The potential of Potential Functional Theory
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Electronic structure problem
- What atoms, molecules and solids can exist?
- What properties (ground-state energy, electron density geometry, bond distances, angles, nuclear vibrations, ionization energies, bond dissociation, etc.) do they have?

PFT is an alternative approach
- Enables *ab-initio calculations* of very large molecular systems.
- Avoids most-costly step by approximating the KS kinetic and exact exchange energy as a functional of the KS potential.

Combines elements of today’s lectures on Hohenberg-Kohn theorem, KS equations, Local density approximation, Density matrices and holes.
Atomic units throughout \((e^2 = \hbar = m_e = 1)\); suppress spin indices.

Ground-state energy of \(N\) electrons:

\[
E_0 = \min_{\Psi} \langle \Psi | \hat{H} | \Psi \rangle = \min_{\Psi} \langle \Psi | \hat{T} + \hat{V}_{ee} + \hat{V} | \Psi \rangle,
\]

where

\[
\hat{T} = -\frac{1}{2} \sum_j \nabla_j^2, \quad \hat{V}_{ee} = \frac{1}{2} \sum_j \sum_{j \neq k} \frac{1}{|r_j - r_k|}, \quad \hat{V} = \sum_j v(r_j),
\]

and \(\Psi\) are \(N\)-particle wave functions that are antisymmetric, normalized, and have finite kinetic energy.
Use Hohenberg-Kohn mapping for interacting and noninteracting particles:

\[ v(\mathbf{r}) \leftrightarrow n(\mathbf{r}) \leftrightarrow v_S(\mathbf{r}) \, . \]

Write universal part of Hohenberg-Kohn functional as functional of the KS potential:

\[ F[\tilde{v}_S] = T_S[\tilde{v}_S] + U[\tilde{v}_S] + E_{XC}[\tilde{v}_S] \, . \]

Obtain true gs energy from the variational principle

\[ E_0 = \min_{\tilde{v}_S} \left( F[\tilde{v}_S] + \int d\mathbf{r} \ n_S[\tilde{v}_S](\mathbf{r}) \ v(\mathbf{r}) \right) \, . \]
At the minimum the gs energy satisfies

$$\frac{\delta E_0[\tilde{v}_S]}{\delta \tilde{v}_S(r)} \bigg|_{v_S} = 0.$$ 

Given $n_S[v_S](r)$ and $E_{XC}[v_S]$, 

$$v'_S[v_S](r) = v(r) + \int dr' \chi^{-1}_S[v_S](r', r) \frac{\delta E_{HXC}[\tilde{v}_S]}{\delta \tilde{v}_S(r')} \bigg|_{v_S},$$

$$v'_S[v_S](r) = -\int dr' \chi^{-1}_S[v_S] \frac{\delta T_S[\tilde{v}_S]}{\delta \tilde{v}_S} \bigg|_{v_S}$$

determine the minimizing $v_S(r)$, and hence, the true gs energy, where 

$$\chi_S[v_S](r', r) = \frac{\delta n_S[\tilde{v}_S](r')}{\delta \tilde{v}_S(r)} \bigg|_{v_S}$$

denotes the one-body density-density response function.
Introduce a coupling-constant $\lambda \in [0, 1]$ in the KS potential:

$$v^\lambda_S(r) = \lambda v_S(r) + (1 - \lambda) v^R_r(r), \quad \Delta v_S(r) = v_S(r) - v^R_r(r).$$

Obtain the KS kinetic energy just from the density as a functional of the KS potential

$$T_S[v_S] = E^R_S + \int d\mathbf{r} \left\{ \bar{n}_S(\mathbf{r}) \Delta v_S(\mathbf{r}) - n_S[v_S](\mathbf{r}) v_S(\mathbf{r}) \right\},$$

where $\bar{n}_S[v_S](\mathbf{r}) = \int_0^1 d\lambda n_S[v^\lambda_S](\mathbf{r})$. 
Obtain the exchange energy through the 1RDM:

\[ E_x[v_S] = \int dr \int dr' \gamma_s^*[v_S](r,r') \gamma_s[v_S](r,r') v_{ee}(r,r') \, . \]

