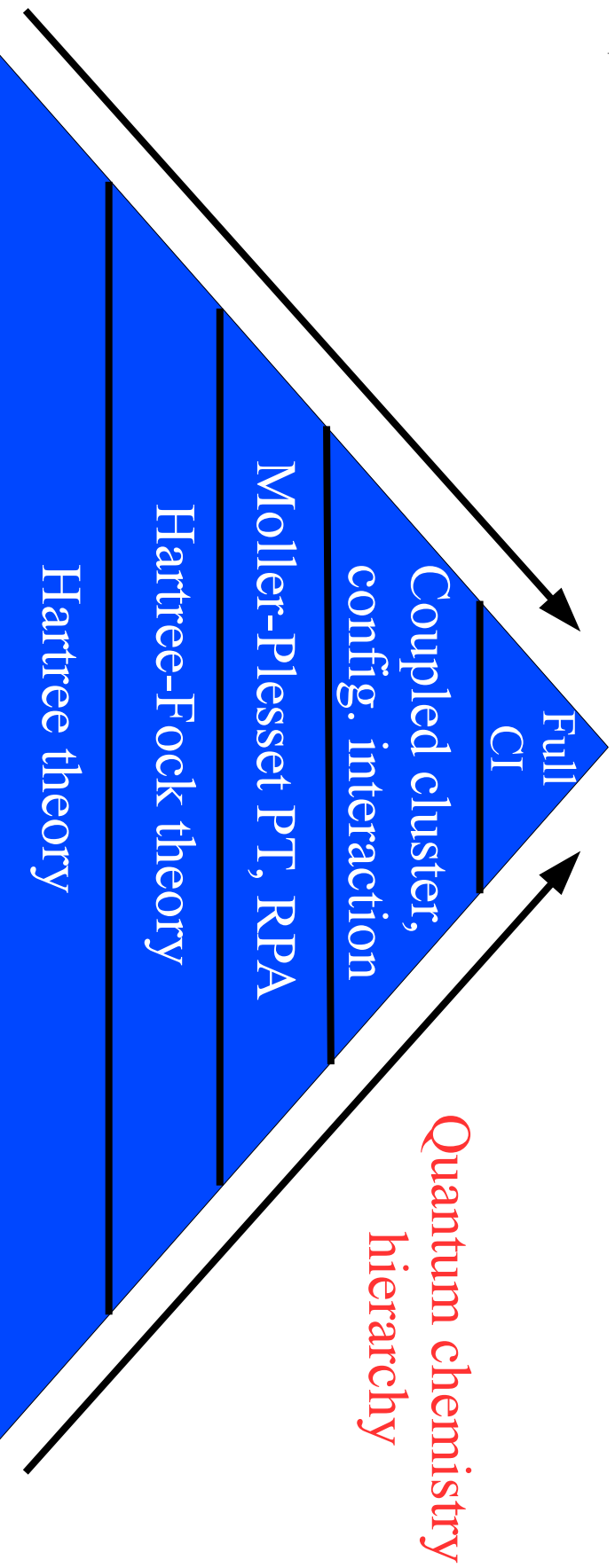- HF is still an effective single-particle theory, amenable to conceptual analysis and insights:

$$\hat{\mathcal{F}}_i \varphi_i = \epsilon_i \varphi_i$$

Fock operator   orbitals   orbital energies

Beyond Hartee-Fock theory: Taming electron correlation
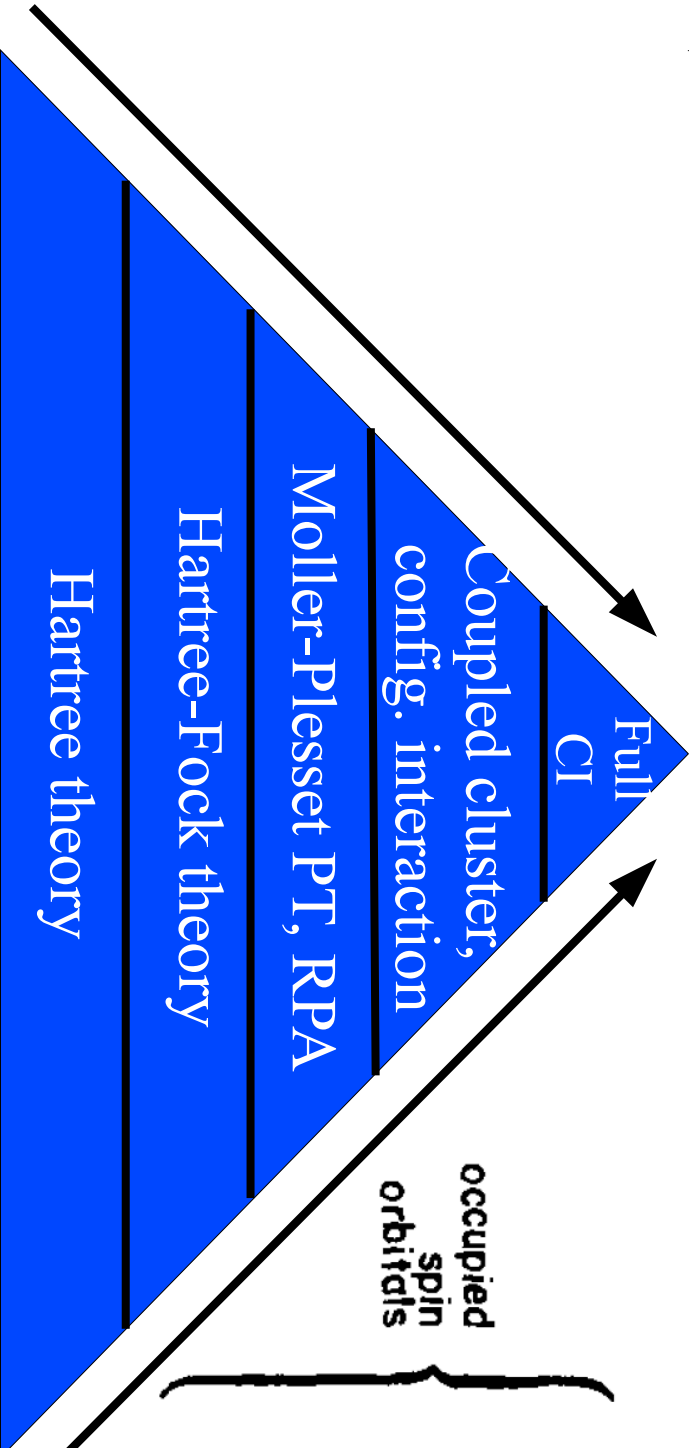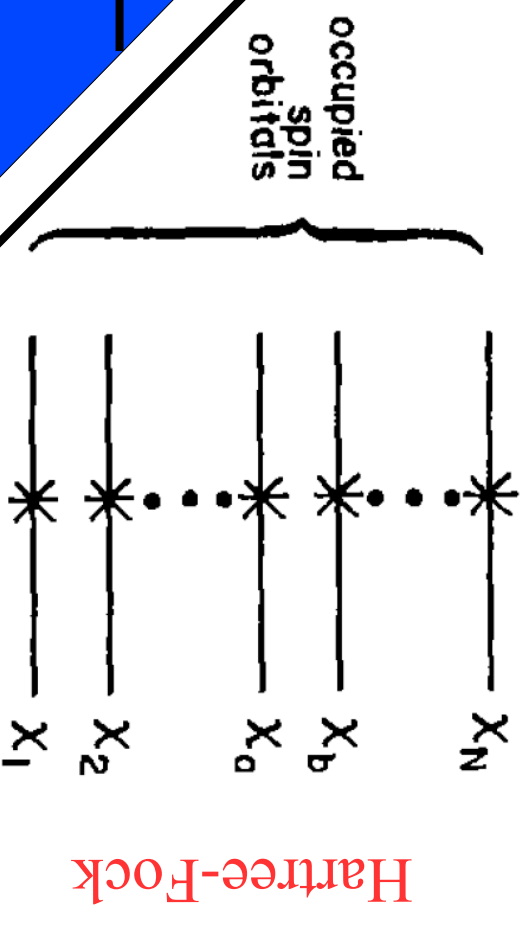
$$E^e_{corr} = E^e - E^e_{HF}$$

$$H\Psi = E\Psi$$

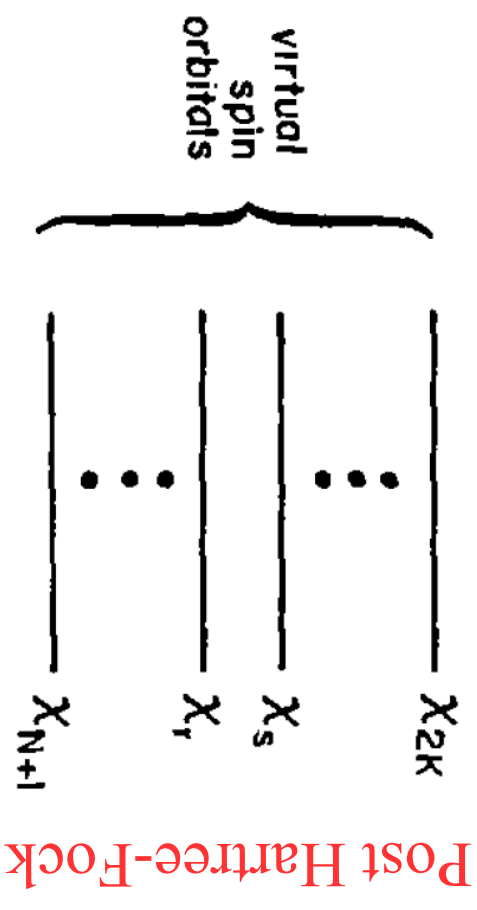Small ($\sim$1-2%), but fundamental part of electronic energy. Responsible for van der Waals interactions and cohesion in a wide range of molecules and materials

Hartree theory

Hartree-Fock theory

Moller-Plesset PT, RPA

Coupled cluster, config. interaction

Full CI

Quantum chemistry hierarchy

Beyond Hartee-Fock theory:
Taming electron correlation

$$H\Psi = E\Psi$$

Hartree theory

Hartree-Fock theory

Moller-Plesset PT, RPA

Coupled cluster, config. interaction

Full CI

occupied spin orbitals

virtual spin orbitals

χ_1 χ_2 χ_a χ_b χ_N

χ_{N+1} χ_r χ_s χ_{2K}

Hartree-Fock

Post Hartree-Fock

Moller-Plesset perturbation theory

$$\hat{\mathcal{H}}' = \hat{\mathcal{H}}_e - \sum_i^N \hat{\mathcal{F}}_i = \sum_{i,j;i<j} \frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}_j|} - \sum_i [v^{\mathrm{H}}(\boldsymbol{r}_i) - v^{\mathrm{x}}(\boldsymbol{r}_i)]$$

$$\boxed{E^{\mathrm{MP2}} = E_{\mathrm{HF}} + \frac{1}{4} \sum_{ijab} \frac{|\langle ij \| ab \rangle|^2}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}}$$

$$\langle ij \| ab \rangle = \int \int \frac{\phi_i^*(\boldsymbol{r}) \phi_j^*(\boldsymbol{r}') \phi_a^*(\boldsymbol{r}) \phi_b^*(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} d^3\boldsymbol{r} d^3\boldsymbol{r}'$$

Coupled-cluster theory

$$\Psi_{CC} = e^{\hat{T}}\Psi_0 = \left(1 + \hat{T} + \frac{\hat{T}^2}{2!} + \frac{\hat{T}^3}{3!} + \cdots \right)\Psi_0$$

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \cdots$$

$$\hat{T}_1\Psi_0 = \sum_{i}^{occ.}\sum_{a}^{unocc.} t_i^a \Psi_i^a$$

$$\hat{T}_2\Psi_0 = \sum_{ij}^{occ.}\sum_{ab}^{unocc.} t_{ij}^{ab} \Psi_{ij}^{ab}$$

$$\hat{T}_3\Psi_0 = \sum_{ijk}^{occ.}\sum_{abc}^{unocc.} t_{ijk}^{abc} \Psi_{ijk}^{abc}$$

...

