The potential of Potential Functional Theory

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P. Elliott, **AC**, S. Pittalis, E.K.U. Gross, K. Burke, PRA **92**, 022513 (2015).

Going beyond DFT

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.

Hamiltonian and ground-state energy

Atomic units throughout ($e^2 = \hbar = m_e = 1$); suppress spin indices.

Ground-state energy of N electrons:

$$E_0 = \min_{\Psi} \langle \Psi \mid \hat{H} \mid \Psi \rangle = \min_{\Psi} \langle \Psi \mid \hat{T} + \hat{V}_{\mathrm{ee}} + \hat{V} \mid \Psi \rangle \,,$$

where

$$\hat{T} = -\frac{1}{2} \sum_j \nabla_j^2 \,, \quad \hat{V}_{\mathrm{ee}} = \frac{1}{2} \sum_j \sum_{j \neq k} \frac{1}{|\mathbf{r}_j - \mathbf{r}_k|} \,, \quad \hat{V} = \sum_j v(\mathbf{r}_j) \,,$$

and Ψ are N-particle wave functions that are antisymmetric, normalized, and have finite kinetic energy.

Universal functional in PFT

Use Hohenberg-Kohn mapping for interacting and noninteracting particles:

$$v(\mathbf{r}) \leftrightarrow n(\mathbf{r}) \leftrightarrow v_{\mathrm{S}}(\mathbf{r}) \ .$$

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

$$F[\tilde{v}_{\mathrm{S}}] = T_{\mathrm{S}}[\tilde{v}_{\mathrm{S}}] + U[\tilde{v}_{\mathrm{S}}] + E_{\mathrm{XC}}[\tilde{v}_{\mathrm{S}}] \ .$$

Obtain true gs energy from the variational principle

$$E_0 = \min_{\tilde{v}_{\mathrm{S}}} \left(F[\tilde{v}_{\mathrm{S}}] + \int d\mathbf{r} \ n_{\mathrm{S}}[\tilde{v}_{\mathrm{S}}](\mathbf{r}) \, v(\mathbf{r}) \right) \ .$$

Self-consistent equations

At the minimum the gs energy satisfies

$$\left.\frac{\delta E_0[\tilde{v}_{\rm S}]}{\delta \tilde{v}_{\rm S}(\mathbf{r})}\right|_{v_{\rm S}} = 0 \ .$$

Given $n_{\rm S}[v_{\rm S}](\mathbf{r})$ and $E_{\rm XC}[v_{\rm S}]$,

$$v'_{\rm S}[v_{\rm S}](\mathbf{r}) = v(\mathbf{r}) + \int d\mathbf{r}' \ \chi_{\rm S}^{-1}[v_{\rm S}](\mathbf{r}', \mathbf{r}) \ \left.\frac{\delta E_{\rm HXC}[\tilde{v}_{\rm S}]}{\delta \tilde{v}_{\rm S}(\mathbf{r}')}\right|_{v_{\rm S}} ,$$

$$v'_{\rm S}[v_{\rm S}](\mathbf{r}) = -\int d\mathbf{r}' \ \chi_{\rm S}^{-1}[v_{\rm S}] \ \left.\frac{\delta T_{\rm S}[\tilde{v}_{\rm S}]}{\delta \tilde{v}_{\rm S}}\right|_{v_{\rm S}}$$

determine the minimizing $v_{\rm S}(\mathbf{r})$, and hence, the true gs energy, where

$$\chi_{\rm S}[v_{\rm S}](\mathbf{r}', \mathbf{r}) = \left.\delta n_{\rm S}[\tilde{v}_{\rm S}](\mathbf{r}')/\delta \tilde{v}_{\rm S}(\mathbf{r})\right|_{v_{\rm S}}$$

denotes the one-body density-density response function.

