An efficient real-space density functional algorithm[1,2]

with S. A. Chin[3], S. Janecek[1,4], M. Liebrecht[1]and R. Zillich[1]

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[4]Institut de Ciència de Materials de Barcelona (ICMAB–CSIC), Campus de Bellaterra, 08193 Barcelona, Spain

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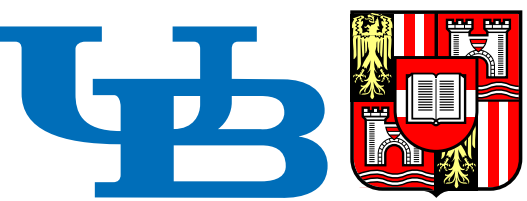


Der Wissenschaftsfonds.

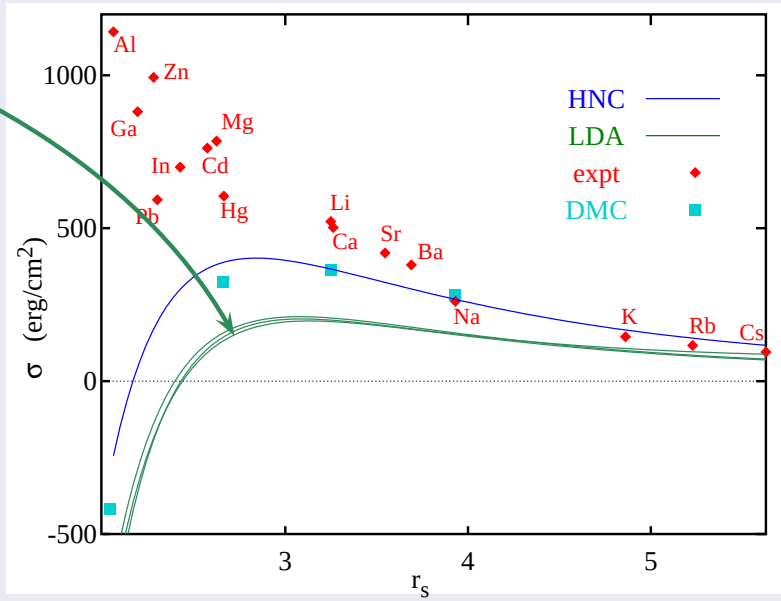
Outline

My first exposures to DFT

E. K. and Walter Kohn, **PRL57**, 862 (1986)

Surface energy for simple model systems in:

- LDA (Lang, Kohn, 1971)



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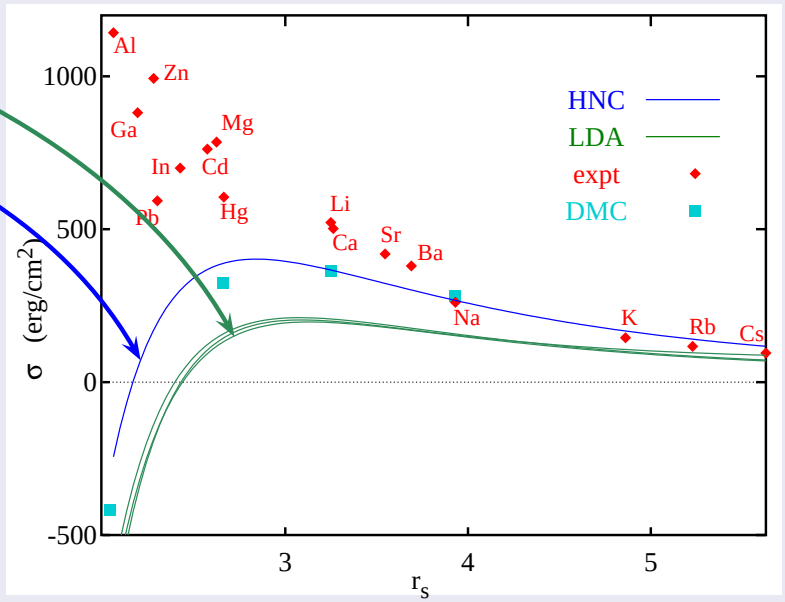

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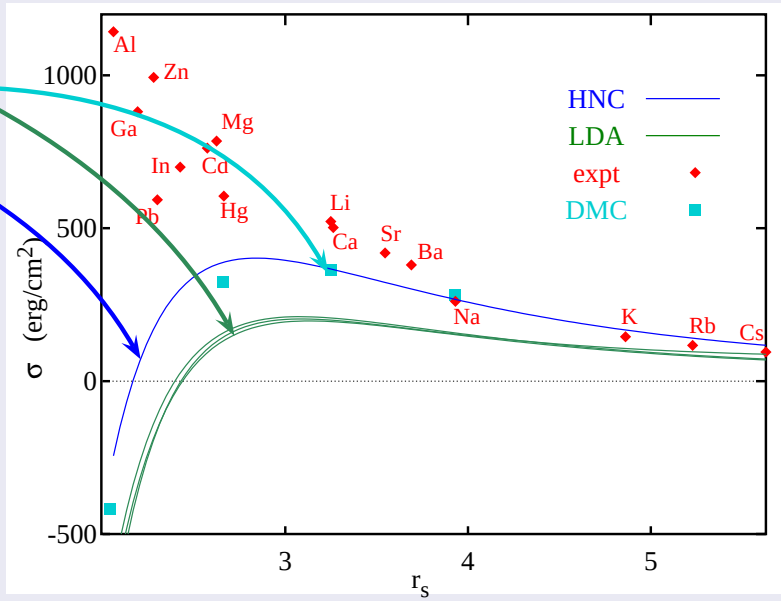

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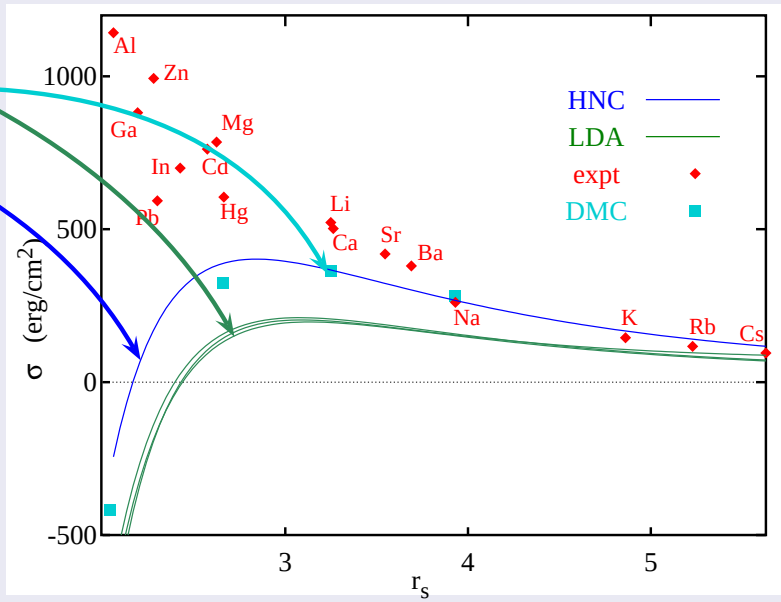

Conclusion

- LDA is significantly off
- LDA must be fixed by ad-hoc corrections (GGA) BUT
- LDA is the only choice in complicated geometries

Surface energy of simple metals
Poking into a wasp-nest

- FHNC-EL generalizable to non-uniform Fermi systems (E. K. and W. Kohn and G.-X. Qian: PR **B32**, 5693 (1985); E. K. and W. Kohn: PRL **57**, 862 (1986).)

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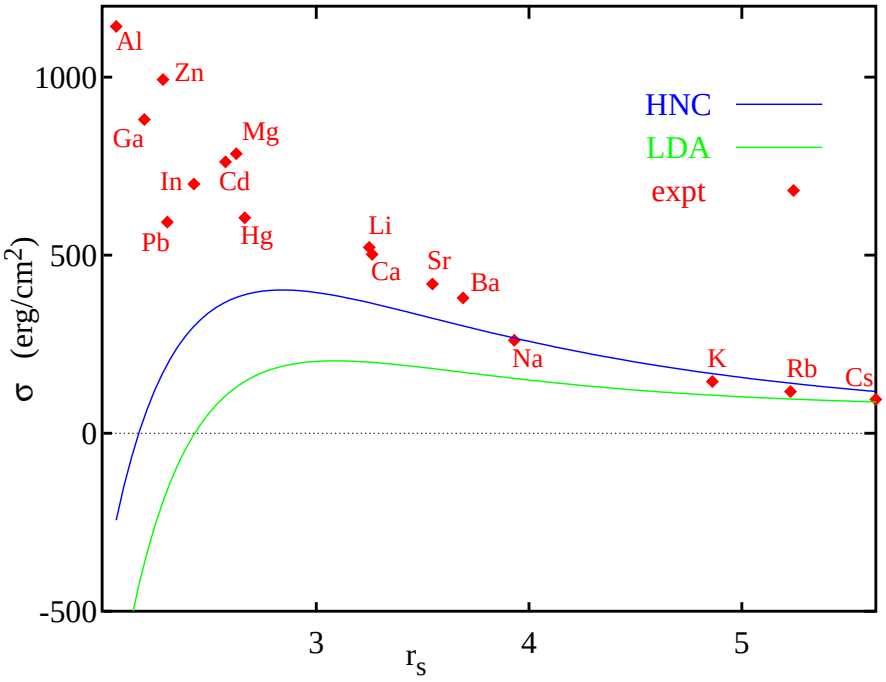

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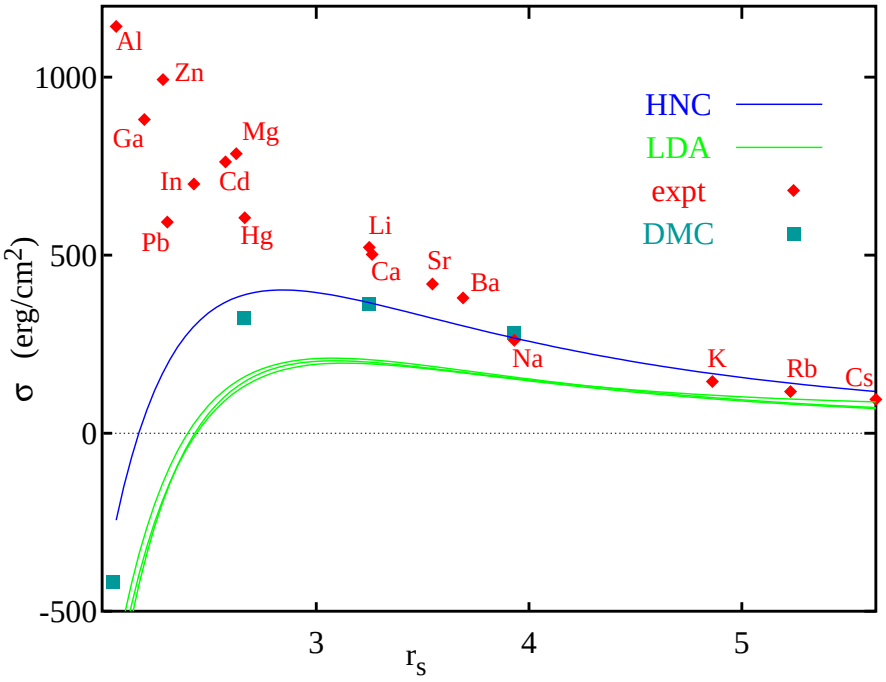
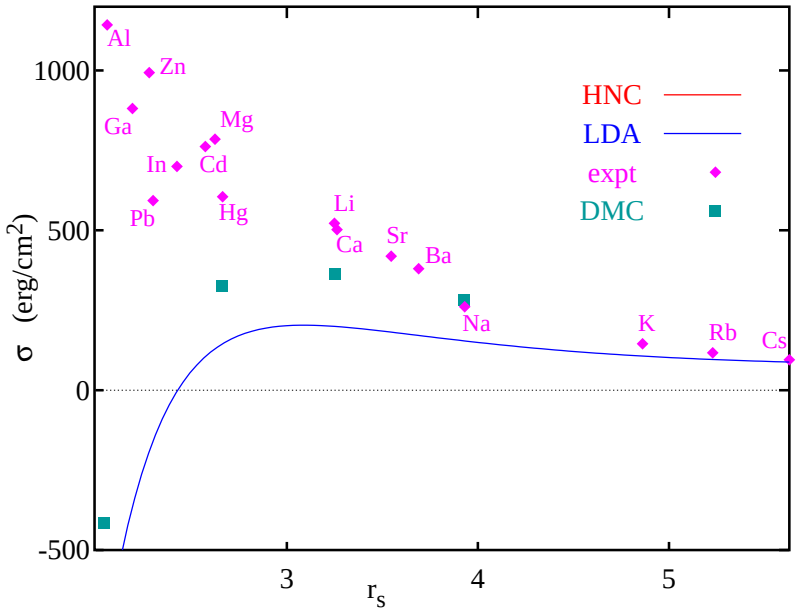
- Excellent agreement of FHNC-EL for metallic surface energies with GFMC ☺



