Functional derivative of the Zero Point Energy functional from the strong Coupling limit of Density Functional Theory

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Why?

$$F_\lambda[\rho] \equiv \min_{\Psi\to\rho}\langle\Psi_\lambda|\hat{T}+\lambda\hat{V}_e|\Psi_\lambda\rangle$$

$$E_\lambda[\rho] = \min_{\tilde{\rho}}\left(F_\lambda[\tilde{\rho}] + \int \mathrm{d}\mathbf{r}\,\tilde{\rho}(\mathbf{r})v^\lambda[\rho](\mathbf{r})\right)$$

$$\frac{\delta F_\lambda[\tilde{\rho}]}{\delta\tilde{\rho}(\mathbf{r})}|_{\tilde{\rho}=\rho} = -v^\lambda[\rho](\mathbf{r})$$

$$F^{\mathrm{ZPE}}[\rho] = 2W'_\infty[\rho]$$

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

Why?

$$F_\lambda[\rho] \sim \lambda V_{ee}^{\mathrm{SCE}}[\rho] + \sqrt{\lambda} F^{\mathrm{ZPE}}[\rho]$$

Features of the XC- potential in the KS equation

$$E_{\mathrm{xc}}[\rho] \sim E_{\mathrm{xc}}^{\mathrm{ZPE}}[\rho] = V_{ee}^{\mathrm{SCE}}[\rho] - U_H[\rho] + F^{\mathrm{ZPE}}[\rho]$$

$$v_{\mathrm{xc}}[\rho](\mathbf{r}) \sim -v^{\mathrm{SCE}}(\mathbf{r}) - v_{\mathrm{H}}(\mathbf{r}) + \frac{\delta F^{\mathrm{ZPE}}[\rho]}{\delta \rho(x)}$$

Third term in the large λ expansion

$$\frac{\delta F_\lambda[\tilde{\rho}]}{\delta \tilde{\rho}(\mathbf{r})}\Big|_{\tilde{\rho}=\rho} = -v^\lambda[\rho](\mathbf{r})$$

$$v^\lambda[\rho](\mathbf{r}) \sim \lambda v^{\mathrm{SCE}}[\rho](\mathbf{r}) + \sqrt{\lambda}\, \underbrace{v^{ZPE}[\rho](\mathbf{r})}_{???}$$

$$\hat{H}_\lambda \sim \hat{H}^{\mathrm{ZPE}} + \lambda^{-1/4}\Big(-\frac{1}{2}\sum_{D+1}^{DN} \Delta_\mu(\mathbf{s}) \frac{\partial}{\partial u_\mu} + \sum_{\sigma=1}^{DN} V_\sigma{}^{\mathrm{ZPE}}(\mathbf{s}) \sum_{\mu=D+1}^{3N} e_\sigma^\mu(\mathbf{s}) u_\mu + \frac{1}{3!}\sum_{\mu,\nu,\sigma=D+1}^{DN} E^{(3)}_{\mu\nu\sigma}(\mathbf{s}) u_\mu u_\nu u_\sigma + \text{const.}\Big)$$

Outline

- ZPE overview
- Functional derivative of the ZPE functional
- Kinetic peaks in the xc correlation potential: the case of a 1D dimer
- Wrap up and conclusions

ZPE overview

Disclaimer: N=2, D=1!

$$F_{\lambda}[\rho] \sim \lambda V_{ee}^{\mathrm{SCE}} + \sqrt{\lambda} F^{\mathrm{ZPE}}[\rho]$$

$$v_{ee}(x) = \frac{1}{1+|x|}$$

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

$$\hat{H}_{\lambda}[\rho] \sim \lambda \hat{H}^{\mathrm{SCE}} + \sqrt{\lambda} \hat{H}^{\mathrm{ZPE}}$$

$$E_{pot}(x_1, x_2) = v_{ee}(x_1 - x_2) + v^{\mathrm{SCE}}(x_1) + v^{\mathrm{SCE}}(x_2)$$

