Large-coupling strength expansion in DFT and Hartree-Fock adiabatic connections

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Notation

Many-electron Schrödinger equation (in the Born-Oppenheimer approximation):

$$\hat{H} = \underbrace{-\frac{1}{2}\sum_{i=1}^{N}\nabla^2_{\mathbf{r}_i}}_{\hat{T}} + \underbrace{\sum_{1\le i<j\le N}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}}_{\hat{V}_{ee}} + \underbrace{\sum_{i=1}^{N} v_{\mathrm{ne}}(\mathbf{r}_i)}_{\hat{V}_{\mathrm{ext}} \text{ or } \hat{V}_{ne}}$$

$$\mathbf{r}_i, \mathbf{R}_\alpha \in \mathbb{R}^3$$

$$v_{\mathrm{ne}}(\mathbf{r}) = -\sum_{\alpha=1}^{M}\frac{Z_\alpha}{|\mathbf{r}-\mathbf{R}_\alpha|}$$

ground state electronic energy as a function of the nuclear positions

$$E_0 = E_0(\mathbf{R}_1, \ldots \mathbf{R}_M) = \min_{\Psi\in\mathcal{W}^N}\langle\Psi|\hat{H}|\Psi\rangle$$

fermionic N-particle wfs.

$$E_0 = \inf_{\Phi\in\mathcal{S}^N}\left\{\langle\Phi|\hat{T}+\hat{V}_{\mathrm{ne}}|\Phi\rangle + E_{\mathrm{Hxc}}[\rho_\Phi]\right\}$$ Kohn-Sham DFT

$$E_0^{\mathrm{HF}} = \inf_{\Phi\in\mathcal{S}^N}\langle\Phi|\hat{T}+\hat{V}_{ee}+\hat{V}_{\mathrm{ne}}|\Phi\rangle$$ Hartree-Fock

Slater determinants

$$\boxed{E_c = \langle\Psi|\hat{H}|\Psi\rangle - \langle\Phi|\hat{H}|\Phi\rangle}$$

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Kohn-Sham DFT

$$\rho_\Psi(\mathbf{r}) = N\int_{\{\uparrow,\downarrow\}\times(\mathbb{R}^3\times\{\uparrow,\downarrow\})^{N-1}}|\Psi(\mathbf{x},\mathbf{x}_2,\ldots,\mathbf{x}_N)|^2\,\mathrm{d}\sigma\mathrm{d}\mathbf{x}_2\ldots\mathrm{d}\mathbf{x}_N$$

$$E_0^{\mathrm{HF}} = \inf_{\Phi\in\mathcal{S}^N}\langle\Phi|\hat{T}+\hat{V}_{ee}+\hat{V}_{\mathrm{ne}}|\Phi\rangle$$

Hartree-Fock

Slater determinants

$$\boxed{E_c = \langle\Psi|\hat{H}|\Psi\rangle - \langle\Phi|\hat{H}|\Phi\rangle}$$

Adiabatic connections

DFT

$$\hat{H}_\lambda^{\mathrm{DFT}} = \hat{T} + \lambda \hat{V}_{ee} + \hat{V}_{\mathrm{ext}} + \hat{V}_\lambda[\rho]$$

$$\hat{V}_\lambda[\rho] \ : \ \rho_\lambda = \rho_1 = \rho \ \ \forall \lambda$$

$$W_{c,\lambda}^{\mathrm{DFT}} = \langle \Psi_\lambda | \hat{V}_{ee} | \Psi_\lambda \rangle - \langle \Psi_0 | \hat{V}_{ee} | \Psi_0 \rangle$$

$$E_c^{\mathrm{DFT}} = \int_0^1 W_{c,\lambda}^{\mathrm{DFT}} \, d\lambda$$

$\lambda \to 0$

$$W_{c,\lambda}^{\mathrm{DFT}} \to \sum_{n=2}^{\infty} n \, E_c^{\mathrm{GL}n} \, \lambda^{n-1}$$

$\lambda \to \infty$

$$W_{c,\lambda}^{\mathrm{DFT}} \to W_{c,\infty}^{\mathrm{SCE}} + \frac{W_{\frac{1}{2}}^{\mathrm{SCE}}}{\sqrt{\lambda}} + \dots$$

Hartree-Fock

$$\hat{H}_\lambda^{\mathrm{HF}} = \hat{T} + \hat{V}^{\mathrm{HF}} + \hat{V}_{\mathrm{ext}} + \lambda \left(\hat{V}_{ee} - \hat{V}^{\mathrm{HF}} \right)$$

$$\hat{V}^{\mathrm{HF}} = \hat{J}[\rho^{\mathrm{HF}}] - \hat{K}[\{\phi_i^{\mathrm{HF}}\}] \quad \lambda\text{−independent}$$

$$\rho_\lambda \qquad \rho_{\lambda=0} = \rho^{\mathrm{HF}} \quad \rho_{\lambda=1} = \rho$$

$$W_{c,\lambda}^{\mathrm{HF}} = \langle \Psi_\lambda | \hat{V}_{ee} - \hat{V}^{\mathrm{HF}} | \Psi_\lambda \rangle - \langle \Psi_0 | \hat{V}_{ee} - \hat{V}^{\mathrm{HF}} | \Psi_0 \rangle$$

$$E_c^{\mathrm{HF}} = \int_0^1 W_{c,\lambda}^{\mathrm{HF}} \, d\lambda$$

$\lambda \to 0$

$$W_{c,\lambda}^{\mathrm{HF}} \to \sum_{n=2}^{\infty} n \, E_c^{\mathrm{MP}n} \, \lambda^{n-1}$$

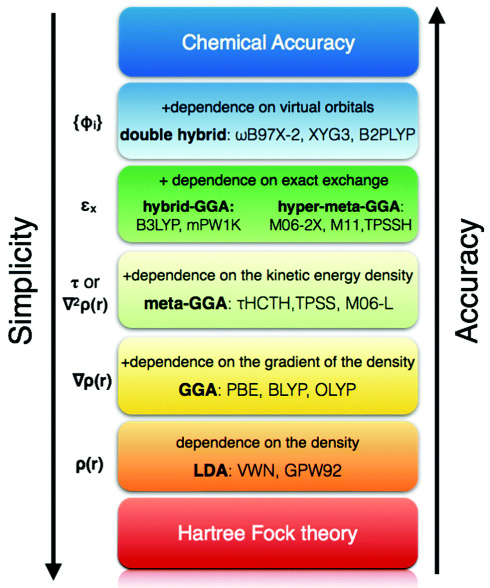
$\lambda \to \infty$

$$W_{c,\lambda}^{\mathrm{HF}} \to W_{c,\infty}^{\mathrm{MP}} + \frac{W_{\frac{1}{2}}^{\mathrm{MP}}}{\sqrt{\lambda}} + \frac{W_{\frac{3}{4}}^{\mathrm{MP}}}{\lambda^{3/4}} + \dots$$

Why studying the large-coupling strength limit?

DFT: ideas on how the density is transformed into an electron-electron interaction:

Which ingredients appear in this exact limit?



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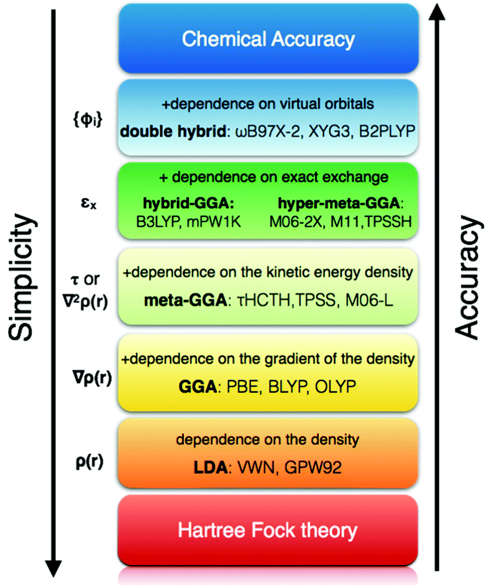

Different structure/ingredients from the strong coupling limit

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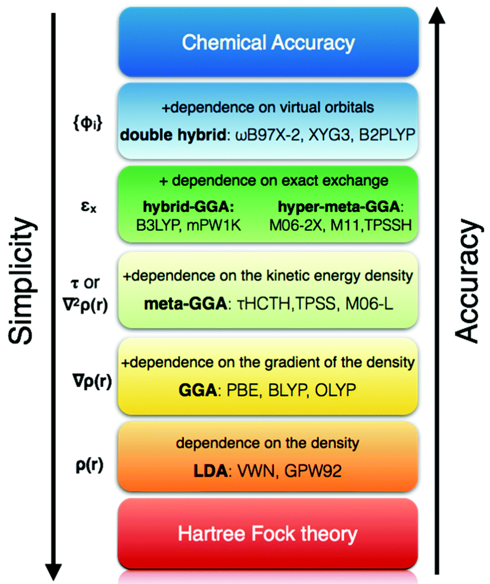
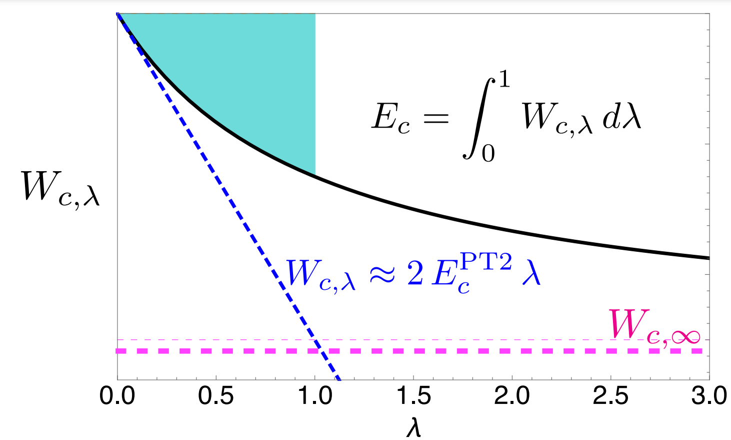


Different structure/ingredients from the strong coupling limit

DFT and HF: Build interpolations between small and large coupling strengths

(can also be done locally, in each point of space)

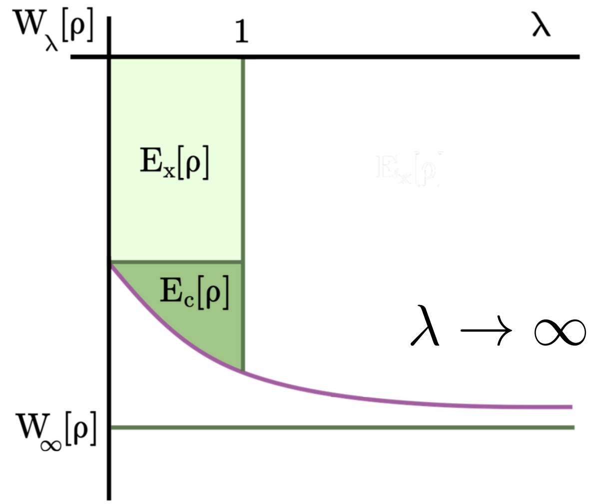


Large coupling in the DFT adiabatic connection

$$E_{xc}[\rho] = \int_0^1 W_\lambda[\rho] d\lambda$$

$$W_\lambda[\rho] = \langle \Psi_\lambda[\rho] | \hat{V}_{ee} | \Psi_\lambda[\rho] \rangle - U[\rho]$$

$$\Psi_\lambda[\rho] = \arg \min_{\Psi \to \rho} \langle \Psi | \hat{T} + \lambda \hat{V}_{ee} | \Psi \rangle$$



$$W_\lambda^{\mathrm{DFT}} \to W_\infty^{\mathrm{SCE}}[\rho] + \frac{W_{\frac{1}{2}}^{\mathrm{SCE}}[\rho]}{\sqrt{\lambda}} + O\left(\lambda^{-5/4}\right) + O(\underbrace{e^{-\sqrt{\lambda}}}_{\text{spin state}})$$

$$W_\infty[\rho] = V_{ee}^{\mathrm{SCE}}[\rho] - U[\rho]$$

$$V_{ee}^{\mathrm{SCE}}[\rho] = \min_{\Psi \to \rho} \langle \Psi | \hat{V}_{ee} | \Psi \rangle$$

*Seidl, PRA **60**, 438 (1999)*
*Seidl, Gori-Giorgi & Savin, PRA **75**, 042511 (2007)*
*Gori-Giorgi, Vignale & Seidl, JCTC **5**, 743 (2009)*
*Grossi, Kooi, Giesbertz, Seidl, Cohen, Mori-Sanchez, Gori-Giorgi, JCTC **13**, 6089 (2017)*
Lewin, arXiv:1706.02199
Cotar, Friesecke, & Kluppelberg, arXiv:1706.05676

XC functional tends to SCE in the low-density or strong-coupling limit

Large coupling in the DFT adiabatic connection

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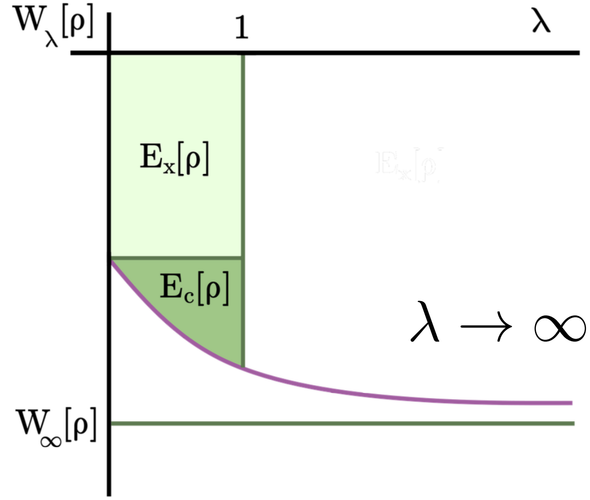

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highly non-local

$$W_{\infty}[\rho] = V_{ee}^{\mathrm{SCE}}[\rho] - U[\rho]$$
$$V_{ee}^{\mathrm{SCE}}[\rho] = \min_{\Psi \to \rho} \langle \Psi | \hat{V}_{ee} | \Psi \rangle$$

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SCE functional: rigorous results

$$V_{ee}^{\mathrm{SCE}}[\rho] = \min_{\Psi \to \rho} \langle \Psi | \hat{V}_{ee} | \Psi \rangle$$

equivalent to an optimal transport (or mass transportation theory) problem with Coulomb cost

- *Buttazzo, De Pascale, & Gori-Giorgi, Phys. Rev. A. 85, 062502 (2012)*
- *Cotar, Friesecke, & Kluppelberg, Comm. Pure Appl. Math. 66, 548 (2013)*
- *Pass, Nonlinearity 26, 2731 (2013)*
- *Mendl & Lin, Phys. Rev. B 87, 125106 (2013)*
- *Chen, Friesecke, & Mendl, J. Chem. Theory Comput 10, 4360 (2014)*
- *Colombo, De Pascale, Di Marino, Can. J. Math. 67, 350 (2015)*
- *Benamou, Carlier, Cuturi, Nenna, L.; Peyré, arXiv:1412.5154*
- *Benamou, Carlier, Nenna, arXiv:1505.01136v2*
- *Friesecke, Mendl, Pass, Cotar & Kluppelberg, J. Chem. Phys. 139, 164109 (2013)*
- *De Pascale, arXiv:1503.07063*
- *Colombo & Stra, arXiv:1507.08522*
- *Lewin, arXiv:1706.02199*
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SCE functional

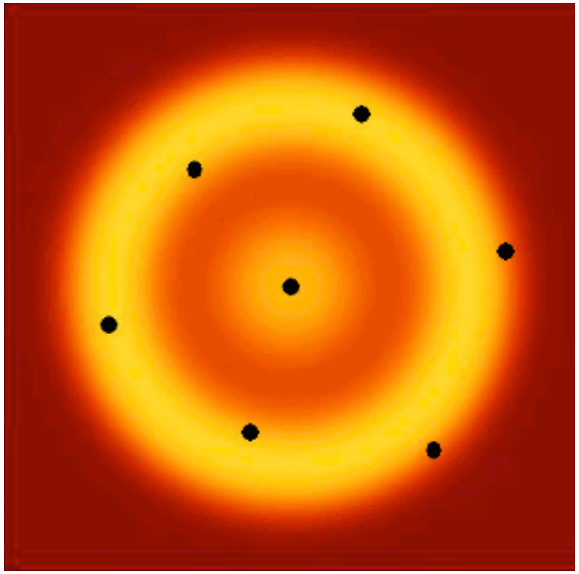
$$W_\infty[\rho] = V_{ee}^{\mathrm{SCE}}[\rho] - U[\rho] \qquad V_{ee}^{\mathrm{SCE}}[\rho] = \min_{\Psi\to\rho}\langle\Psi|\hat{V}_{ee}|\Psi\rangle$$

$$\boxed{|\Psi_{\mathrm{SCE}}(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)|^2 = \frac{1}{N!}\sum_{\mathcal{P}}\int d\mathbf{s}\frac{\rho(\mathbf{s})}{N}\delta(\mathbf{r}_1-\mathbf{f}_{\mathcal{P}(1)}(\mathbf{s}))\delta(\mathbf{r}_2-\mathbf{f}_{\mathcal{P}(2)}(\mathbf{s}))\ldots\delta(\mathbf{r}_N-\mathbf{f}_{\mathcal{P}(N)}(\mathbf{s}))}$$

the wavefunction collapses to a 3D subspace of the full 3N-dimensional configuration space

$$\rho(\mathbf{f}_i(\mathbf{r}))d\mathbf{f}_i(\mathbf{r}) = \rho(\mathbf{r})d\mathbf{r}$$

$$\begin{aligned}
\mathbf{f}_1(\mathbf{r}) &\equiv \mathbf{r},\\
\mathbf{f}_2(\mathbf{r}) &\equiv \mathbf{f}(\mathbf{r}),\\
\mathbf{f}_3(\mathbf{r}) &= \mathbf{f}(\mathbf{f}(\mathbf{r})),\\
\mathbf{f}_4(\mathbf{r}) &= \mathbf{f}(\mathbf{f}(\mathbf{f}(\mathbf{r}))),\\
&\vdots\\
\underbrace{\mathbf{f}(\mathbf{f}(\ldots\mathbf{f}(\mathbf{f}(\mathbf{r}))))}_{N\text{ times}} &= \mathbf{r}.
\end{aligned}$$



Seidl, PRA 60, 4387 (1999)
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*Malet, Mirtschink, Cremon, Reimann & Gori-Giorgi, PRB **87** 115146 (2013)*

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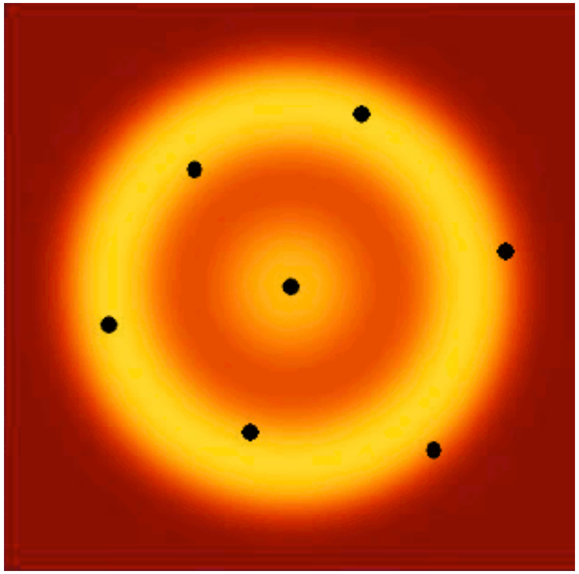

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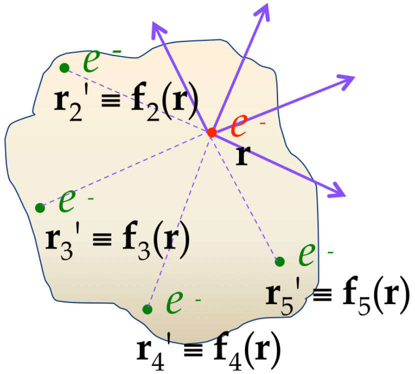
SCE functional and functional derivative

$$V_{ee}^{\mathrm{SCE}}[\rho] = \int d\mathbf{r}\,\frac{\rho(\mathbf{r})}{N}\sum_{i=1}^{N}\sum_{j=i+1}^{N}\frac{1}{|\mathbf{f}_i(\mathbf{r})-\mathbf{f}_j(\mathbf{r})|}$$
$$= \frac{1}{2}\int \rho(\mathbf{r})\sum_{i=2}^{N}\frac{1}{|\mathbf{r}-\mathbf{f}_i(\mathbf{r})|}$$



$$\frac{\delta V_{ee}^{\mathrm{SCE}}[\rho]}{\delta\rho(\mathbf{r})} = v_{\mathrm{SCE}}(\mathbf{r})$$

$$\nabla v_{\mathrm{SCE}}(\mathbf{r}) = -\sum_{i=2}^{N}\frac{\mathbf{r}-\mathbf{f}_i(\mathbf{r})}{|\mathbf{r}-\mathbf{f}_i(\mathbf{r})|^3}$$

shortcut to the functional derivative

$$v_{\mathrm{Hxc}}(\mathbf{r}) \to v_{\mathrm{SCE}}(\mathbf{r})$$

low-density (strong coupling) limit

*Seidl, Gori-Giorgi and Savin, PRA **75**, 042511 (2007)*

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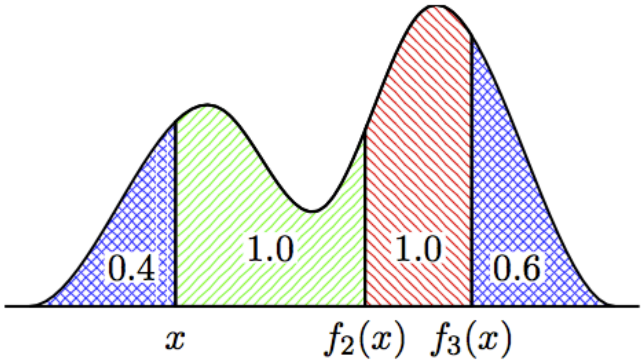
1D case is transparent (and as cheap as LDA)



$$N_e(x) = \int_{-\infty}^{x} \rho(x')\, dx'$$

$$a_k = N_e^{-1}(k)$$

$$f_i(x) = \begin{cases} N_e^{-1}[N_e(x) + i - 1] & x \le a_{N+1-i} \\ N_e^{-1}[N_e(x) + i - 1 - N] & x > a_{N+1-i}, \end{cases}$$

Written on simple physical considerations: *M. Seidl, PRA **60**, 4387 (1999)*

Rigorous Proof: *M. Colombo, L. De Pascale, S. Di Marino, Can. J. Math. 67, 350 (2015)*

KS SCE applied to 1D physics: *Malet & Gori-Giorgi, PRL 109 246402 (2012);*
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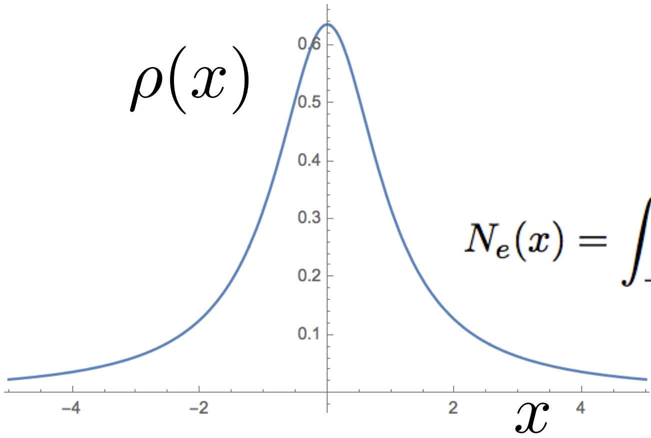
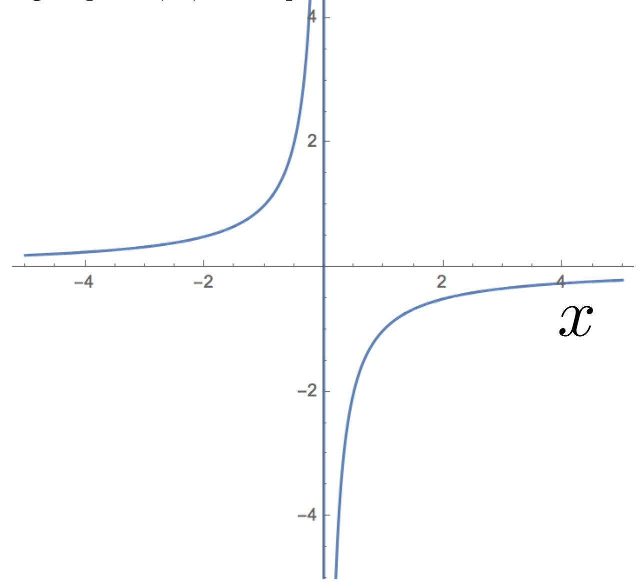
N=2 electrons in 1D: SCE and exact functional



$$N_e(x) = \int_{-\infty}^{x} \rho(x')\, dx'$$

$$f(x) = N_e^{-1}[N_e(x) \pm 1]$$



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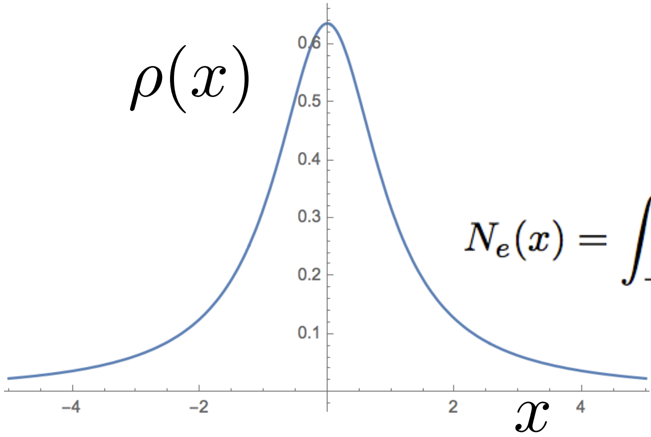