KS kinetic energy

Introduce a coupling-constant $\lambda \in [0,1]$ in the KS potential:

$$v_{\rm S}^{\lambda}(\mathbf{r}) = \lambda\, v_{\rm S}(\mathbf{r}) + (1-\lambda)\, v^{R}(\mathbf{r})\,, \qquad \Delta v_{\rm S}(\mathbf{r}) = v_{\rm S}(\mathbf{r}) - v^{R}(\mathbf{r})\ .$$

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

$$T_{\rm S}[v_{\rm S}] = E_{\rm S}^{R} + \int d\mathbf{r}\ \{\bar{n}_{\rm S}(\mathbf{r})\, \Delta v_{\rm S}(\mathbf{r}) - n_{\rm S}[v_{\rm S}](\mathbf{r})\, v_{\rm S}(\mathbf{r})\}\ ,$$

where $\bar{n}_{\rm S}[v_{\rm S}](\mathbf{r}) = \int_0^1 d\lambda\, n_{\rm S}[v_{\rm S}^{\lambda}](\mathbf{r})$.

Exchange energy

Obtain the exchange energy through the 1RDM:

$$E_{\mathrm{X}}[v_{\mathrm{S}}] = \int d\mathbf{r} \int d\mathbf{r}' \, \gamma^*_{\mathrm{S}}[v_{\mathrm{S}}](\mathbf{r},\mathbf{r}')\gamma_{\mathrm{S}}[v_{\mathrm{S}}](\mathbf{r},\mathbf{r}') \, v_{\mathrm{ee}}(\mathbf{r},\mathbf{r}') \ .$$

The corresponding exchange hole is defined as:

$$n_{\mathrm{X}}(\mathbf{r},\mathbf{r}') = -\frac{\gamma^*_{\mathrm{S}}[v_{\mathrm{S}}](\mathbf{r},\mathbf{r}')\gamma_{\mathrm{S}}[v_{\mathrm{S}}](\mathbf{r},\mathbf{r}')}{n(\mathbf{r})} \ ,$$

obeying the sum rule $\int d\mathbf{r}' \, n_{\mathrm{X}}(\mathbf{r},\mathbf{r}') = -1 \ \forall \ \mathbf{r}$.

Up to now everything was exact.

Semiclassical approxmiation to the 1RDM

$$\gamma_{\mathrm{S}}^{sc}(x,x') = \sum_{\lambda=\pm} \frac{\lambda \sin[\theta_{\mathsf{F}}^{\lambda}(x,x')]\mathrm{cosec}[\alpha_{\mathsf{F}}^{\lambda}(x,x')/2]}{2T_{\mathsf{F}}\sqrt{k_{\mathsf{F}}(x)k_{\mathsf{F}}(x')}} \ .$$

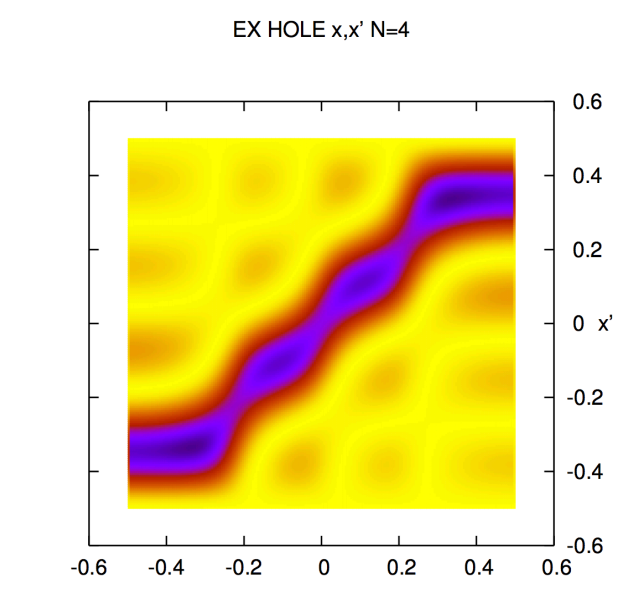
Classical momentum: $k(x) = \sqrt{2\left(\epsilon - v_{\mathrm{S}}(x)\right)}$.