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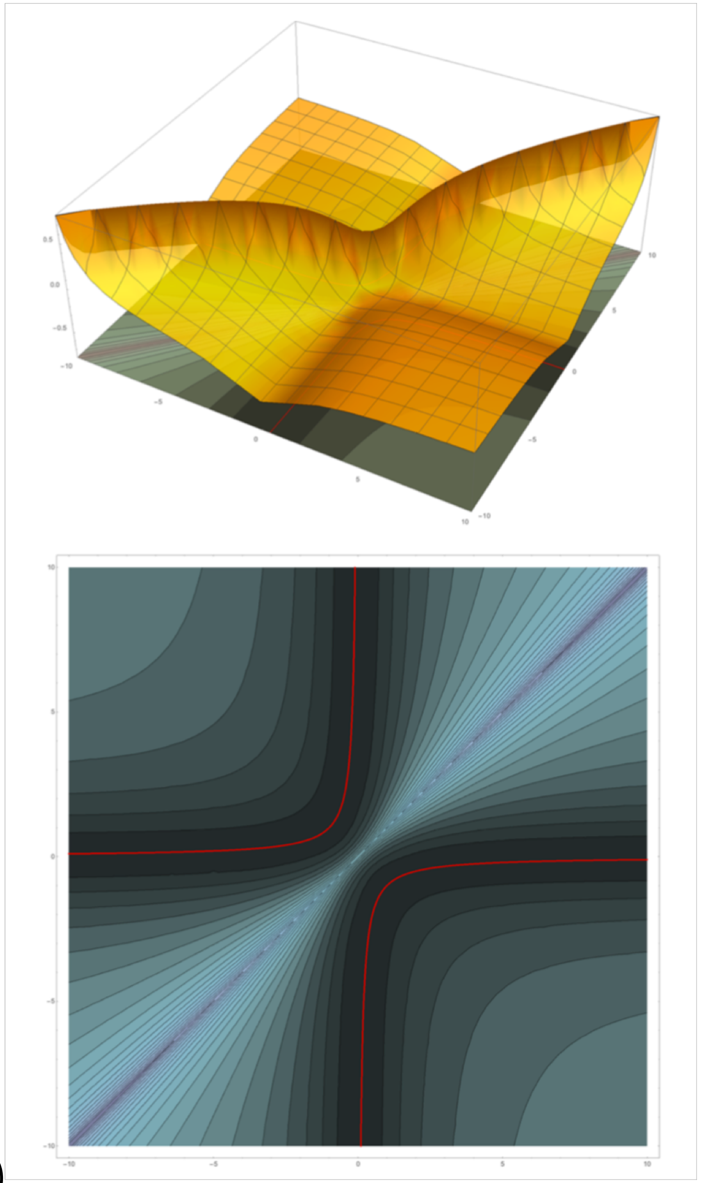

J. Grossi, D. P. Kooi, K. J. H. Giesbertz, M. Seidl, A. J. Cohen, P. Mori-Sánchez, and P. Gori-Giorgi, J. Chem. Theory Comput. **13**, 6089 (2017).

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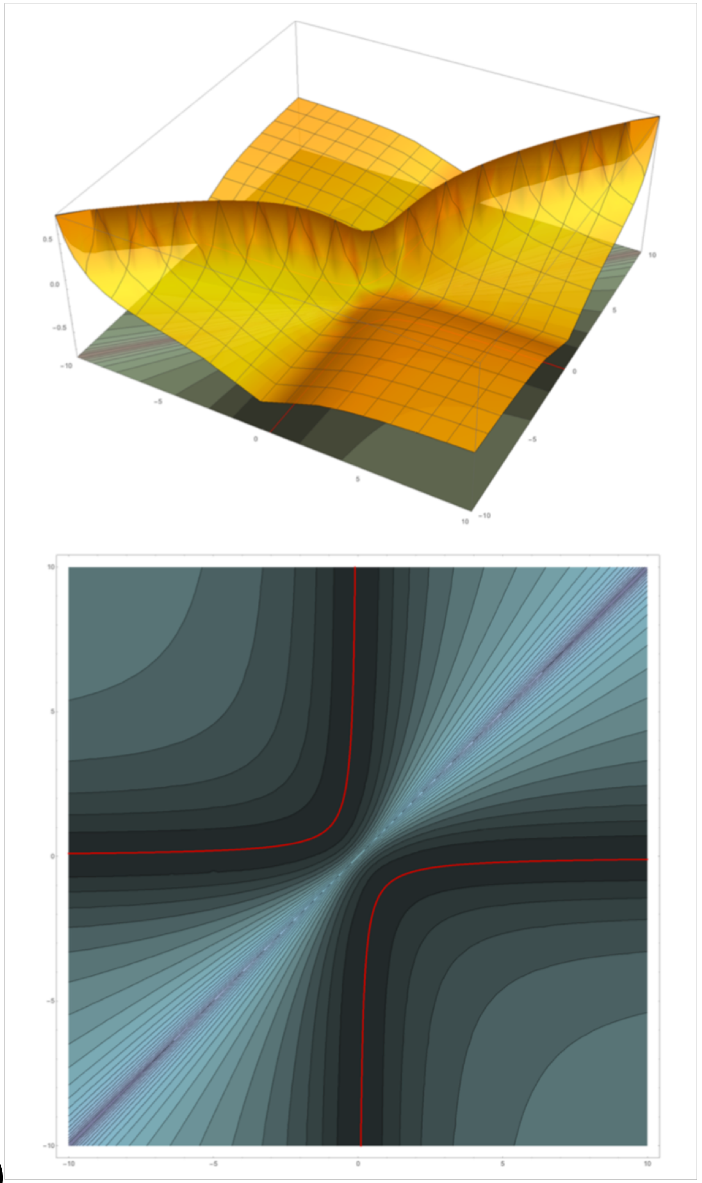