Analysis of surface energies
... a learning experience in many-body physics

- Try LDA;



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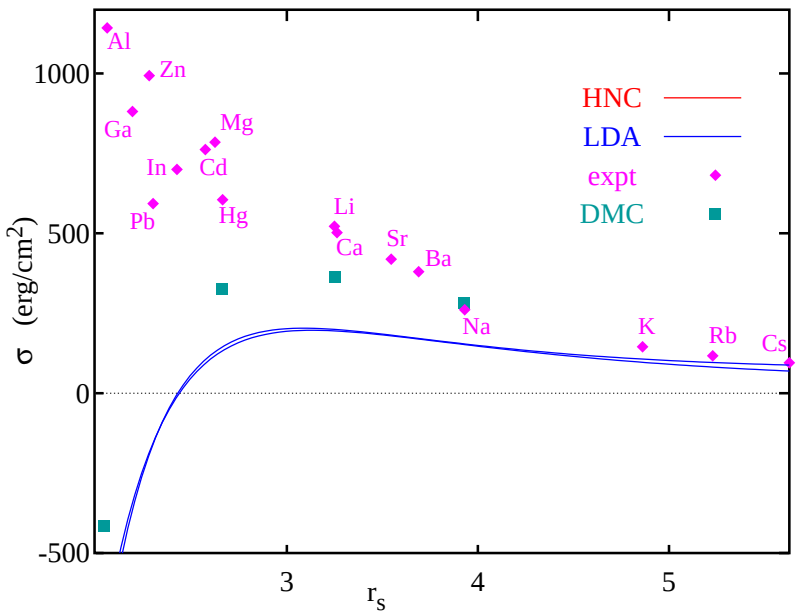

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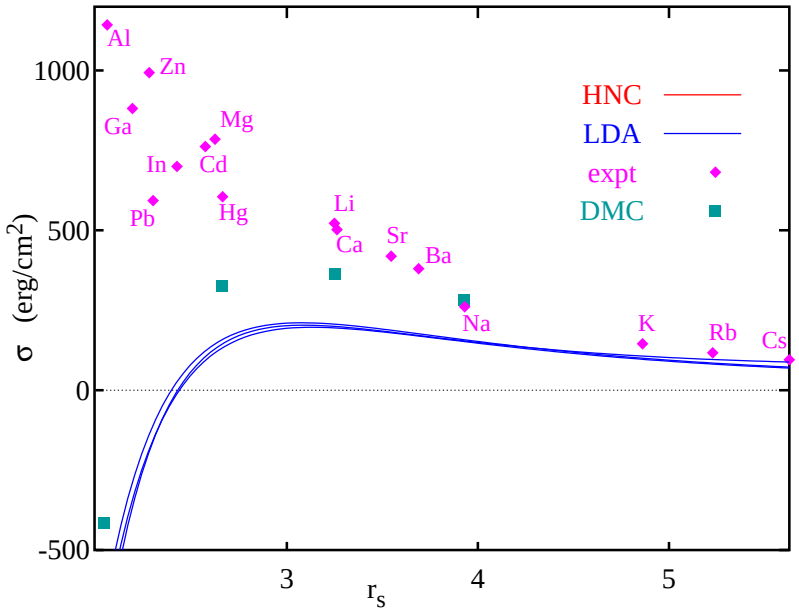
  $V_{ph}(r) = v_c(r) C_{bulk}(r, r_{cm})$;



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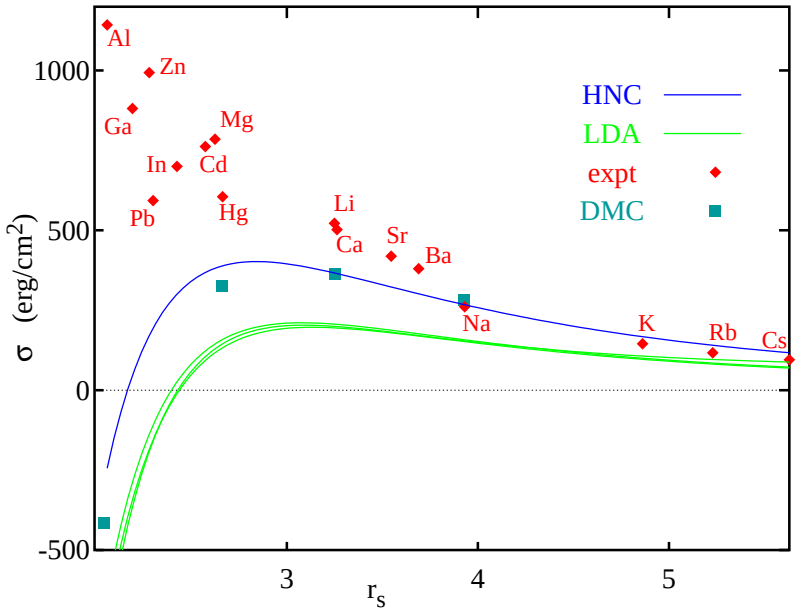

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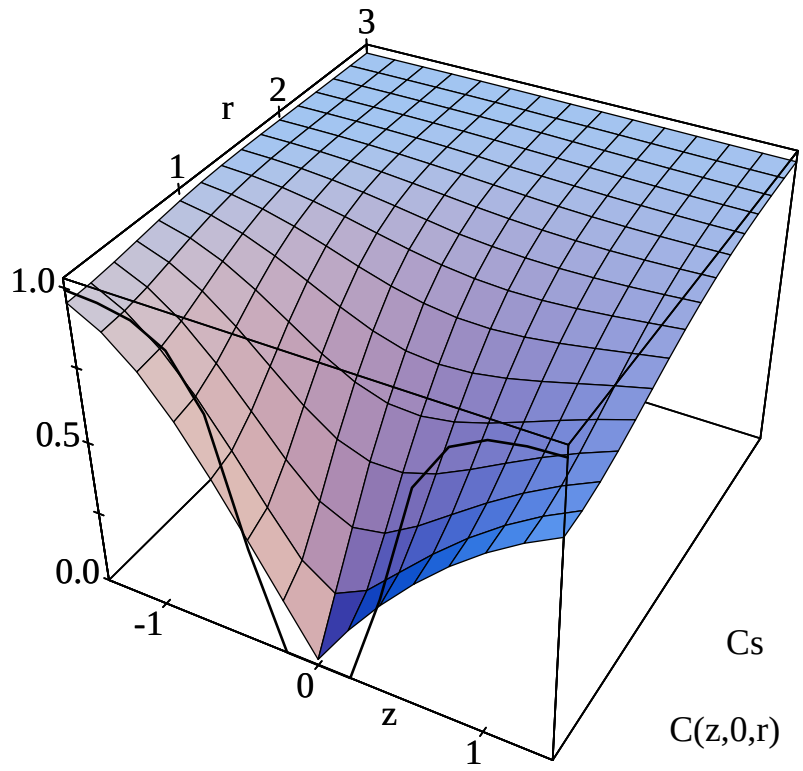
- Conclusion: The local structure is just different !



Closed-shell atoms

Correlation energy – everything beyond Hartree-Fock

	expt.	*FHNC*	*LDA*	*GGA*	*GGA′*
Be	-0.0944	-0.107	-0.224	-0.099	-0.094
Ne^{+6}	-0.18	-0.109	-0.333	-0.026	-0.136
Ne	-0.393	-0.421	-0.74	-0.41	-0.39
Na^{+1}	-0.396	-0.419			
Mg^{+2}	-0.402	-0.418			
Al^{+3}	-0.409	-0.418			
Si^{+4}	-0.417	-0.419			
P^{+5}	-0.426	-0.419			
S^{+6}	-0.434	-0.421			
...					

"LDA is 99.5 percent accurate" (A well known DFT practitioner)

Electronic Hamiltonian in a magnetic field

$$H = \underbrace{\frac{1}{2m}\sum_{i=1}^{N}\left[-i\hbar\nabla_i + e\mathbf{A}(\mathbf{r}_i)\right]^2}_{1} + \underbrace{\sum_{i<j}^{N}\frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}}_{2} + \underbrace{\sum_{i=1}^{N} V_{ext}(\mathbf{i})}_{3}$$

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(3) Ion core (pseudo-)potentials. A mess....

Kohn-Sham Equation

Mapping the many-body problem onto a one-body problem

Kohn-Sham equations:

Effective Schödinger ("Kohn-Sham") equation

$$\left[\frac{1}{2m}(\mathbf{p}+e\mathbf{A}(\mathbf{r}))^2+\hat{V}^{\sigma}_{\mathrm{KS}}[\rho^{\uparrow},\rho^{\downarrow}](\mathbf{r})\right]\psi_{i,\sigma}(\mathbf{r})=\epsilon_{i,\sigma}\psi_{i,\sigma}(\mathbf{r})$$

KS-wavefunctions $\psi_{i,\sigma}(\mathbf{r})$

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Densities

$$\rho_{\sigma}(\mathbf{r})=\sum_{i=1}^{N_{\sigma}}|\psi_{i,\sigma}(\mathbf{r})|^2,\ \rho(\mathbf{r})=\sum_{\sigma}\rho_{\sigma}(\mathbf{r})$$

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Self-consistency iterations

Define: *evolution operator* $\mathcal{T}(\epsilon) \equiv e^{-\epsilon \hat{H}}$

Solving Schrödinger-like equations
The imaginary timestep method

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Then:

- The sequence $\{\psi_i^{(k)}(\mathbf{r})\}$ converges towards the low-lying eigenstates.

Eigenvalue solver – operator factorizations

Calculating $e^{-\epsilon \hat{H}} = e^{-\epsilon(\hat{T}+\hat{V})}$

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"Trotter Formula" - Second order factorization

$$\mathcal{T}_2(\epsilon) = e^{-\frac{1}{2}\epsilon\hat{V}} e^{-\epsilon\hat{T}} e^{-\frac{1}{2}\epsilon\hat{V}} + \mathcal{O}(\epsilon^3)$$

- Calculate $e^{-\frac{1}{2}\epsilon\hat{V}}$ in real space, $e^{-\epsilon\hat{T}}$ in momentum space.