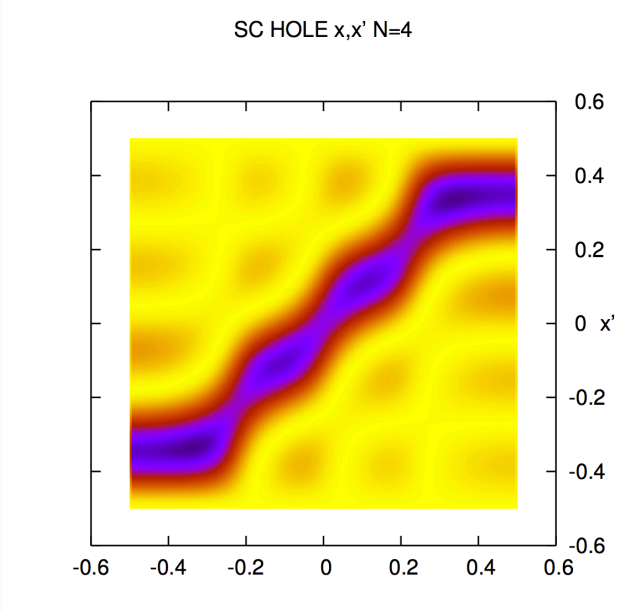
Classical action: $\theta(x) = \int_0^x dx'\, k(x')\,, \quad \theta_{\mathsf{F}}(L) = (N+1/2)\pi.$

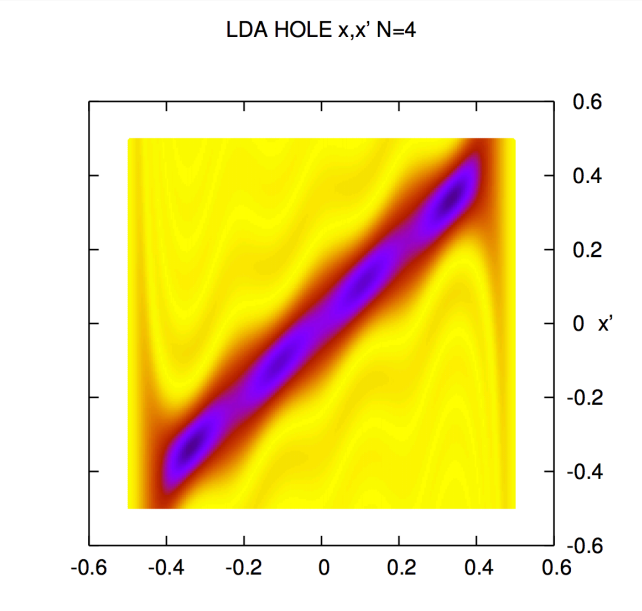
Classical time: $t(x) = \int_0^x \frac{1}{k(x')}\,, \quad T = t(L)\,, \quad \alpha(x) = \pi t(x)/T.$

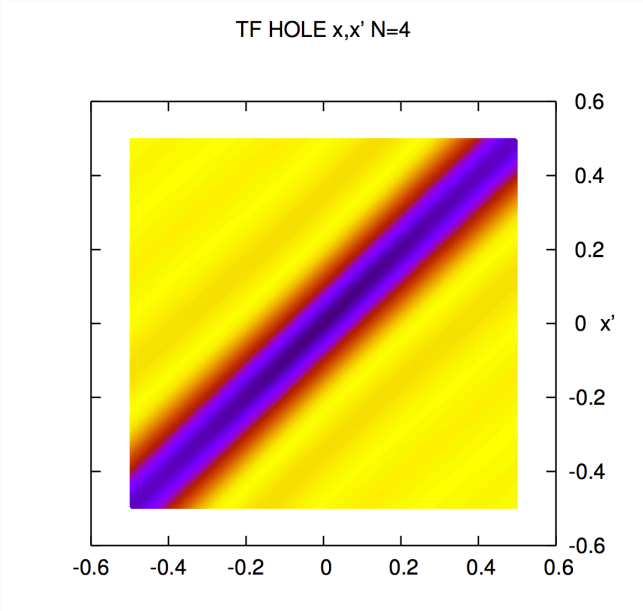
Abbreviations:
$\theta^{\pm}(x,x') = \theta(x) \pm \theta(x')\,, \alpha^{\pm}(x,x') = \alpha(x) \pm \alpha(x')$.