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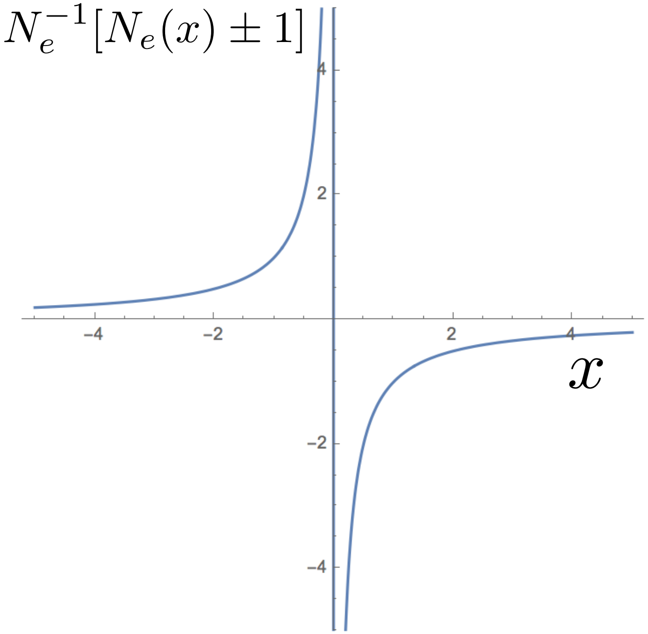
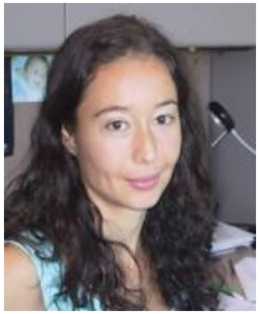


Aron Cohen



Paula Mori-Sanchez

$$\Psi_{\lambda}[\rho] = \arg\min_{\Psi\to\rho} \langle \Psi | \hat{T} + \lambda \hat{V}_{ee} | \Psi \rangle$$

Morí-Sanchez & Cohen, J. Phys. Chem. Lett. 9, 4910 (2018)

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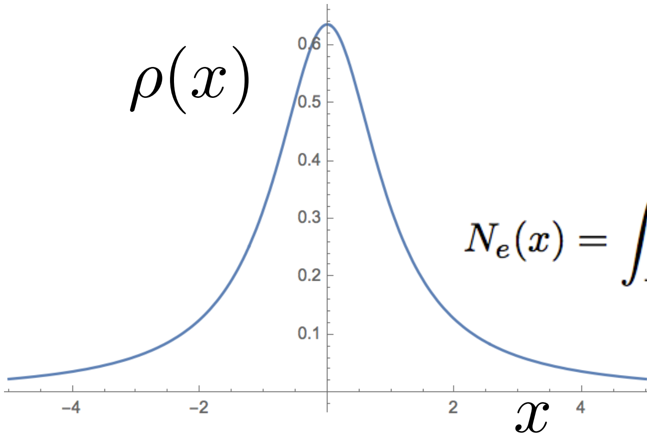

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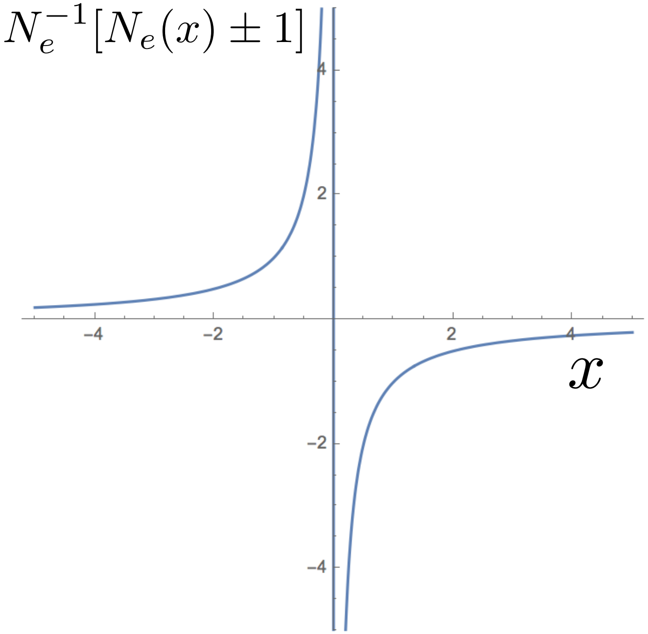

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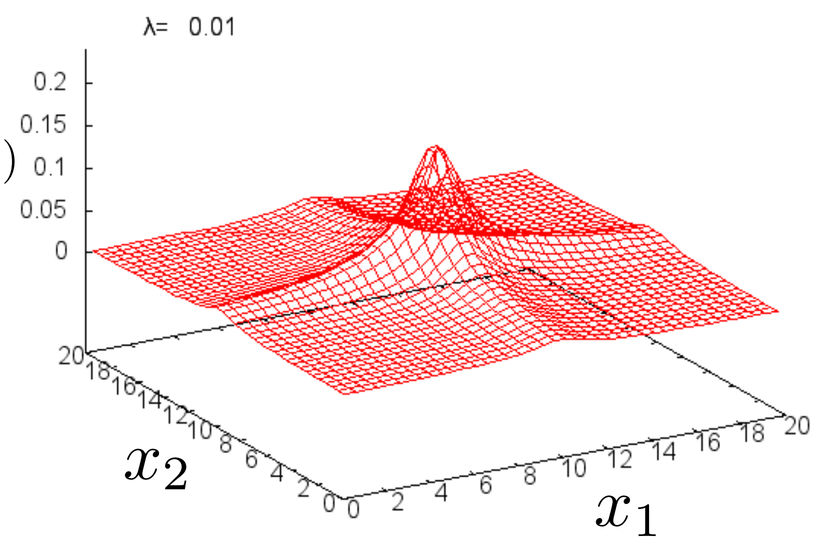
$\Psi_\lambda[\rho](x_1, x_2)$



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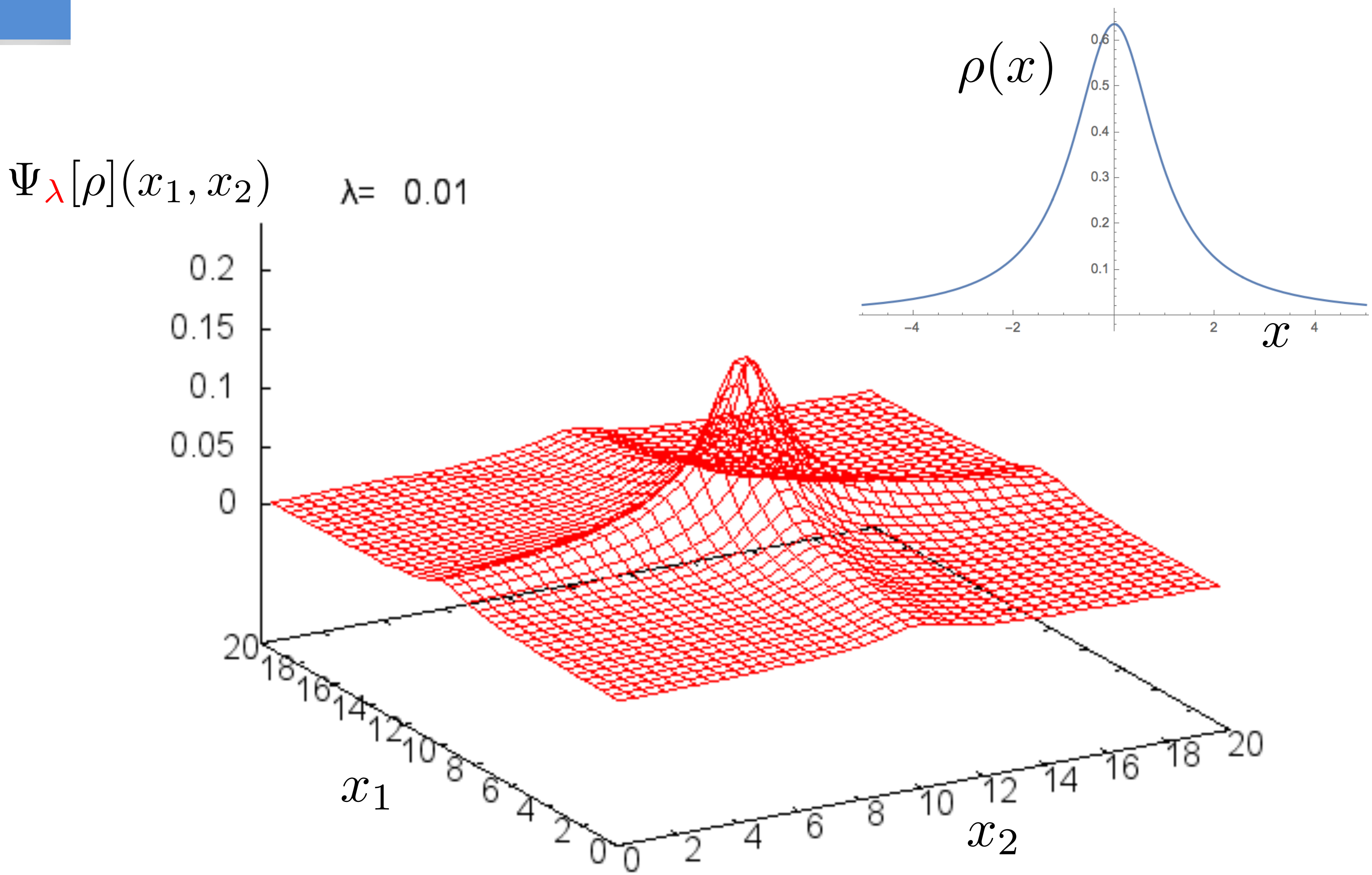
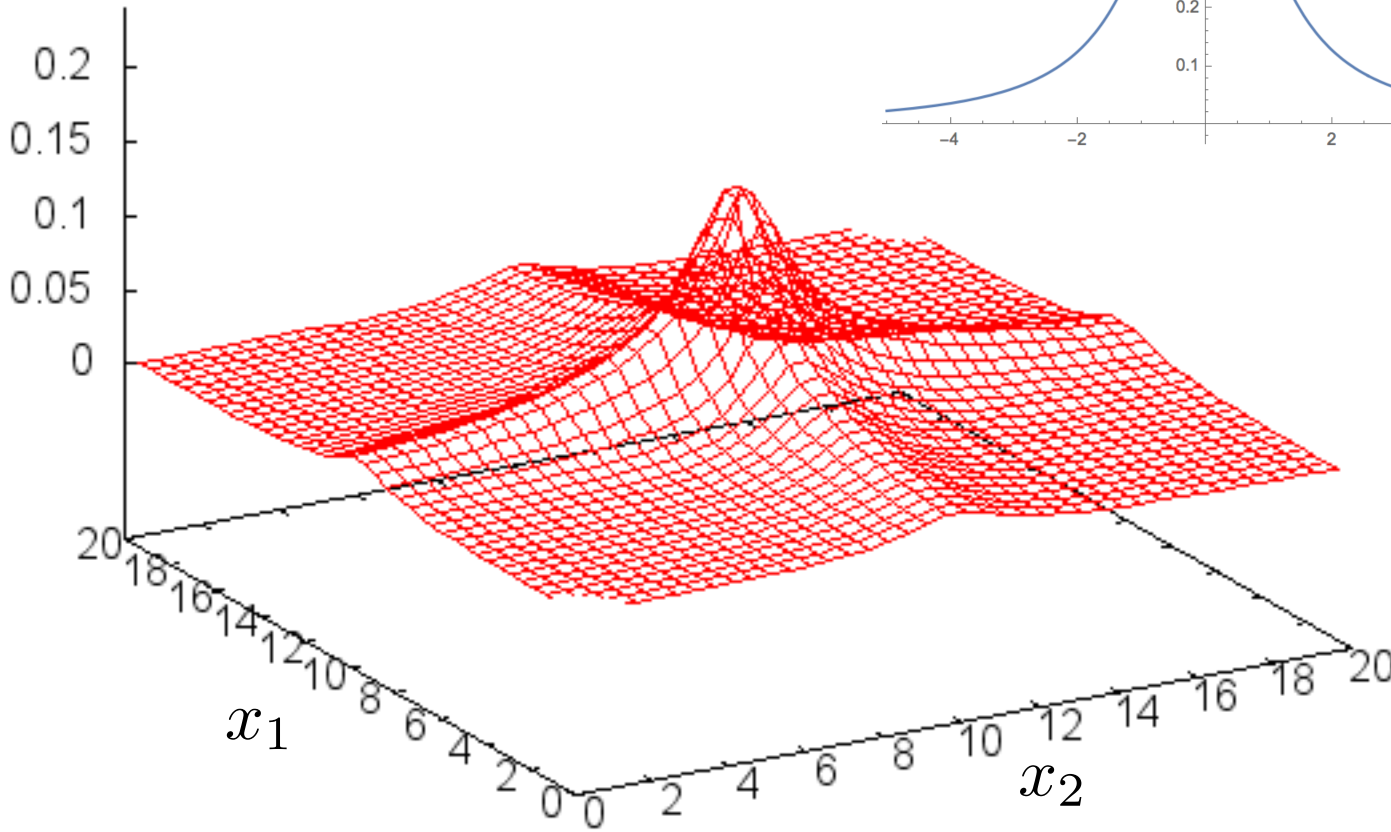
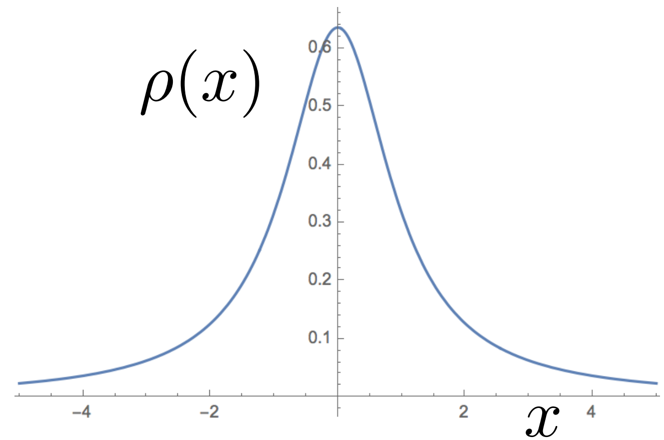
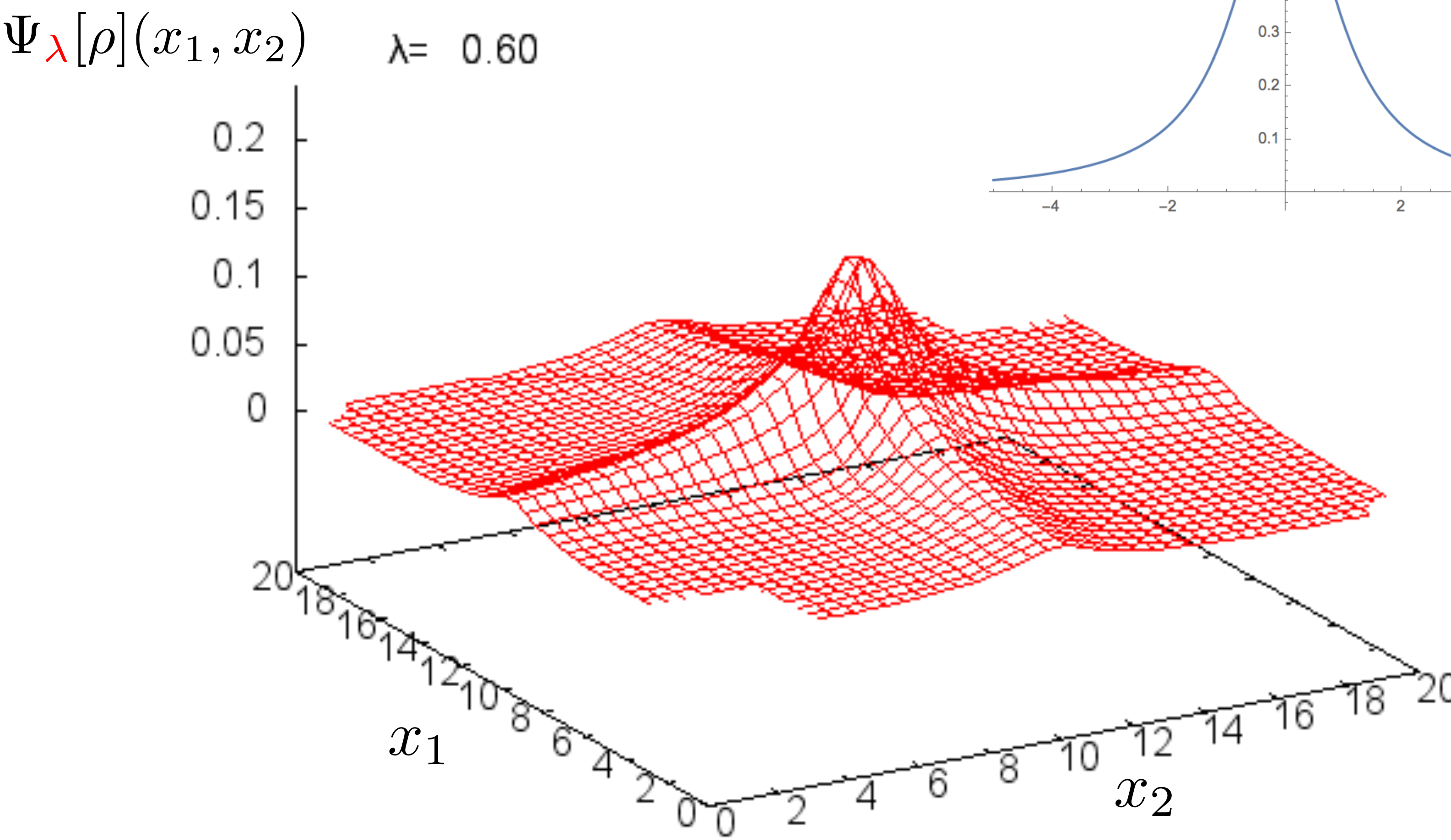
Morí-Sanchez & Cohen, J. Phys. Chem. Lett. 9, 4910 (2018)

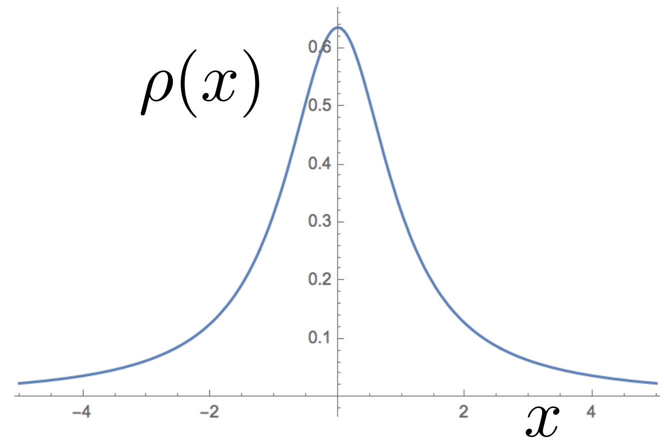

$\Psi_\lambda[\rho](x_1, x_2)$
λ= 0.01
0.2
0.15
0.1
0.05
0
x_1
x_2
$\rho(x)$
x

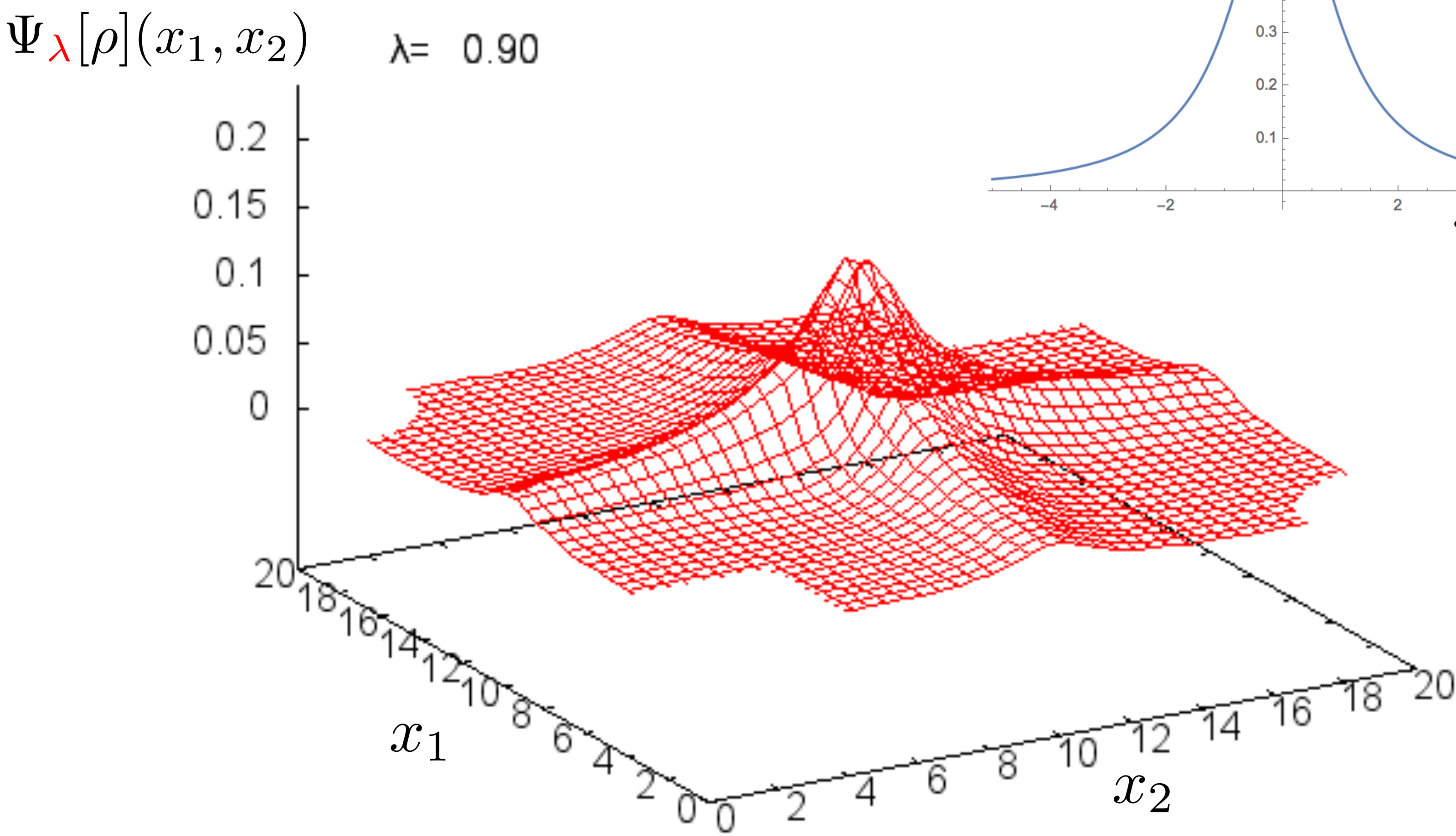
$\Psi_\lambda[\rho](x_1, x_2)$ λ= 0.30



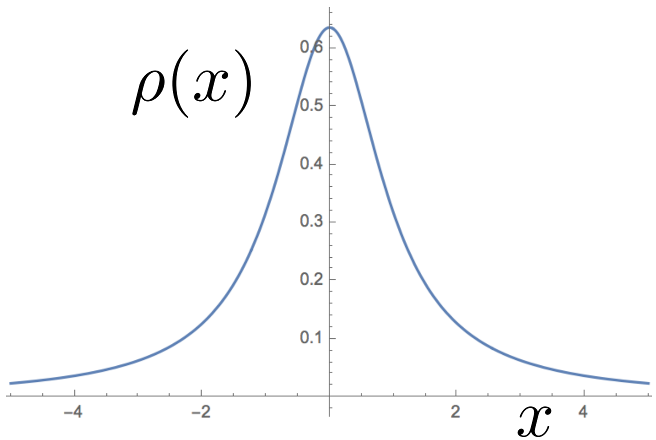



$\Psi_\lambda[\rho](x_1, x_2)$
λ= 0.60
0.2
0.15
0.1
0.05
0
20
18
16
14
12
10
8
6
4
2
0
x_1
0
2
4
6
8
10
12
14
16
18
20
x_2