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Large ϵ
Small ϵ
$\Leftrightarrow$
Fast convergence, poor accuracy
Slow convergence, good accuracy

Fourth order factorization

Suzuki '96, Chin '97, Chin and Forbert '01

$$\begin{aligned}
\mathcal{T}_4(\epsilon) &= e^{-\frac{1}{6}\epsilon\hat{V}} e^{-\frac{1}{2}\epsilon\hat{T}} e^{-\frac{2}{3}\epsilon\widetilde{V}} e^{-\frac{1}{2}\epsilon\hat{T}} e^{-\frac{1}{6}\epsilon\hat{V}} + \mathcal{O}(\epsilon^5) \\
\widetilde{V} &= \hat{V} + \frac{\epsilon^2}{48}[\hat{V},[\hat{T},\hat{V}]] \quad \Rightarrow \quad \widetilde{V}(\mathbf{r}) = V(\mathbf{r}) + \frac{\hbar^2\epsilon^2}{48m}|\nabla V(\mathbf{r})|^2
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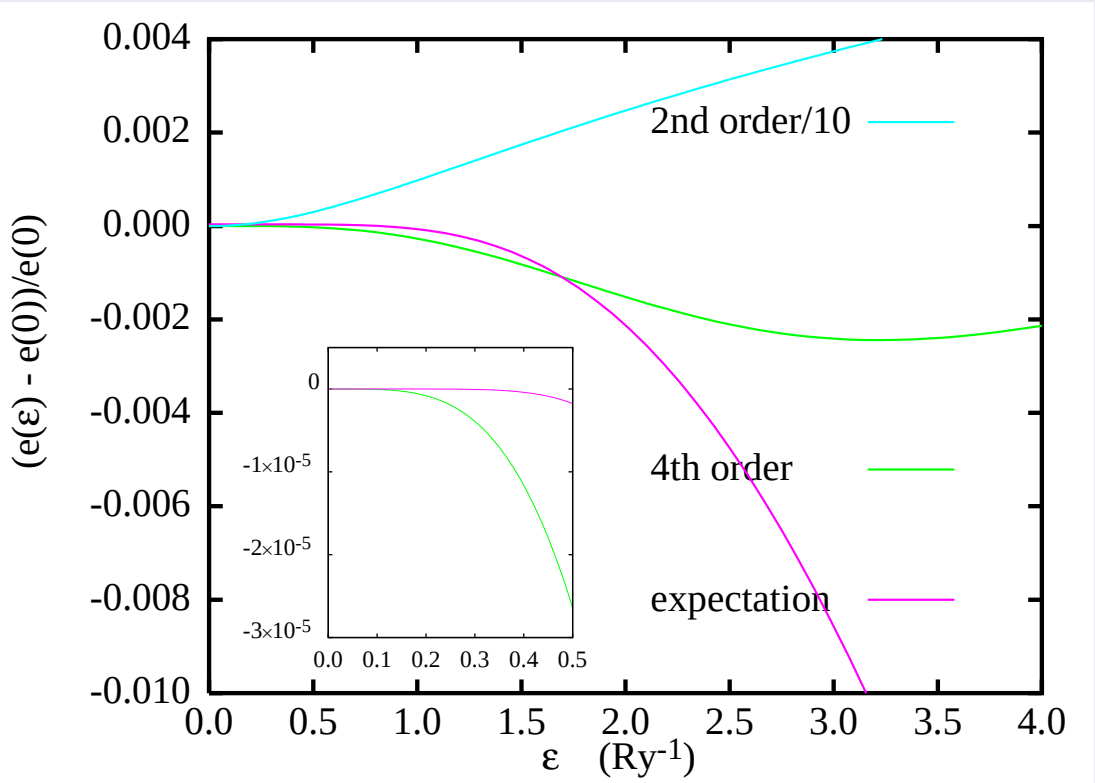
- Local potential: $\Rightarrow$ calculate in coordinate space
- Double commutator term $\propto |\nabla V(\mathbf{r})|^2$: $\Rightarrow$ calculate in coordinate space.
- Kinetic energy: $\Rightarrow$ calculate in momentum space
  Plane waves are eigenstates of $\hat{T}$ in any uniform discretization

$$t_n(k) = \left(\frac{2\sin\kappa}{h}\right)^2 \left[1 + \frac{1}{3}\sin^2\kappa + \frac{8}{45}\sin^4\kappa + \frac{4}{35}\sin^6\kappa + \ldots\right]$$

$$\kappa = kh/2 \quad h\text{: discretization step size}$$

Convergence Comparison



- typical speed gain (system dependent): 10 - 100
- expectation energy $\langle\psi_i(\epsilon)|\,\hat{H}\,|\psi_i(\epsilon)\rangle = e_i(\epsilon) + \mathcal{O}(\epsilon^8)$ gives good convergence tests.

High-order propagation: . . .
Can we do even better ?

The “nogo theorem” (Chin, Suzuki)

- There is no factorization of the diffusion operator of the form

$$\mathcal{T}(\epsilon) = e^{-\epsilon(\hat{T}+\hat{V})} = \prod_{i=1}^{M} e^{-a_i\,\epsilon\hat{T}}\, e^{-b_i\,\epsilon\hat{V}} + \mathcal{O}(\epsilon^N)$$

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- Multi-Product Expansion are a way out

$$e^{-\epsilon(\hat{T}+\hat{V})} = \sum_{k=1}^{n} c_k \mathcal{T}_2^k\left(\frac{\epsilon}{k}\right) + \mathcal{O}(\epsilon^{2n+1}) \equiv \mathcal{T}_n(\epsilon) + \mathcal{O}(\epsilon^{2n+1}),$$

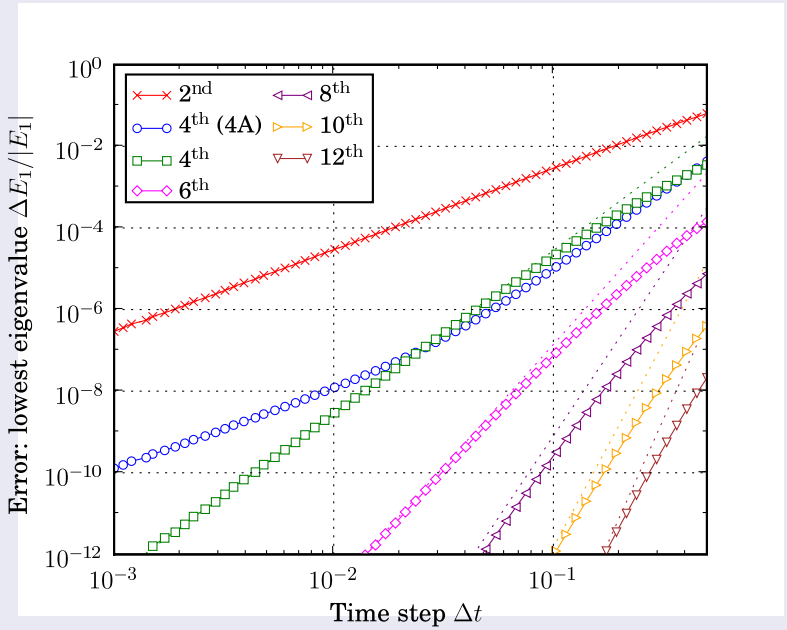
coefficients:

$$c_i = \prod_{j=1(\neq i)}^{n} k_i^2/(k_i^2 - k_j^2)$$

High-Order propagation

How easy is it to solve the Schrödinger equation in 3D ?

- Higher order methods can converge in very few steps



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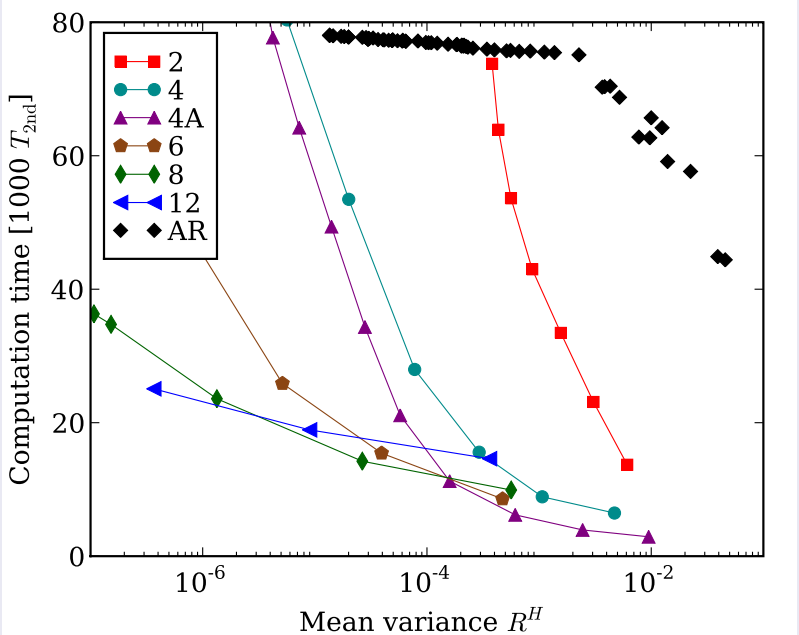

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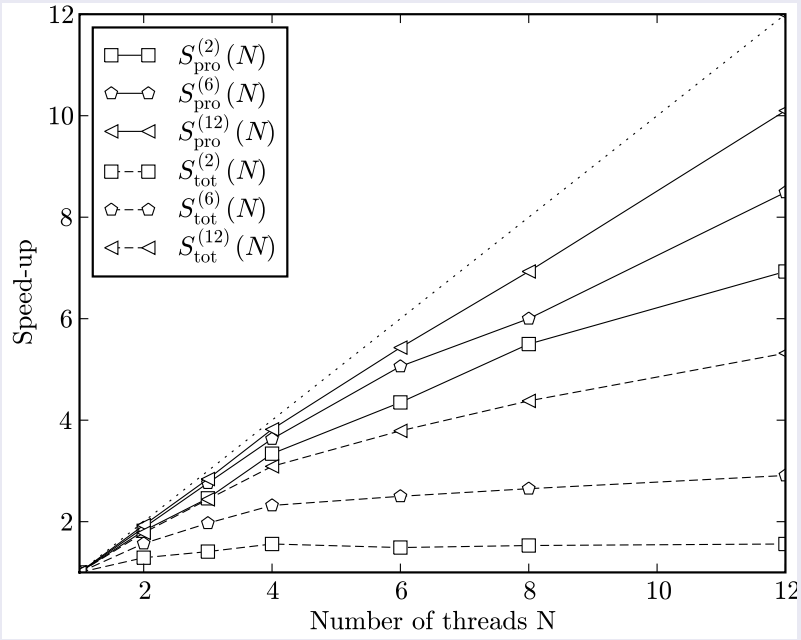

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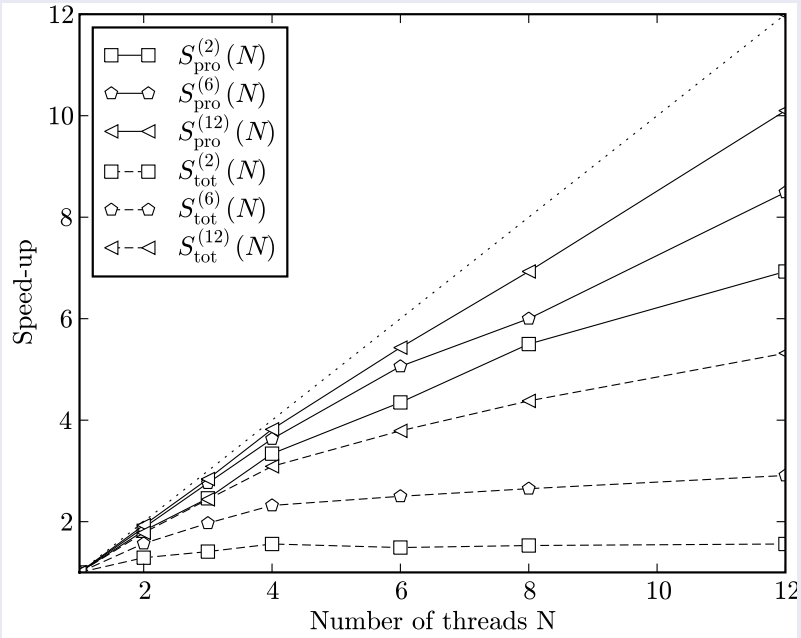
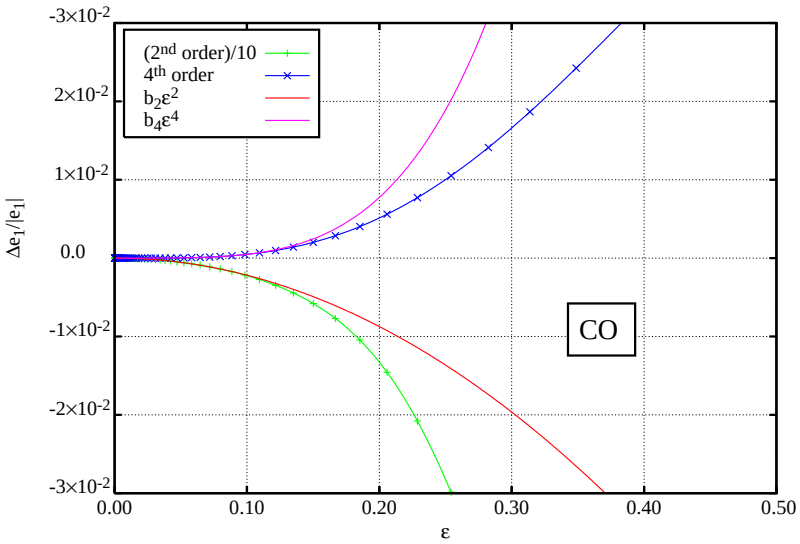