Semiclassical exchange hole









Non-variational calculations

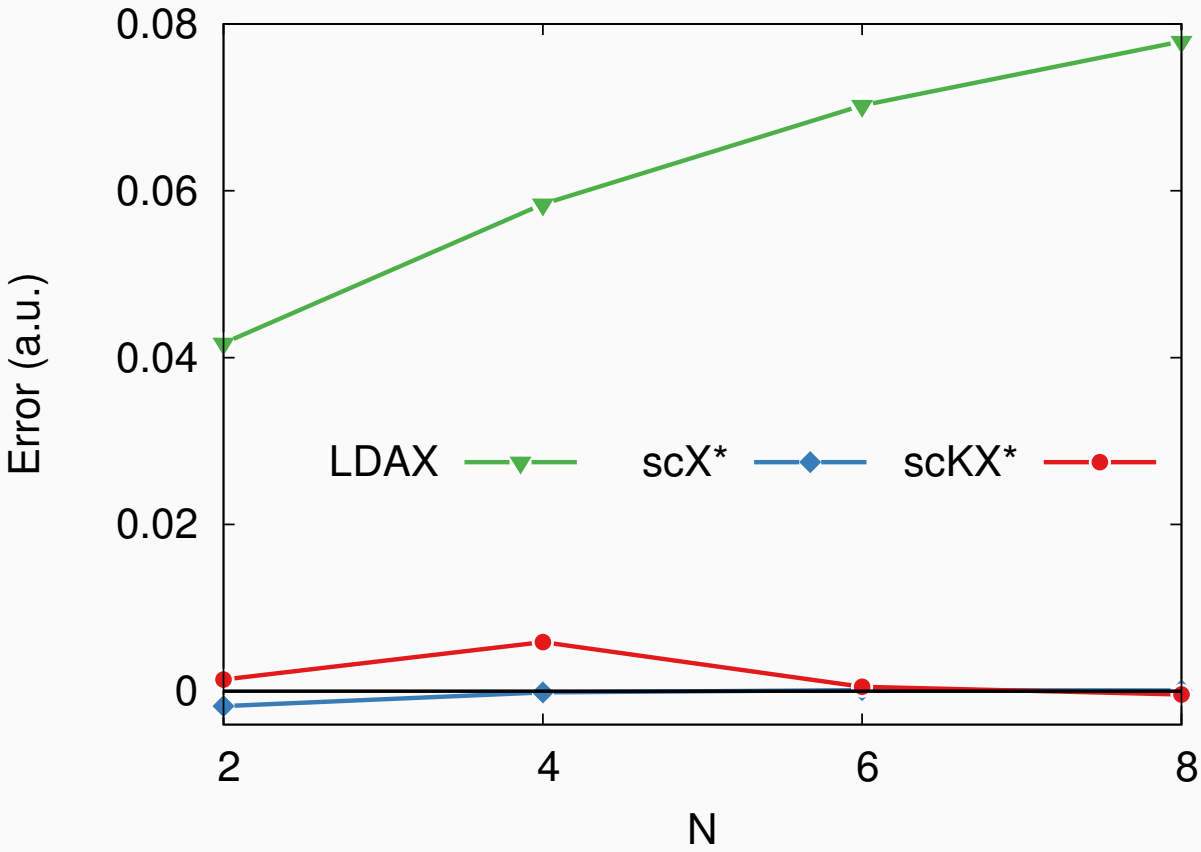


Figure 1: Energy error made by LDA exchange (LDAX), non-variational semiclassical exchange (scX*), and semiclassical kinetic and exchange (scKX*) for N spin-unpolarized, interacting fermions in a 1d well.

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.

N	E^{EXX}	$E_{\mathrm{X}}^{\mathrm{EXX}}$	error$\cdot 10^3$		
			LDAX	scX	scKX
2	2.81	-0.52	41.72	-3.10	-29.60
4	39.04	-1.26	58.41	-3.86	- 1.14
6	126.10	-2.10	70.24	-1.20	0.47
8	283.70	-2.98	77.91	-0.10	- 1.76

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.