The corresponding exchange hole is defined as:

\[ n_x(r, r') = -\frac{\gamma_s^*[v_S](r, r') \gamma_s[v_S](r, r')}{n(r)} \, , \]

obeying the sum rule \[ \int dr' n_x(r, r') = -1 \, \forall \, r. \]
Up to now everything was exact.
Semiclassical approximation to the 1RDM

\[ \gamma_{sc}^{S}(x, x') = \sum_{\lambda=\pm} \frac{\lambda \sin[\theta_F^\lambda(x, x')] \cosec[\alpha_F^\lambda(x, x')]}{2T_F \sqrt{k_F(x)k_F(x')}} \]

Classical momentum: \[ k(x) = \sqrt{2 (\epsilon - v_S(x))} \]

Classical action: \[ \theta(x) = \int_{0}^{x} dx' k(x'), \quad \theta_F(L) = (N + 1/2)\pi. \]

Classical time: \[ t(x) = \int_{0}^{x} \frac{1}{k(x')} \, , \quad T = t(L), \quad \alpha(x) = \pi t(x)/T. \]

Abbreviations:
\[ \theta^\pm(x, x') = \theta(x) \pm \theta(x') \, , \quad \alpha^\pm(x, x') = \alpha(x) \pm \alpha(x') . \]
Semiclassical exchange hole
Figure 1: Energy error made by LDA exchange (LDAX), non-variational semiclassical exchange (scX*), and semiclassical kinetic and exchange (scKX*) for $N$ spin-unpolarized, interacting fermions in a 1d well.
Variational calculations

**Table 1:** Total EXX energy and respective errors of variational calculations within LDAX, scX, and scKX for $N$ spin-unpolarized fermions interacting via $\exp(-4u)$ in an external potential $v(x) = -5 \sin^2(\pi x)$ within a box of unit length.

<table>
<thead>
<tr>
<th>$N$</th>
<th>$E_{\text{EXX}}$</th>
<th>$E_{\text{X}}$</th>
<th>$\text{error} \cdot 10^3$</th>
<th>LDAX</th>
<th>scX</th>
<th>scKX</th>
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Conclusions

• Our exchange approximation (scX) is as accurate as EXX and comes at almost no cost.

• Our orbital-free, pure PFT calculation (scKX) has comparable accuracy and comes at even smaller computational cost.

• Analogous formulas highly desired for potentials in 3D.
The (spin-polarized) LDAX energy per electron in 1D:

$$
\epsilon_x^{\text{LDA}}(n(x)) = -\frac{\arctan \beta}{\pi} + \frac{\ln(1 + \beta^2)}{2\pi \beta}, \quad \beta = 2\pi n/\alpha.
$$
Non-variational, semiclassical exchange approximation evaluated on KS potential from LDAX.

**Table 2:** Total EXX energy and respective errors of perturbative post-LDAX(*) calculations within LDAX, scX, and scKX for $N$ spin-unpolarized fermions interacting via $\exp(-4u)$ in an external potential $v(x) = -5\sin^2(\pi x)$ within a box of unit length.

<table>
<thead>
<tr>
<th>$N$</th>
<th>$E^{\text{EXX}}$</th>
<th>$E_x^{\text{EXX}}$</th>
<th>Error·$10^3$</th>
<th>LDAX</th>
<th>scX*</th>
<th>scKX*</th>
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Figure 2: Upper plot: Converged KS potentials of EXX, LDAX, scX, and scKX runs. Lower plot: Error in the respective, converged densities with respect to EXX.
Figure 3: Exchange energy density (upper) and its error (lower).
Appendix: Variational calculations (energy components)

**Table 3:** Energy components of variational calculations within LDAX, semiclassical exchange (scX), and a semiclassical approximation of all energy components (scKX) for 4 ‘electrons’ in the same problem as in Tab. 2.

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<th>error · 10^3</th>
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