Coupled-cluster theory

$$e^{\hat{T}} = 1 + \hat{T}_1 + \left(\hat{T}_2 + \frac{\hat{T}_1^2}{2}\right) + \left(\hat{T}_3 + \hat{T}_1\hat{T}_2 + \frac{\hat{T}_1^3}{6}\right) + \left(\hat{T}_4 + \hat{T}_3\hat{T}_1 + \frac{\hat{T}_2^2}{2} + \frac{\hat{T}_2\hat{T}_1^2}{2} + \frac{\hat{T}_1^4}{48}\right) + \cdots$$

$$E^{CC} = \langle \Psi_0 | e^{-\hat{T}} \hat{\mathcal{H}} e^{\hat{T}} | \Psi_0 \rangle$$

Configuration interaction (CI)

$|\Psi_a^r\rangle$ $|\Psi_{ab}^{rs}\rangle$

X_{2k}, X_s, X_r, X_{N+1}, X_N, X_b, X_a, X_2, X_1
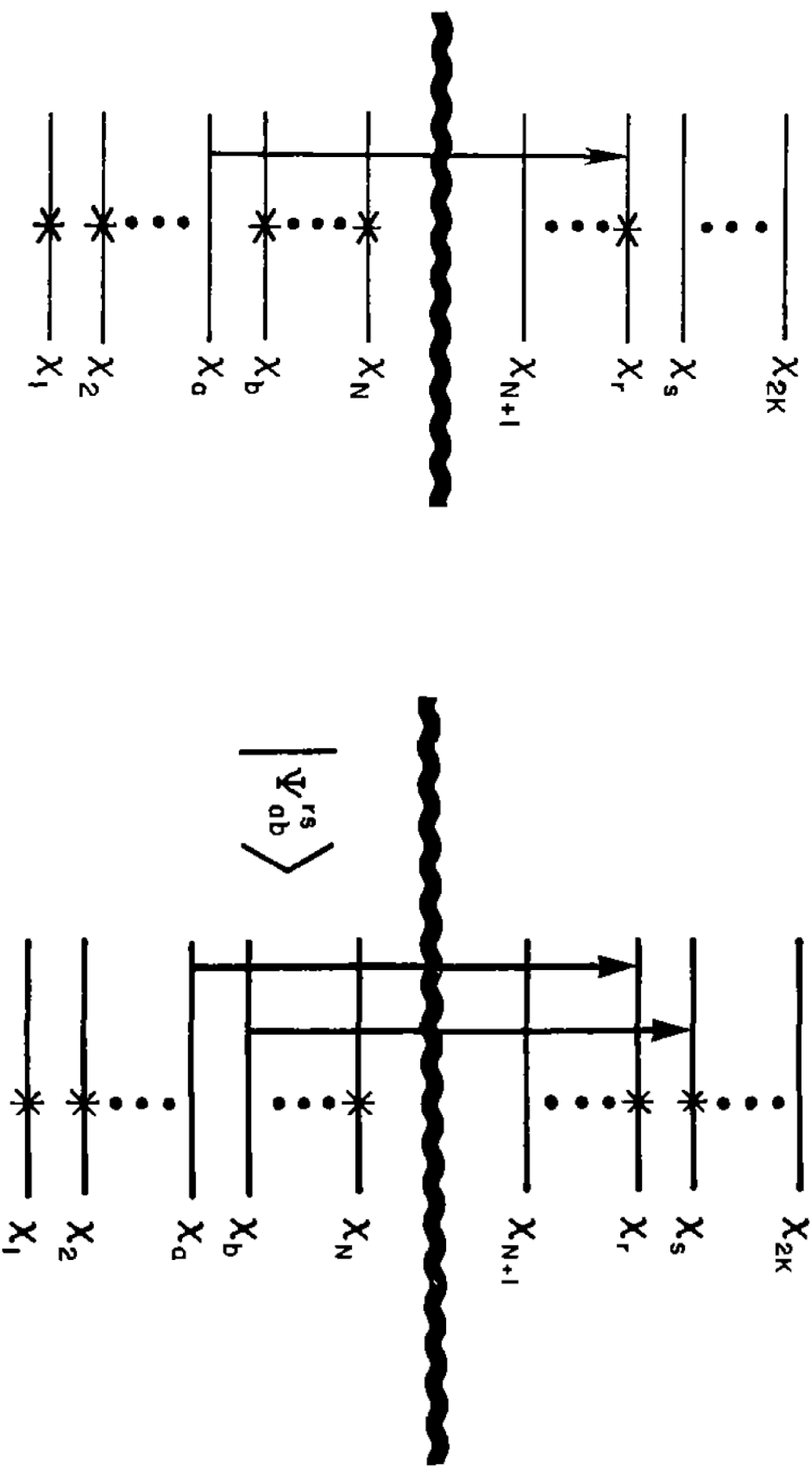
$$|\Phi\rangle = c_0|\Psi_0\rangle + \sum_{ra} c_a^r|\Psi_a^r\rangle + \sum_{\substack{a<b \\ r<s}} c_{ab}^{rs}|\Psi_{ab}^{rs}\rangle + \sum_{\substack{a<b<c \\ r<s<t}} c_{abc}^{rst}|\Psi_{abc}^{rst}\rangle + \cdots$$

Post-Hartree-Fock methods: Summary

- Electronic exchange and correlation are purely quantum-mechanical phenomena (absent in classical mechanics)

- Hartree-Fock describes exchange (or antisymmetry of the wavefunction to exchange of two electrons), but has no correlation

- Electron correlation is difficult to calculate accurately: MP2/3 theory gets 90% of correlation, CCSD(T) gets 98%.

- MP2 scales as N^5, CCSD as N^6, CCSD(T) as N^7

- CI (in a converged basis) is exact, but VERY expensive, exponentially scaling, and essentially a "dumb" brute force method.

- Some newer methods exploit sparsity in the many-electron wavefunction or derive model Hamiltonians, hopefully with minimal empiricism.

- Post HF methods obey the variational principle: Lower energy = better wavefunction.

Is Ψ absolutely essential ?

Density-functional theory of nucleo-electronic systems

$H\Psi = E\Psi$

Accuracy,
Reliability,
and
Predictive
Power

Full
CI

Wavefunction
based methods
(MP2, RPA, CCSD(T),...)

Density-functional theory
with (semi)-local and hybrid functionals

Semi-empirical methods
(AM1, PM6, CNDO, tight-binding)

Empirical potentials ("force fields")
(no explicit electrons)

Computational
Cost;
Loss of
Conceptual
Understanding ?
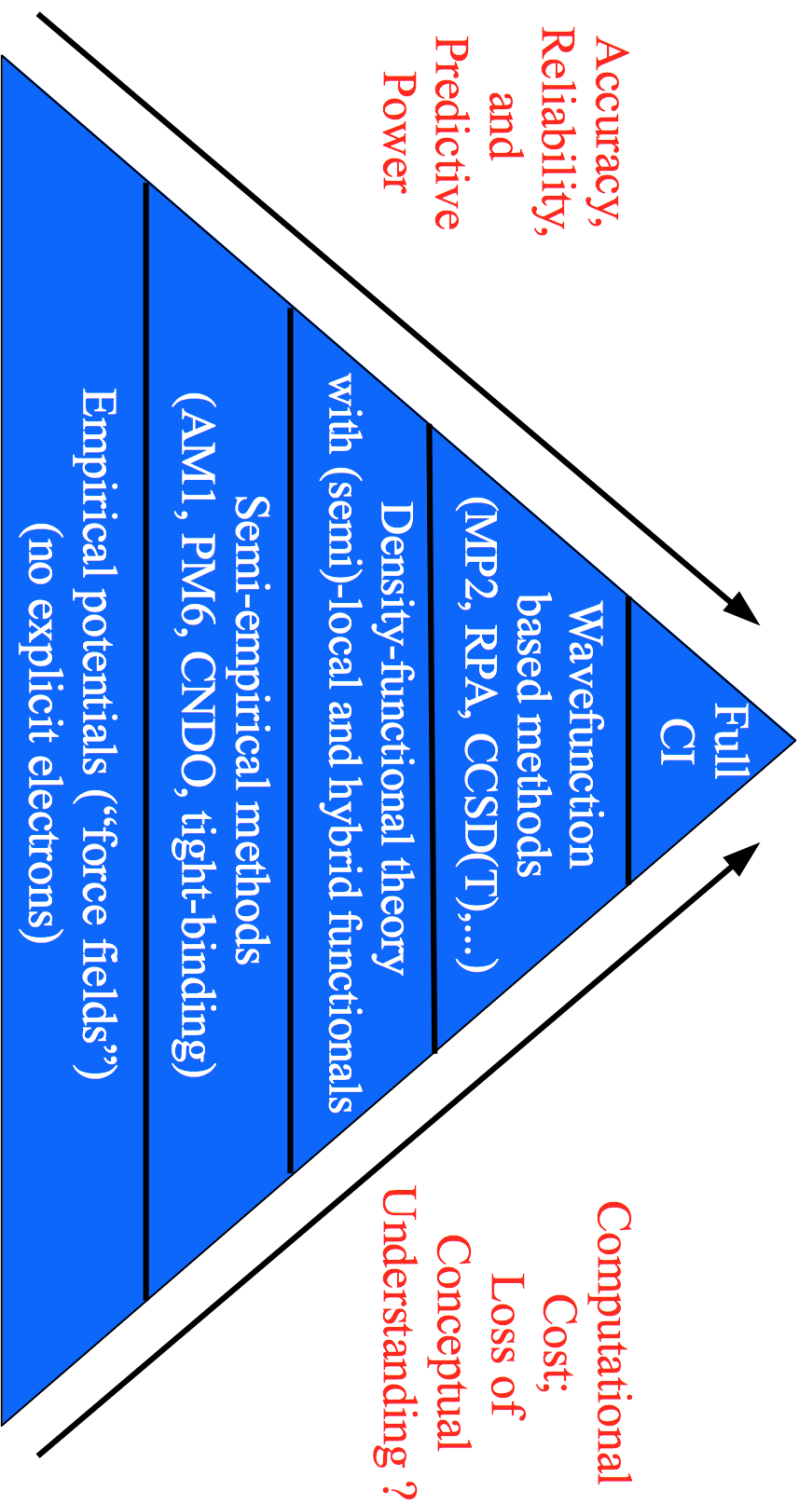
$$\Psi(\vec{r}_1, \vec{r}_2, \vec{r}_3, \ldots, \vec{r}_n) \longrightarrow n(\vec{r}) \quad \text{or} \quad \rho(\vec{r})$$
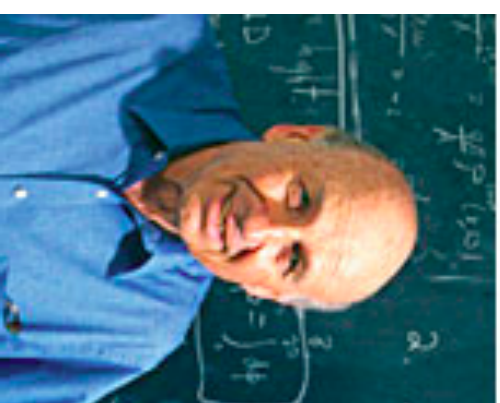
UCSB PHOTO SERVICES