Solving a local Schrödinger equation in 3D is embarrassingly easy

Program for download:

S. Janecek and E. K., Computer Physics Communications 178, 835 (2008)

Convergence for realistic systems

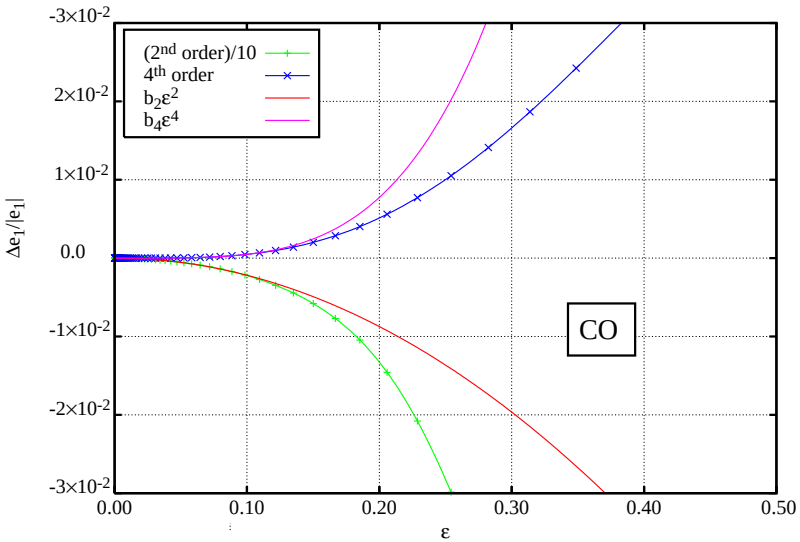


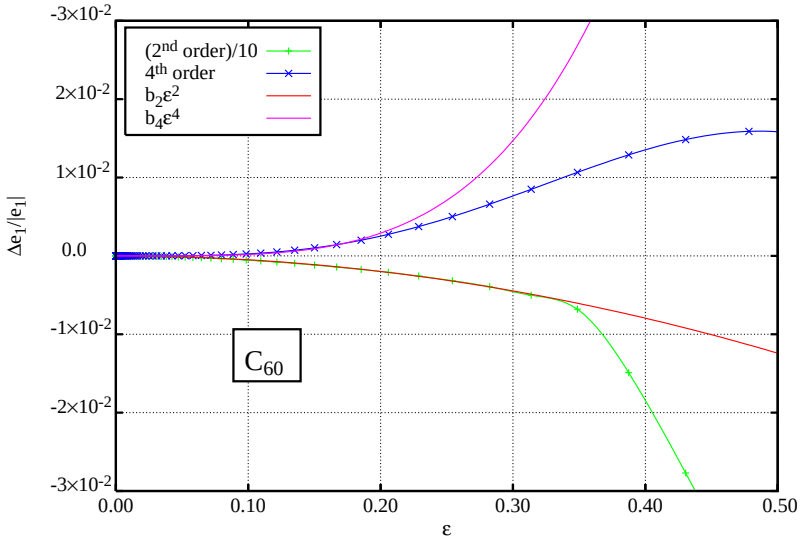
Convergence deteriorates very little

- for small systems: CO

Recall $N \propto 1/\epsilon$

Convergence for realistic systems





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- for large systems: C_{60}

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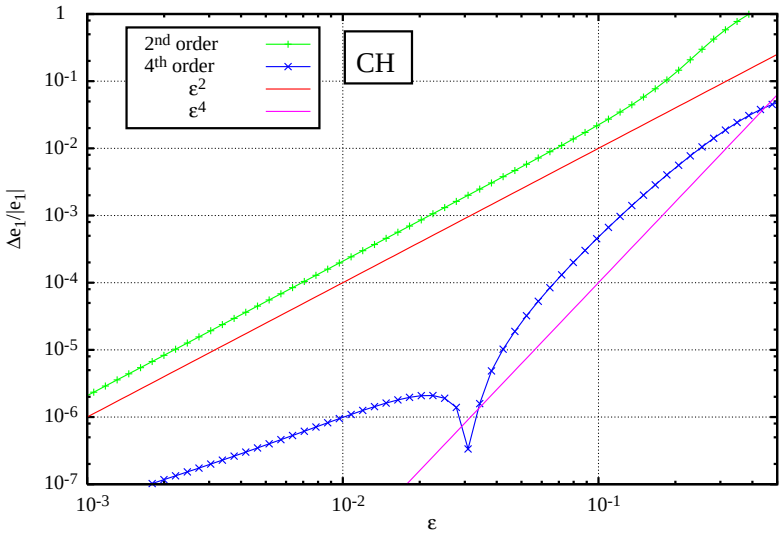

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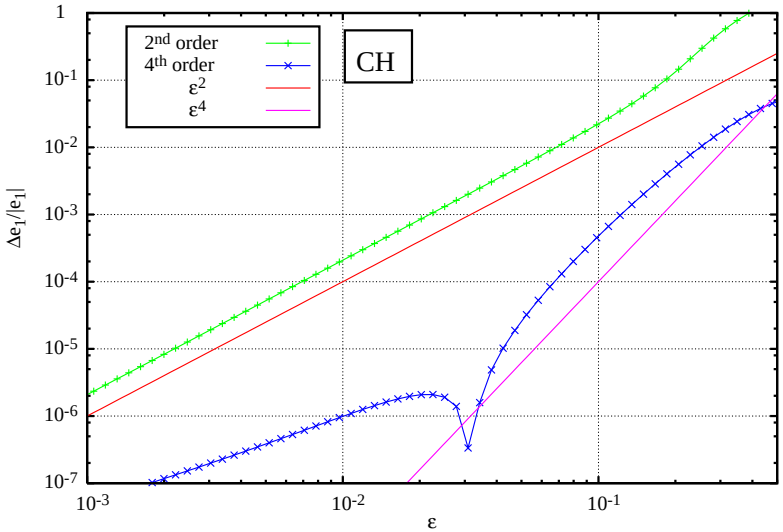
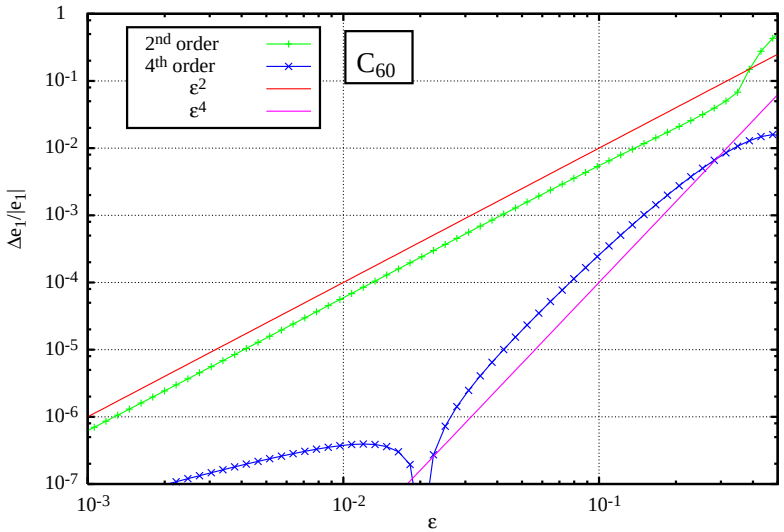
Convergence for realistic systems





Convergence deteriorates very little

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Homogenous Magnetic Fields

$$e^{-\frac{1}{2}\epsilon\hat{T}}: \hat{T} = \frac{1}{2m}\boldsymbol{P}^2 \rightarrow \hat{T} = \frac{1}{2m}\boldsymbol{\Pi}^2 = \frac{1}{2m}(\Pi_x^2 + \Pi_y^2),$$
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Exact Factorization

$$e^{-\frac{\epsilon}{2m}(\Pi_x^2+\Pi_y^2)} = e^{-\frac{\epsilon}{4m}C_E(\xi)\Pi_x^2} e^{-\frac{\epsilon}{2m}C_M(\xi)\Pi_y^2} e^{-\frac{\epsilon}{4m}C_E(\xi)\Pi_x^2}$$

$$\xi = \epsilon\frac{\hbar eB}{m},\ C_E(\xi), C_M(\xi): \text{ simple analytic functions}$$

Exact calculation of the kinetic energy: Algorithm

Redo kinetic energy:

$$\underbrace{e^{-\epsilon \hat{T}}\psi(x,y,z)}_{(4)} = \underbrace{e^{-\frac{\epsilon}{4m}C_E(\xi)\Pi_x^2}}_{(3)}\underbrace{e^{-\frac{\epsilon}{2m}C_M(\xi)\Pi_y^2}}_{(2)}\underbrace{e^{-\frac{\epsilon}{4m}C_E(\xi)\Pi_x^2}e^{-\frac{\epsilon}{2m}p_z^2}\psi(x,y,x)}_{(1)}$$

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Algorithm: Choose an n-point derivative formula

- (1) For all y, Fourier transform the x and the z -coordinate of each state to (k_x, k_z)-space.
  Multiply by $e^{-\frac{\epsilon\hbar^2}{2m}C_E(\xi)t_n(k_x+eBy/\hbar)-\frac{\epsilon\hbar^2}{2m}t_n(k_z)}$.
  $\Rightarrow$ N 2d-Fourier transforms.

Counting operations

$N \times N^2 \ln N^2$

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Algorithm: Choose an n-point derivative formula

- (2) For all k_x, k_z, Fourier transform now y to k_y-space.

  Multiply by $e^{-\frac{\epsilon\hbar^2 t_n(k_y)}{2m}C_M(\xi)}$.

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- (3) For all k_x, k_z, do the inverse transformation back to y.
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$$N \times N^2 \ln N^2 + N^2 \times N \ln N + N^2 \times N \ln N + N \times N^2 \ln N^2 = 2N^3 \ln N^3$$

Operations: $\Rightarrow$ Same as two 3D-FFt's !

Gauge invariance

What we learned in E&M and quantum mechanics

- The gauge tansformation

$$\begin{aligned} \mathbf{A}(\mathbf{r}) &\rightarrow \mathbf{A}'(\mathbf{r}) = \mathbf{A}(\mathbf{r}) + \boldsymbol{\nabla}\chi(\mathbf{r}) \\ \psi(\mathbf{r}) &\rightarrow \psi'(\mathbf{r}) = e^{ie\chi(\mathbf{r})/\hbar}\psi(\mathbf{r}) \end{aligned}$$

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- This is true only if we have no discretization errors.
  For example: For a discretized derivative operator

$$f'(x) \approx \frac{f(x+h) - f(x-h)}{2h}$$

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  chain- and product rules are only approximately satisfied.
- However: To be efficient, we want the mesh as coarse as possible.

Discrete gauge invariance

Why is this relevant ?

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The simple reason:

$$\frac{\partial}{\partial x} e^{ie\chi(x)/\hbar} = \frac{ie}{\hbar} \frac{\partial \chi(x)}{\partial x} e^{ie\chi(x)/\hbar)}$$

but

$$\frac{e^{ie\chi(x+h)/\hbar} - e^{ie\chi(x-h)/\hbar}}{2h} \neq \frac{ie}{\hbar} \left[\frac{\chi(x+h) - \chi(x-h)}{2h} \right] e^{ie\chi(x)/\hbar}$$

Is there a solution ?

What we find in the literature:

Indeed, within a finite linear variational subspace, gauge-origin invariance can never be obtained exactly, only approximately for small displacements of the gauge origin. In such cases, therefore, the calculated energies and properties will depend on the choice of gauge origin.

T. Helgaker, M. Jazuński, and K. Ruud, Chem. Rev. **99**, 293 (1999).

The way out

Let's solve the problem anyway !