Appendix: LDA exchange in 1D

The (spin-polarized) LDAX energy per electron in 1D:

$$\epsilon_{\mathrm{X}}^{\mathrm{LDA}}(n(x)) = -\frac{\arctan\beta}{\pi} + \frac{\ln(1+\beta^2)}{2\pi\beta}\,, \quad \beta = 2\pi\, n/\alpha\ .$$

Appendix: Non-variational calculations (energetics)

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.

N	E^{EXX}	$E_{\mathrm{X}}^{\mathrm{EXX}}$	error$\cdot 10^3$		
			LDAX	scX*	scKX*
2	2.81	-0.52	41.72	-1.79	1.40
4	39.04	-1.26	58.41	-0.15	5.89
6	126.10	-2.10	70.24	0.14	0.53
8	283.70	-2.98	77.91	0.08	-0.40

Appendix: Variational calculations (KS potentials)

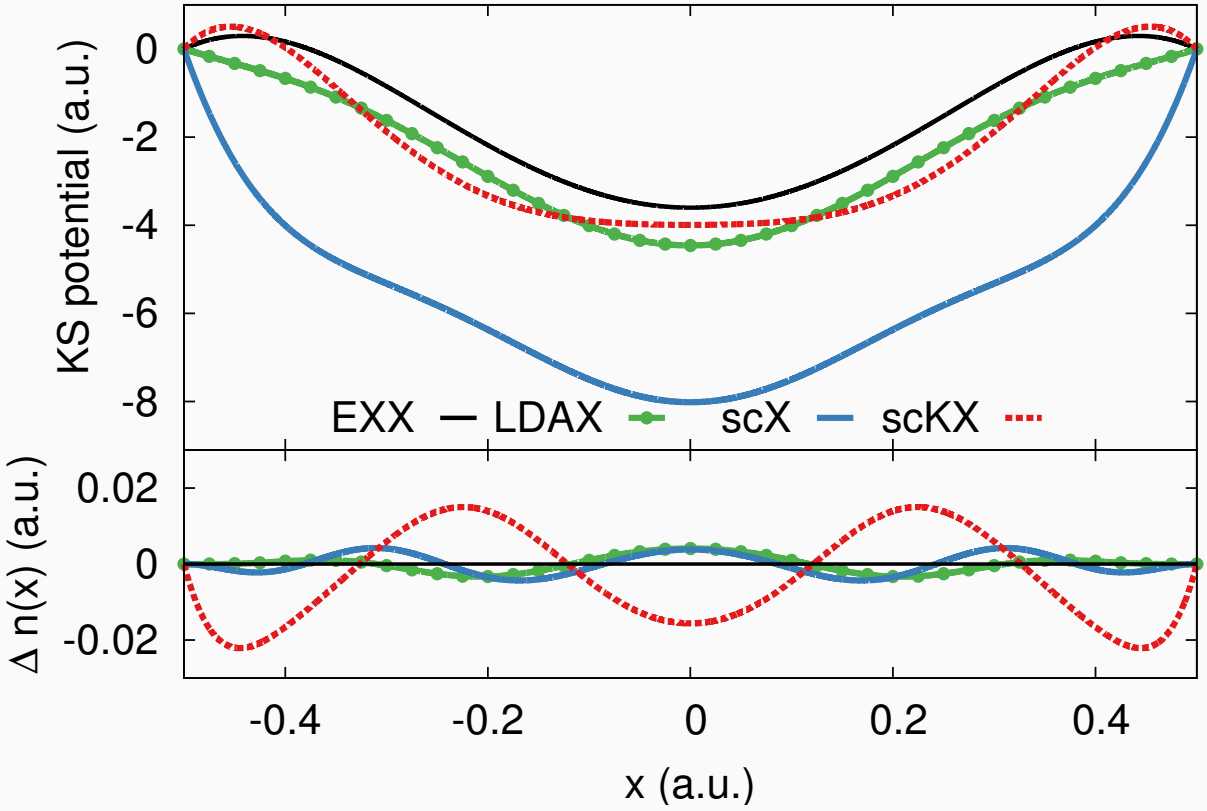


Figure 2: Upper plot: Converged KS potentials of EXX, LDAX, scX, and scKX runs. Lower plot: Error in the respective, converged densities with respect to EXX.