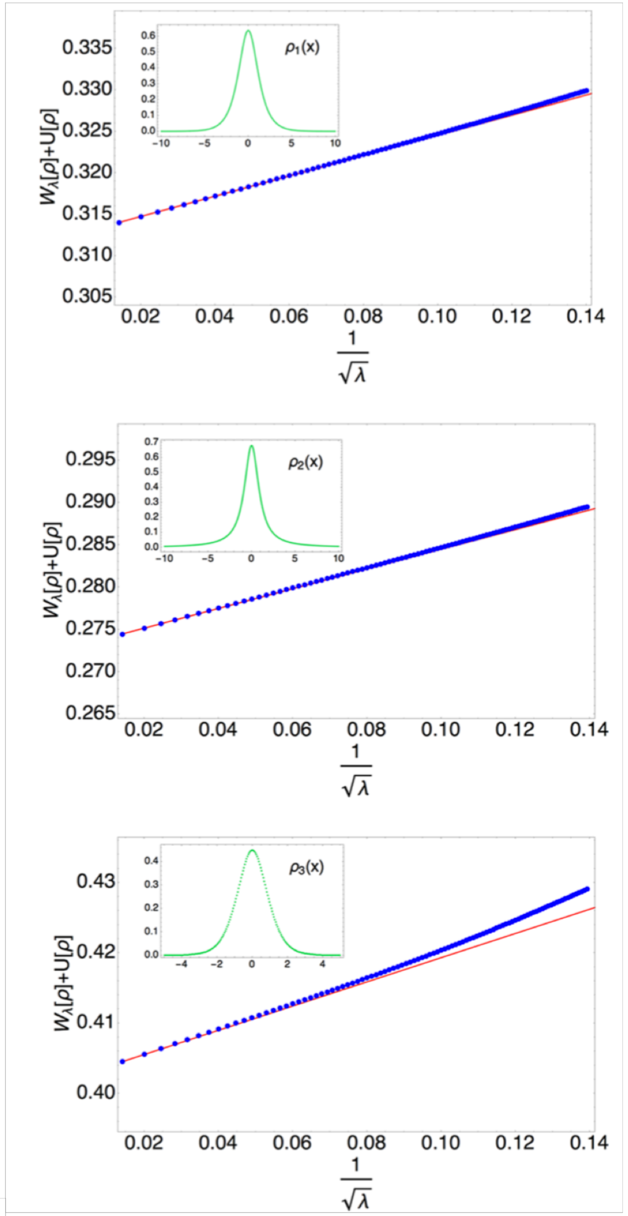

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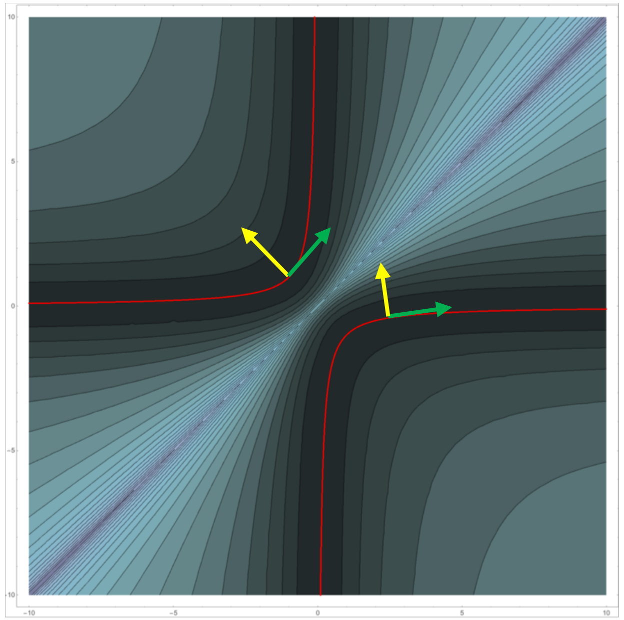
ZPE overview

$$\hat{H}_{\lambda}[\rho] \sim \lambda \hat{H}^{\text{SCE}} + \sqrt{\lambda}\hat{H}^{\text{ZPE}}$$



$$\sqrt{\lambda}\left(-\frac{1}{2}\frac{\partial^2}{\partial u^2} + \frac{1}{2}\omega(s)u^2 + v^{\text{ZPE}}(s) + v^{\text{ZPE}}(f(s))\right)\Psi_{\lambda}(s,u) = \sqrt{\lambda}E^{\text{ZPE}}\Psi_{\lambda}(s,u)$$