Density-functional theory (DFT)

#	Title	Author(s)
1.	*Self-Consistent Equations Including Exchange and Correlation Effects (1965)*	W. Kohn, L. J. Sham
2.	*Inhomogeneous Electron Gas (1964)*	P. Honenberg, W. Kohn
3.	*Self-Interaction Correction to Density-Functional Approximations for Many-Electron Systems (1981)*	J.P. Perdew, Alex Zunger
4.	*Ground State of the Electron Gas by a Stochastic Method (1980)*	D. M. Ceperley, B.J. Alder
5.	*Theory of Superconductivity (1957)*	J. Bardeen, L.N. Cooper, J.R. Schrieffer
6.	*Model of Leptons (1967)*	S. Weinberg
7.	*Linear Methods in Band Theory (1975)*	O. K. Andersen
8.	*Effects of Configuration Interaction on Intensities and Phase Shifts (1961)*	U. Fano
8.	*Disordered Electronic Systems (1985)*	P.A. Lee, T.V. Ramakrishnan
9.	*The Electronic Properties of Two-Dimensional Systems (1982)*	T. Ando, A.B. Fowler, F. Stern
10.	*Special Points for Brilloun-Zone Integrations (1976)*	H.J. Monkhorst, James D. Pack
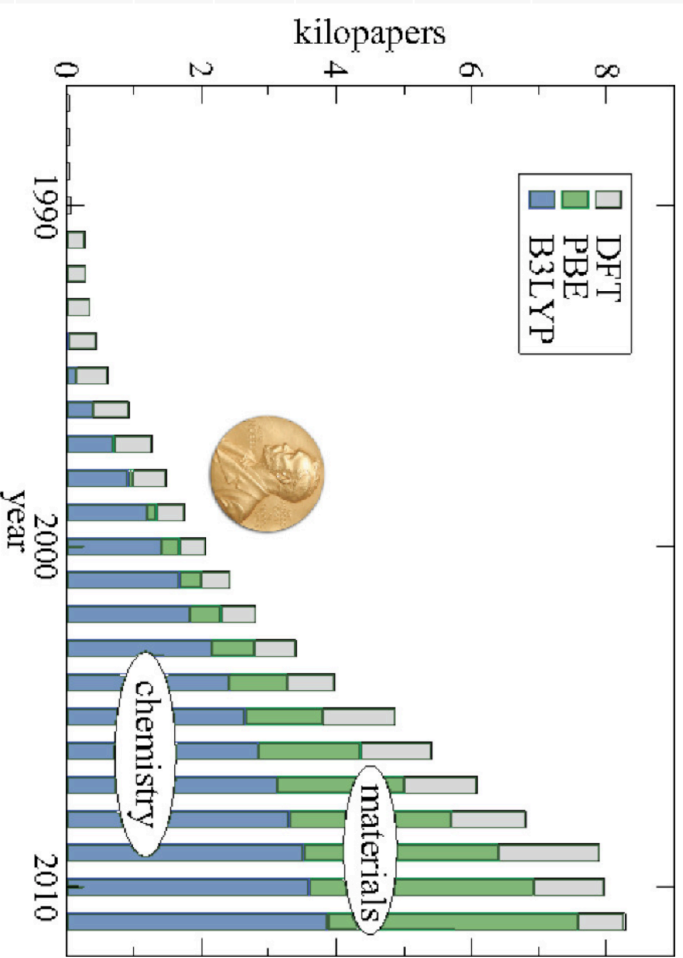
The Hohenberg-Kohn Theorem (1964)

$$n(\mathbf{r'}) = n[\Phi]$$

$$= \langle\Phi|\sum_i^N \delta(\mathbf{r'}-\mathbf{r_i})|\Phi\rangle$$

$\Phi^{(1)}$

$\Phi^{(2)}$

$\Phi^{(3)}$

$\Phi^{(4)}$

$\Phi^{(5)}$

$\Phi^{(6)}$

$\Phi^{(7)}$

$\Phi^{(8)}$

$\Phi^{(9)}$

$\Phi^{(10)}$

$\Phi^{(11)}$

$\Phi^{(12)}$

$\Phi^{(13)}$

$n^{(1)}$

$n^{(2)}$

$n^{(3)}$

$n^{(4)}$

$n^{(5)}$

$n^{(6)}$

$n^{(7)}$

$n^{(8)}$

$n^{(9)}$

$n^{(10)}$

$n^{(11)}$

$n^{(12)}$

$n^{(13)}$
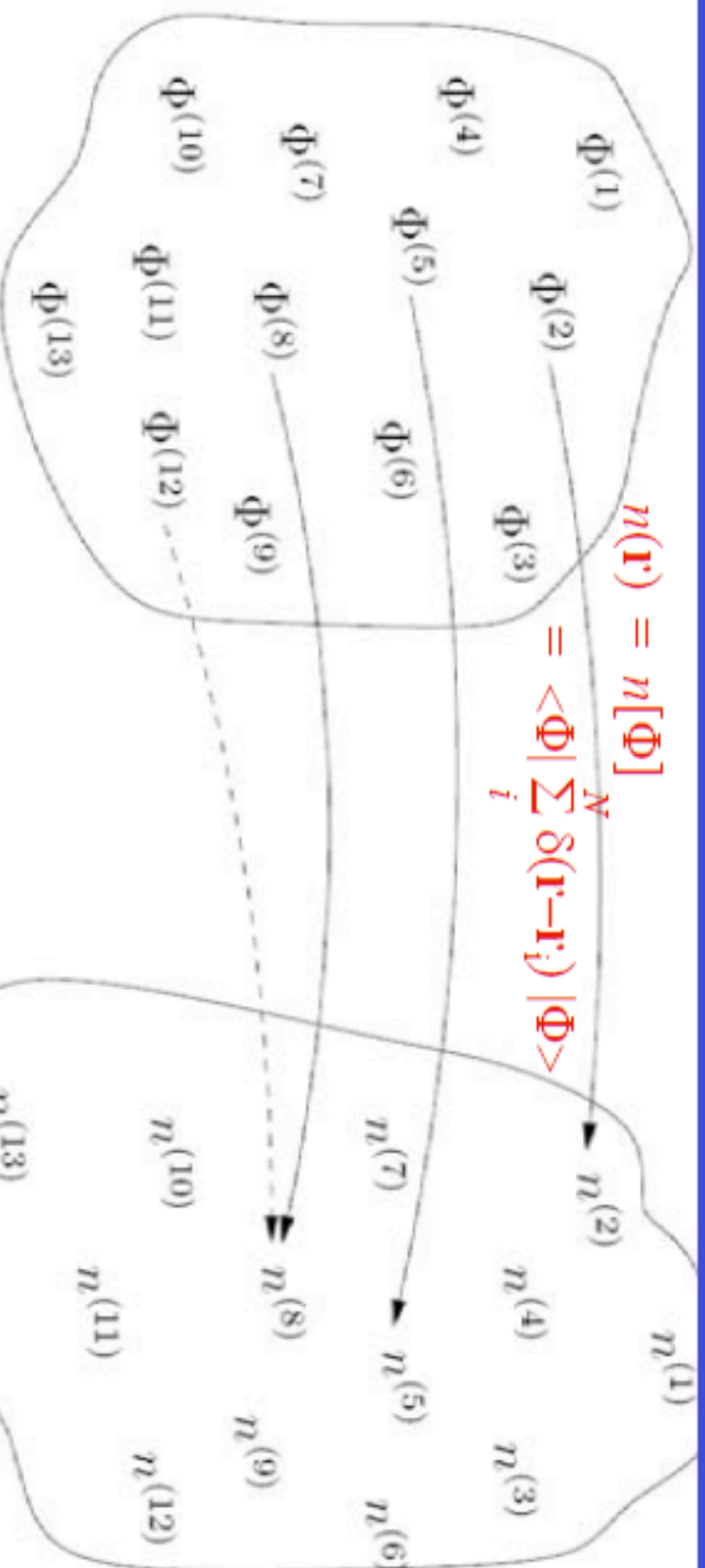
The set of non-degenerate ground state wave functions Φ of arbitrary N-particle Hamiltonians.

The set of particle densities $n(\mathbf{r})$ belonging to non-degenerate ground states of the N-particle problem.

The dashed arrow is not possible

Density Functional Theory

The energy of the ground state of a many-electron system :

$$E_0 \left(\{ \mathbf{R}_I \} \right) = \text{Min}_\Phi \left< \Phi | H^e | \Phi \right>$$

Hohenberg and Kohn (1964):   The functional

$$n(\mathbf{r}) = n[\Phi] = \left< \Phi \right| \sum_i \delta(\mathbf{r} - \mathbf{r}_i) \left| \Phi \right>$$

can be inverted, *i.e.*,

$$\Phi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \Phi[n(\mathbf{r})] \ .$$

This implies:

$$E_0 \left(\{ \mathbf{R}_I \} \right) = \text{Min}_{n(\mathbf{r})} E_{\{ \mathbf{R}_I \}} [n]$$

Summary of Hohenberg-Kohn Density-Functional Theory (DFT) -- 1964

-- There is a one-to-one correspondence between the ground-state wave function and the many-body Hamiltonian [or the nuclear potential, $v^{nuc}(\mathbf{r})$].

-- The many-body Hamiltonian determines everything.

-- There is a one-to-one correspondence between the ground-state electron-density and the ground-state wave function.

Kohn and Sham (1965):

$$E_v[n] = T_s[n] + \int v(\mathbf{r})n(\mathbf{r})d^3\mathbf{r} + E^{\text{Hartree}}[n] + E^{\text{xc}}[n]$$

with

$$E^{\text{Hartree}}[n] = \frac{1}{2}\frac{e^2}{4\pi\epsilon_0}\iint \frac{n(\mathbf{r})n(\mathbf{r'})}{|\mathbf{r} - \mathbf{r'}|}d^3\mathbf{r}\,d^3\mathbf{r'}$$

And $T_s[n]$ the functional of the kinetic energy of **non-interacting electrons**. $E^{\text{xc}}[n]$ **contains all the unknowns**.