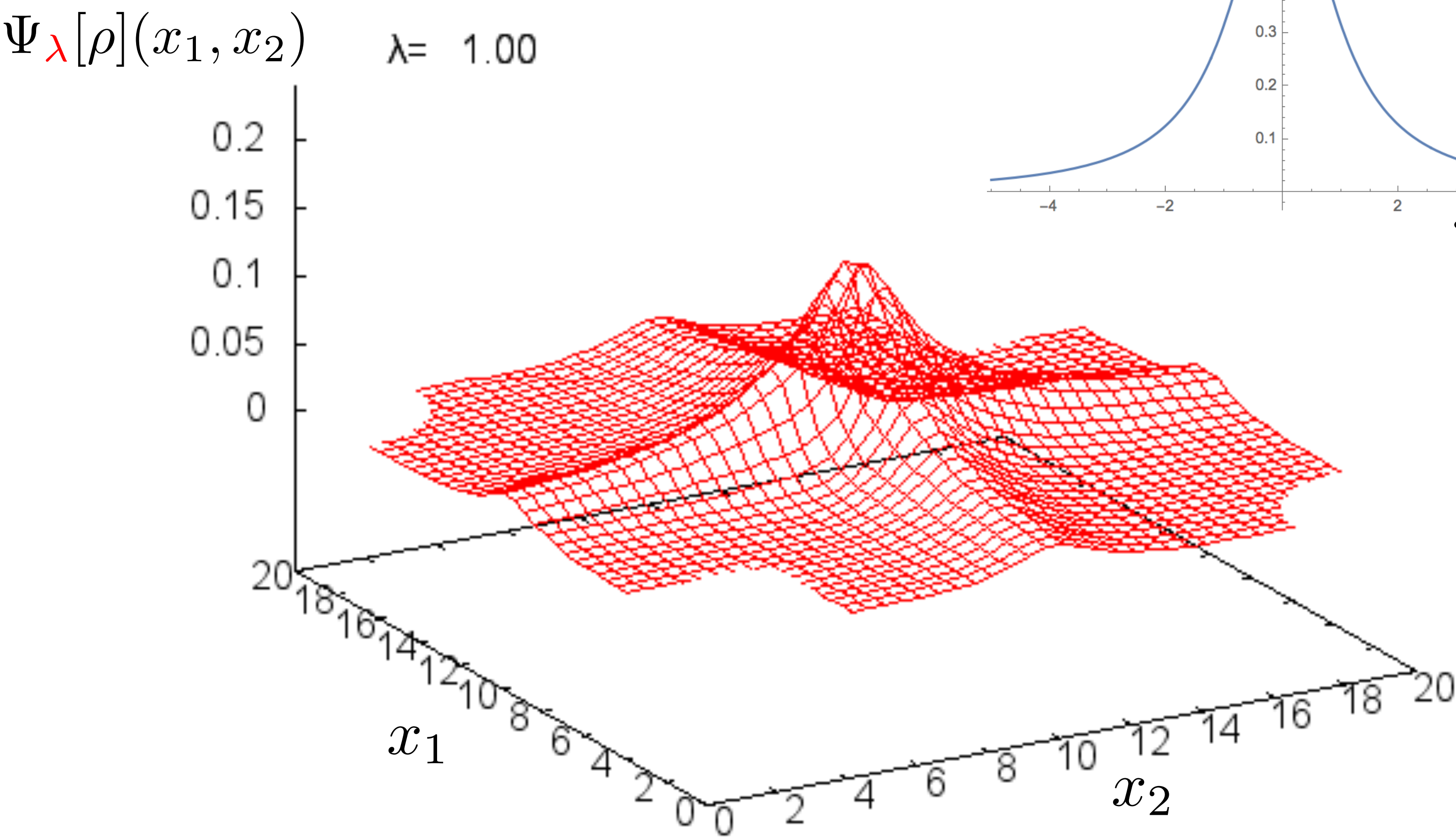

$\rho(x)$
0.6
0.5
0.4
0.3
0.2
0.1
−4
−2
2
4
x

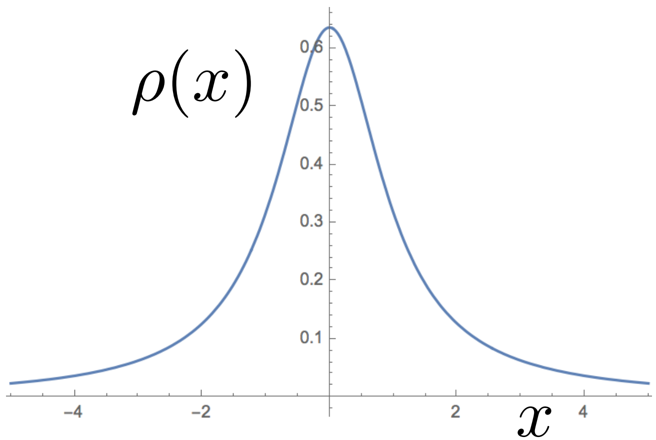


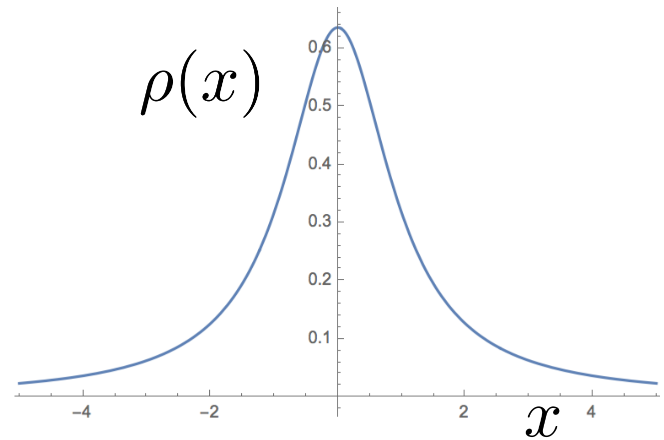
$\Psi_\lambda[\rho](x_1, x_2)$
λ= 0.90
0.2
0.15
0.1
0.05
0
20
18
16
14
12
10
8
6
4
2
0
x_1
0
2
4
6
8
10
12
14
16
18
20
x_2

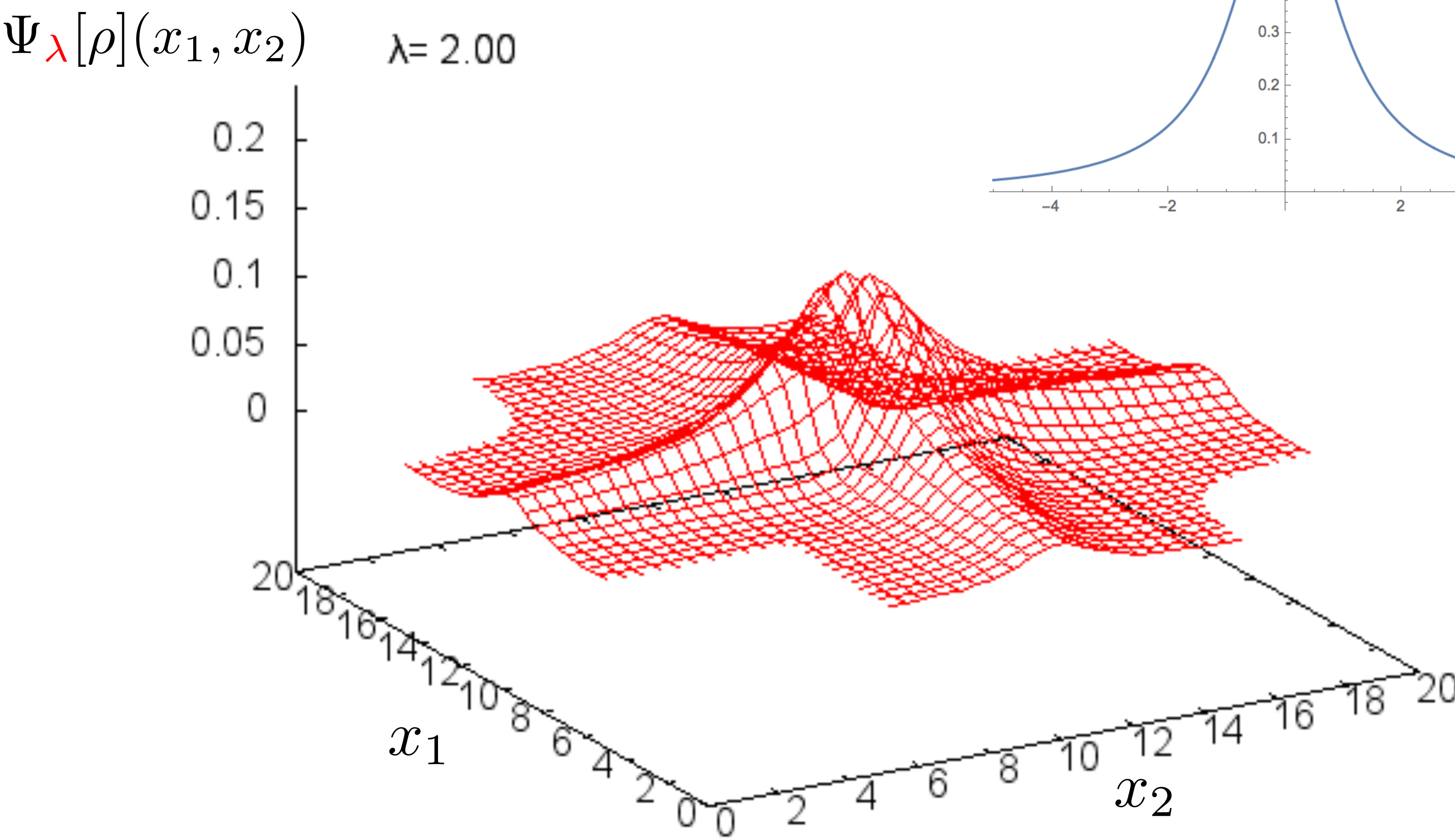


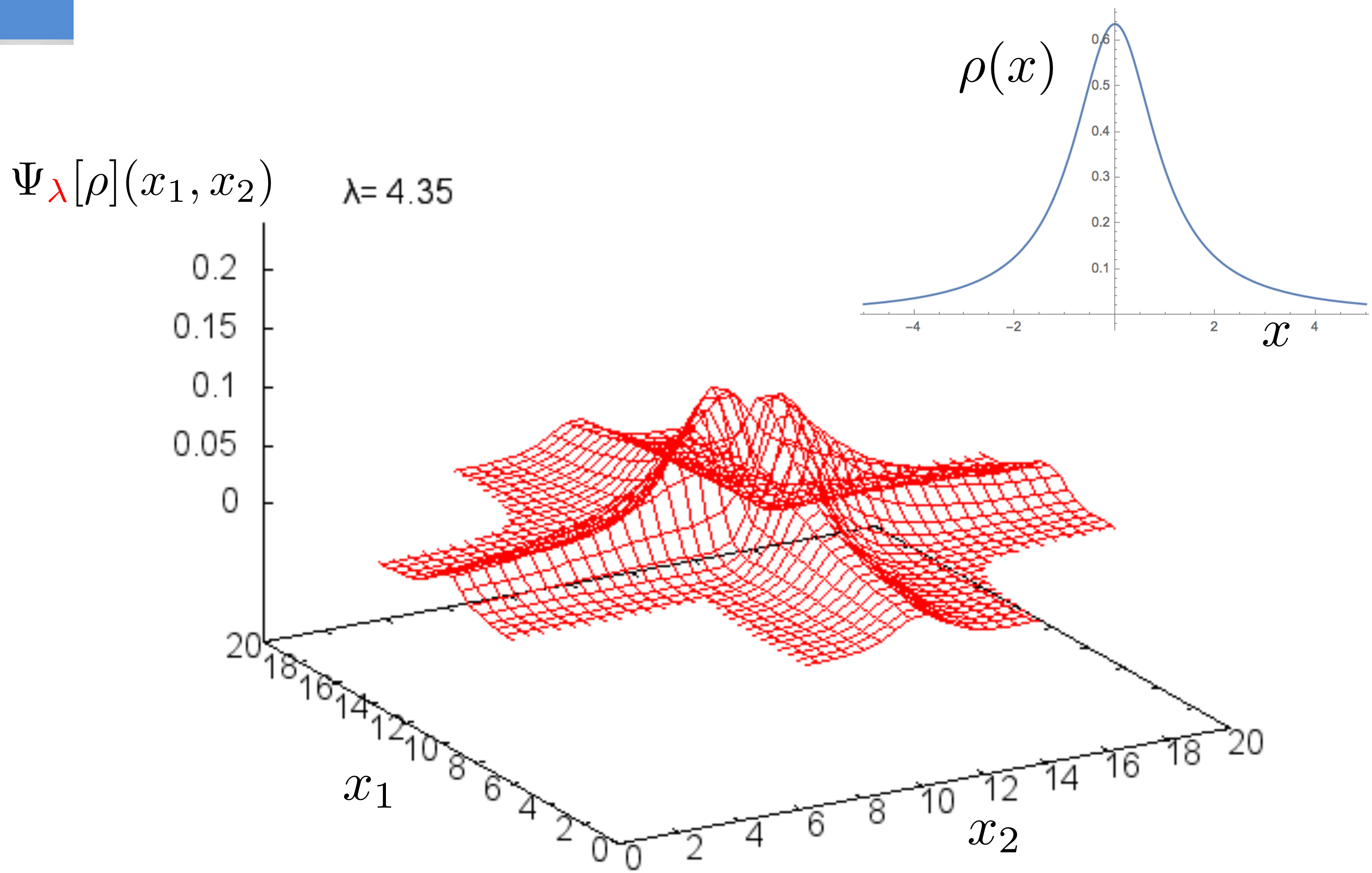
$\rho(x)$
0.6
0.5
0.4
0.3
0.2
0.1
−4
−2
2
4
x

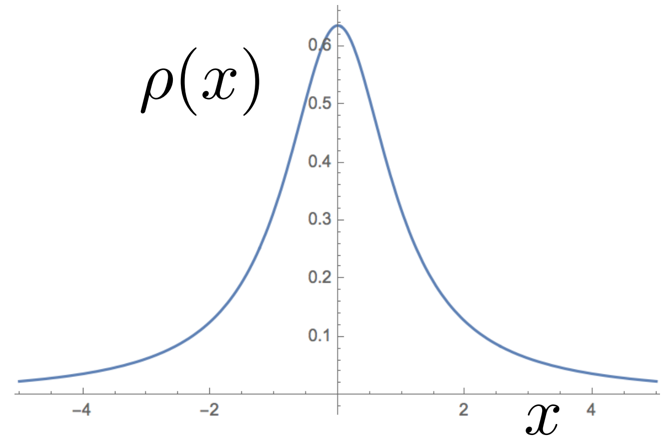

$\Psi_{\lambda}[\rho](x_1, x_2)$
λ= 1.00
0.2
0.15
0.1
0.05
0
20 18 16 14 12 10 8 6 4 2 0
x_1
0 2 4 6 8 10 12 14 16 18 20
x_2

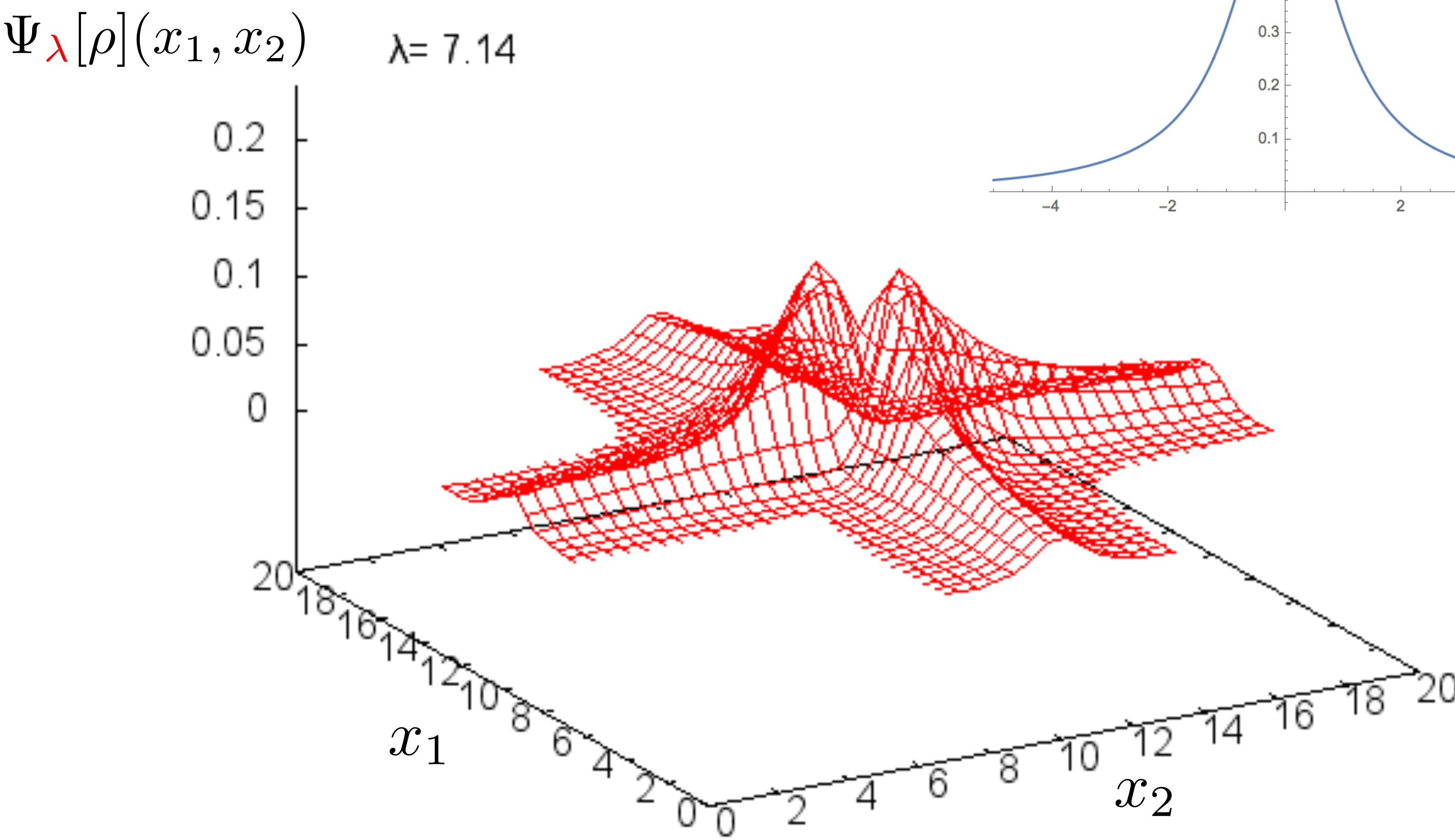

$\rho(x)$
0.6
0.5
0.4
0.3
0.2
0.1
−4 −2 2 4
x


$\rho(x)$
0.6
0.5
0.4
0.3
0.2
0.1
−4
−2
2
4
x


$\Psi_{\lambda}[\rho](x_1, x_2)$
λ= 2.00
0.2
0.15
0.1
0.05
0
20
18
16
14
12
10
8
6
4
2
0
x_1
0
2
4
6
8
10
12
14
16
18
20
x_2


$\rho(x)$
0.6
0.5
0.4
0.3
0.2
0.1
−4
−2
2
4
x
$\Psi_{\lambda}[\rho](x_1, x_2)$
λ= 4.35
0.2
0.15
0.1
0.05
0
20
18
16
14
12
10
8
6
4
2
0
x_1
0
2
4
6
8
10
12
14
16
18
20
x_2