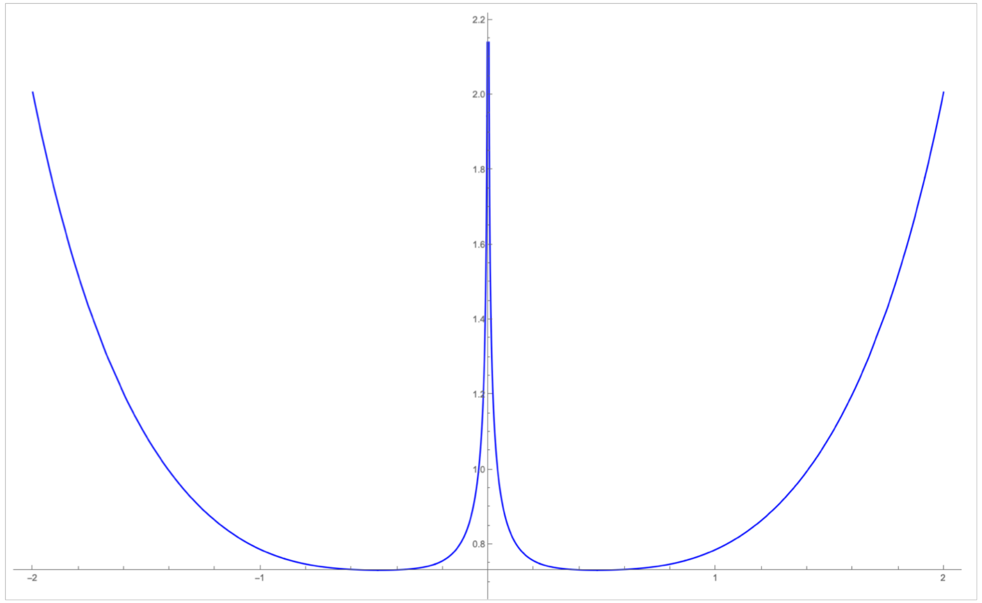
$$v^{\text{ZPE}}(s) + v^{\text{ZPE}}(f(s)) = -\frac{\omega(s)}{2}$$

P. Gori-Giorgi, G. Vignale, and M. Seidl, J. Chem. Theory Comput. **5**, 743 (2009).

ZPE overview

$$F^{\mathrm{ZPE}}[\rho] = \frac{1}{4}\int \mathrm{d}s\,\rho(s)\omega(s)$$

$$\omega(s) = \sqrt{v''_{ee}(|s - f(s)|)\left(\frac{\rho(s)}{\rho(f(s))} + \frac{\rho(f(s))}{\rho(s)}\right)}$$