At fixed electron number N the variational principle gives

$$\delta\left\{E_v[n] - \mu\left(\int n(\mathbf{r})d^3\mathbf{r} - N\right)\right\} = 0$$

or

$$\boxed{\frac{\delta E_v[n]}{\delta n} = \mu = \frac{\delta T_s[n]}{\delta n(\mathbf{r})} + v^{\text{eff}}(\mathbf{r})}$$

Kohn-Sham
equation

Kohn and Sham (1965):

$$v^{\text{eff}}(\mathbf{r}) = v(\mathbf{r}) + \frac{e^2}{4\pi\varepsilon_0} \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r' + \frac{\delta E^{\text{xc}}[n]}{\delta n(\mathbf{r})}$$

Because $T_s[n]$ is the functional of non-interacting particles we effectively "restrict" the allowed densities to those that can be written as

$$n(\mathbf{r}) = \sum_{i=1}^{N} |\varphi_i(\mathbf{r})|^2$$

This implies:

$$\left\{ -\frac{\hbar^2}{2m} \nabla^2 + v^{\text{eff}}(\mathbf{r}) \right\} \varphi_i(\mathbf{r}) = \epsilon_i \varphi_i(\mathbf{r})$$

Kohn-Sham equation

$$
\begin{aligned}
T_s[n] &= \sum_{k=1}^{N} \left\langle \varphi_k \left| -\frac{\hbar^2}{2m} \nabla^2 \right| \varphi_k \right\rangle \\
&= \sum_{k=1}^{N} \epsilon_k - \int v^{\text{eff}}[n^{\text{in}}](\mathbf{r}) n(\mathbf{r}) d^3r \ .
\end{aligned}
$$

$v^{\text{eff}}(\mathbf{r})$ depends on the density that we are seeking.

The Kohn-Sham Ansatz

- Kohn-Sham (1965) – Replace the original many-body problem with an independent electron problem **that can be solved!**

- Only the ground state density and the ground state energy are required to be the same as in the original many-body problem.

$$E_v[n] = T_s[n] + \int v(\mathbf{r}) n(\mathbf{r}) d^3\mathbf{r} + E^{\text{Hartree}}[n] + E^{\text{xc}}[n]$$

- Maybe the exact $E^{xc}[n]$ functional cannot be written as a closed mathematical expression. Maybe there is a detour similar to that taken for $T_s[n]$? The challenge is to find useful, approximate xc functionals.

Density-functional theory (DFT): No free lunch

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

Exchange and Correlation functions
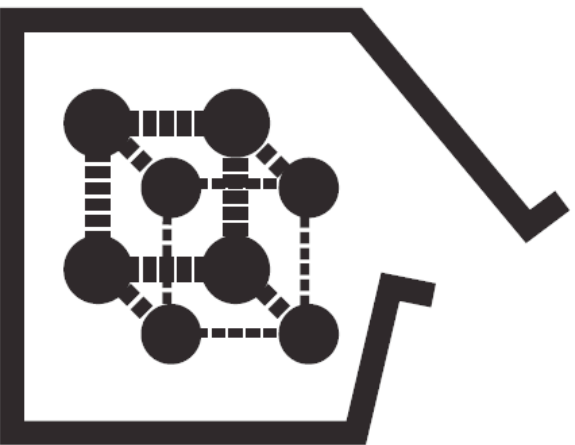
$$n(\vec{r}); \; \vec{\nabla} n(\vec{r}); \; \nabla^2 n(\vec{r}); \; \ldots$$

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

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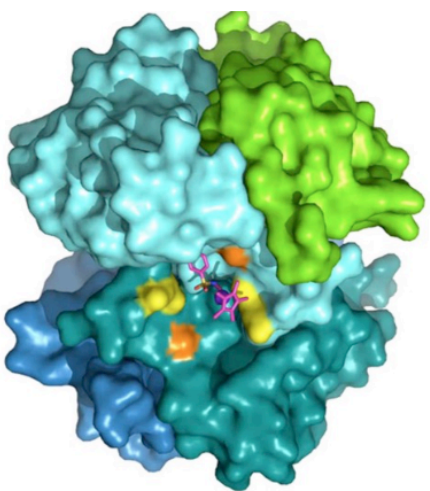
Water

Proteins

Van der Waals
interactions
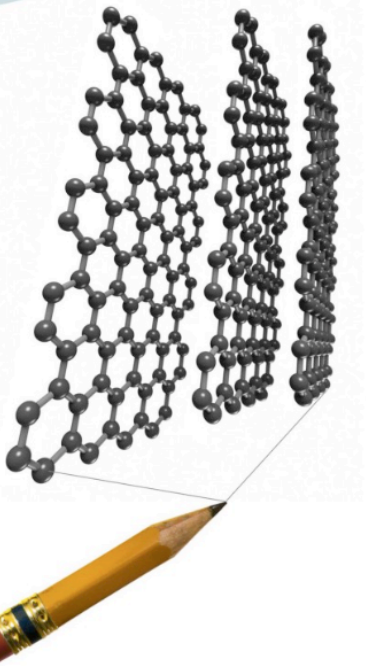
Gecko
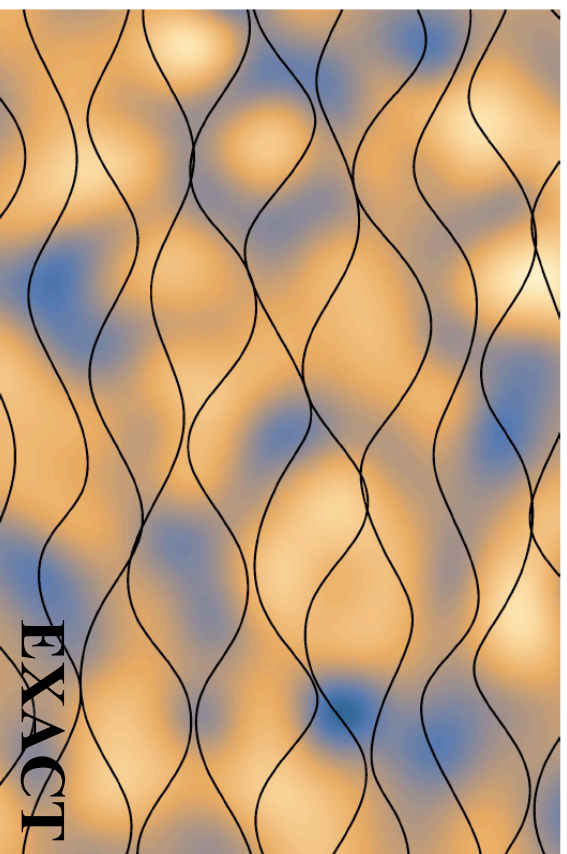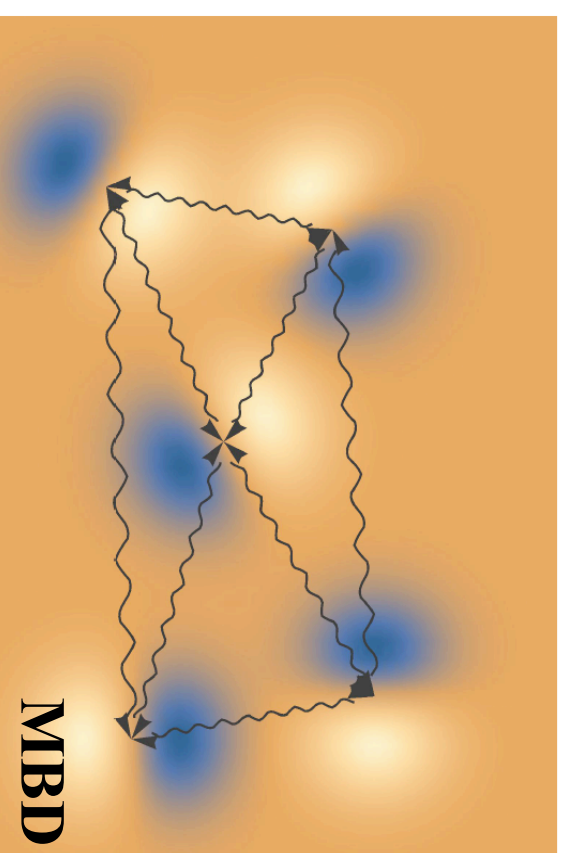
Polymers

Graphite sheets

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

a

$$-\frac{1}{2\pi}\int_0^\infty du\,\mathrm{Tr}\left[(\chi_{\tilde{\imath}} - \chi_0)v\right]$$

EXACT

b

$$-\frac{1}{2\pi}\int_0^\infty du\sum_{n=2}^\infty \frac{1}{n}\mathrm{Tr}\left[(\boldsymbol{\alpha}_m\tilde{\mathbf{T}})^n\right]$$

MBD

c

$$-\frac{1}{2}\sum_{ij} C_{6,ij}\, f(\mathbf{R})\mathbf{R}^{-6}$$

D2/D3, XDM, TS

d

$$-\frac{1}{2}\iint \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'\, n(\mathbf{r})\Phi(\mathbf{r},\mathbf{r}')n(\mathbf{r}')$$