$\rho(x)$
0.6
0.5
0.4
0.3
0.2
0.1
−4
−2
2
4
x


$\Psi_{\lambda}[\rho](x_1, x_2)$
λ= 7.14
0.2
0.15
0.1
0.05
0
20
18
16
14
12
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8
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4
2
0
x_1
0
2
4
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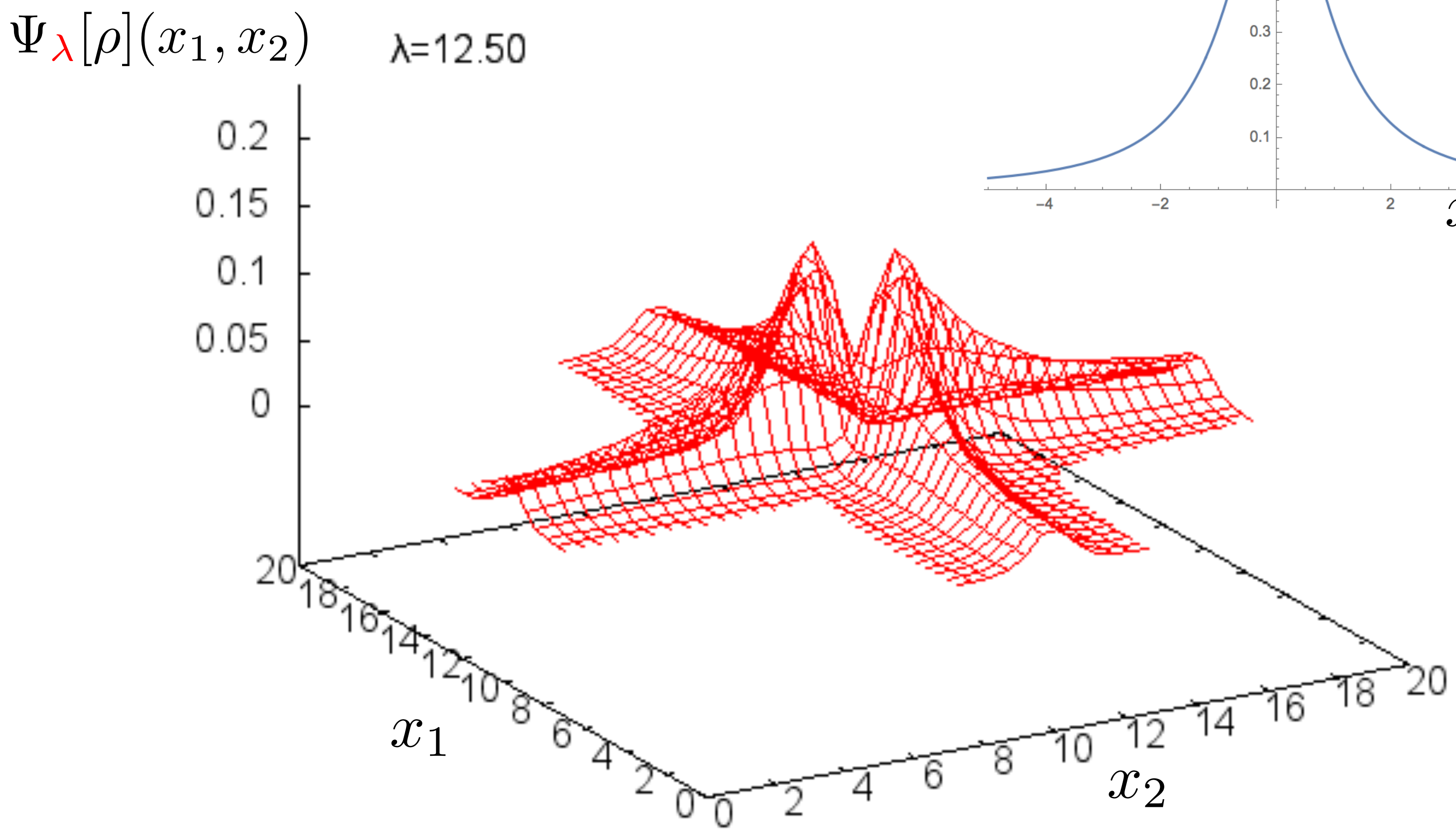
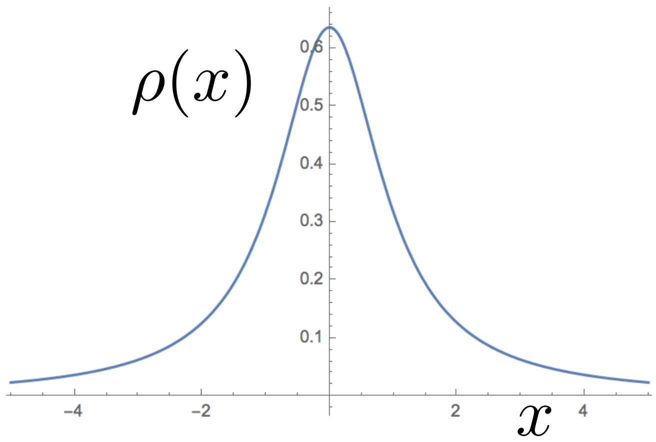
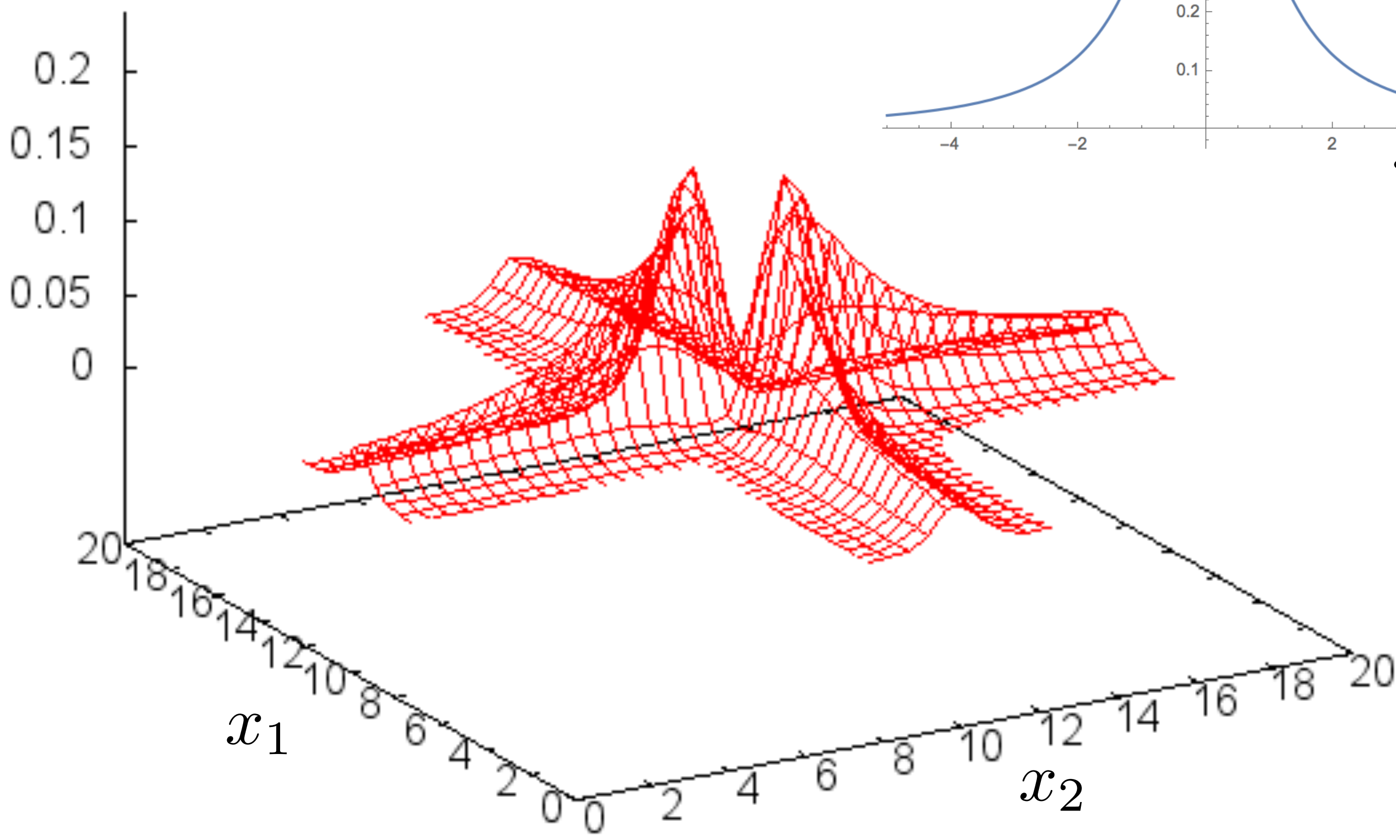
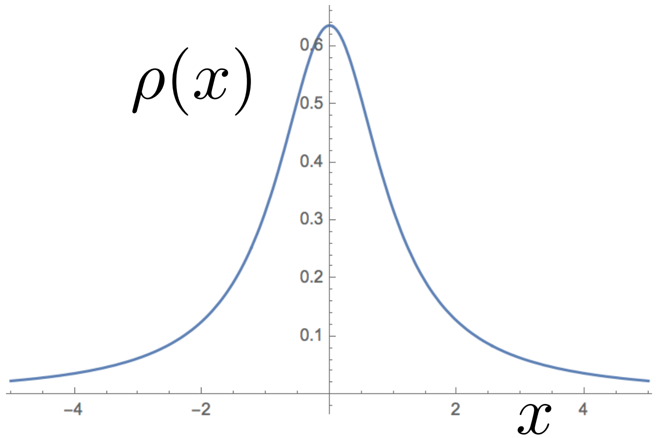
8
10
12
14
16
18
20
x_2


$\Psi_\lambda[\rho](x_1, x_2)$
λ=12.50
0.2
0.15
0.1
0.05
0
x_1
x_2
0 2 4 6 8 10 12 14 16 18 20
0 2 4 6 8 10 12 14 16 18 20

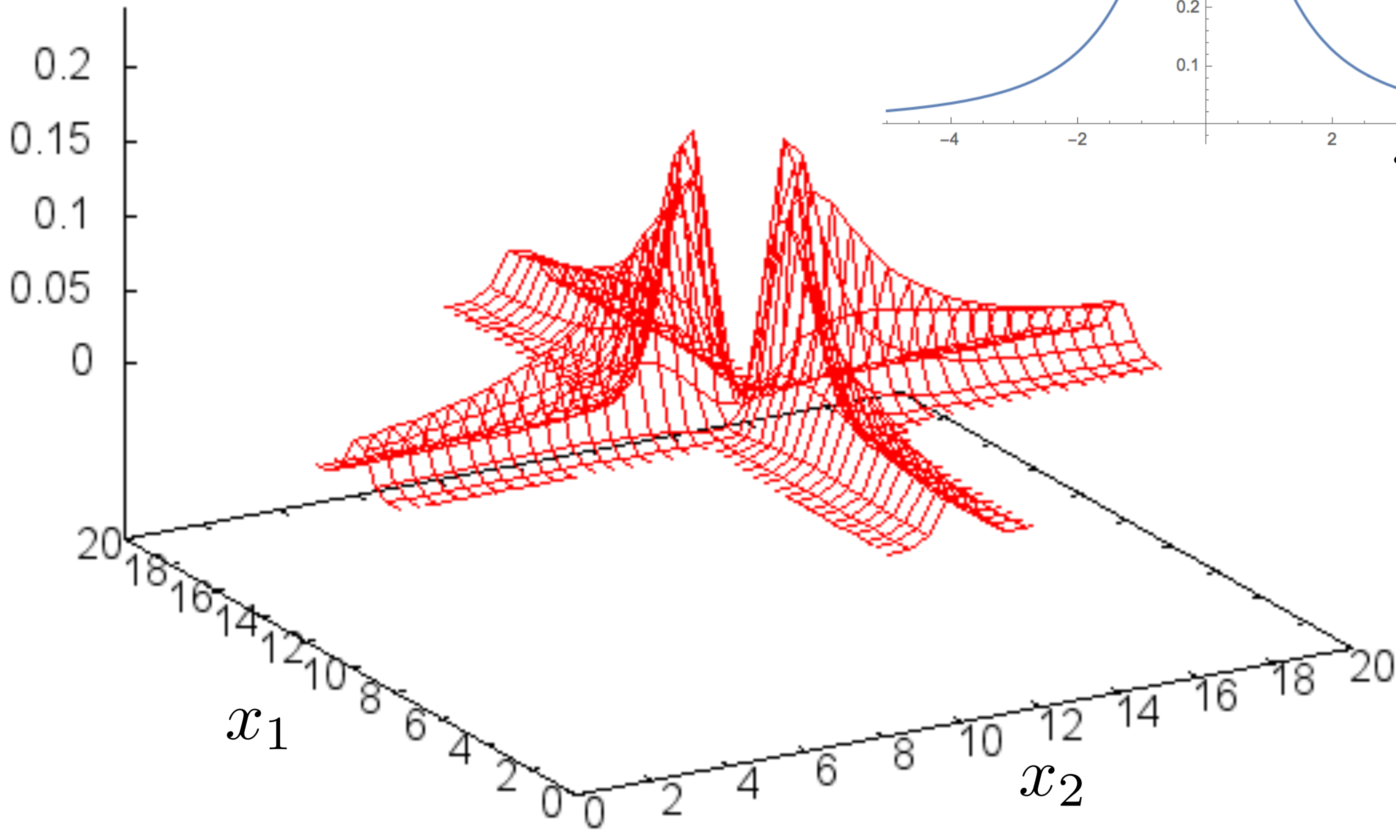

$\rho(x)$
0.6
0.5
0.4
0.3
0.2
0.1
−4
−2
2
4
x

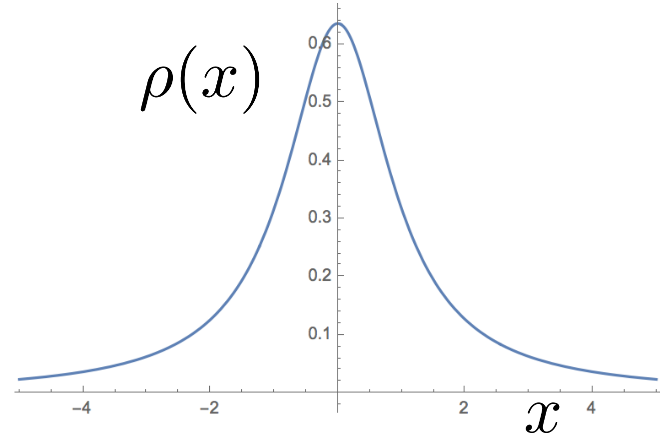
$\Psi_{\lambda}[\rho](x_1, x_2)$ λ=20.00

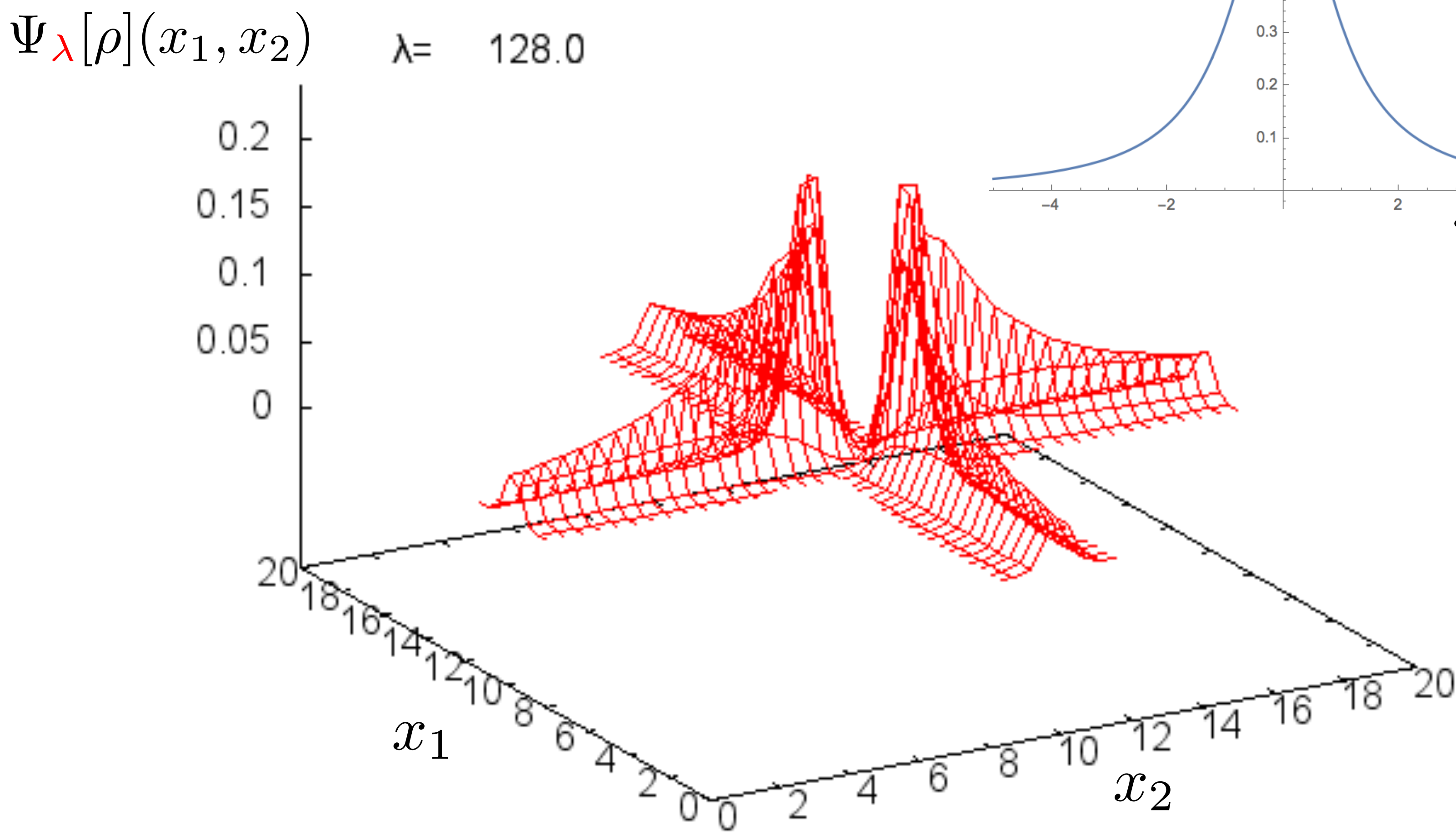


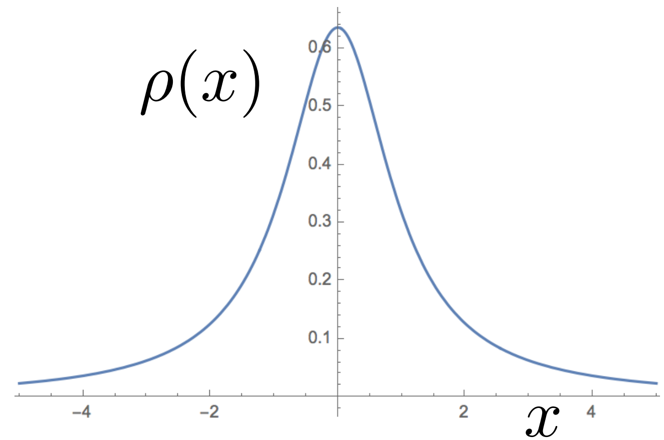


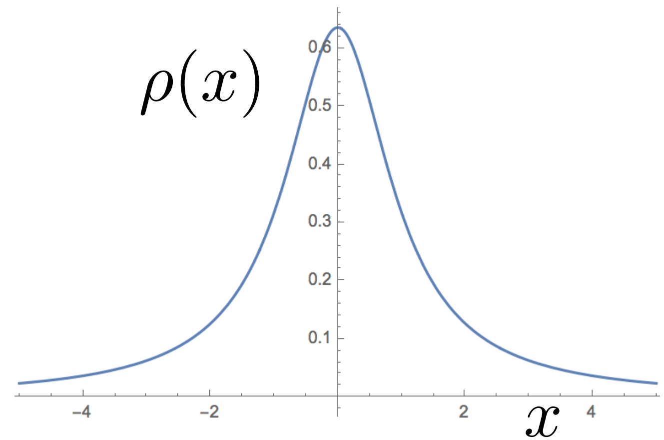
$\Psi_{\lambda}[\rho](x_1, x_2)$ λ= 50.0

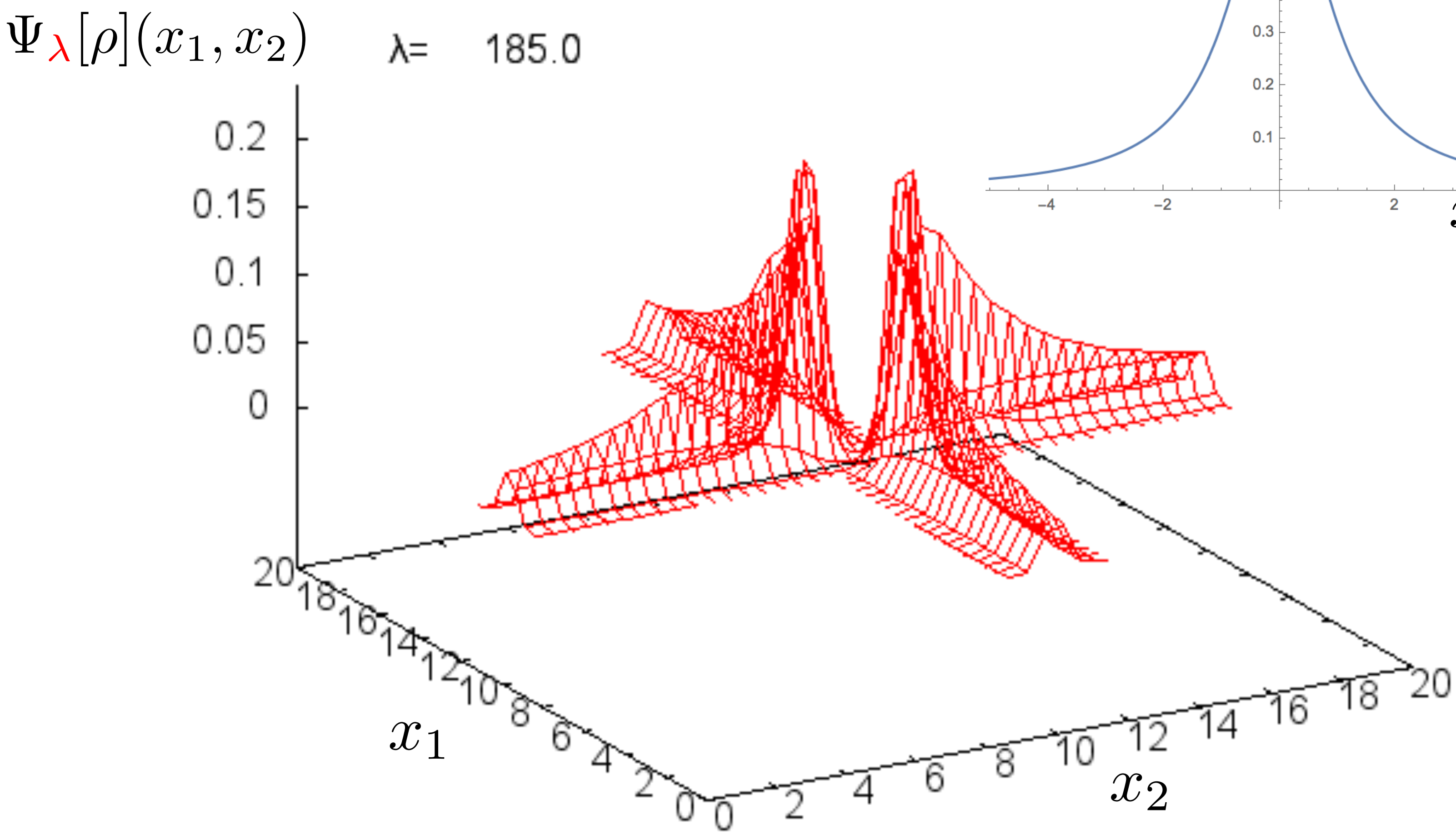


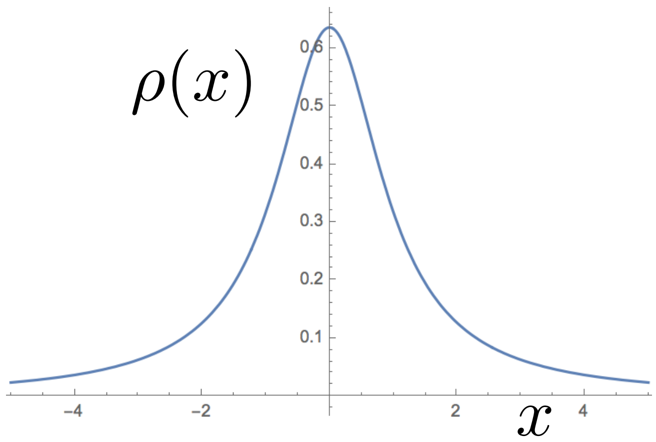



$\Psi_{\lambda}[\rho](x_1, x_2)$
λ= 128.0
0.2
0.15
0.1
0.05
0
x_1
x_2
20 18 16 14 12 10 8 6 4 2 0
0 2 4 6 8 10 12 14 16 18 20