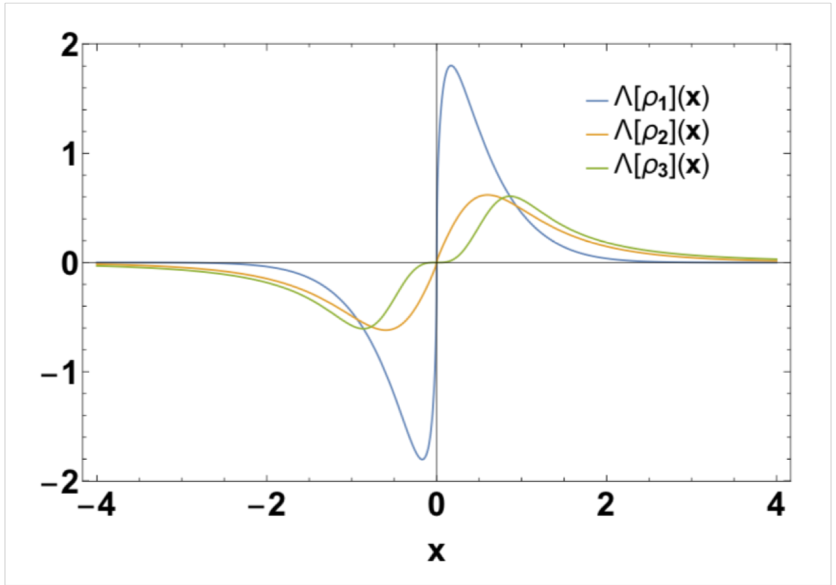


$$\frac{\delta f([\rho];x)}{\delta\rho(x')} = (\theta(x-x') - \theta(f([\rho];x)-x'))\left(\frac{1}{\rho(f([\rho];x))} + \frac{f([\rho];0^+) - f([\rho];0^-)}{\rho(0)}\delta(x)\right)$$

G. Lani, S. Di Marino, A. Gerolin, R. van Leeuwen, and P. Gori-Giorgi, Phys. Chem. Chem. Phys. **18**, 21092 (2016).

Functional derivative of the ZPE functional

$$\frac{\delta F^{\mathrm{ZPE}}[\rho]}{\delta\rho(x)} = \frac{\omega(x)}{4} + \frac{1}{4}\int_x^{f(x)} \mathrm{d}y\Lambda(y)$$



$$\Lambda(y) = \frac{v_{ee}'''(f(y)-y)}{\omega(y)} + \frac{v_{ee}''(f(y)-y)\rho'(f(y))(3f'(y^2)+1)}{\omega(y)\rho(f(y))(f'(y)^2+1)}$$

$$\omega(s) = \sqrt{v_{ee}''(|s-f(s)|)\left(\frac{\rho(s)}{\rho(f(s))} + \frac{\rho(f(s))}{\rho(s)}\right)}$$

Functional derivative of the ZPE functional

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$$\frac{\delta F_\lambda[\tilde{\rho}]}{\delta \tilde{\rho}(\mathbf{r})}\Big|_{\tilde{\rho}=\rho} = -v^\lambda[\rho](\mathbf{r})$$

$$v^\lambda[\rho](\mathbf{r}) \sim \lambda v^{\mathrm{SCE}}[\rho](\mathbf{r}) + \sqrt{\lambda}\underbrace{v^{ZPE}[\rho](\mathbf{r})}_{???}$$

$$\Lambda(y) = \frac{v'''_{ee}(f(y)-y)}{\omega(y)} + \frac{v''_{ee}(f(y)-y)\rho'(f(y))(3f'(y^2)+1)}{\omega(y)\rho(f(y))(f'(y)^2+1)}$$

$$v^{\mathrm{ZPE}}(s) + v^{\mathrm{ZPE}}(f(s)) = -\frac{\omega(s)}{2}$$

$$f(x) = f^{-1}(x)$$

$$\omega(s) = \sqrt{v''_{ee}(|s-f(s)|)\left(\frac{\rho(s)}{\rho(f(s))} + \frac{\rho(f(s))}{\rho(s)}\right)}$$