Appendix: Variational calculations (energy density)

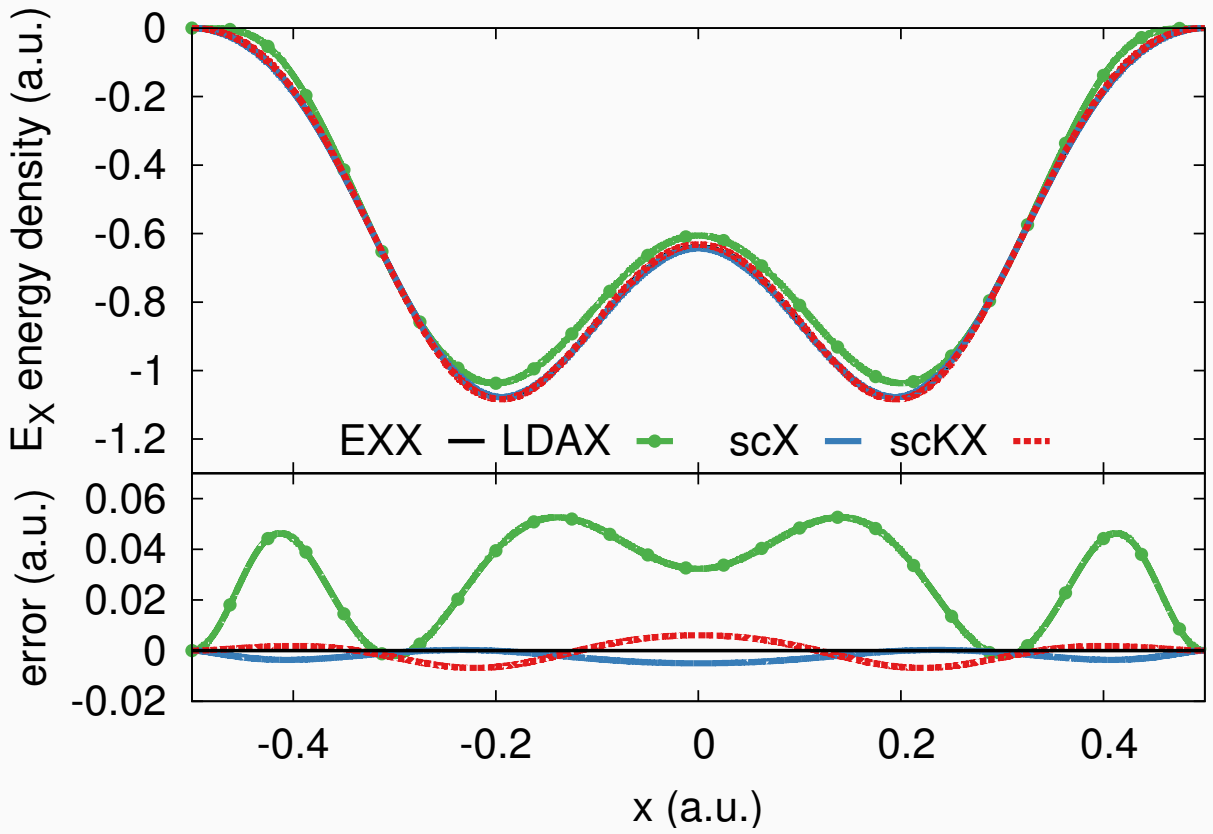


Figure 3: Exchange energy density (upper) and its error (lower).

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.

	EXX	error$\cdot 10^3$		
		LDAX	scX	scKX
E	39.04	58.41	-3.86	-1.14
T_{S}	49.44	1.22	0.34	1.22
V_{ext}	-12.72	-1.38	0.07	4.56
U	3.58	0.003	0.02	-5.90
E_{X}	-1.26	58.56	-4.29	-1.02