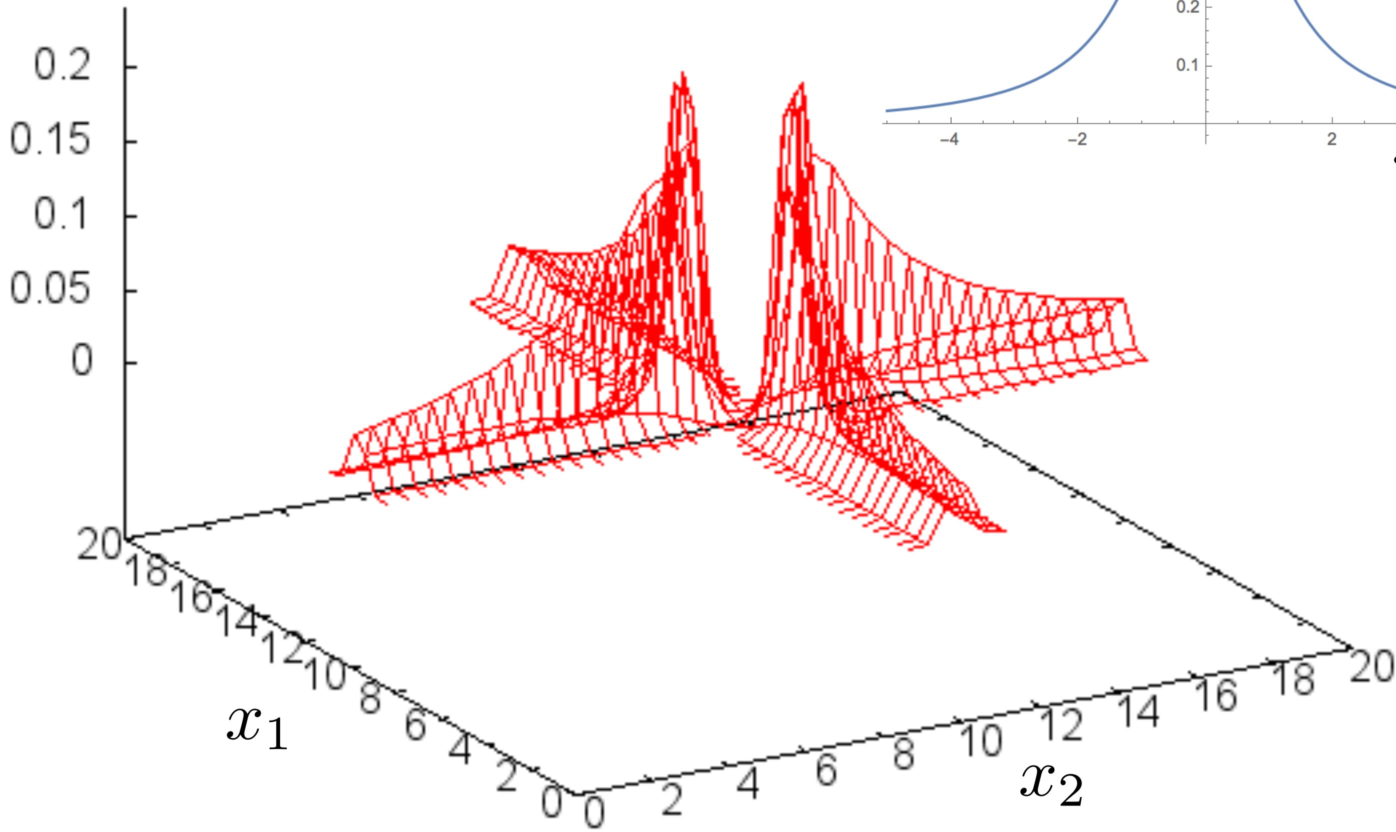

$\rho(x)$
0.6
0.5
0.4
0.3
0.2
0.1
−4 −2 2 4
x

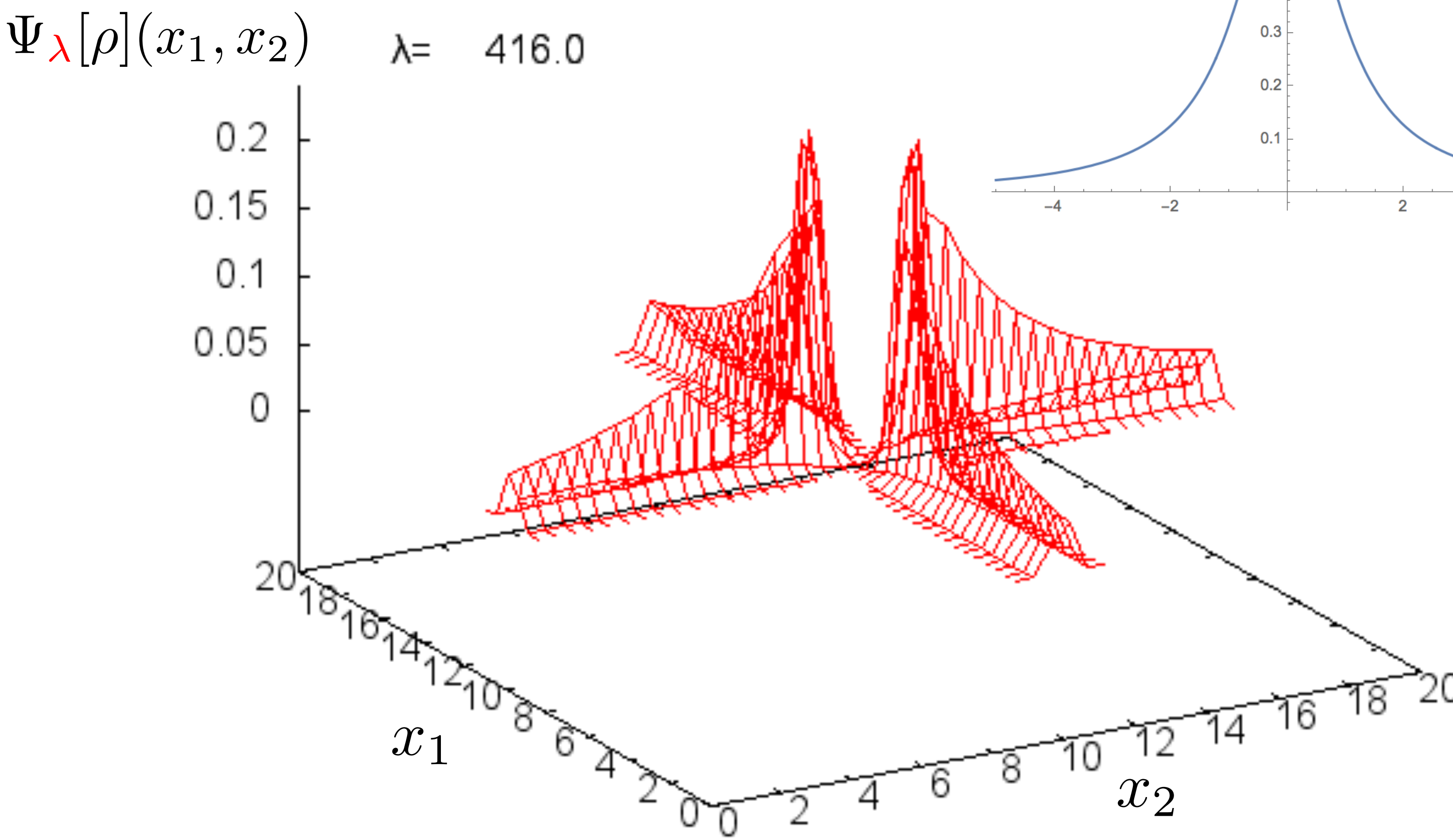

$\rho(x)$
0.6
0.5
0.4
0.3
0.2
0.1
−4
−2
2
4
x


$\Psi_{\lambda}[\rho](x_1, x_2)$
λ= 185.0
0.2
0.15
0.1
0.05
0
20 18 16 14 12 10 8 6 4 2 0
x_1
0 2 4 6 8 10 12 14 16 18 20
x_2

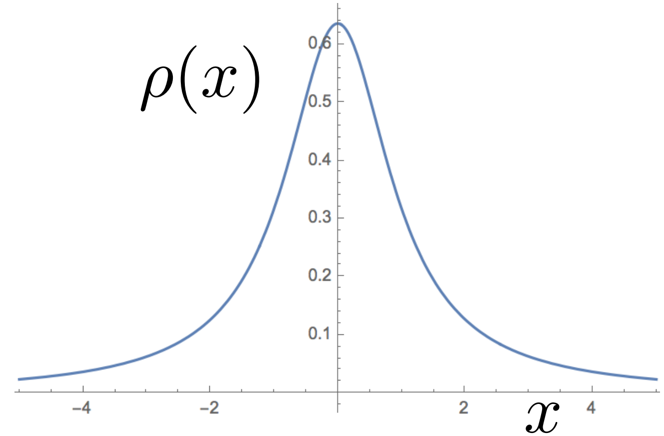


$\Psi_{\lambda}[\rho](x_1, x_2)$ λ= 277.0

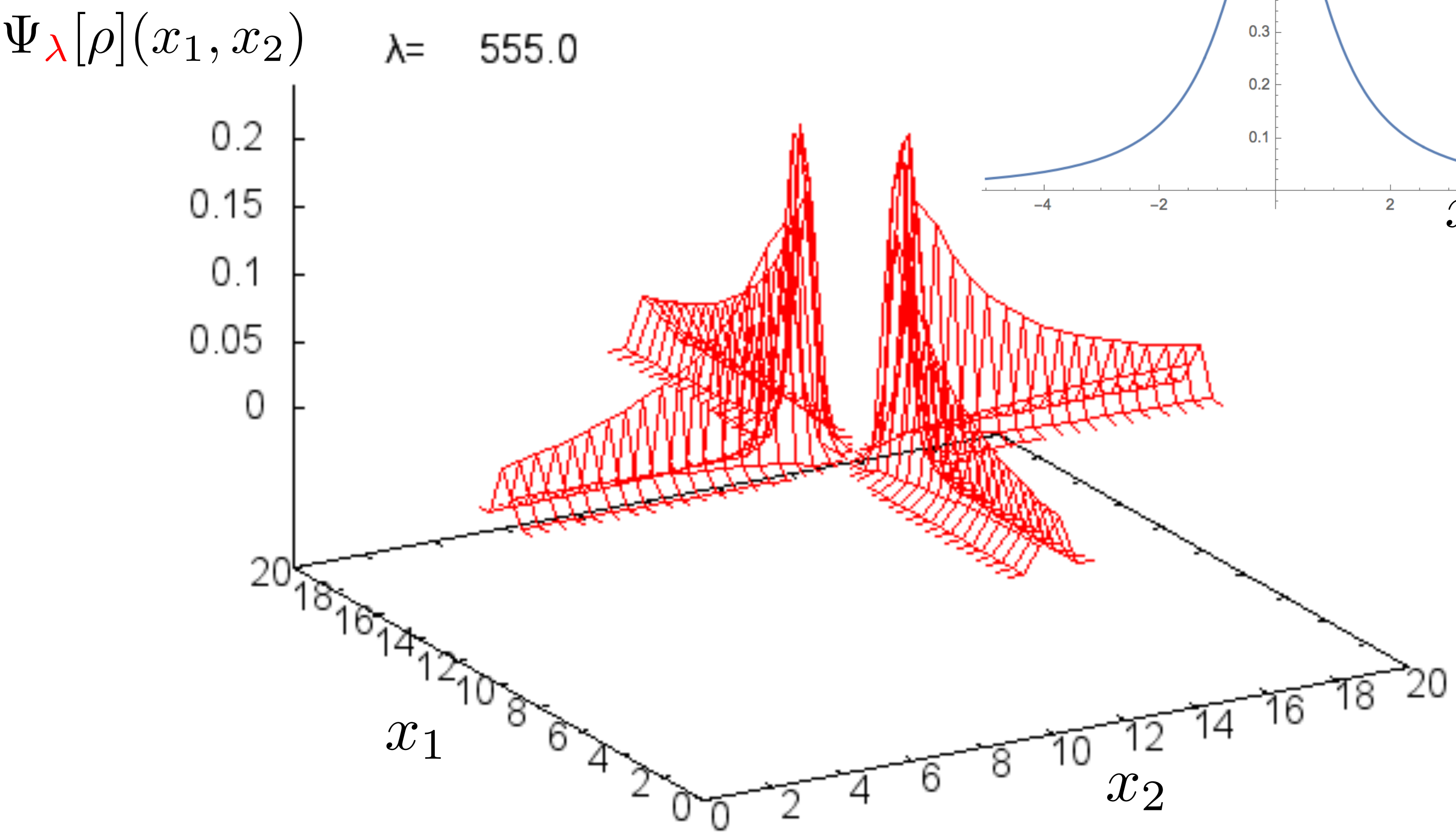


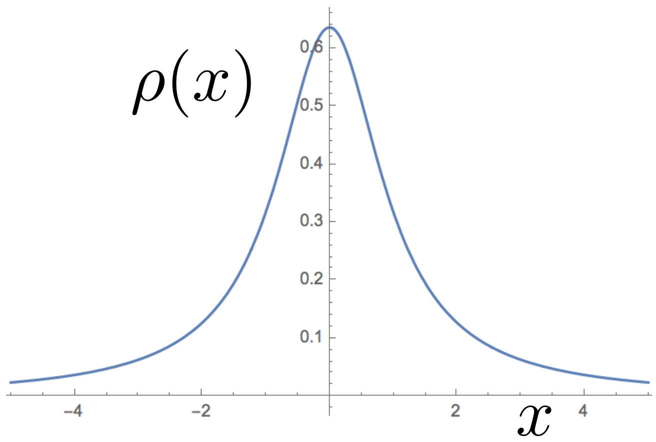


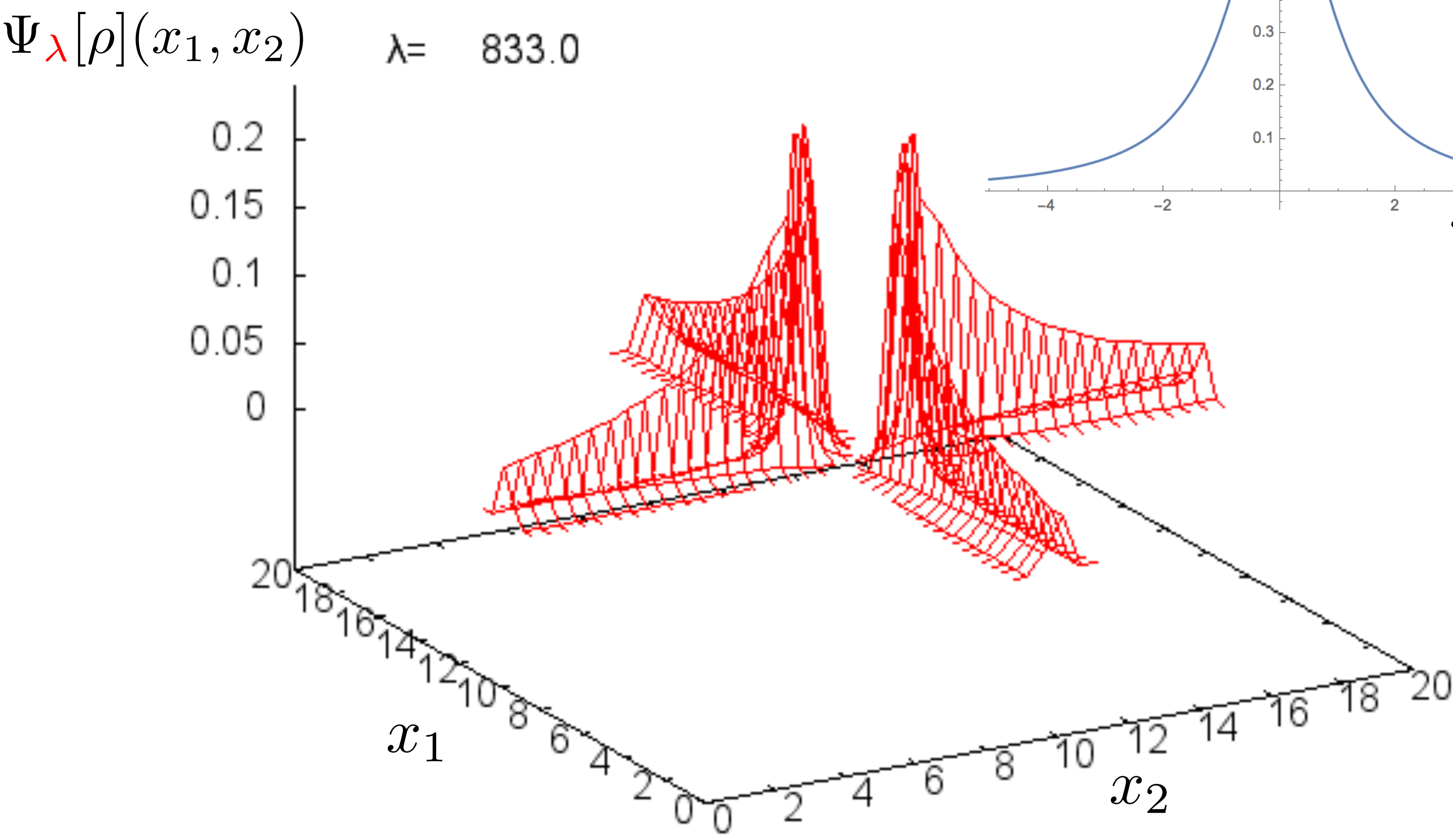
$\Psi_{\lambda}[\rho](x_1, x_2)$
λ= 416.0
0.2
0.15
0.1
0.05
0
20
18
16
14
12
10
8
6
4
2
0
x_1
0
2
4
6
8
10
12
14
16
18
20
x_2



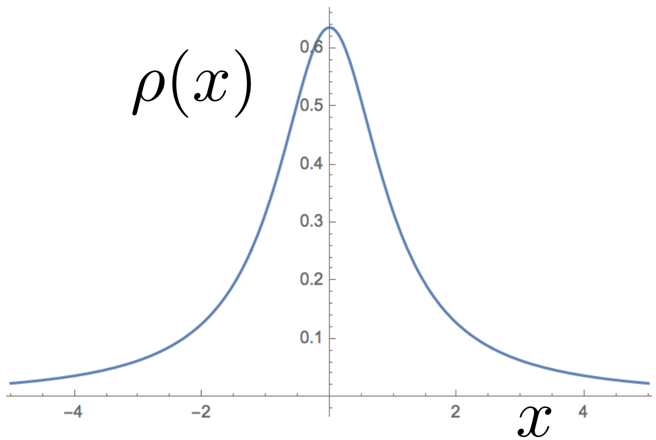
$\rho(x)$
0.6
0.5
0.4
0.3
0.2
0.1
−4
−2
2
4
x


$\Psi_{\lambda}[\rho](x_1, x_2)$
λ= 555.0
0.2
0.15
0.1
0.05
0
20
18
16
14
12
10
8
6
4
2
0
x_1
0
2
4
6
8
10
12
14
16
18
20
x_2

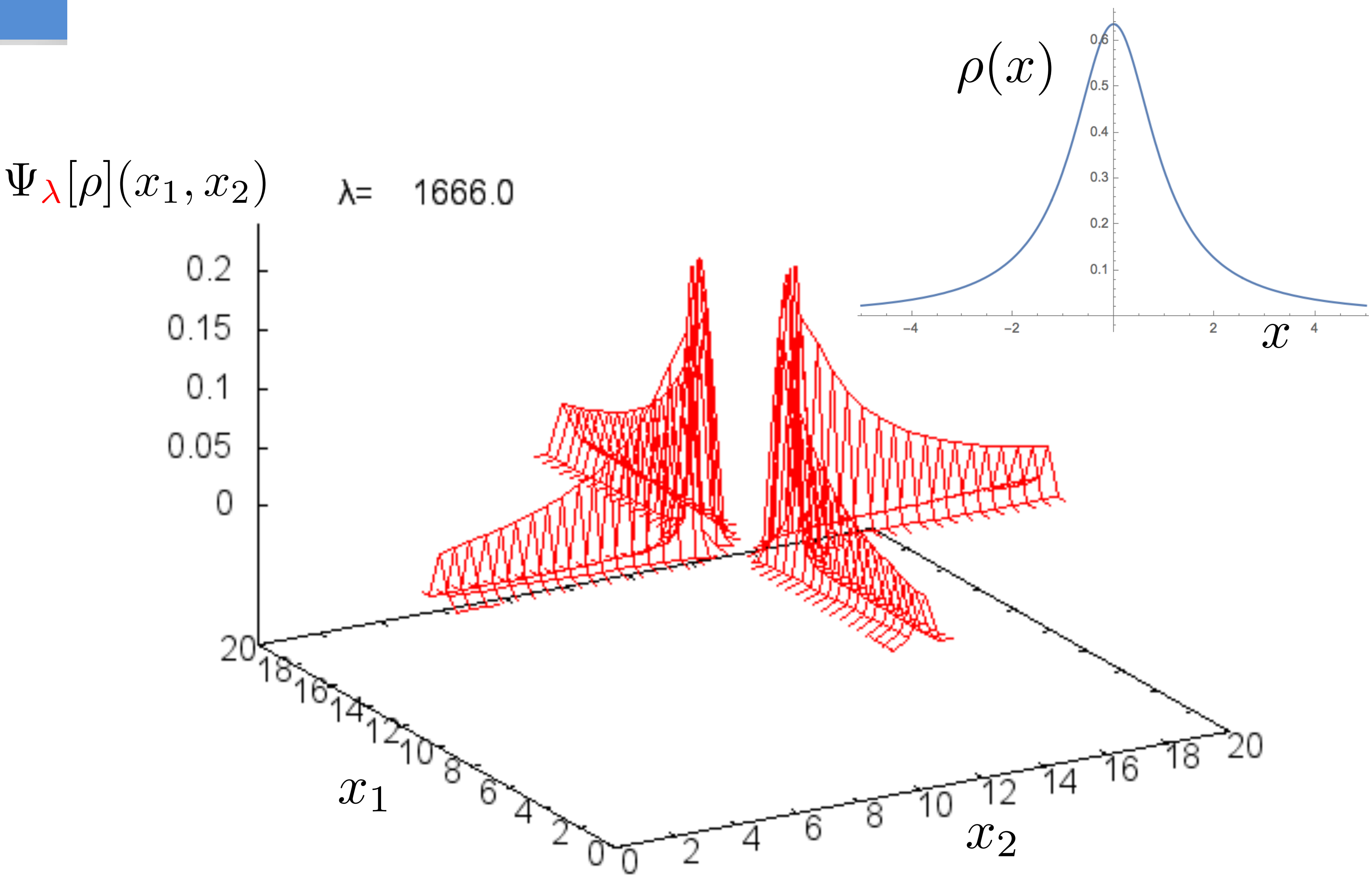

$\rho(x)$
0.6
0.5
0.4
0.3
0.2
0.1
-4
-2
2
4
x

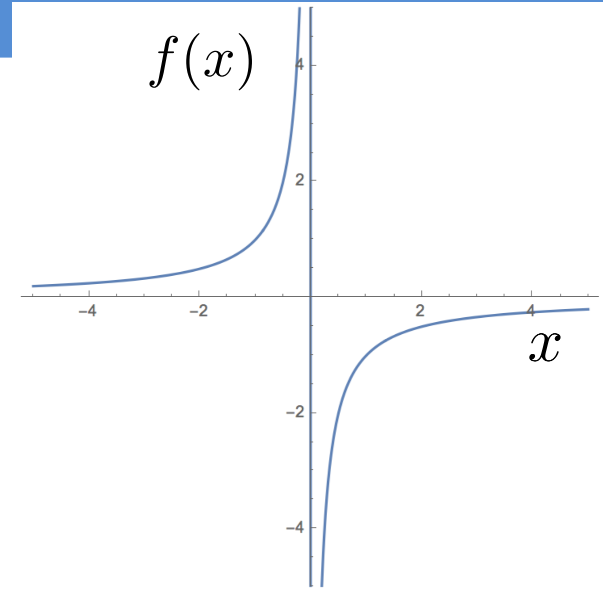


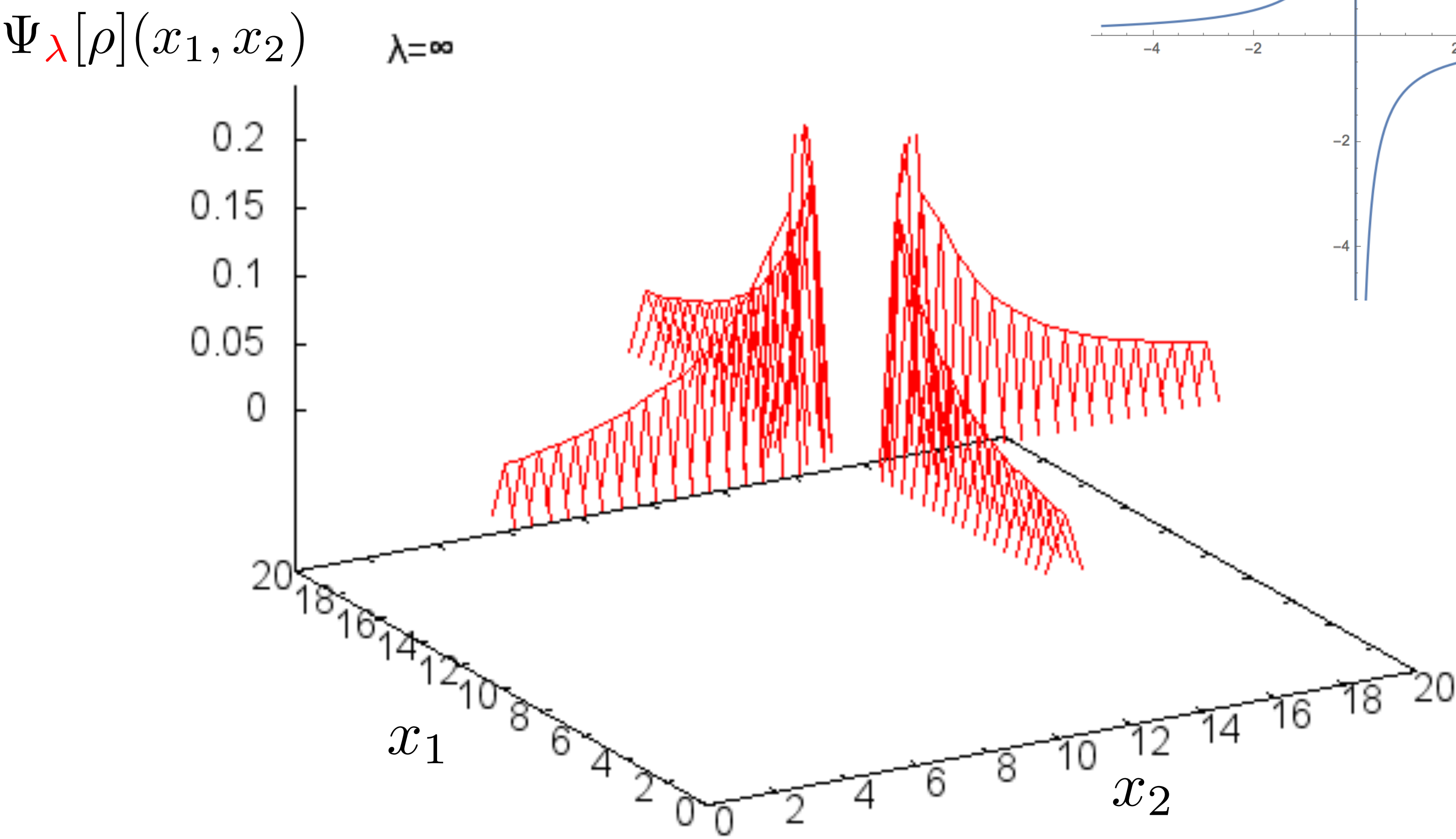
$\Psi_\lambda[\rho](x_1,x_2)$
λ= 833.0
0.2
0.15
0.1
0.05
0
x_1
x_2