Functional derivative of the ZPE functional

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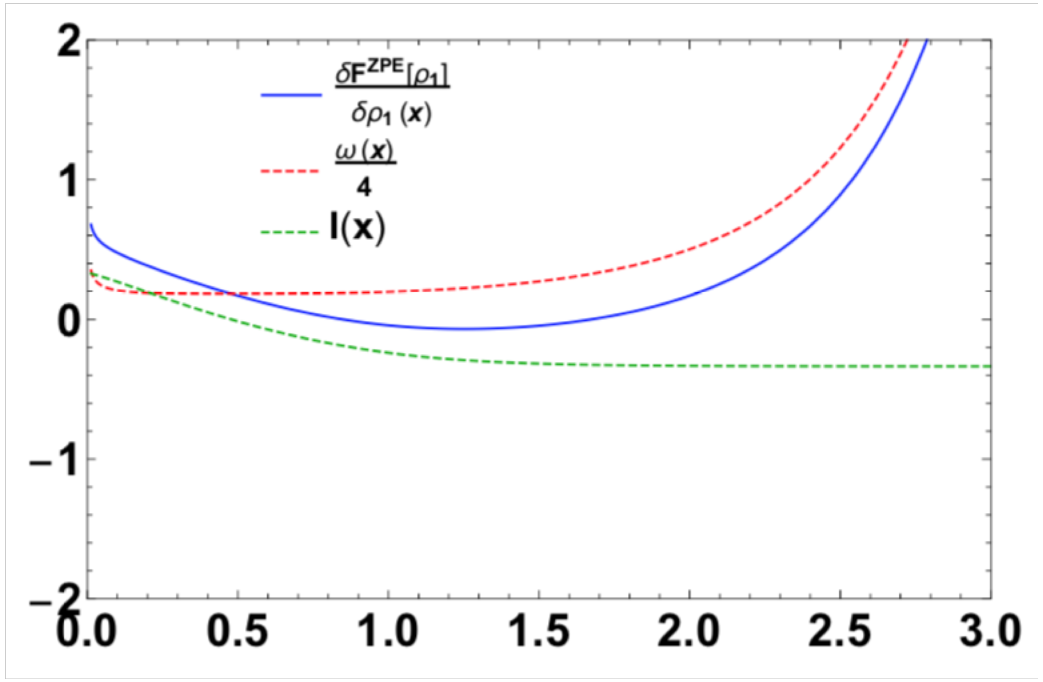