Schwinger's gauge transport function

Let

$$f_i(\mathbf{r}) = \int^{x_i} A_i(\mathbf{r}) dx_i$$

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$\Rightarrow$ takes care of the phase factor in the wave function.

Homogeneous fields:

Let $\mathbf{A} = -By\mathbf{e}_x$, $f_x(\mathbf{r}) = -Bxy$.
Represent the wave function in momentum space:

$$\psi(x) = \sum_k \psi_k e^{ikx} .$$

$$\left[-i\hbar\frac{\partial}{\partial x_i} + eA_i(\mathbf{r})\right]^2 \psi(x) = e^{ieBxy/\hbar}\frac{\partial^2}{\partial x^2}e^{-ieBxy/\hbar}\sum_k \psi_k e^{lkx}$$

$$= \sum_k \psi_k e^{ieBxy/\hbar}\frac{\partial^2}{\partial x^2}e^{i(k-eBy/\hbar)x} = \sum_k t_n(k - eBy/\hbar)\psi_k e^{lkx}$$

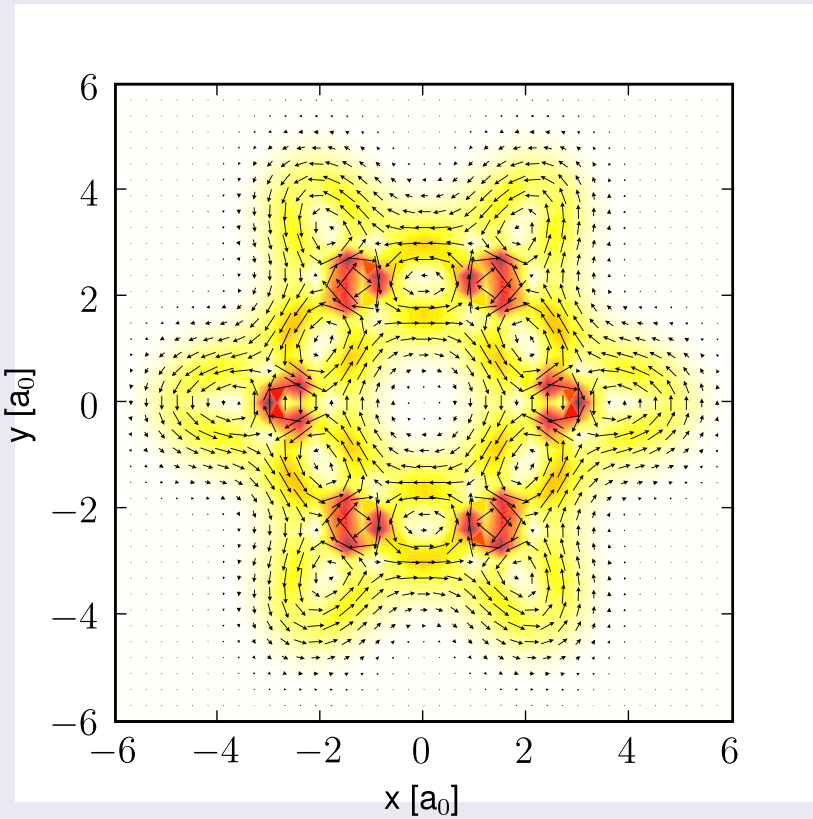
with – for an n-point second derivative fomula

$$t_n(k) = \left(\frac{2\sin\kappa}{h}\right)^2 \left[1 + \frac{1}{3}\sin^2\kappa + \frac{8}{45}\sin^4\kappa + \frac{4}{35}\sin^6\kappa + \ldots\right] .$$

Induced currents

Current density:

$$\mathbf{j}(\mathbf{r}) = \frac{e}{2m} \sum_i \left[\psi_i^* \mathbf{\Pi} \psi_i + \psi_i \left(\mathbf{\Pi} \psi_i\right)^*\right] = \frac{e}{m} \sum_i \Re e \left\{\psi_i^* \mathbf{\Pi} \psi_i\right\},$$



Induced current density in a C_6H_6 molecule at 1Tesla

Featured in Phys. Rev. B Kaleidoscope

S. Janecek and E. K., Phys. Rev. B77, 245115 (2008)

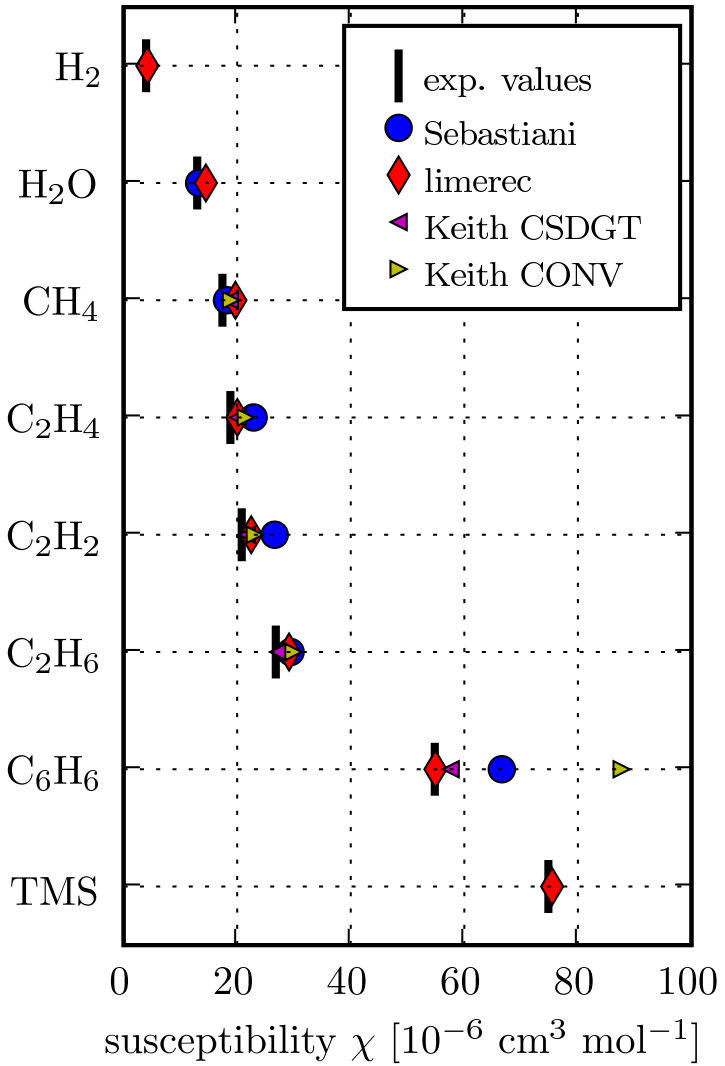
Magnetic susceptibility

Induced magnetic dipole moment

$$\mathbf{m} = \frac{1}{2} \int \mathbf{r} \times \mathbf{j}(\mathbf{r})\, d^3\mathbf{r}.$$

Susceptibility:

$$\begin{aligned} \chi_{ij} &= \frac{\partial M_i}{\partial H_j} = \frac{\partial B_j}{\partial H_j} \frac{\partial M_i}{\partial B_j} \\ &= \frac{N\mu_0}{V} \frac{\partial}{\partial B_i} m_j. \end{aligned}$$



NMR shifts: Measure local field strengths

Induced magnetic field:

$$\mathbf{B}^{\mathrm{ind}}(\mathbf{r}) = \frac{\mu_0}{4\pi} \int d^3r' \, \frac{\mathbf{r}' - \mathbf{r}}{|\mathbf{r}' - \mathbf{r}|^3} \times \mathbf{j}(\mathbf{r}')$$

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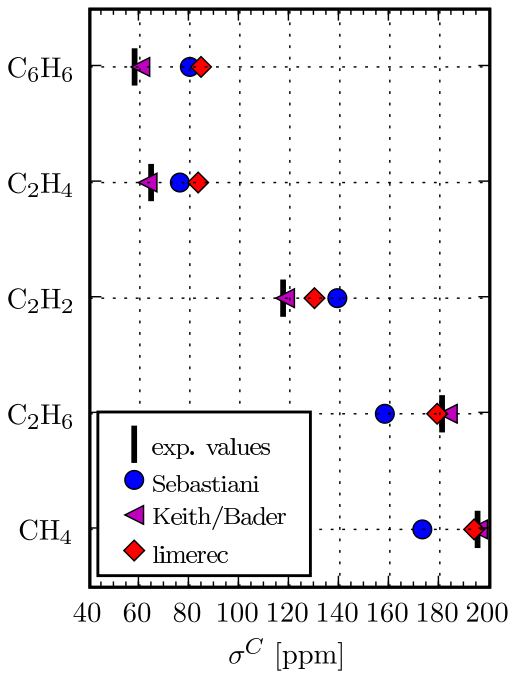
Chemical shift tensor

$$\sigma(\mathbf{R}) = \frac{\partial \mathbf{B}^{\text{ind}}(\mathbf{R})}{\partial \mathbf{B}^{\text{ext}}}.$$

NMR shift for C atoms in C_6H_6



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Results are just as good as DFT lets them be.

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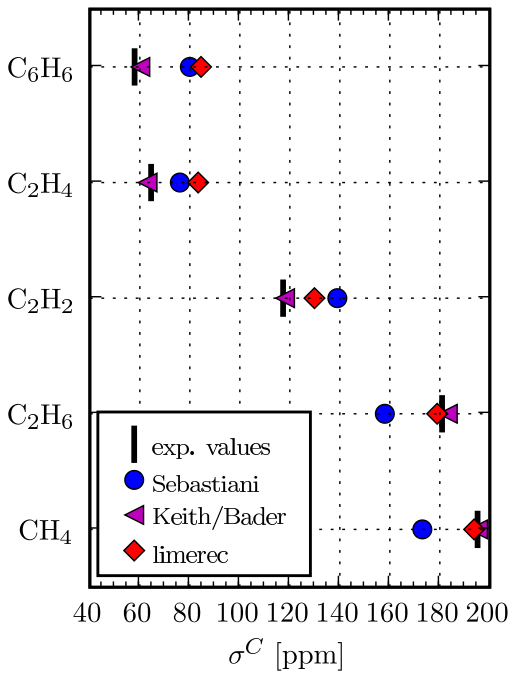

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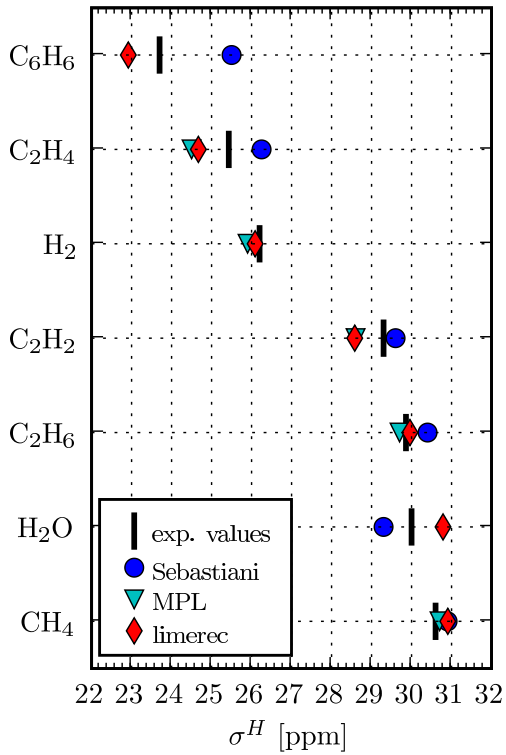
NMR shift for H atoms in C_6H_6



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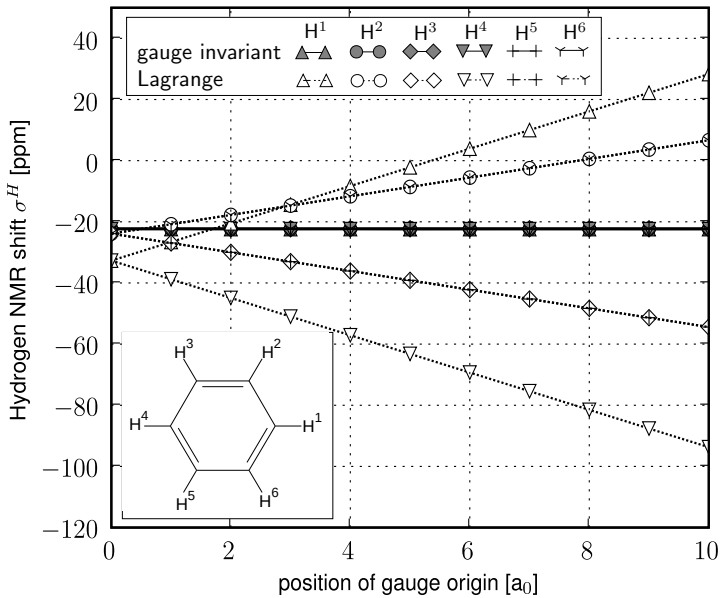
Gauge invariance

Results are stable against gauge transformations,

Sensitive against gauge transformations
(if one does it wrong !)