vdW-DF
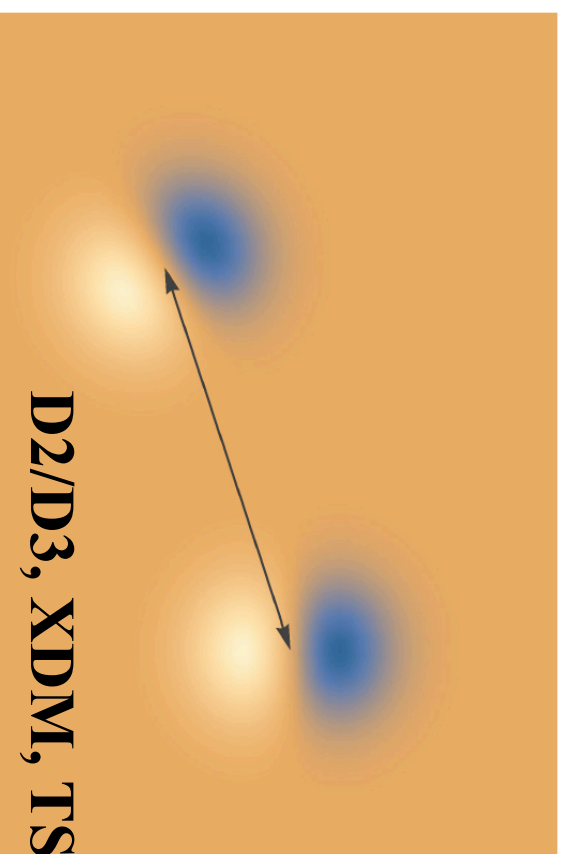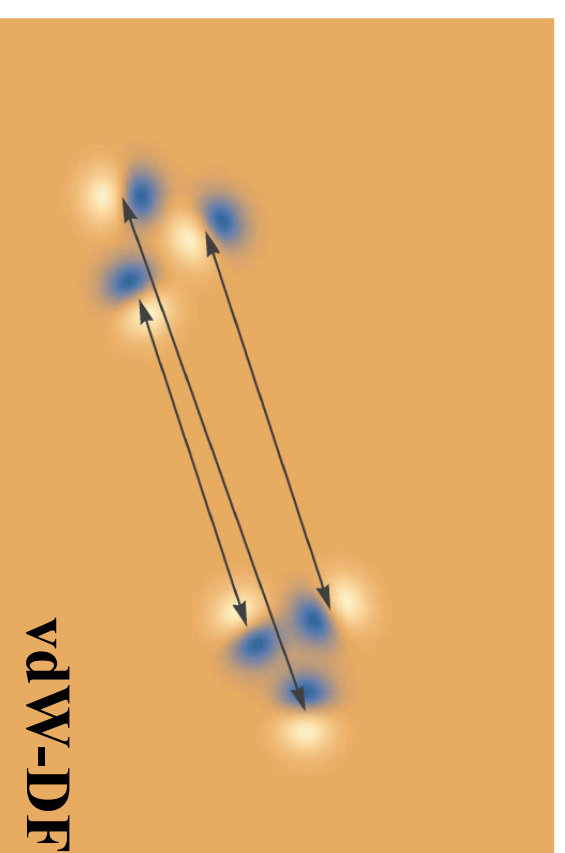
Physicist's Dream: Mapping Electrons to Quantum Harmonic Oscillators (QHO)
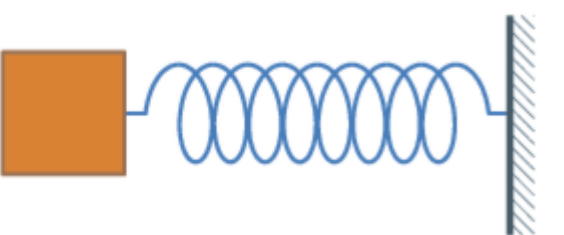
Nucleus (*q*)

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; F. Manby; ...*

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**)

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

From Dream to Reality:

Argon dimer described accurately by two oscillators

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

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

  $$\{\alpha(0), C_6, C_8\} \rightarrow \{m, q, \omega\}$$
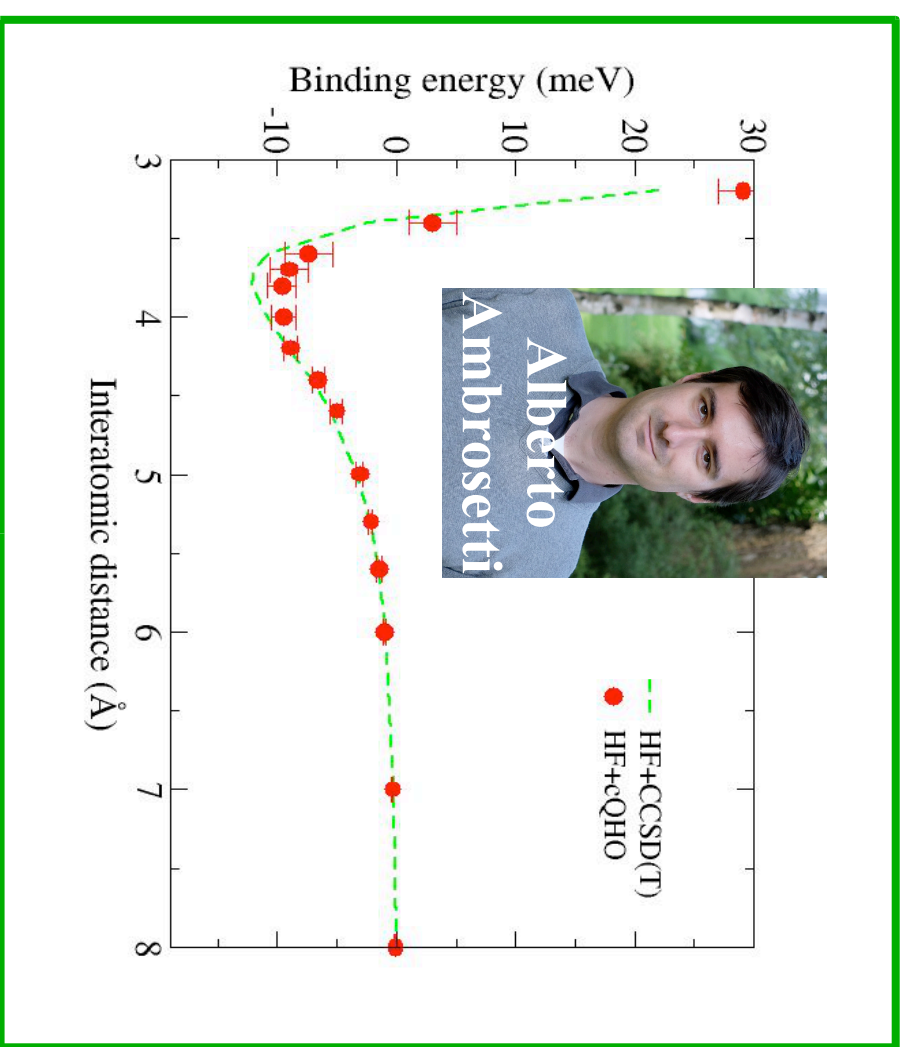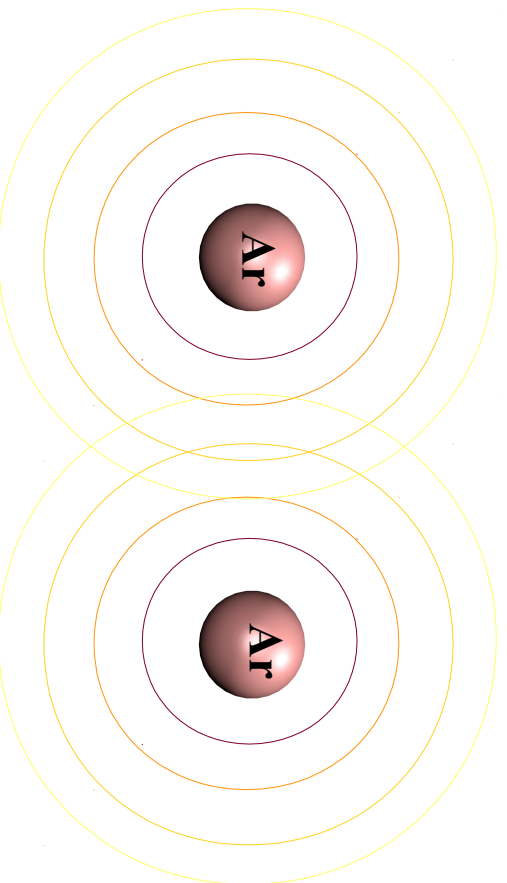
HF+cQHO: almost exact binding energy curve (within 3 meV at minimum) without any specific adjustments.

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

Binding energy (meV)

Interatomic distance (Å)

- - - HF+CCSD(T)
- HF+cQHO

Alberto Ambrosetti

Modeling Real Materials: DFT+MBD Method

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

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

A. Ambrosetti,
R. A. Distasio Jr.,
A. M. Reilly,
A. Tkatchenko,
J. Chem. Phys. (2014)
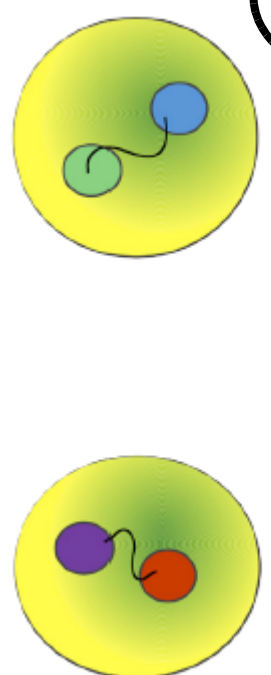
1
$$\alpha_0 = \frac{V[n]}{V_{free}} \alpha_{0,free}$$

Valence electrons
projected to oscillators
(Tkatchenko-Scheffler)
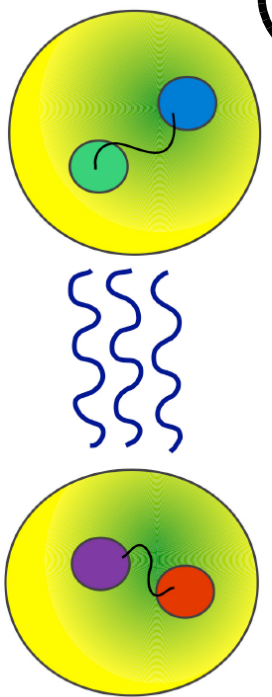
2
$$\tilde{\alpha} = \alpha - \alpha T_{<R} \tilde{\alpha}$$

Dyson-like
short-range
electrodynamic
screening

3
$$\hat{\mathcal{H}}_{>R} \Psi = E\Psi$$

Long-range
correlation
energy
calculated
using SE

From First-Principles Quantum Methods to Semi-Empirical and Classical Approaches

Coarse-graining QC and DFT

Semi-empirical quantum chemistry and tight-binding

$$H\Psi = E\Psi$$

Accuracy,
Reliability,
and
Predictive
Power

Computational
Cost;
Loss of
Conceptual
Understanding ?

Full
CI

Wavefunction
based methods
(MP2, RPA, CCSD(T),...)