$\rho(x)$
x

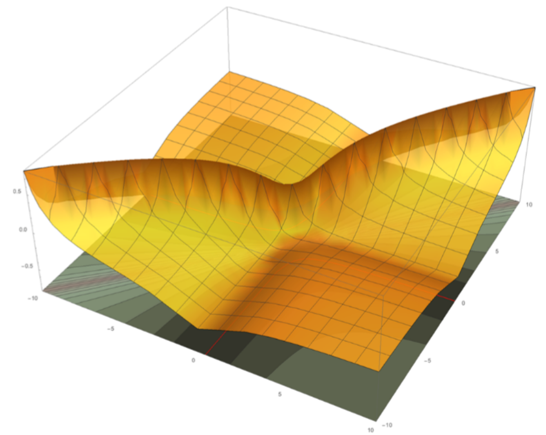

$\Psi_{\lambda}[\rho](x_1, x_2)$
λ= 1666.0
0.2
0.15
0.1
0.05
0
x_1
x_2
0 2 4 6 8 10 12 14 16 18 20
$\rho(x)$
0.6
0.5
0.4
0.3
0.2
0.1
−4 −2 2 4
x



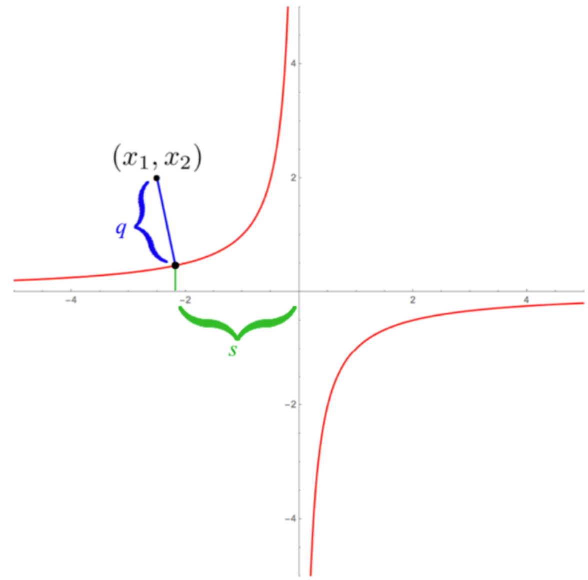


see also: Chen & Friesecke, Multiscale Modeling & Simulation 13, 1259 (2015)

Next leading term in DFT



$$V_{ee} + V_\infty$$



$$W_{\lambda}^{\mathrm{DFT}} \to W_{\infty}^{\mathrm{SCE}}[\rho] + \frac{W_{\frac{1}{2}}^{\mathrm{SCE}}[\rho]}{\sqrt{\lambda}} + \ldots$$

$$W_{\frac{1}{2}}^{\mathrm{SCE}}[\rho] = \frac{1}{2}\int d^3 s \frac{\rho(\mathbf{s})}{N} \sum_{\mu=4}^{3N} \frac{\omega_\mu(\mathbf{s})}{2}$$

PGG, Vignale, Seidl, JCTC 5, 743 (2009)
Grossi, Kooi, Giesbertz, Seidl, Cohen, Mori-Sanchez, P.GG, JCTC 13, 6089 (2017)
Colombo, Di Marino, Stra, arXiv:2106.06282

Spherically symmetric systems

ansatz: 1D solution for the radial part + relative angles minimization

Seidl, Gori-Giorgi and Savin, PRA ***75****, 042511 (2007)*

not always the lowest solution (it depends on the density)

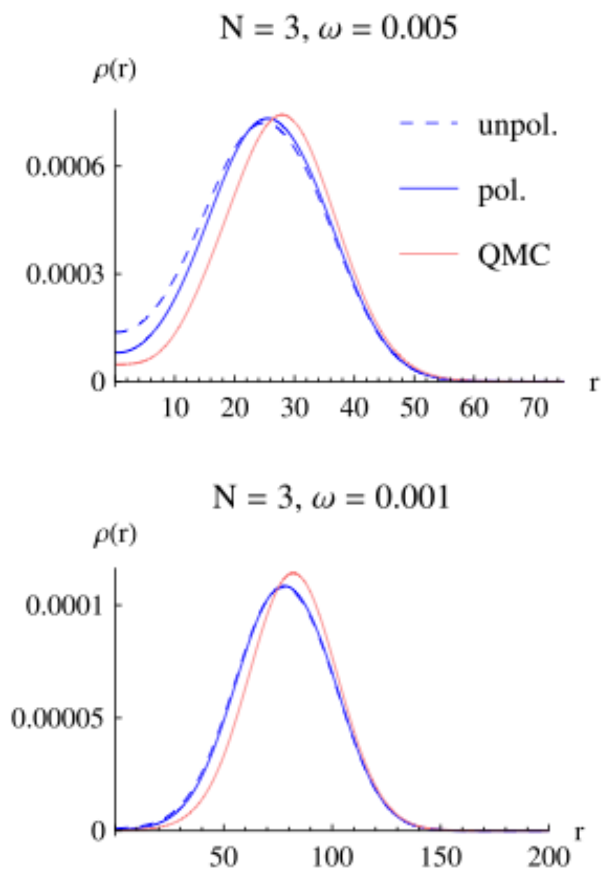
Colombo & Stra, arXiv:1507.08522

however, the 1D-like solution is very close to the true minimum, and the potential computed from it is the functional derivative of the 1D-like SCE functional

Seidl, Di Marino, Gerolin, Nenna, Giesbertz & Gori-Giorgi, arXiv:1702.05022

$$\nabla v_{\mathrm{SCE}}(\mathbf{r}) = -\sum_{i=2}^{N} \frac{\mathbf{r}-\mathbf{f}_i(\mathbf{r})}{|\mathbf{r}-\mathbf{f}_i(\mathbf{r})|^3}$$

Accuracy of KS SCE for low-density



electrons in 2D harmonic trap

$$v_{\text{ext}}(\mathbf{r}) = \frac{1}{2}\omega^2 r^2$$

$$E_{xc}[\rho] \approx W_\infty[\rho]$$

energy accuracy
of ~ 1 mH* (~4%)

QMC: *D. Guclu and C.J. Umrigar*

*Mendl, Malet & Gori-Giorgi, PRB **89**, 125106 (2014)*

General 3D geometry: algorithms from optimal transport

$$V_{ee}^{\mathrm{SCE}}[\rho] = \min_{\Psi\to\rho} \langle \Psi | \hat{V}_{ee} | \Psi \rangle$$ **mass transportation (Monge-Kantorovich) problem**

Kantorovich dual formulation: theory

- Buttazzo, De Pascale, & Gori-Giorgi, Phys. Rev. A. 85, 062502 (2012)

- De Pascale, arXiv:1503.07063

Linear programming algorithm based on the dual formulation:

- Mendl & Lin, Phys. Rev. B 87, 125106 (2013)

Discretised linear programming algorithm

-Chen, Friesecke, Mendl, J. Chem. Theory Comput, 10, 4360 (2014)

Entropic regularization algorithm

- Benamou, Carlier, Nenna, arXiv:1505.01136v2

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Entropic regularization algorithm

- Benamou, Carlier, Nenna, arXiv:15

arXiv.org > math > arXiv:1905.08322

Mathematics > Optimization and Control

Semidefinite relaxation of multi-marginal optimal transport for strictly correlated electrons in second quantization

Yuehaw Khoo, Lin Lin, Michael Lindsey, Lexing Ying

arXiv.org >

Mathematics > Probability

Approximation of Optimal Transport problems with marginal moments constraints

Aurélien Alfonsi, Rafaël Coyaud, Virginie Ehrlacher, Damiano Lombardi

(Submitted on 14 May 2019)

arXiv.org >

Mathemat

Breaking the curse of dimension in multi-marginal Kantorovich optimal transport on finite state spaces

G. Friesecke, D. Vögler

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arXiv.org > math > arXiv:1905.08322

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Mathemat

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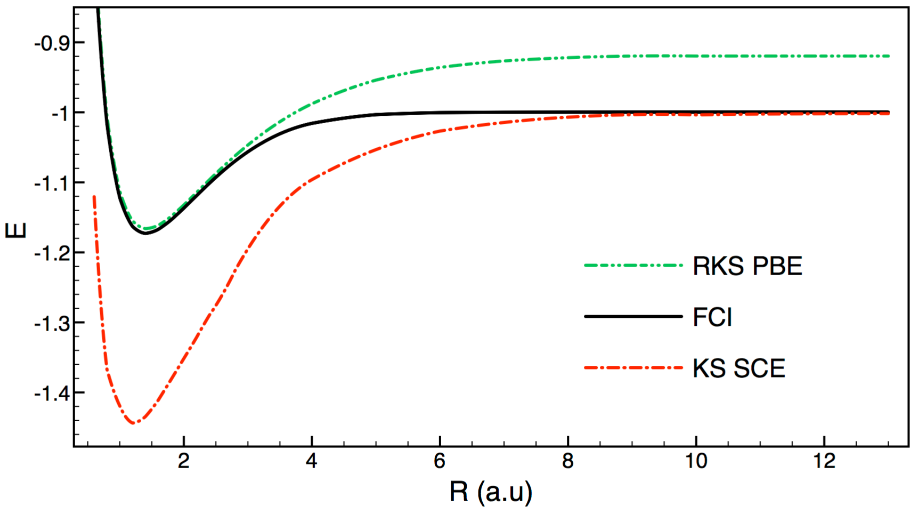
G. Friesecke, D. Vögler

Better to design approximations inspired to the SCE form ?

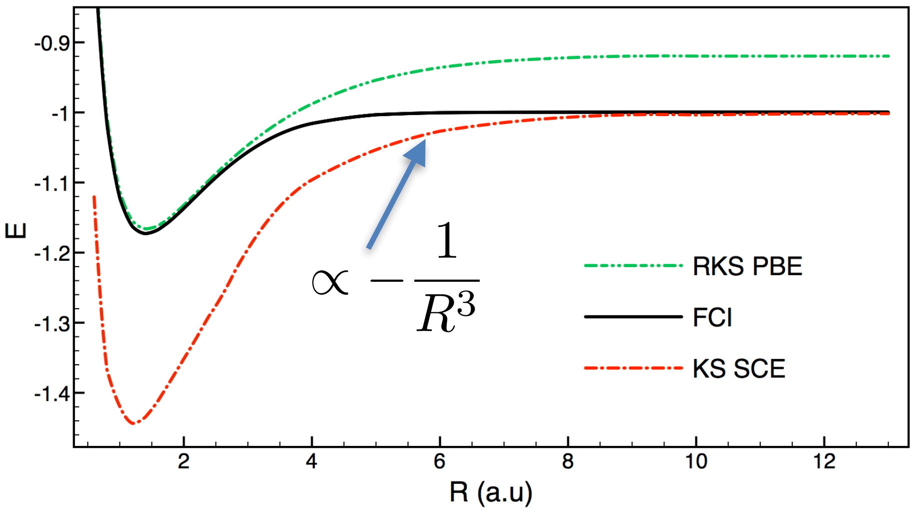
H_2 molecule (SCE from Kantorovich formulation)



$$E_{xc}[\rho] \approx W_\infty[\rho]$$

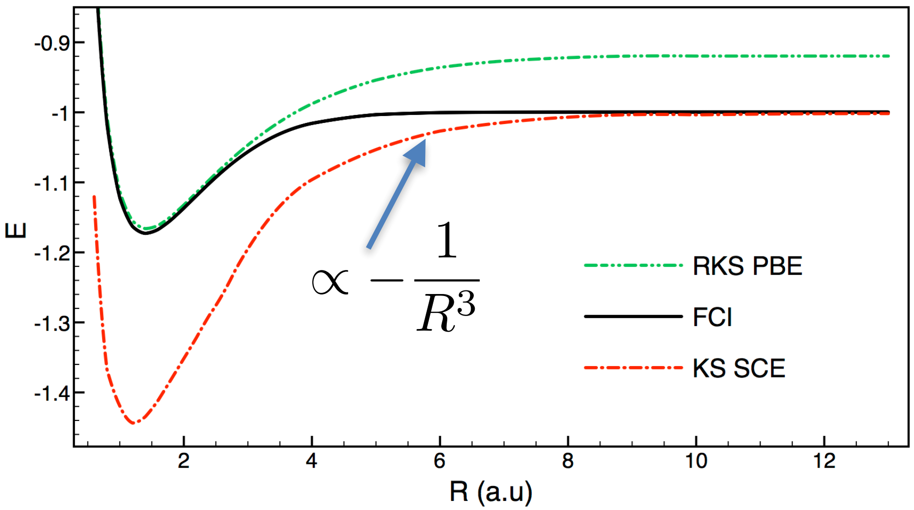
Vuckovic, Wagner, Mirtschink & Gori-Giorgi, JCTC 11, 3153 (2015)

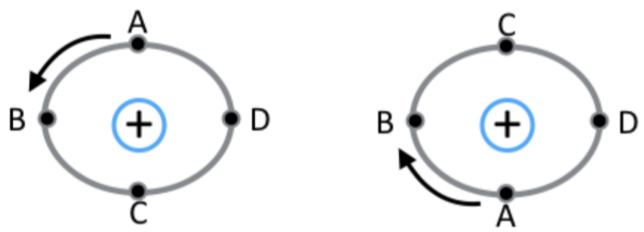
H_2 molecule (SCE from Kantorovich formulation)



$$E_{xc}[\rho] \approx W_\infty[\rho]$$

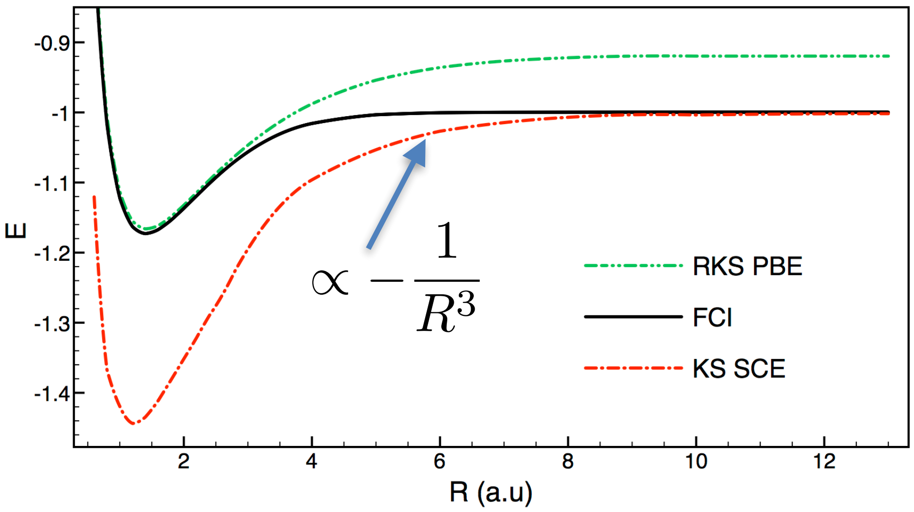
H_2 molecule (SCE from Kantorovich formulation)

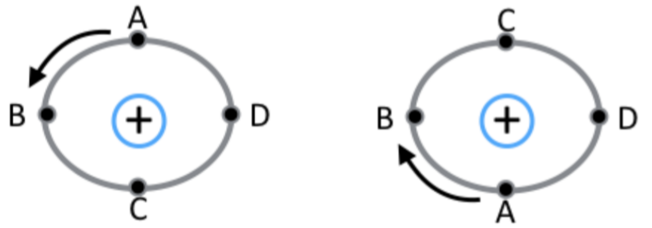




$$E_{xc}[\rho] \approx W_\infty[\rho]$$

H_2 molecule (SCE from Kantorovich formulation)

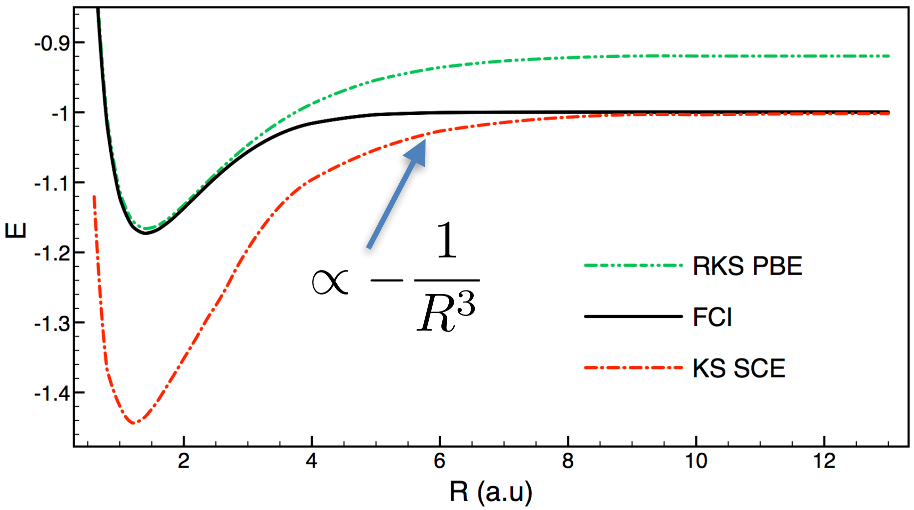


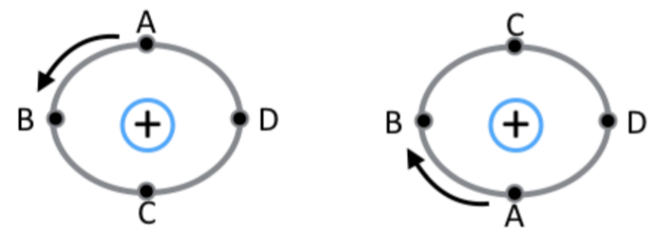


- *we do not account for the "price" in kinetic energy to make this perfect correlation*
- *you get attraction also for perfectly spherical densities*

$$E_{xc}[\rho] \approx W_\infty[\rho]$$

H_2 molecule (SCE from Kantorovich formulation)

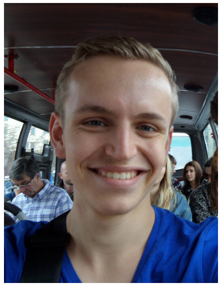




- we do not account for the "price" in kinetic energy to make this perfect correlation
- you get attraction also for perfectly spherical densities

$$E_{xc}[\rho] \approx W_\infty[\rho]$$

Talk today:
FDM approach
to dispersion



Derk Kooi

SCE and chemistry

- approximate SCE density functionals (integrals of the density as main ingredient)

non-local radius (NLR) model

*Wagner & PG-G, PRA **90**, 052512 (2014)*

*Zhou, Bahmann & Ernzerhof, JCP **143**, 124013 (2015)*

shell model

*Bahmann, Zhou & Ernzerhof, JCP **145**, 124014 (2016)*

- use input from the weakly correlated regime

local interpolation along the adiabatic connection

*Vuckovic, Irons, Savin, Teale & PG-G, JCTC **12**, 2598 (2016)*

*Vuckovic, Irons, Wagner, Teale & PG-G, PCCP **19**, 6169 (2017)*

global interpolations (can use semilocal approximations for SCE)

*Fabiano, PG-G, Seidl, Della Sala JCTC **12**, 4885 (2016)*

Giarrusso, PG-G, Della Sala, Fabiano, JCP 148, 134106 (2018)

Vuckovic, PG-G, Della Sala, Fabiano, JPCL 9, 3137 (2018)

- build approximations for the physical coupling strength rescaling SCE

multi-radii functional (MRF)

*Vuckovic & PG-G, J. Phys. Chem. Lett. **8**, 2799 (2017)*

Vuckovic, J. Chem. Theory Comput. 15, 3580 (2019)

SCE and chemistry

- approximate SCE density functionals (integrals of the density as main ingredient)

non-local radius (NLR) model

*Wagner & PG-G, PRA **90**, 052512 (2014)*

*Zhou, Bahmann & Ernzerhof, JCP **143**, 124013 (2015)*

shell model

*Bahmann, Zhou & Ernzerhof, JCP **145**, 124014 (2016)*

- use input from the weakly correlated regime

local interpolation along the adiabatic connection

*Vuckovic, Irons, Savin, Teale & PG-G, JCTC **12**, 2598 (2016)*

*Vuckovic, Irons, Wagner, Teale & PG-G, PCCP **19**, 6169 (2017)*

global interpolations (can use semilocal approximations for SCE)

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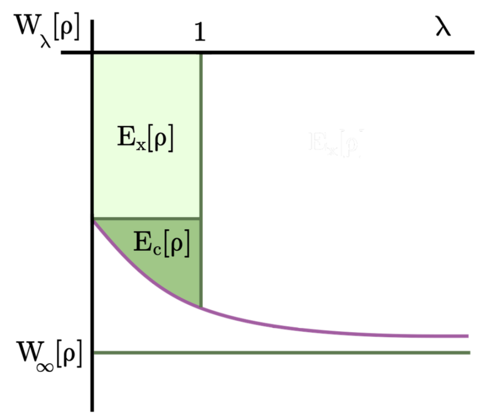
Global interpolations (old idea: Seidl, Perdew, Levy 1999)

global AC integrand

$$E_{xc}[\rho] = \int_0^1 W_\lambda[\rho] \mathrm{d}\lambda$$

$$W_\lambda[\rho] = \langle \Psi_\lambda[\rho] | \hat{V}_{ee} | \Psi_\lambda[\rho] \rangle - U[\rho].$$



Global Interpolations:

- no gauge issue
  (can use semilocal approx.)