Motivation
First set of applications

Cluster physics is a research field of high interest

- Clusters represent the connection between molecules and solids.
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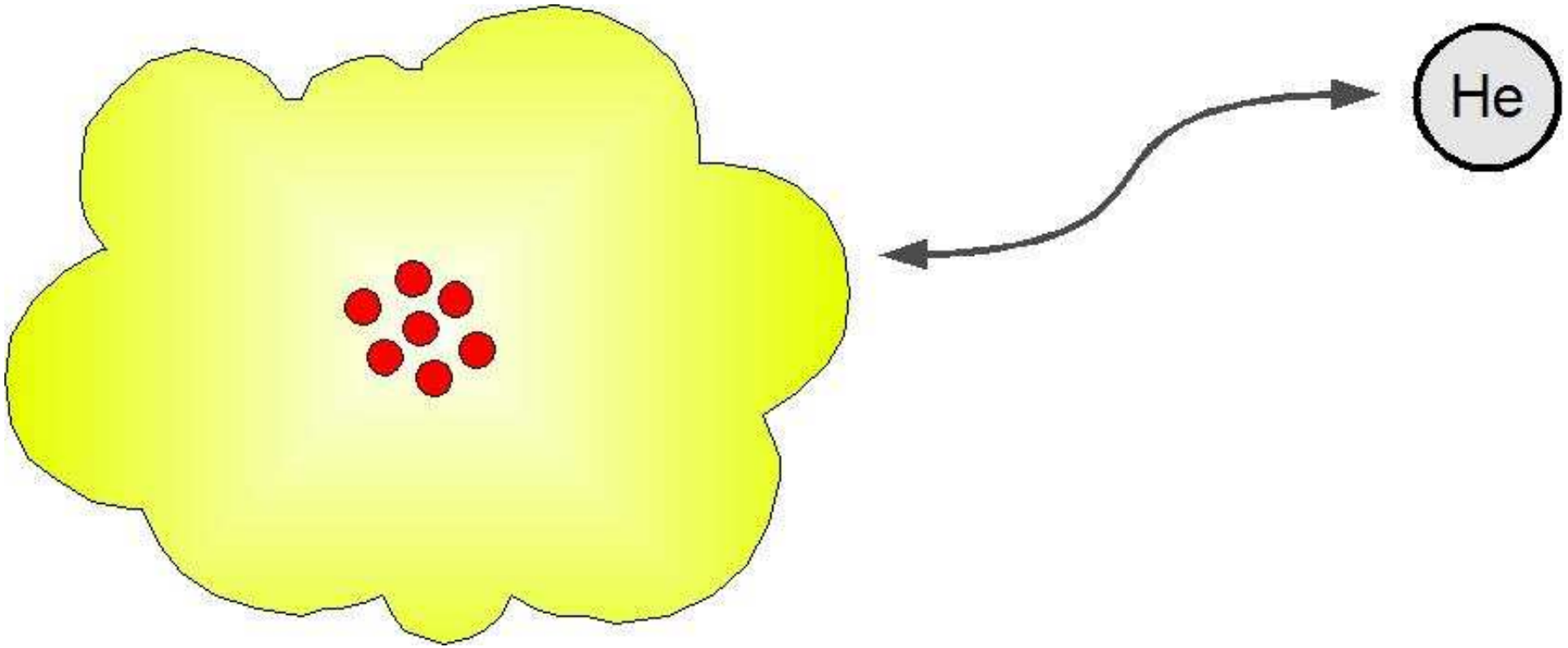
Model for cluster-helium interaction is required!

Physical Model

Helium atoms: quantum mechanics



Ions: fixed positions, classical mechanics

Electrons: quantum mechanics

Magnesium-Helium Interaction Model

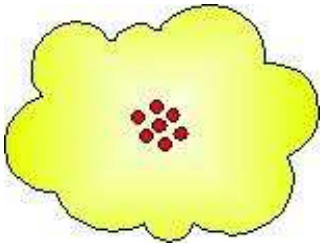
- electrostatic interactions: Helium atoms are considered as polarizable spheres
- Pauli repulsion: Phenomenological
- long-range part: Non-local dispersion corrections

The new interactions have to be added to the **self-consistency** cycle.

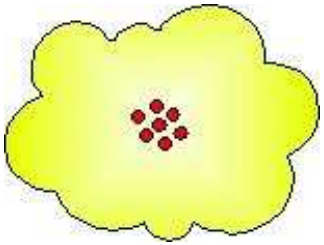
Effective Potential in Helium enviroment:

$$v_s[\rho](\mathbf{r}) = v(\mathbf{r}) + v_H[\rho](\mathbf{r}) + v_{xc}[\rho](\mathbf{r}) + v_C[\rho, \rho_{He}](\mathbf{r}) + v_P[\rho, \rho_{He}](\mathbf{r})$$