Density-functional theory
with (semi)-local and hybrid functionals

Semi-empirical methods
(AM1, PM6, CNDO, tight-binding)

Empirical potentials ("force fields")
(no explicit electrons)
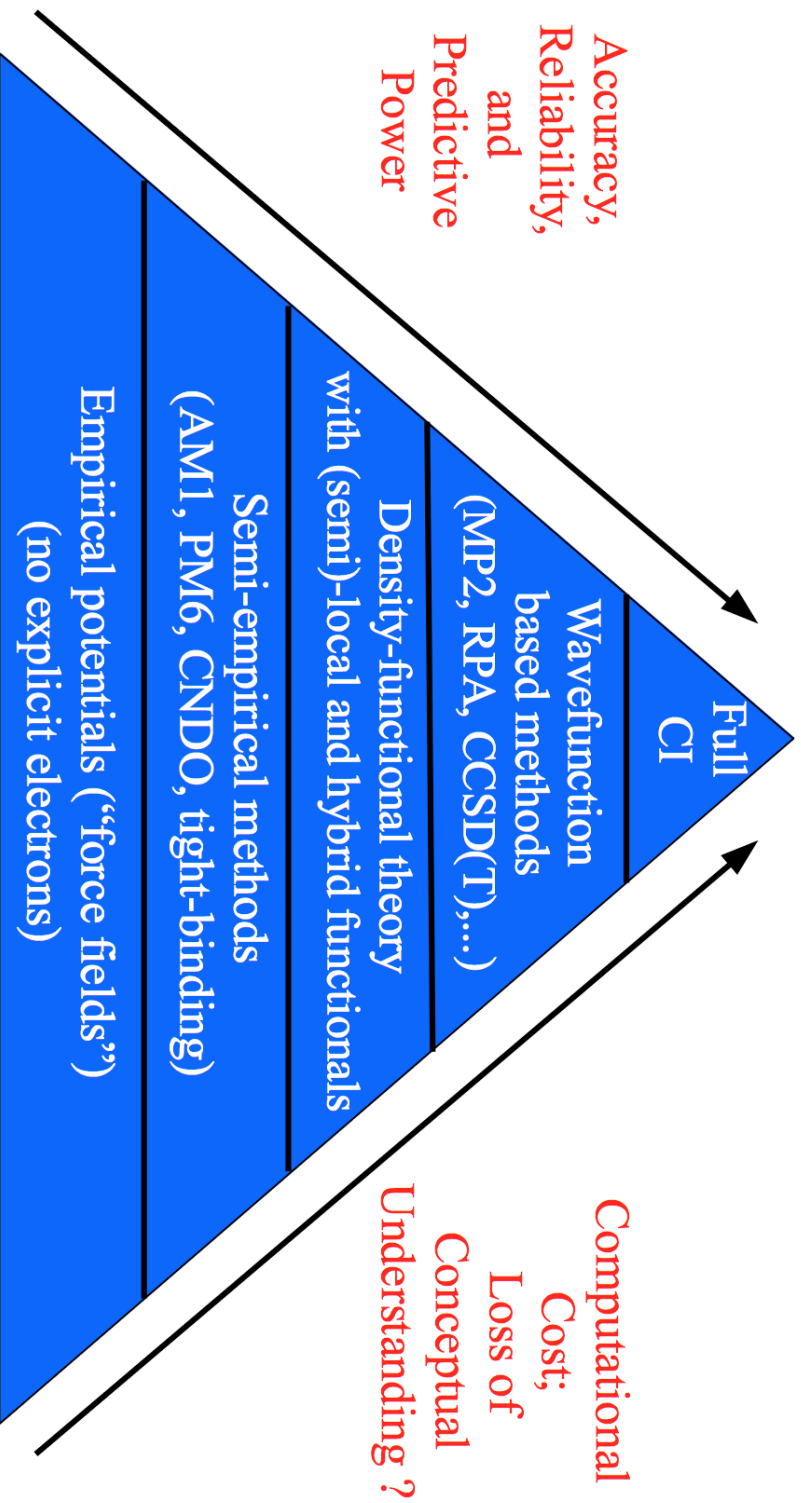
Semi-empirical quantum chemistry and tight-binding

Main idea:

- Semi-empirical QC: Empirically approximate the most expensive integrals in Hartree-Fock or correlated calculations.

- Tight-binding: Expand the density to second (or fourth) order. All integrals become relatively simple and the energy is obtained in a single diagonalization step.

- Weakness: These methods inherit all the problems of approximate QC/DFT, i.e. long-range correlation is absent, exchange is heavily approximated.

- Strength: can be applied to 1,000s of atoms

Throwing away electrons

Empirical potentials ("force fields")

$H\Psi = E\Psi$

Accuracy,
Reliability,
and
Predictive
Power

Full
CI

Wavefunction
based methods
(MP2, RPA, CCSD(T),...)

Density-functional theory
with (semi)-local and hybrid functionals

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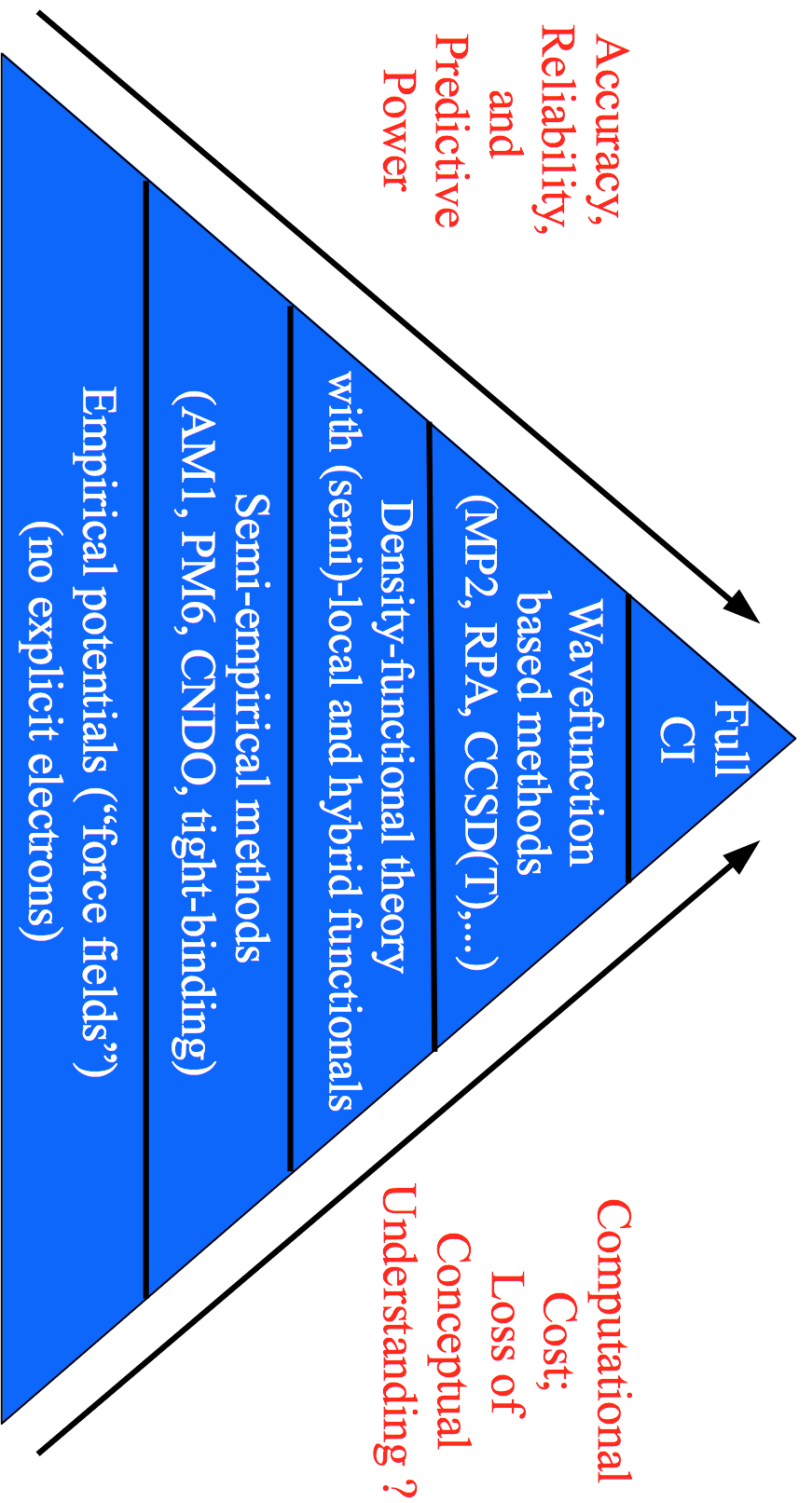
Classical force fields