- size-consistency error
  can be corrected: JPCL 9, 3137 (2018)

Results:

- work reasonably only with HF orbitals
- usually better than MP2, MP3 and MP4 for interaction energies
- small variance

e.g., the S66 data set (kcal/mol)

method	MAE	variance
rev-ISI	0.33	0.08
ISI	0.33	0.09
SPL	0.35	0.11
LB	0.31	0.14
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different interpolation formulas

Vuckovic, PGG, Della Sala, Fabiano, JPCL 9, 3137 (2018)
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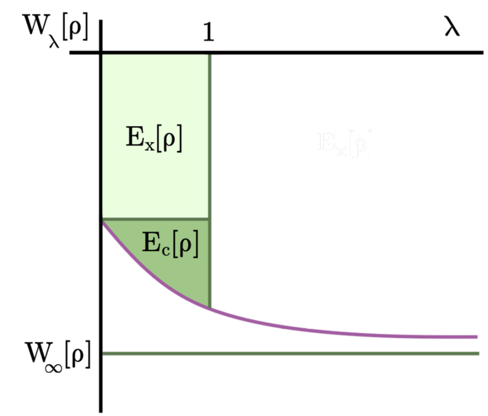

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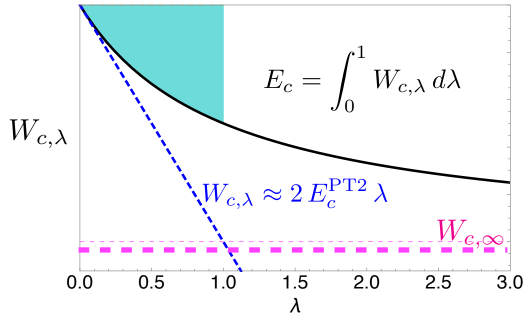
Size consistency: The problem and the correction

Typical example of an interpolation formula:

$$W_{c,\lambda}^{\mathrm{SPL}} = W_{c,\infty}\left(1 - \frac{1}{\sqrt{1 + b\lambda}}\right) \qquad b = \frac{4\,E_c^{\mathrm{MP2}}}{W_{c,\infty}}$$



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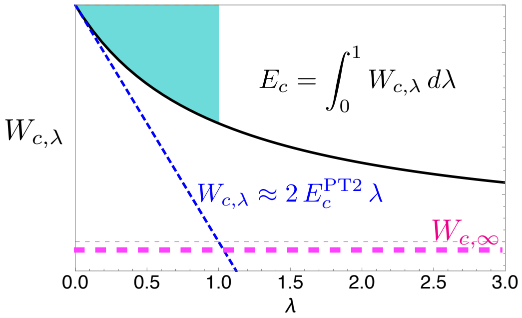

It is size-extensive

A A A

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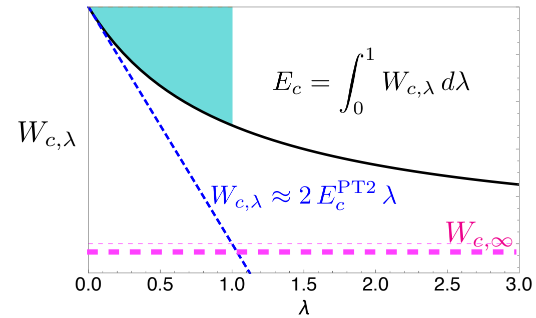

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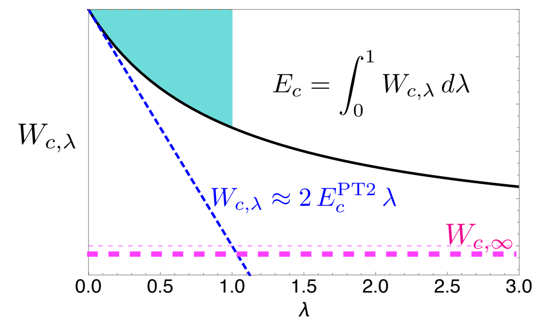

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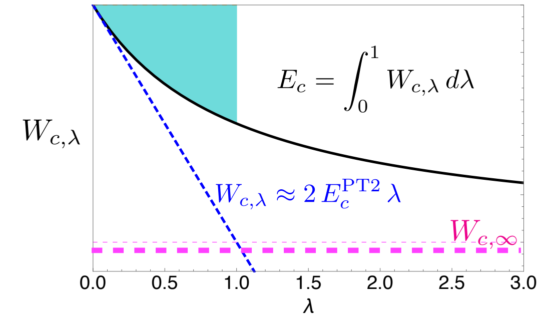

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Same computational cost as the sum of the energies

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Typical example of an interpolation formula:

$$W_{c,\lambda}^{\mathrm{SPL}} = W_{c,\infty}\left(1 - \frac{1}{\sqrt{1 + b\lambda}}\right) \qquad b = \frac{4}{W}$$

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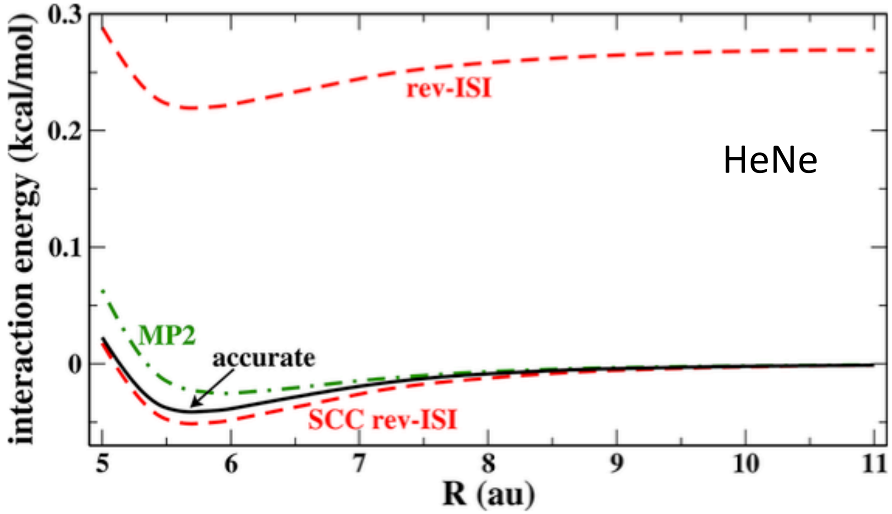

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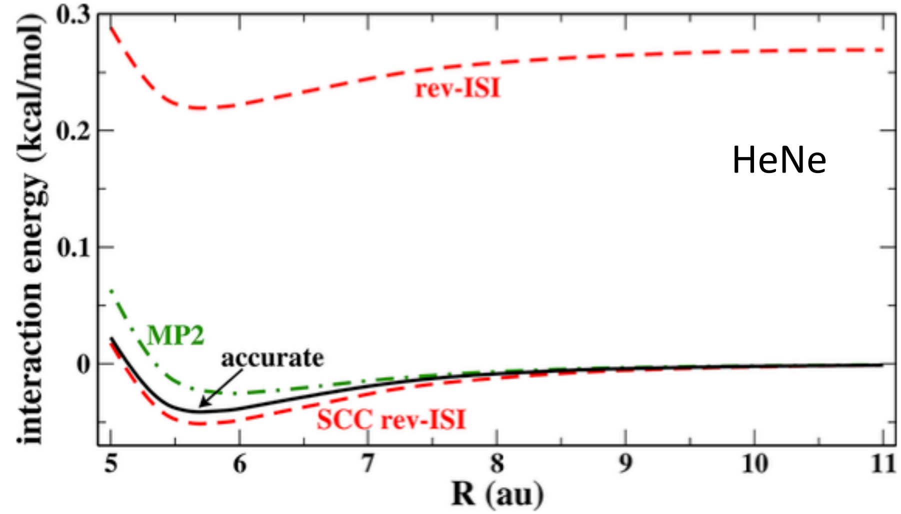

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The Journal of Physical Chemistry Letters

Letter

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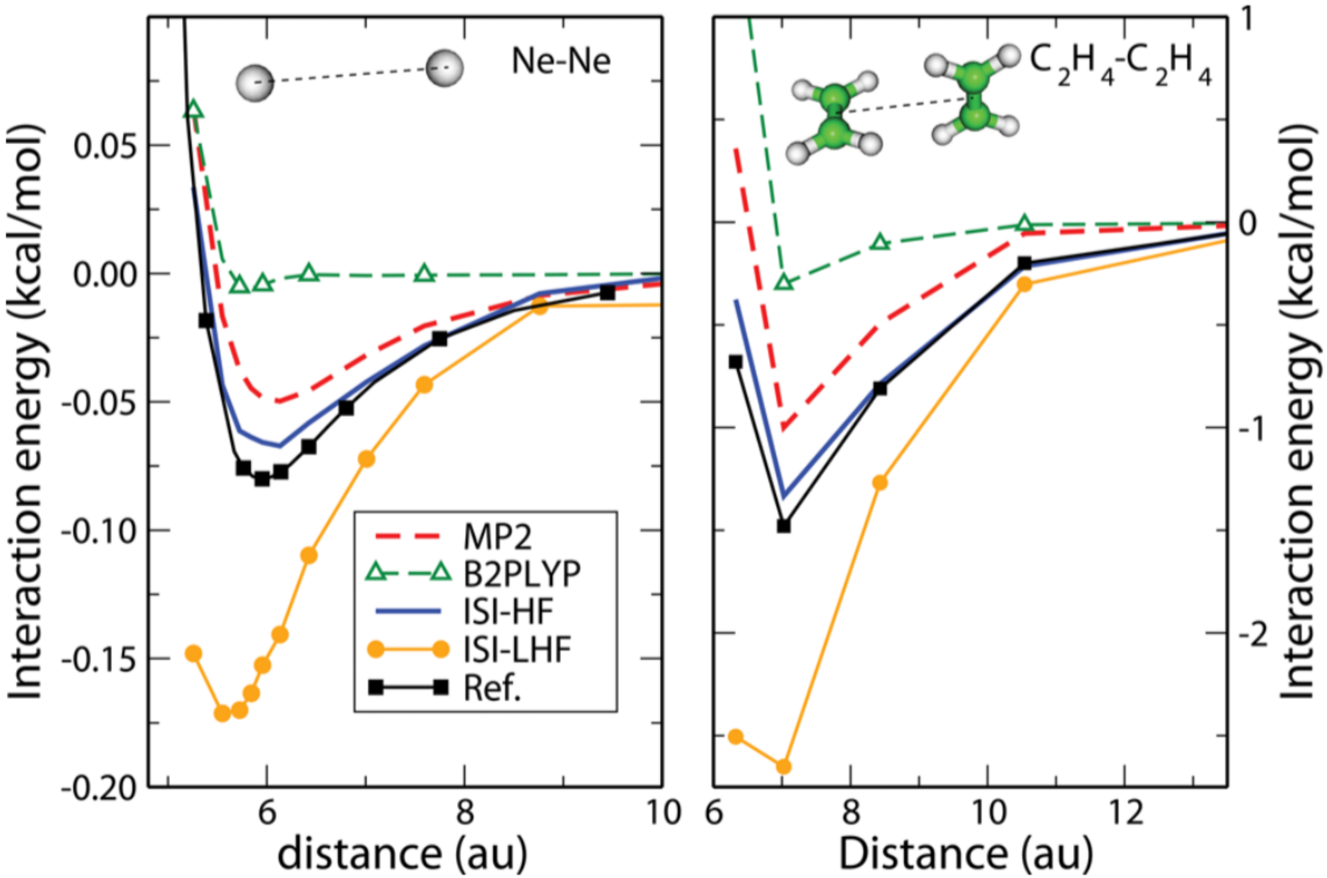
Restoring Size Consistency of Approximate Functionals Constructed from the Adiabatic Connection

Stefan Vuckovic,[*,†] Paola Gori-Giorgi,[†] Fabio Della Sala,[‡,§] and Eduardo Fabiano[‡,§]

Dispersion bonded complexes



Fabiano, Gori-Giorgi, Seidl & Della Sala, JCTC 12, 4885 (2016)

Adiabatic connections

DFT

$$\hat{H}_\lambda^{\mathrm{DFT}} = \hat{T} + \lambda\,\hat{V}_{ee} + \hat{V}_{\mathrm{ext}} + \hat{V}_\lambda[\rho]$$

$$\hat{V}_\lambda[\rho] \;:\; \rho_\lambda = \rho_1 = \rho \;\; \forall\lambda$$

$$W_{c,\lambda}^{\mathrm{DFT}} = \langle\Psi_\lambda|\hat{V}_{ee}|\Psi_\lambda\rangle - \langle\Psi_0|\hat{V}_{ee}|\Psi_0\rangle$$

$$E_c^{\mathrm{DFT}} = \int_0^1 W_{c,\lambda}^{\mathrm{DFT}}\, d\lambda$$

$\lambda \to 0$

$$W_{c,\lambda}^{\mathrm{DFT}} \to \sum_{n=2}^{\infty} n\, E_c^{\mathrm{GL}n}\, \lambda^{n-1}$$

$\lambda \to \infty$

$$W_{c,\lambda}^{\mathrm{DFT}} \to W_{c,\infty}^{\mathrm{SCE}} + \frac{W_{\frac{1}{2}}^{\mathrm{SCE}}}{\sqrt{\lambda}} + \dots$$

Hartree-Fock

$$\hat{H}_\lambda^{\mathrm{HF}} = \hat{T} + \hat{V}^{\mathrm{HF}} + \hat{V}_{\mathrm{ext}} + \lambda\,(\hat{V}_{ee} - \hat{V}^{\mathrm{HF}})$$

$$\hat{V}^{\mathrm{HF}} = \hat{J}[\rho^{\mathrm{HF}}] - \hat{K}[\{\phi_i^{\mathrm{HF}}\}] \quad \lambda\text{−independent}$$

$$\rho_\lambda \qquad \rho_{\lambda=0} = \rho^{\mathrm{HF}} \qquad \rho_{\lambda=1} = \rho$$

$$W_{c,\lambda}^{\mathrm{HF}} = \langle\Psi_\lambda|\hat{V}_{ee} - \hat{V}^{\mathrm{HF}}|\Psi_\lambda\rangle - \langle\Psi_0|\hat{V}_{ee} - \hat{V}^{\mathrm{HF}}|\Psi_0\rangle$$

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$\lambda \to \infty$

$$W_{c,\lambda}^{\mathrm{HF}} \to W_{c,\infty}^{\mathrm{MP}} + \frac{W_{\frac{1}{2}}^{\mathrm{MP}}}{\sqrt{\lambda}} + \frac{W_{\frac{3}{4}}^{\mathrm{MP}}}{\lambda^{3/4}} + \dots$$

Hartree-Fock/Møller-Plesset adiabatic connection

$$\hat{J} = \hat{J}[\rho^{\mathrm{HF}}] = \sum_{i=1}^{N} v_h(\mathbf{r}_i, [\rho^{\mathrm{HF}}])$$

$$\hat{H}_\lambda^{\mathrm{HF}} = \hat{T} + \hat{V}_{\mathrm{ext}} + \hat{J} - \hat{K} + \lambda(\hat{V}_{ee} - \hat{J} + \hat{K})$$

$$v_h(\mathbf{r}, [\rho]) = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'$$

Ψ_λ

$\lambda = 0$ Hartree-Fock Slater determinant

$\lambda = 1$ Exact wave function

$$\hat{K} = \hat{K}[\{\phi_{\mathrm{occ}}^{\mathrm{HF}}\}] = \sum_{i=1}^{N} \hat{k}[\{\phi_{\mathrm{occ}}^{\mathrm{HF}}\}](\mathbf{r}_i, \sigma_i, \mathbf{r}_i'\sigma_i')$$

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$$W_{c,\lambda}^{\mathrm{HF}} = \langle\Psi_\lambda|\hat{V}_{ee} - \hat{J} + \hat{K}|\Psi_\lambda\rangle + U[\rho^{\mathrm{HF}}] + E_x[\{\phi_i^{\mathrm{HF}}\}]$$

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Previous work on radius of convergence, negative coupling strength….

Journal of Physics: Condensed Matter

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Perturbation Theory in the Complex Plane: Exceptional Points and Where to Find Them

Antoine Marie[1], Hugh G A Burton[2] and Pierre-Francois Loos[1]

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What happens when $\lambda \to \infty$?

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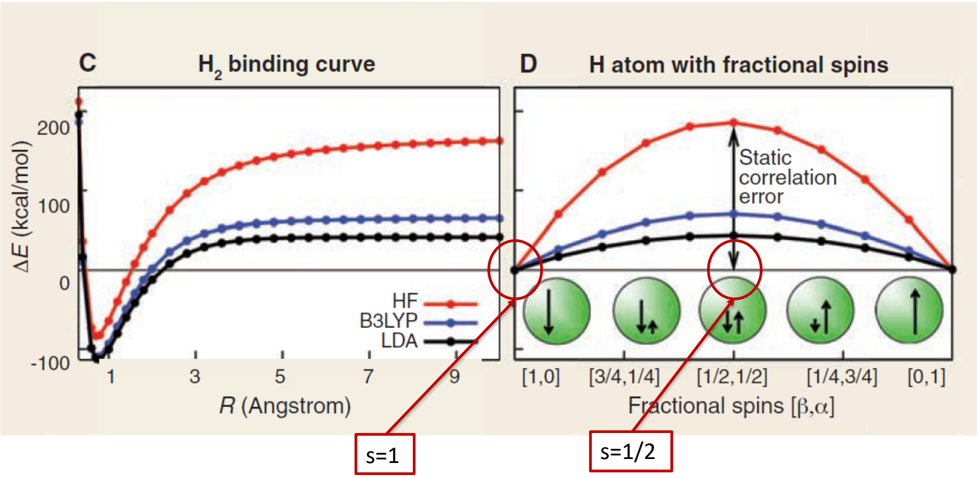
A. J. Cohen, P. Mori-Sánchez, and W. Yang, Science **321**, 792 (2008)



Forbidding spin flip along the AC:

$$\hat{H}_\lambda^{\mathrm{HF}} = \hat{T} + \hat{V}_{\mathrm{ext}} + (1-\lambda)\left(\hat{J}[\phi_s] - s\hat{K}[\phi_s]\right)$$

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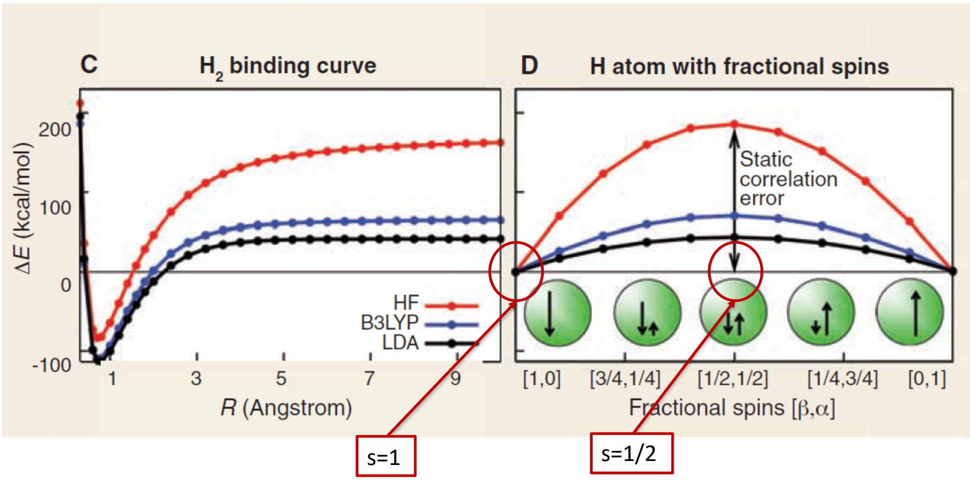

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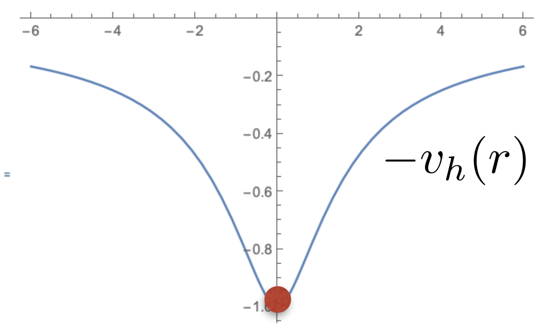

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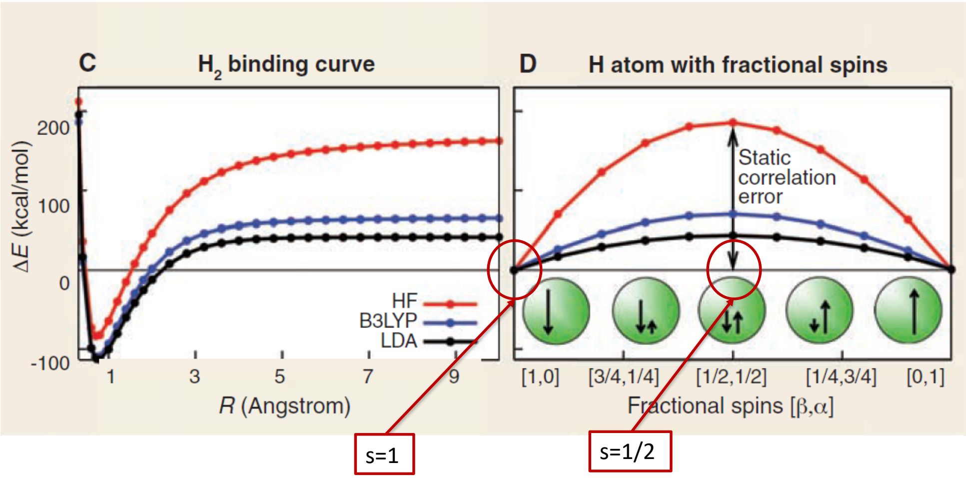

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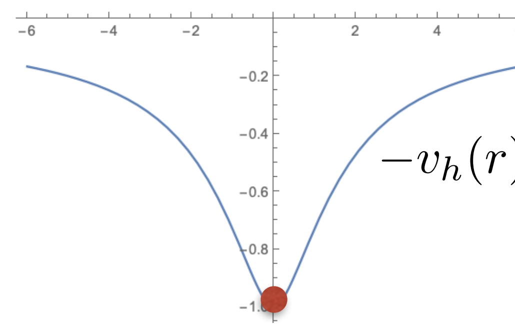

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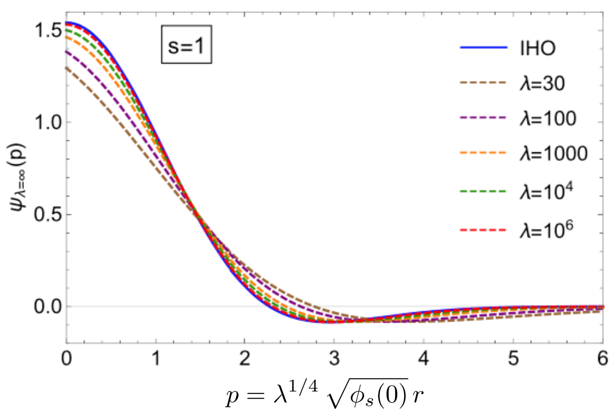

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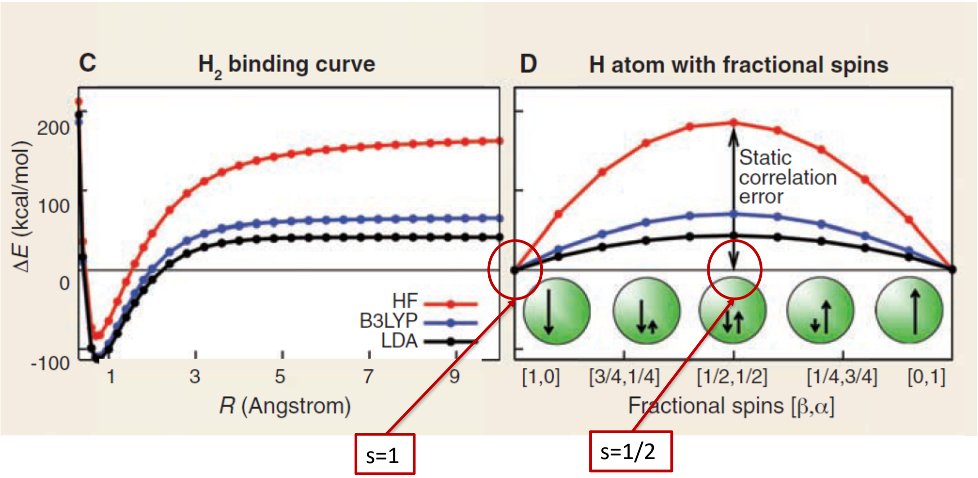
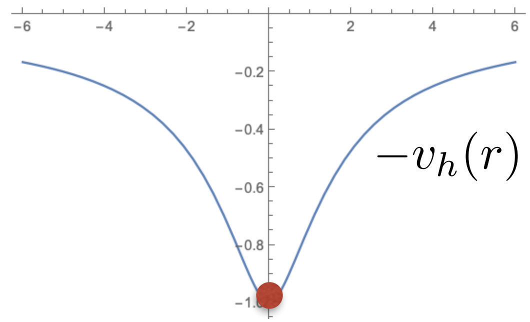


Forbidding spin flip along the AC:

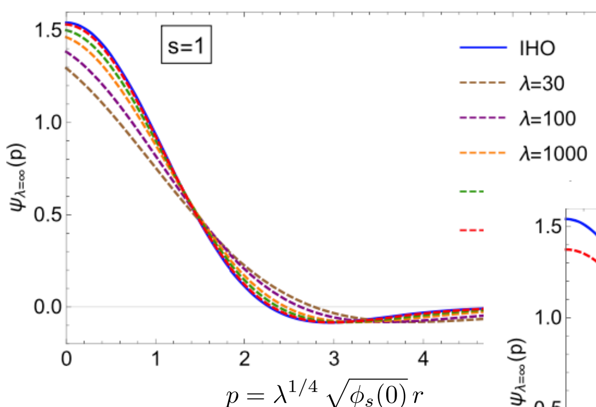
$$\hat{H}_\lambda^{\mathrm{HF}} = \hat{T} + \hat{V}_{\mathrm{ext}} + (1-\lambda)\left(\hat{J}[\phi_s] - s\hat{K}[\phi_s]\right)$$

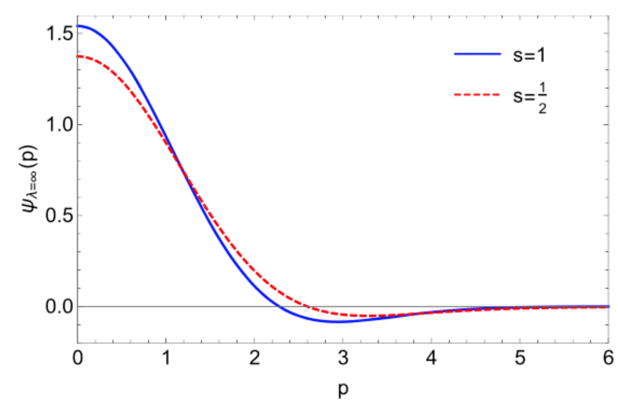
$$\phi_s(\mathbf{r}) = \arg\min_\phi \langle \phi | \hat{T} + \hat{V}_{\mathrm{ext}} + \frac{1}{2}(\hat{J}[\phi] - s\hat{K}[\phi]) | \phi \rangle$$

$$\hat{J} = \int d\mathbf{r}' \frac{|\phi_s(\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|} = v_h(\mathbf{r})$$



$$E_c^{\mathrm{HF}} = \int_0^1 W_{c,\lambda}^{\mathrm{HF}}\, d\lambda$$





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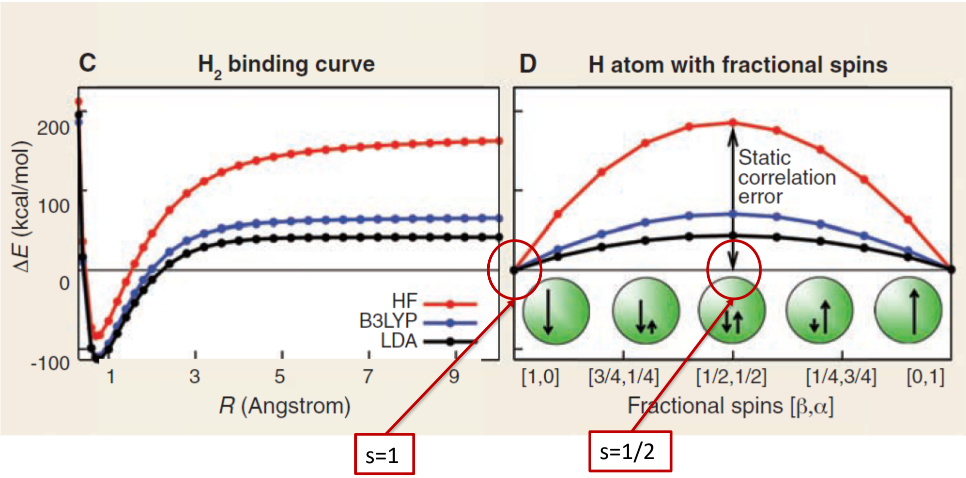