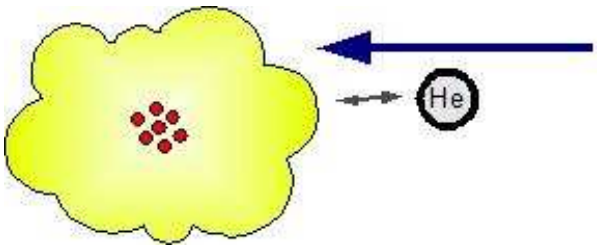
Calculating Cluster-Helium Potentials



calculate reference energy of undisturbed cluster

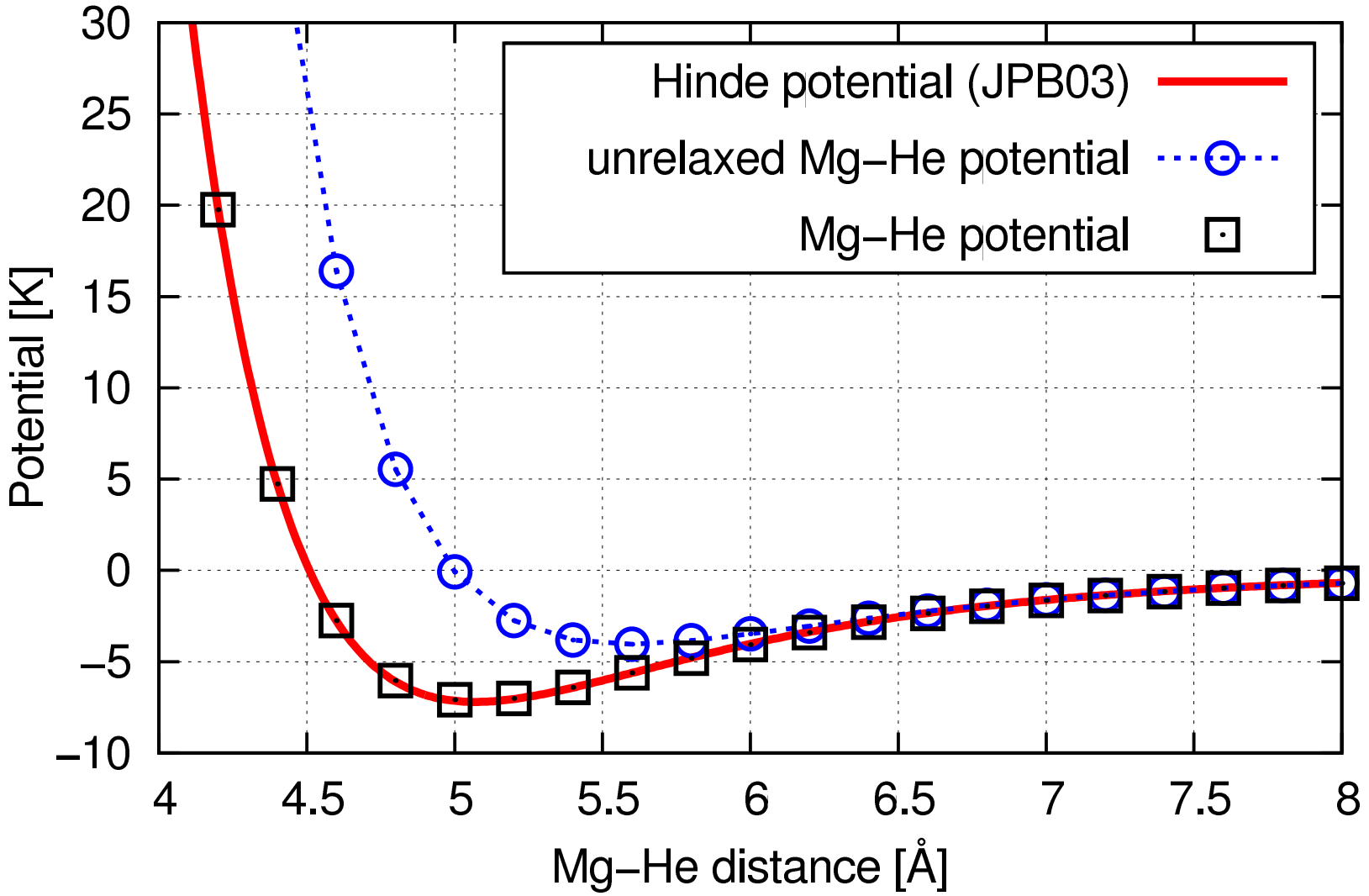


calculate energy-response of cluster to He-atom

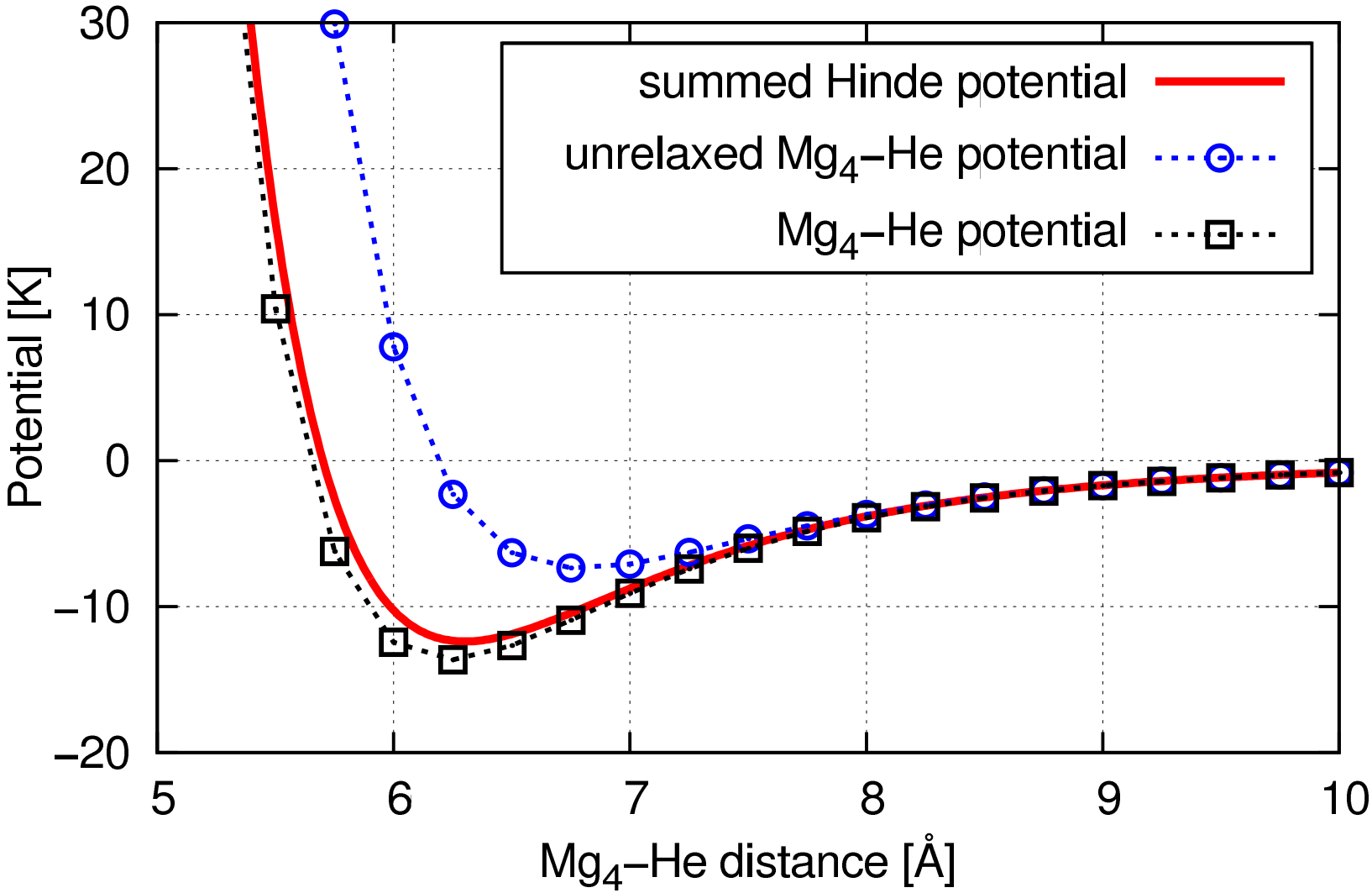


move He-atom

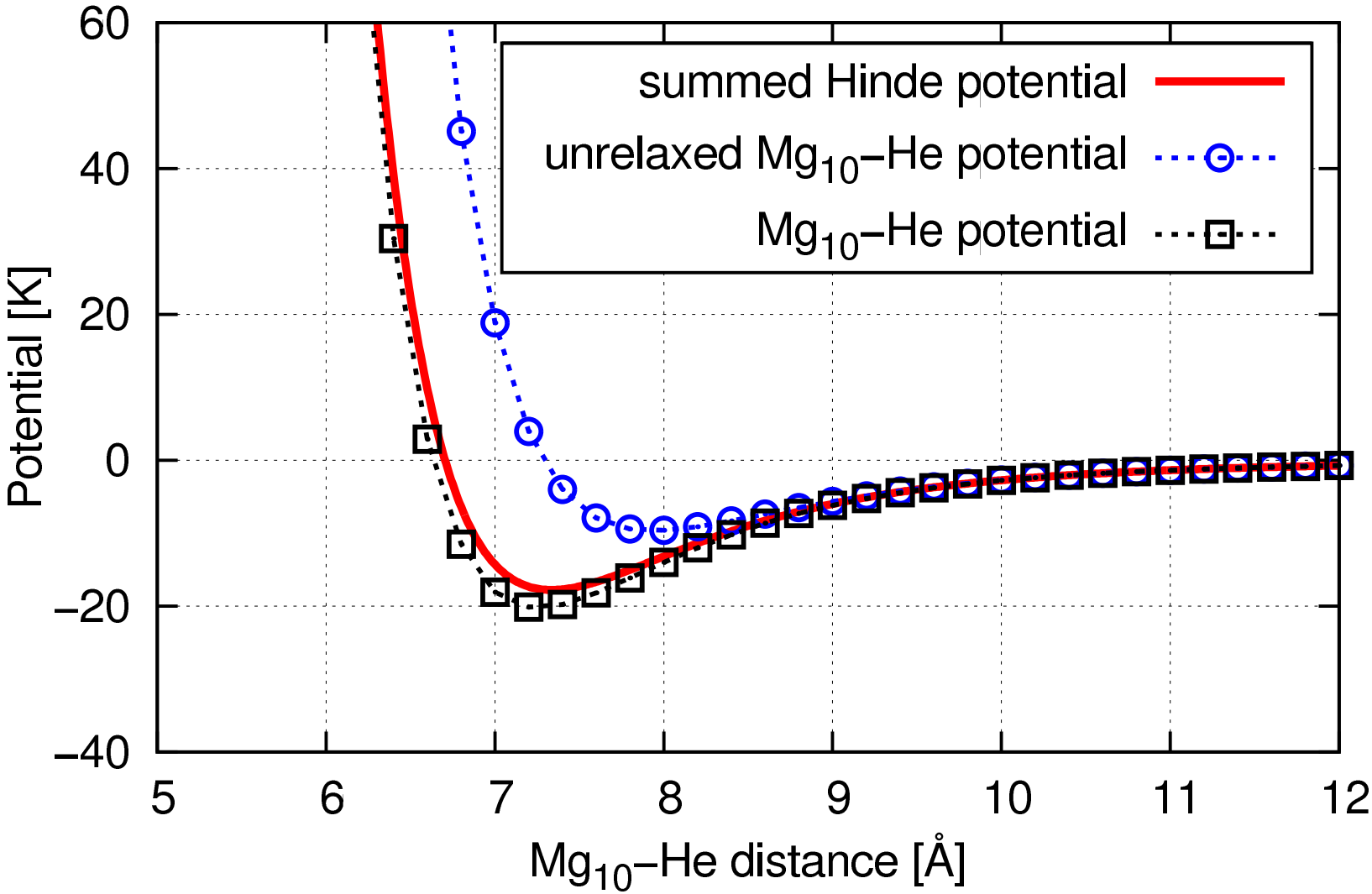
Mg-He Potential



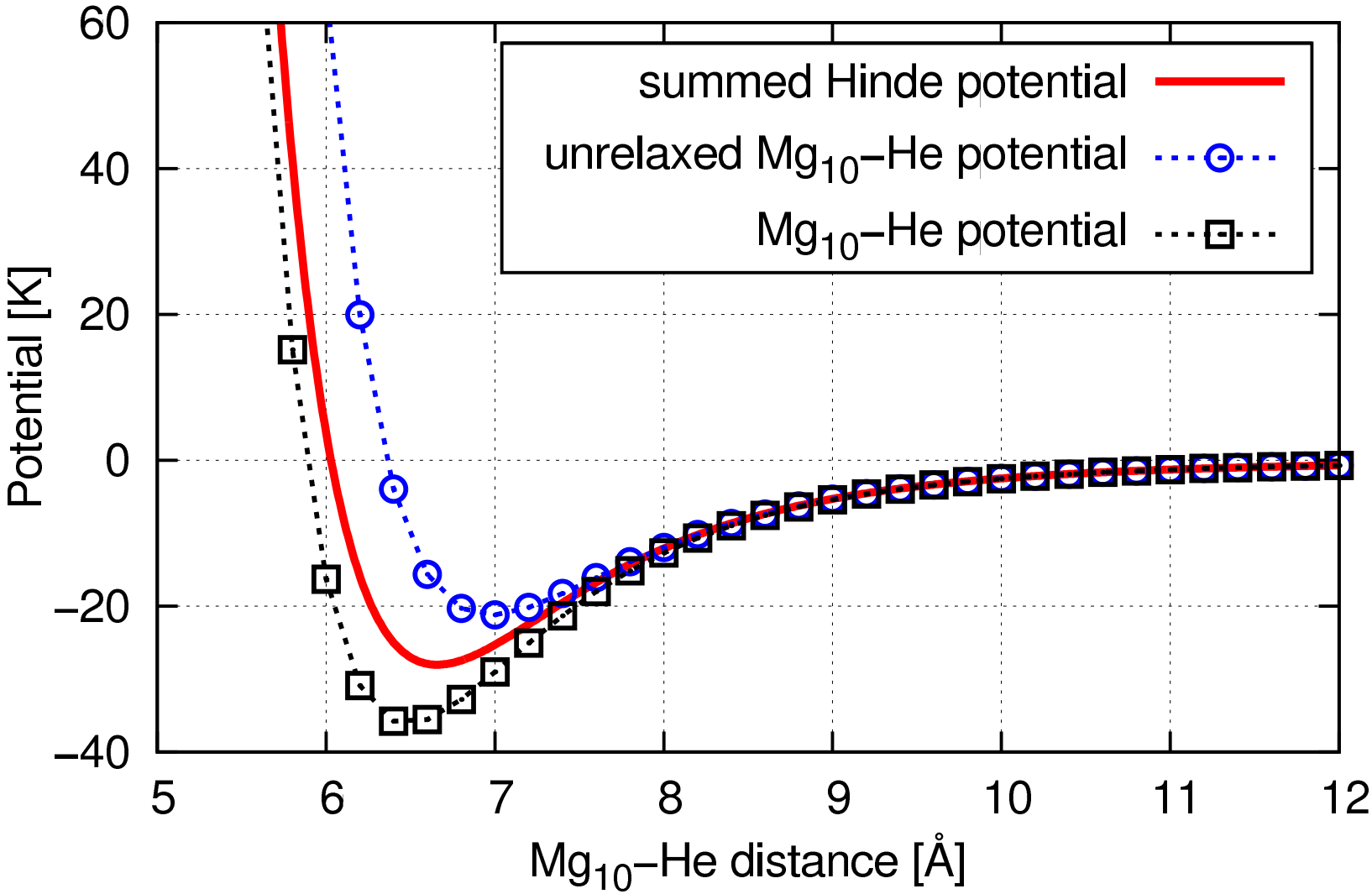
Mg_4-He Potential in z-Direction



Mg_{10}-He Potential in x-Direction



Mg_{10}-He Potential in z-Direction



Path Integral Monte Carlo - PIMC

- Quantum Monte Carlo method in the path integral formulation of quantum mechanics
- well suited for condensed systems like liquid Helium
- in every move the total potential energy is needed

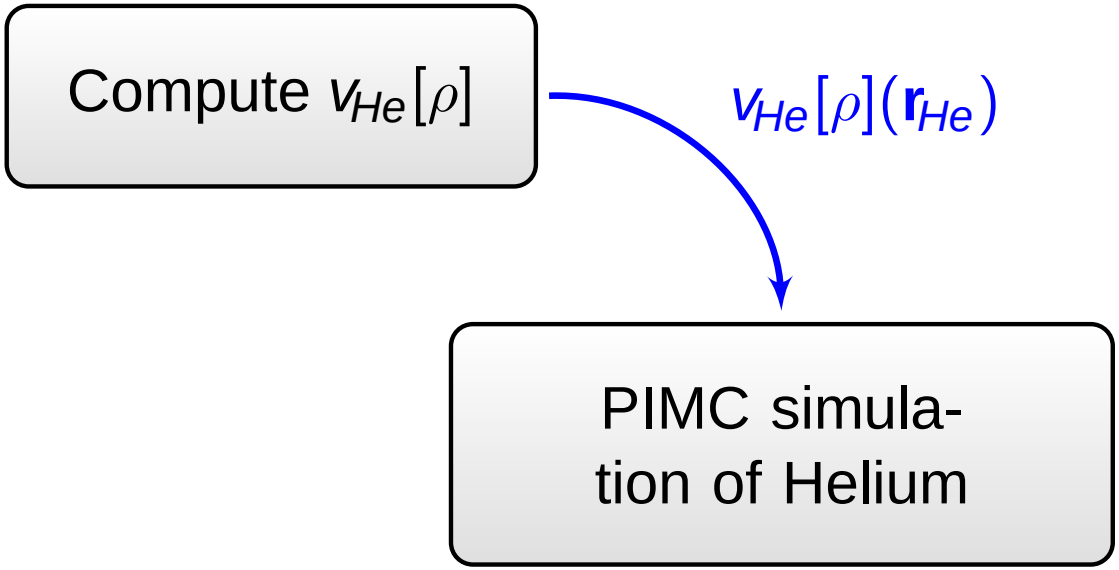
Helium Potential caused by one Mg-cluster

$$v_{He}[\rho](\mathbf{r}_{He}) = v_C[\rho](\mathbf{r}_{He}) + v_P[\rho](\mathbf{r}_{He}) + v_{nl}(\mathbf{r}_{He})$$