Source: Wikipedia

Hydrophobic effect is roughly proportional to surface area

Continuum solvent model

water

Lennard Jones

Distance

bond length or 3-atom angle

torsion angle

Classical force fields with ML
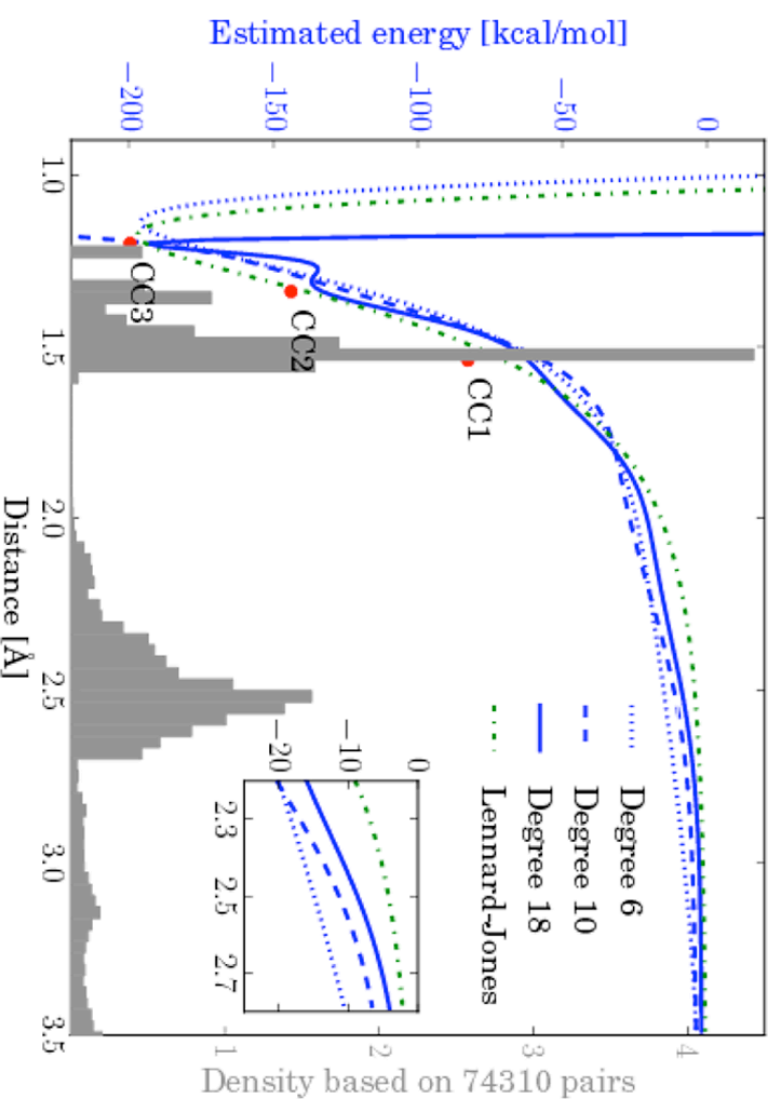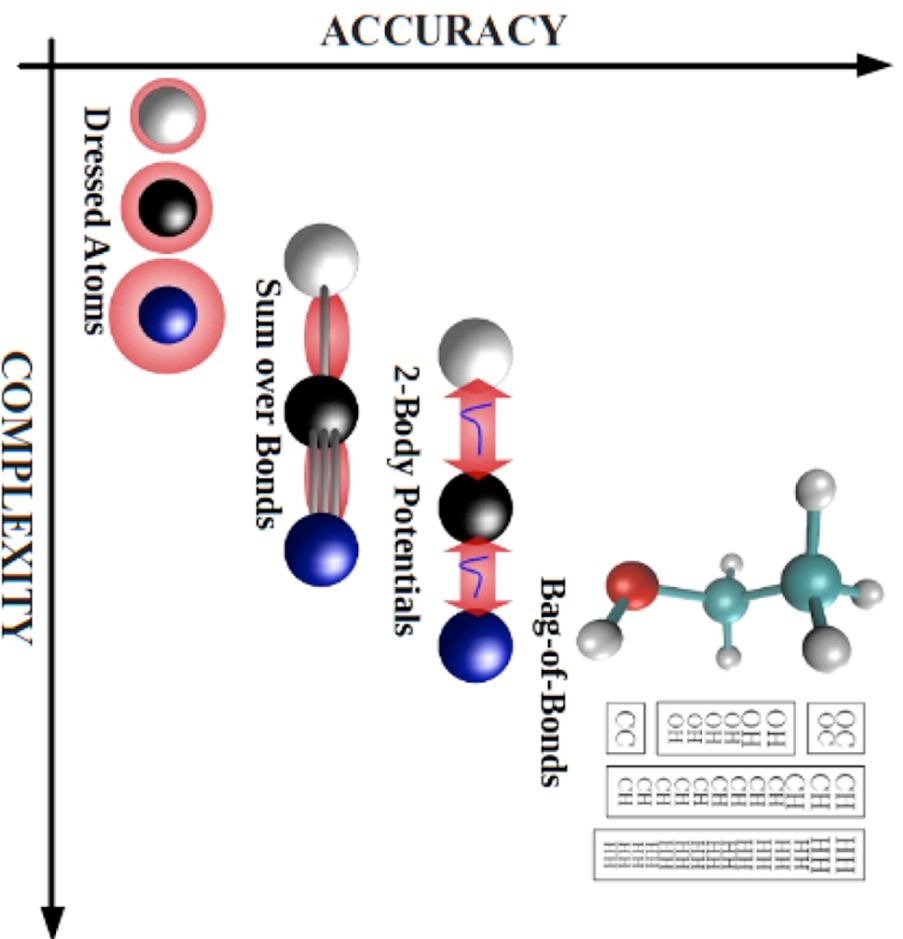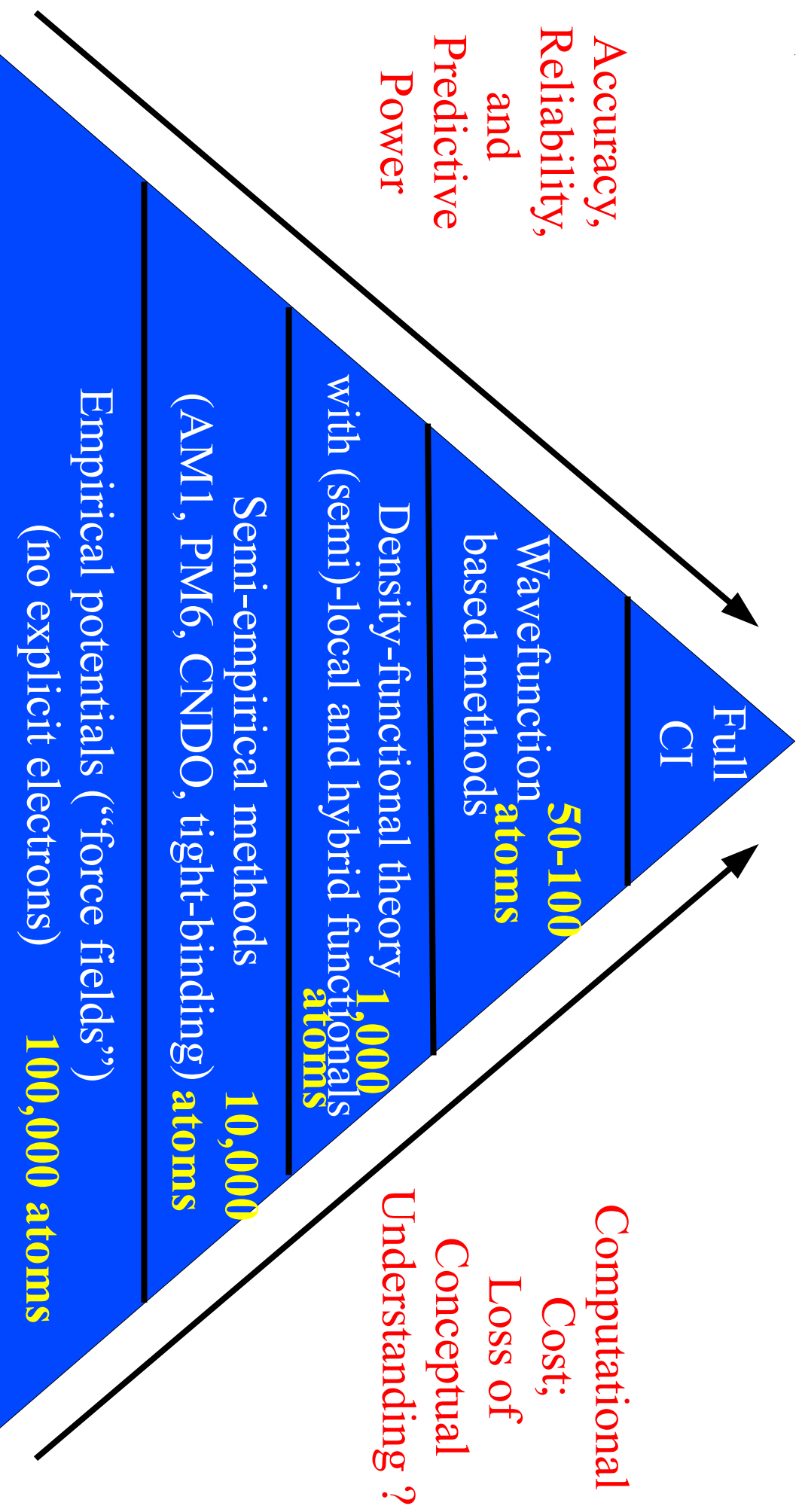
K. Hansen, F. Biegler, ..., K. R. Mueller, and A. Tkatchenko, *J. Phys. Chem. Lett.* 6, 2326 (2015).

Current state-of-the-art of atomistic modeling

$H\Psi = E\Psi$

Accuracy,
Reliability,
and
Predictive
Power

Computational
Cost;
Loss of
Conceptual
Understanding ?

Full CI

Wavefunction based methods
50-100 atoms

Density-functional theory with (semi)-local and hybrid functionals
1,000 atoms

Semi-empirical methods (AM1, PM6, CNDO, tight-binding)
10,000 atoms

Empirical potentials ("force fields") (no explicit electrons)
100,000 atoms

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

- Innocent looking, but powerful and hard to solve equation

- Encodes (almost) all the physics (+ chemistry and biology) of real materials

- Wide range of useful and powerful approximations

- Can ML techniques enable future breakthroughs in modeling and understanding nucleoelectronic systems?

Application: Molecular Crystal Structure Prediction
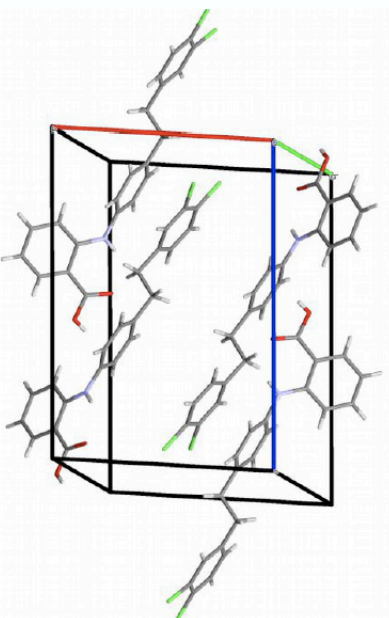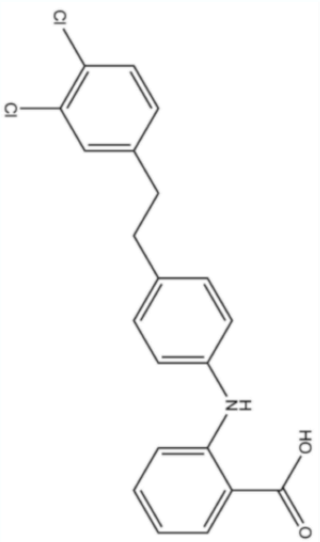
Or

?
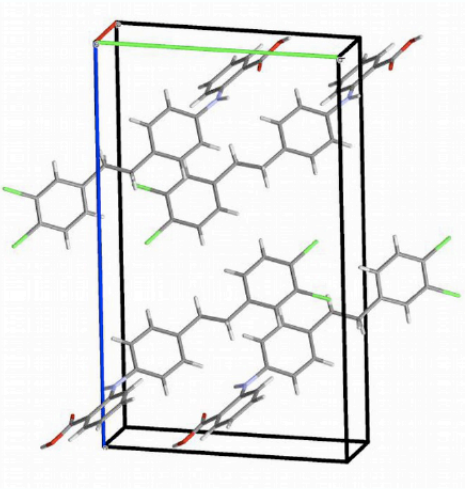
- Solids composed of molecular moieties
- Held together by intermolecular interactions
- Different crystal-packing motifs (polymorphs) possible
- Energy difference between polymorphs ~ 1 - 4 kJ/mol
  - ~ 1 - 2 % **of lattice energy**

Pharmaceuticals

Organic electronics

Explosives

Polymorphs can exhibit completely different
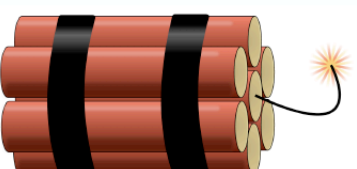
- Kinetic stabilities
- Solubilities
- Densities
- Vibrational Spectra (THz)
- NMR chemical shifts
- Melting Points
- Conductivities
- Refractive Indices
- Vapor pressure
- Elastic constants
- Heat capacities
- …