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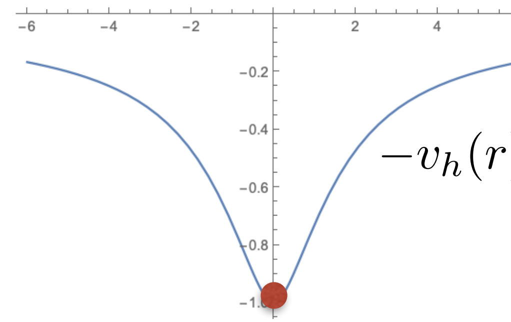


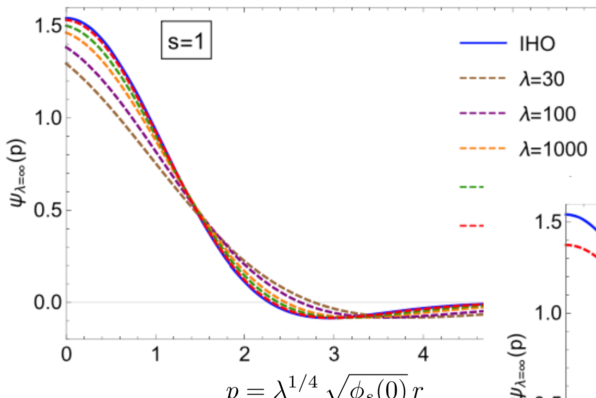
$$E_c^{\mathrm{HF}} = \int_0^1 W_{c,\lambda}^{\mathrm{HF}}\, d\lambda,$$

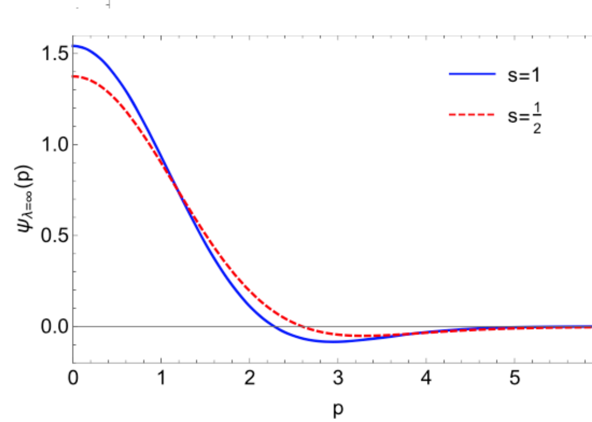
$$W_{c,\lambda\to\infty}^{\mathrm{HF}} = W_{c,\infty}^{\mathrm{HF}} + \frac{W_{\frac{1}{2}}^{\mathrm{HF}}}{\sqrt{\lambda}} + \frac{W_{\frac{3}{4}}^{\mathrm{HF}}}{\lambda^{\frac{3}{4}}} + \cdots,$$

$$W_{c,\infty}^{\mathrm{HF}} = -v_h(0) + (1-s)\,U,$$

$$W_{\frac{1}{2}}^{\mathrm{HF}} = \tilde{\epsilon}_{\frac{1}{2}} \frac{\sqrt{4\pi}}{2} \sqrt{\rho^{\mathrm{HF}}(0)},$$

$$W_{\frac{3}{4}}^{\mathrm{HF}} = Z\,\tilde{\epsilon}_{\frac{1}{4}} \frac{\sqrt[4]{4\pi}}{4} \sqrt[4]{\rho^{\mathrm{HF}}(0)}.$$





General many-electron closed-shell case

$$\Psi_\lambda^h(\mathbf{r}_1,\ldots,\mathbf{r}_N) = \prod_{i=1}^N \mathcal{L}_{i,\lambda}(|\mathbf{r}_i - \mathbf{r}_i^{\min}|),$$

$$\mathcal{L}_{i,\lambda}(r) = \lambda^{\frac{3n}{2}} \mathcal{L}_i(\lambda^n r),$$

$$\int dt\, \mathcal{L}_i^2(t) = 1,$$

$$W_{c,\lambda\to\infty}^{\mathrm{HF}} = W_{c,\infty}^{\mathrm{HF}} + \frac{W_{\frac{1}{2}}^{\mathrm{HF}}}{\sqrt{\lambda}} + \frac{W_{\frac{3}{4}}^{\mathrm{HF}}}{\lambda^{\frac{3}{4}}} + \cdots,$$

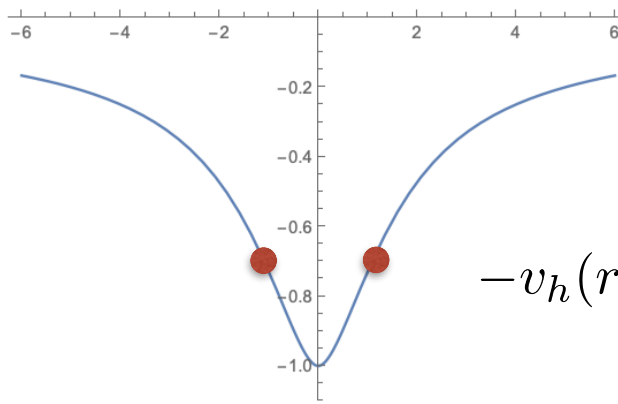
$$W_{c,\infty}^{\mathrm{HF}} = E_{el}[\rho^{\mathrm{HF}}] + E_x,$$

$$W_{\frac{1}{2}}^{\mathrm{HF}} \approx 2.8687 \sum_{i=1}^N \left(\rho^{\mathrm{HF}}(\mathbf{r}_i^{\min})\right)^{1/2},$$

$$W_{\frac{3}{4}}^{\mathrm{HF}} \approx -1.272 \sum_{\mathbf{r}_{Z_k}} Z_k\left(\rho^{\mathrm{HF}}(\mathbf{r}_{Z_k})\right)^{1/4},$$

$$E_{el}[\rho] = \min_{\{\mathbf{r}_1\ldots\mathbf{r}_N\}}\left\{\sum_{\substack{i,j=1\\j>i}}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{i=1}^N v_h(\mathbf{r}_i;[\rho]) + U[\rho]\right\}.$$

Example: 2-electron atom



$-v_h(r)$

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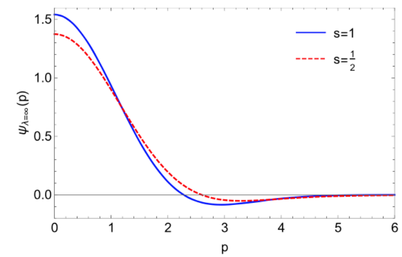

$$W^{\mathrm{HF}}_{c,\lambda\to\infty} = W^{\mathrm{HF}}_{c,\infty} + \frac{W^{\mathrm{HF}}_{\frac{1}{2}}}{\sqrt{\lambda}} + \frac{W^{\mathrm{HF}}_{\frac{3}{4}}}{\lambda^{\frac{3}{4}}} + \cdots,$$

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$$W^{\mathrm{HF}}_{\frac{1}{2}} \approx 2.8687 \sum_{i=1}^{N} \left(\rho^{\mathrm{HF}}(\mathbf{r}_i^{\min})\right)^{1/2},$$

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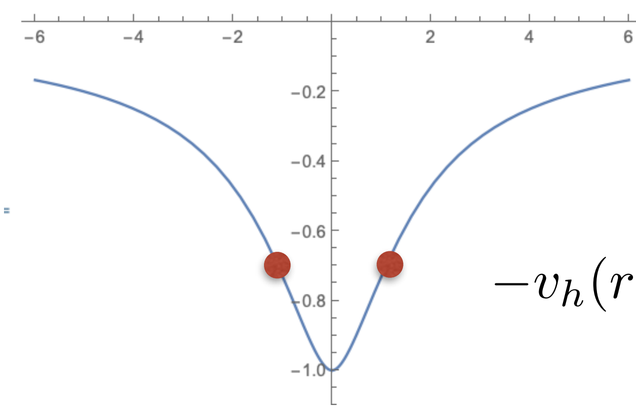

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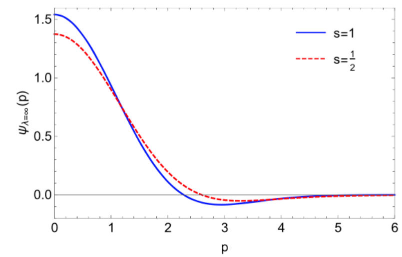

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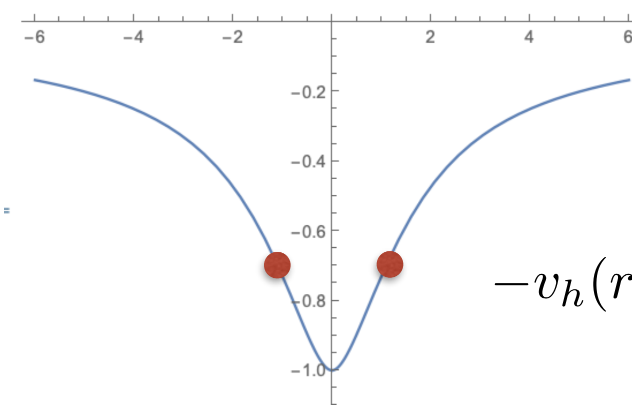

$-v_h(r)$

Large coupling-strength expansion of the Møller–Plesset adiabatic connection: From paradigmatic cases to variational expressions for the leading terms

Cite as: J. Chem. Phys. 153, 214112 (2020); doi: 10.1063/5.0029084
Submitted: 9 September 2020 • Accepted: 11 November 2020 •
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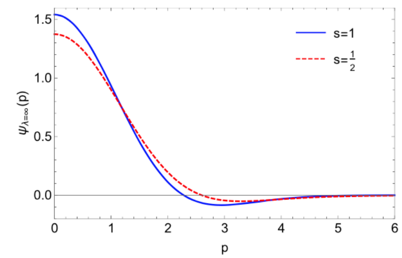

$$W^{\rm HF}_{c,\lambda\to\infty}=W^{\rm HF}_{c,\infty}+\frac{W^{\rm HF}_{\frac{1}{2}}}{\sqrt{\lambda}}+\frac{W^{\rm HF}_{\frac{3}{4}}}{\lambda^{\frac{3}{4}}}+\cdots,$$

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construction of GGA's

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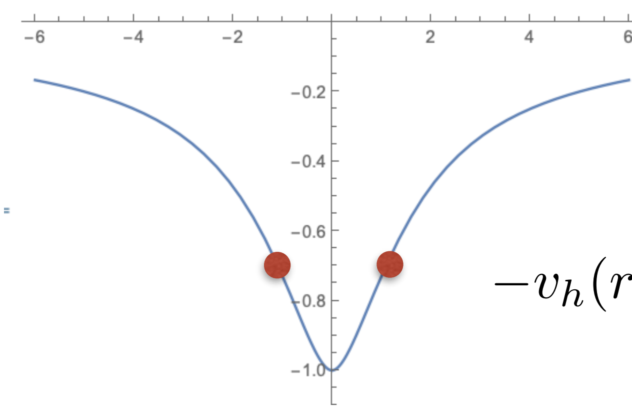

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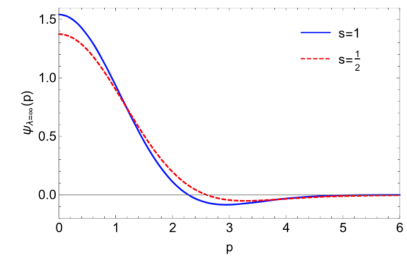

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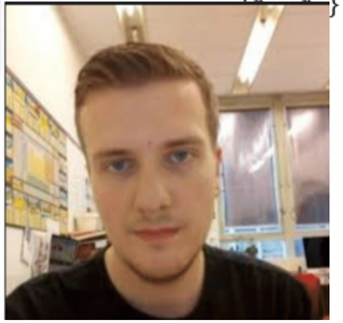

Talk by Tim Daas

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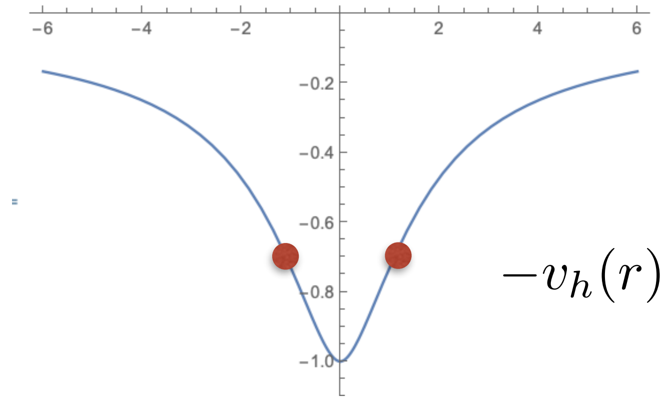

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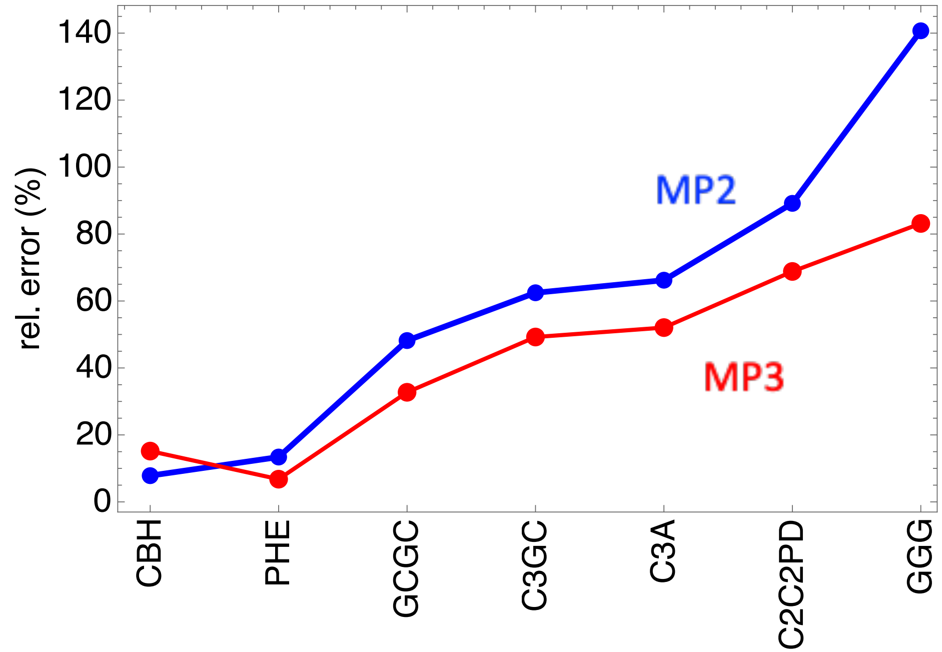
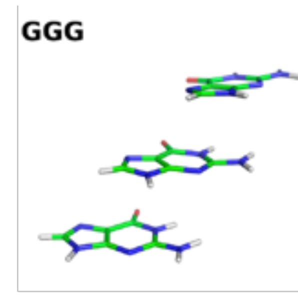
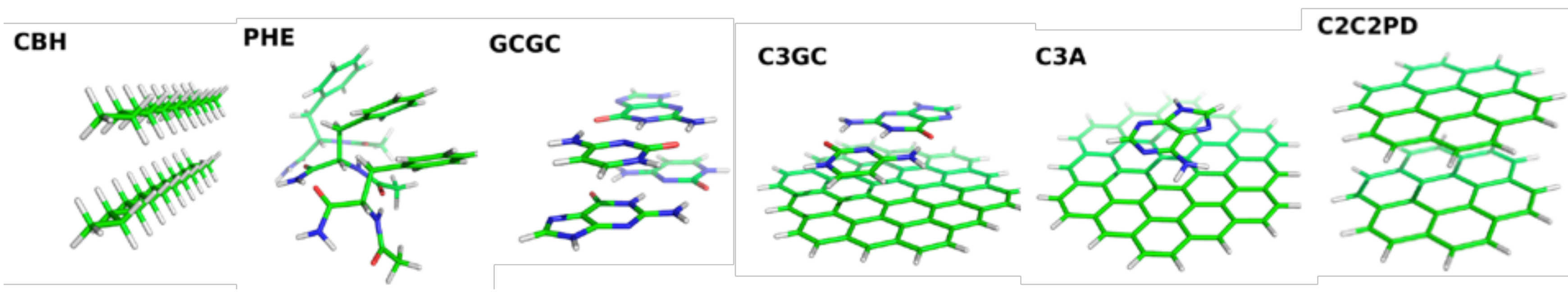
MP2 failure for large molecules – L7 dataset







Divergence of Many-Body Perturbation Theory for Noncovalent Interactions of Large Molecules

Brian D. Nguyen, Guo P. Chen, Matthew M. Agee, Asbjörn M. Burow, Matthew P. Tang, and Filipp Furche*

Cite This: *J. Chem. Theory Comput.* 2020, 16, 2258–2273 **Read Online**

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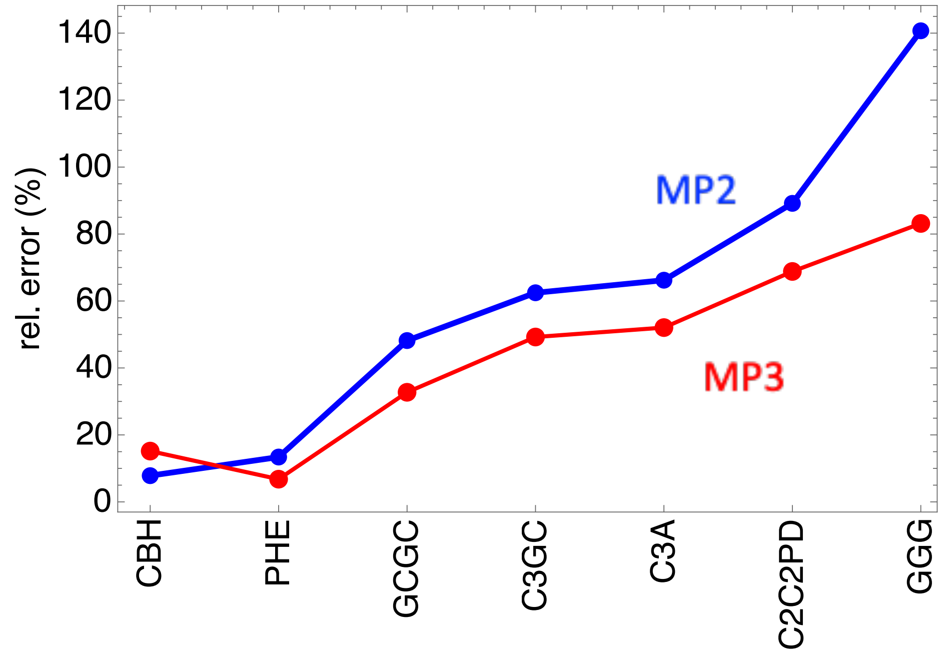
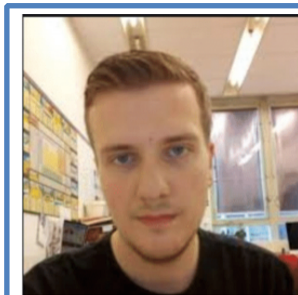
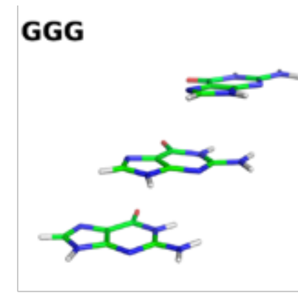
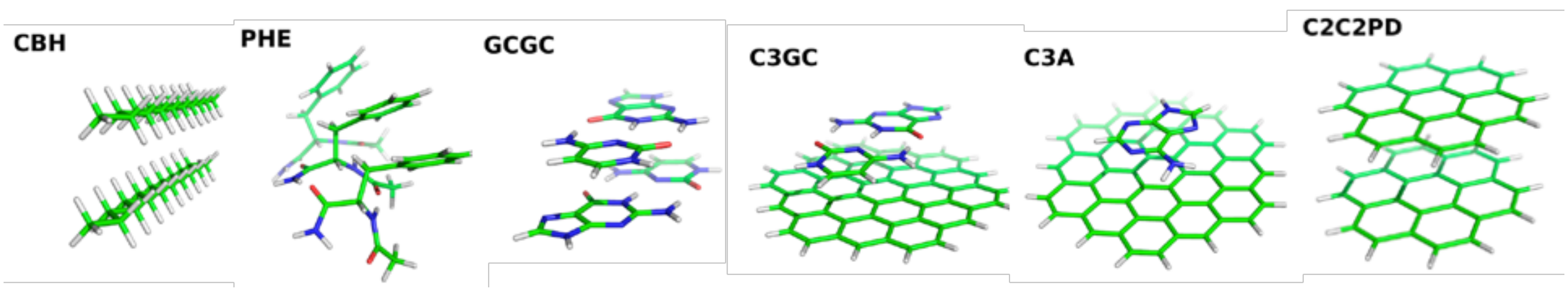




Talk by Tim Daas: correct MP2 errors with interpolations between small and large coupling strengths





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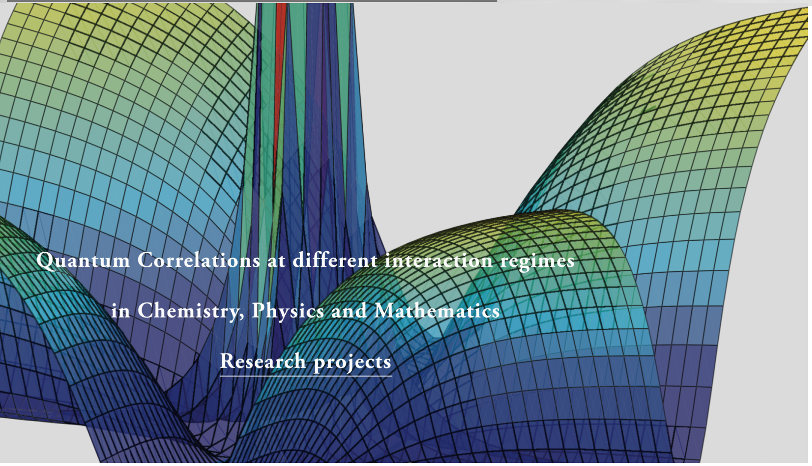


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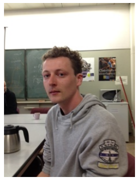
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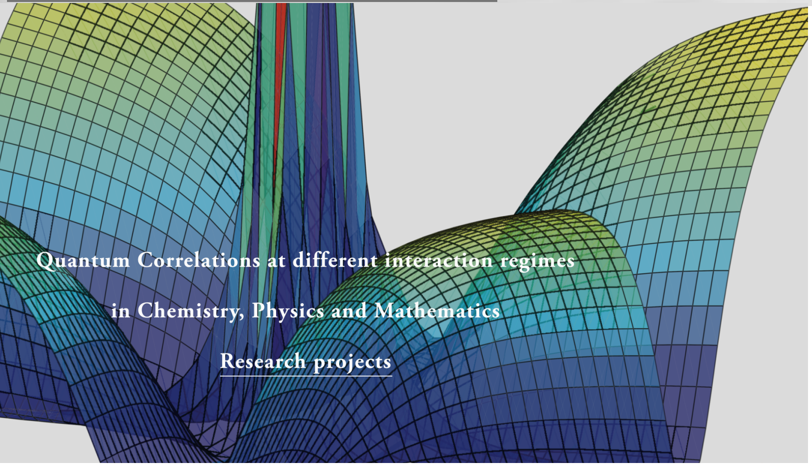


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Thank you for your attention!


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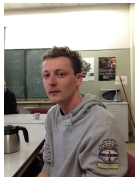
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