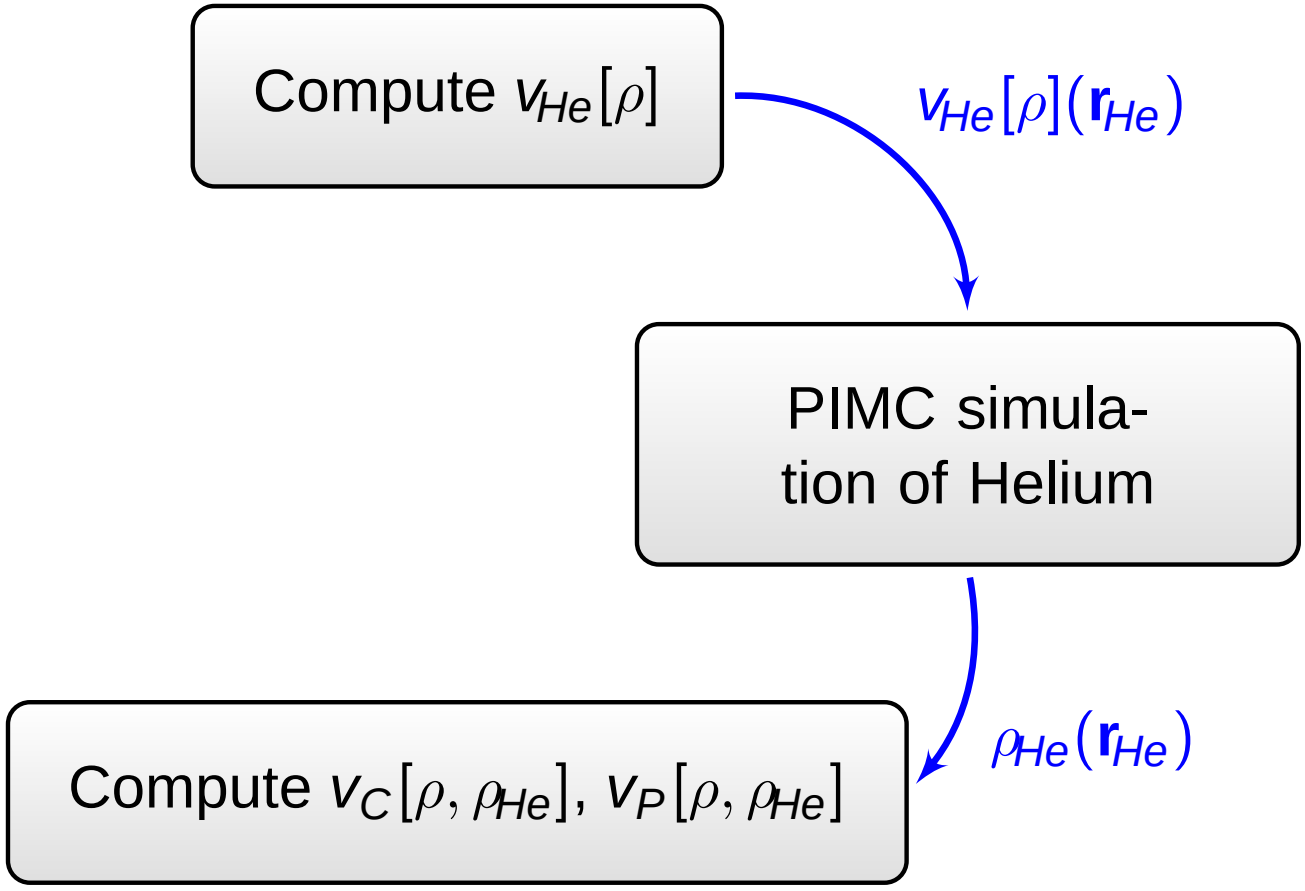
Combination of DFT and PIMC

Compute $v_{He}[\rho]$

Combination of DFT and PIMC



Combination of DFT and PIMC



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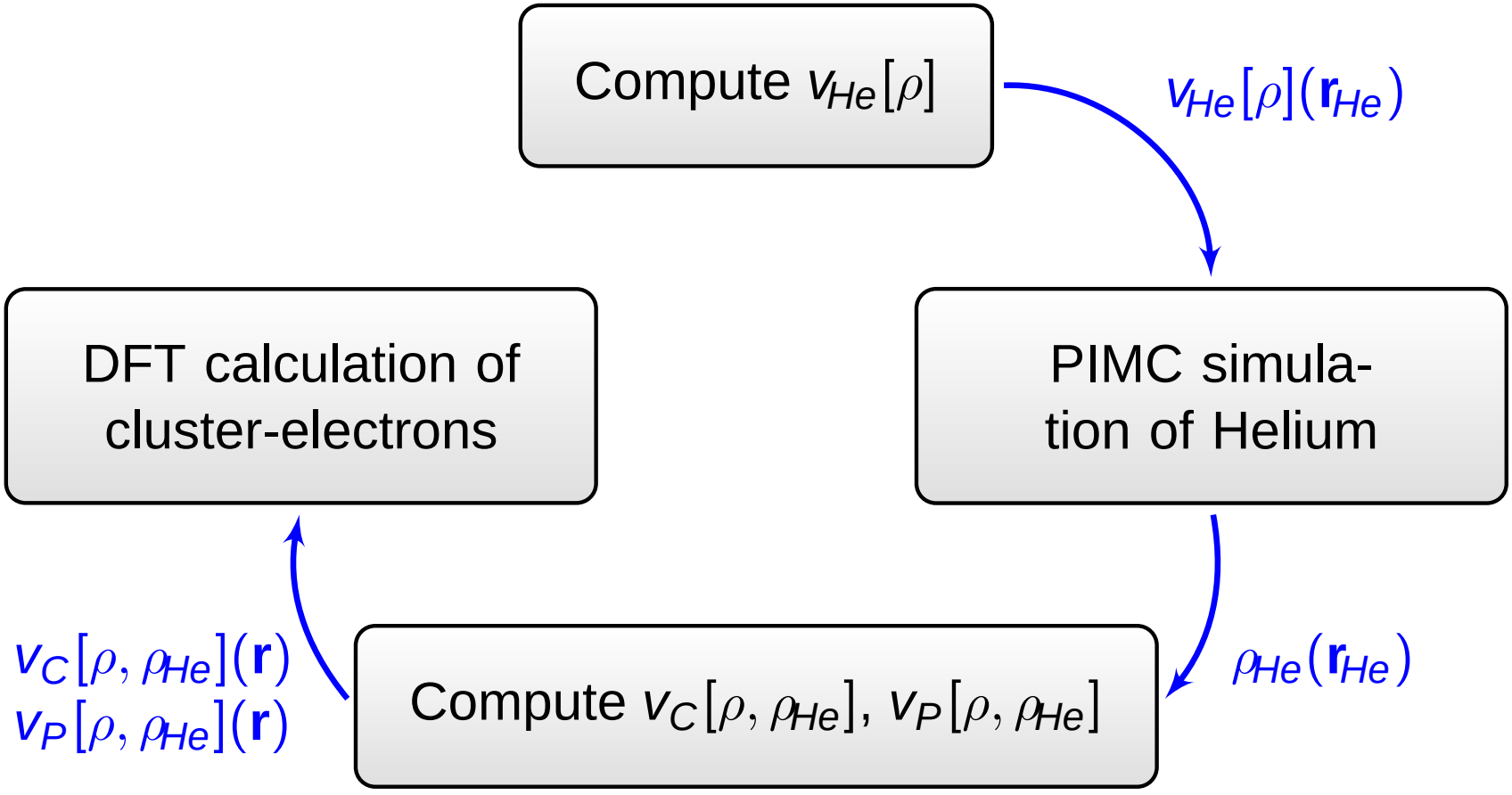

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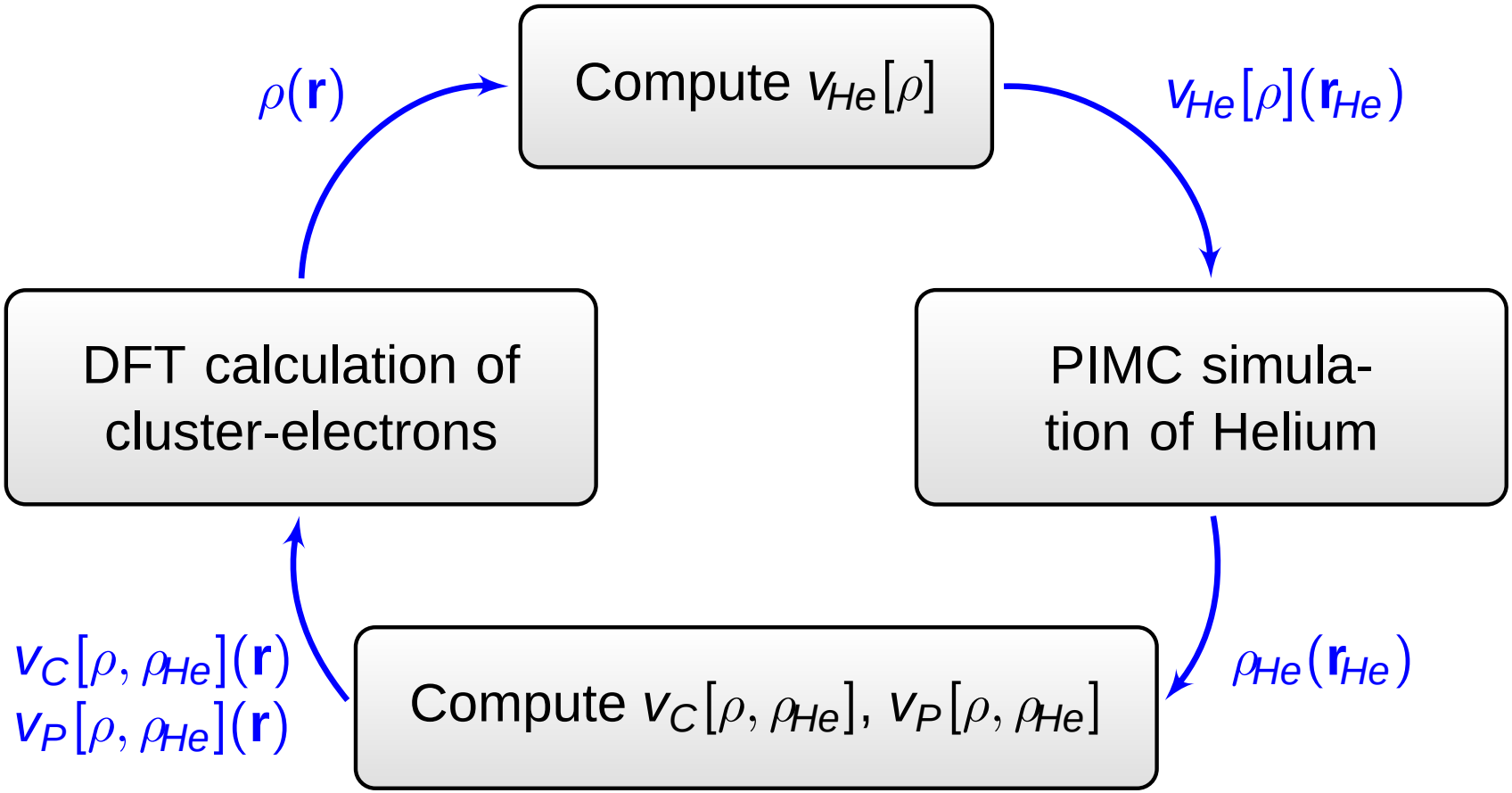

Mg_nHe_m: clusters: Iso-Surfaces of Helium Density

- A Mg_{07} cluster with 40 ^{4}He atoms Mg_7He_{40}
- A Mg_{07} cluster with 80 ^{4}He atoms Mg_7He_{80}
- A Mg_{11} cluster with 60 ^{4}He atoms $Mg_{11}He_{60}$

Summary: A solution looking for problems

Designing a DFT cluster code from scratch

- Forward factorization eigenvalue solver
  - Speed gain in eigenvalue solver by a factor of 10-100
  - Intellectual input from Monte Carlo methods
  - Trivial to parallelize

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Results for magnetic susceptibilities and NMR shifts:
Just as good as the pseudopotentials and density functionals.