Molecular Crystal Structure Prediction (CSP) with DFT+MBD

molecular structure

structural formula

crystal structure generation

energy ranking

(Free) energy

I II III IV V
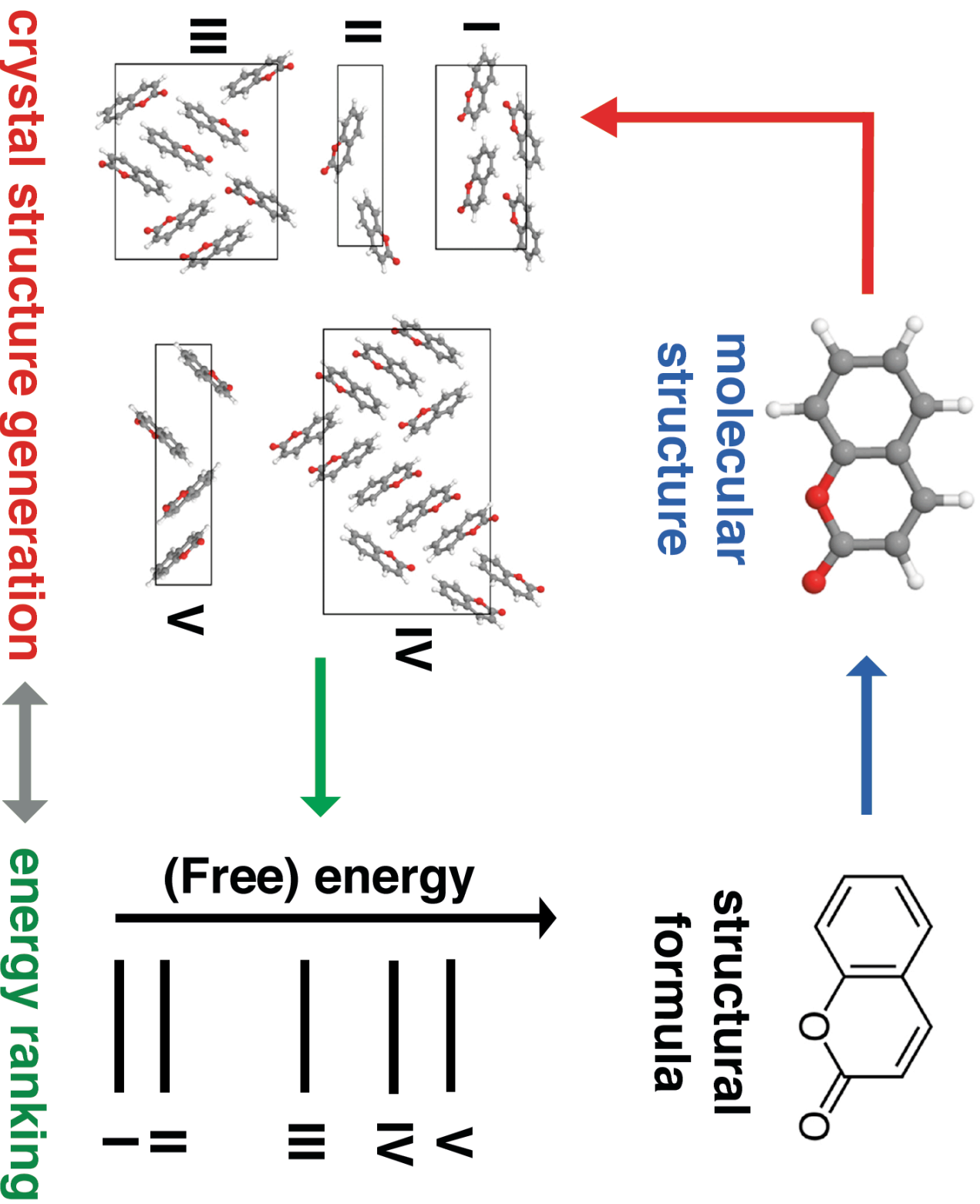
Targets of Cambridge CSP Blind Test 2016
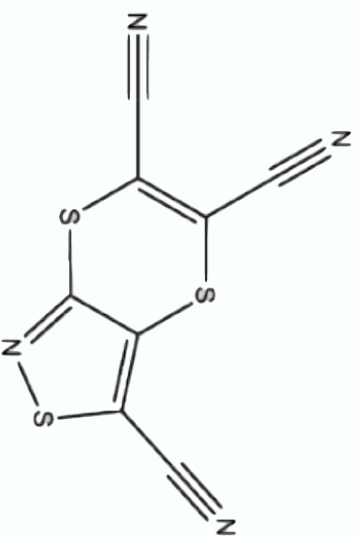
XXII

rigid molecule

XXV

multiple partially flexible molecules
as co-crystal
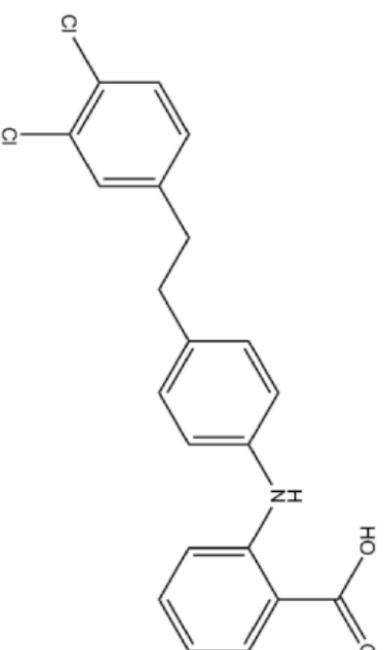
XXIII

partially flexible molecule,
polymorphic system
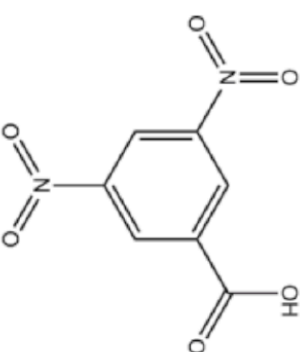
XXVI

molecule with 4-8 internal
degrees of freedom

XXIV

salt
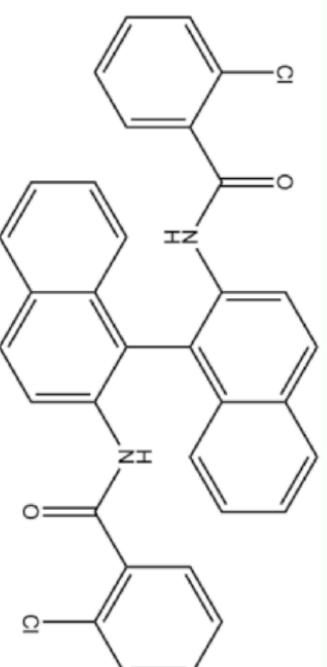
Targets of Cambridge CSP Blind Test 2016
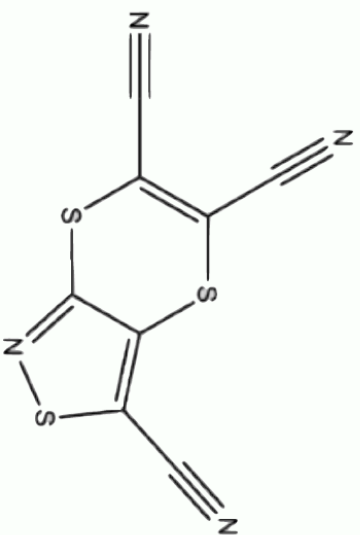
XXII — 57 %

XXIII — 28 %

XXIV — 13 %

XXV — 36 %

XXVI — 25 %

XXV
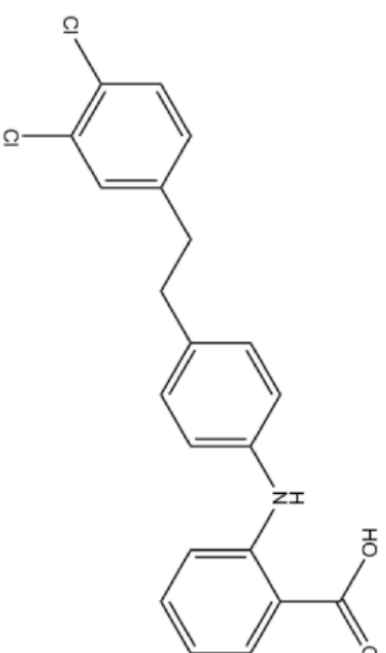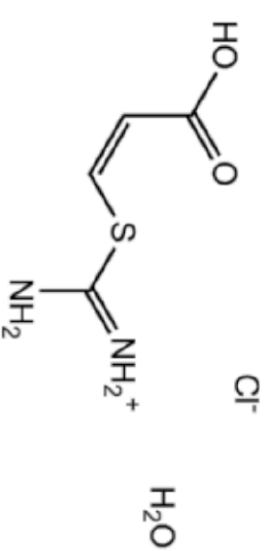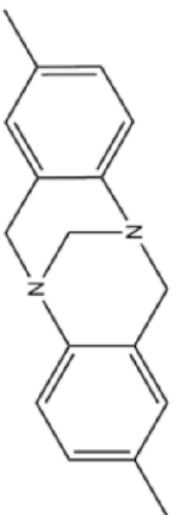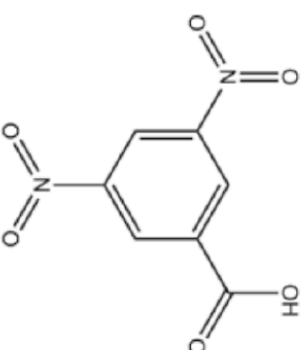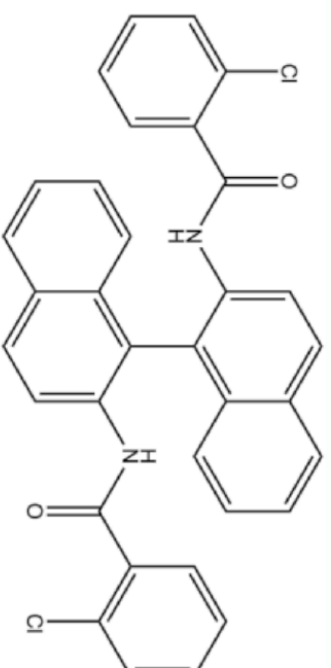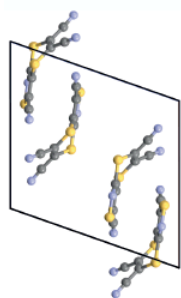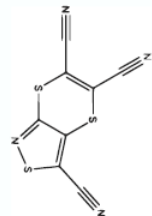
XXII

XXIV

XXVI

Relative lattice energy [kJ/mol/molecule]
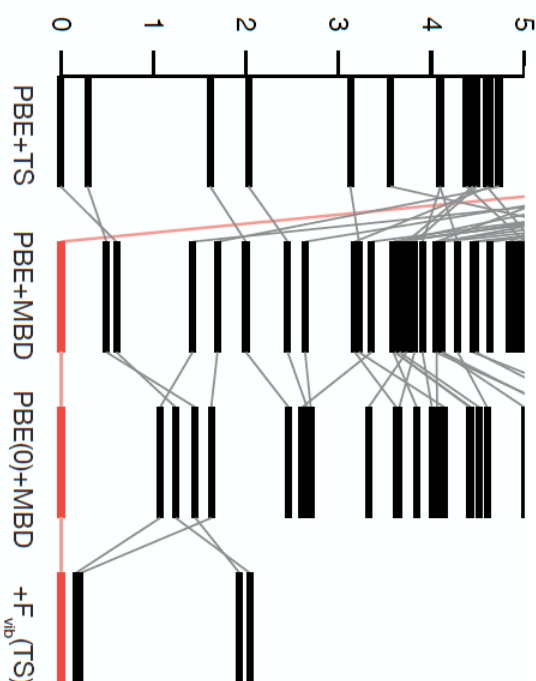
Realistic Drug Molecule

XXIII

Relative stability [kJ/mol]

PBE+TS   PBE+MBD   PBE0+MBD $+F_{vib}^{ha}$ (TS)

3 kJ/mol

Form A
Form B
Form C
Form D
Form E

Z' = 1
Z' > 1

Form A   Form B   Form C   Form D   Form E   Str. N70

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

- Innocent looking, but powerful and hard to solve equation

- Encodes (almost) all the physics (+ chemistry and biology) of real materials

- Wide range of useful and powerful approximations

- Can ML techniques enable future breakthroughs in modeling and understanding nucleoelectronic systems?