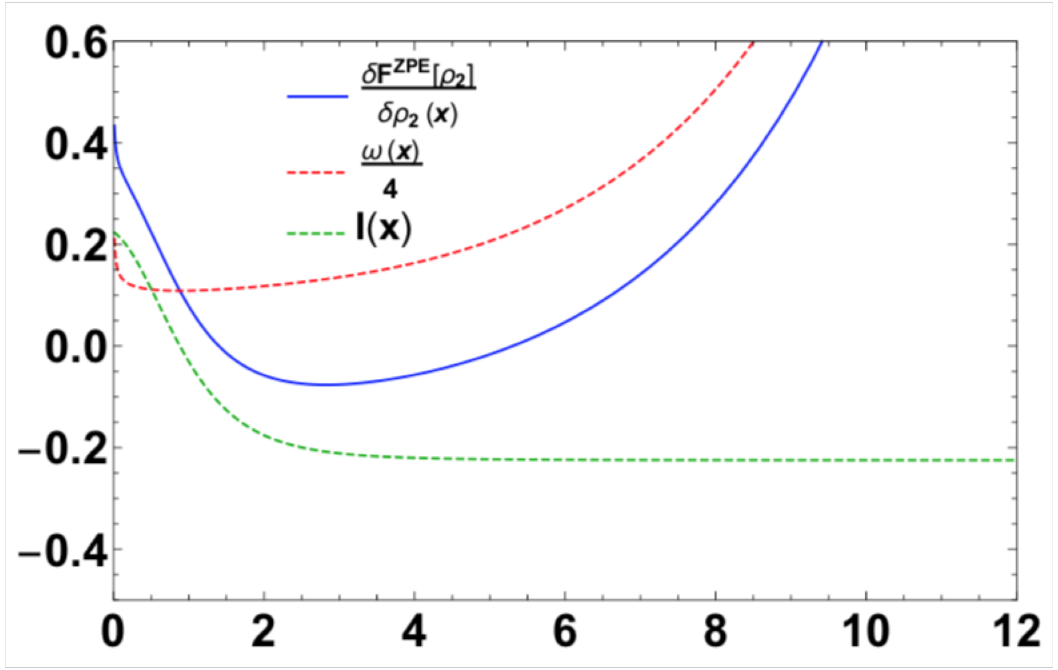

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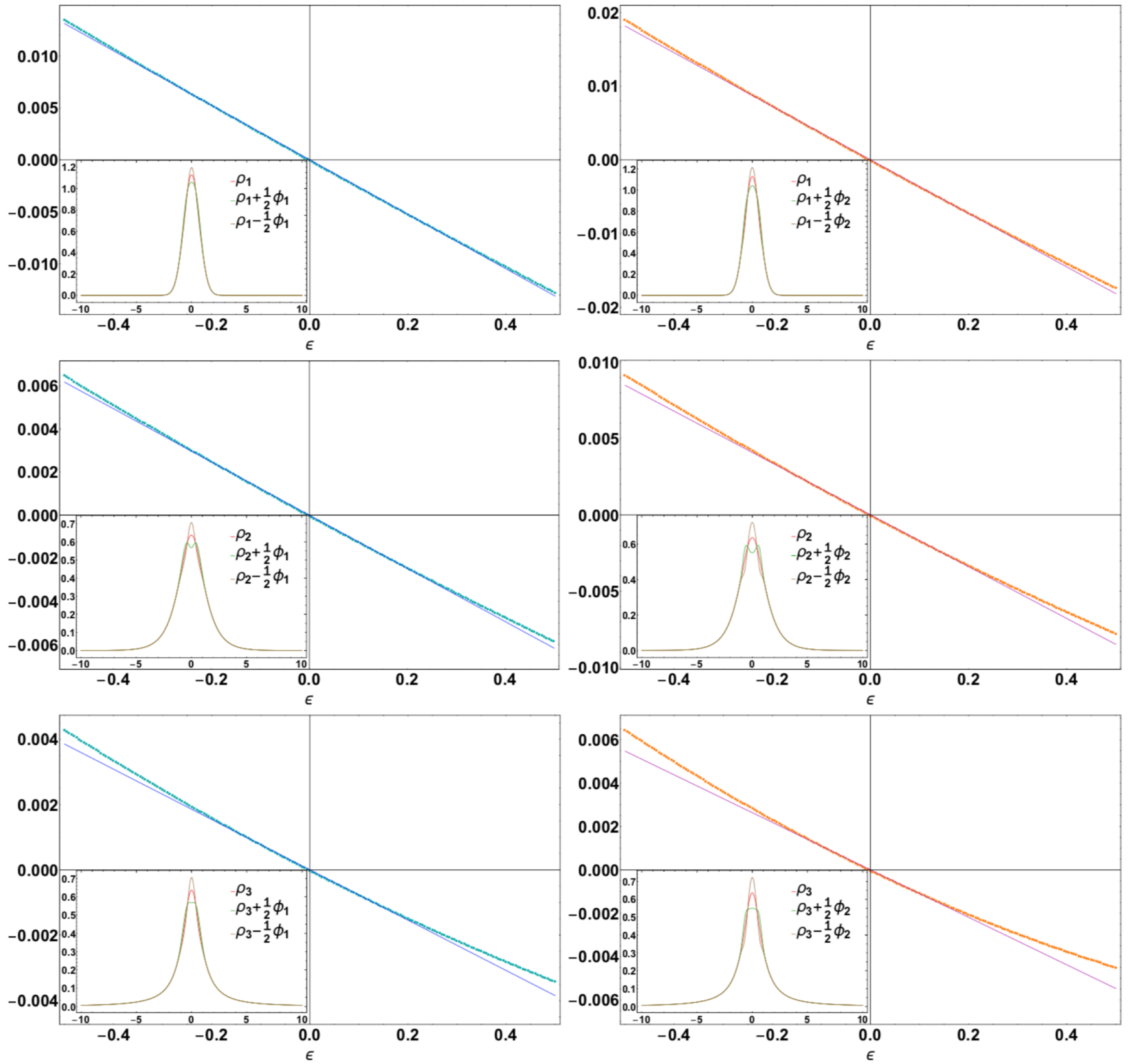
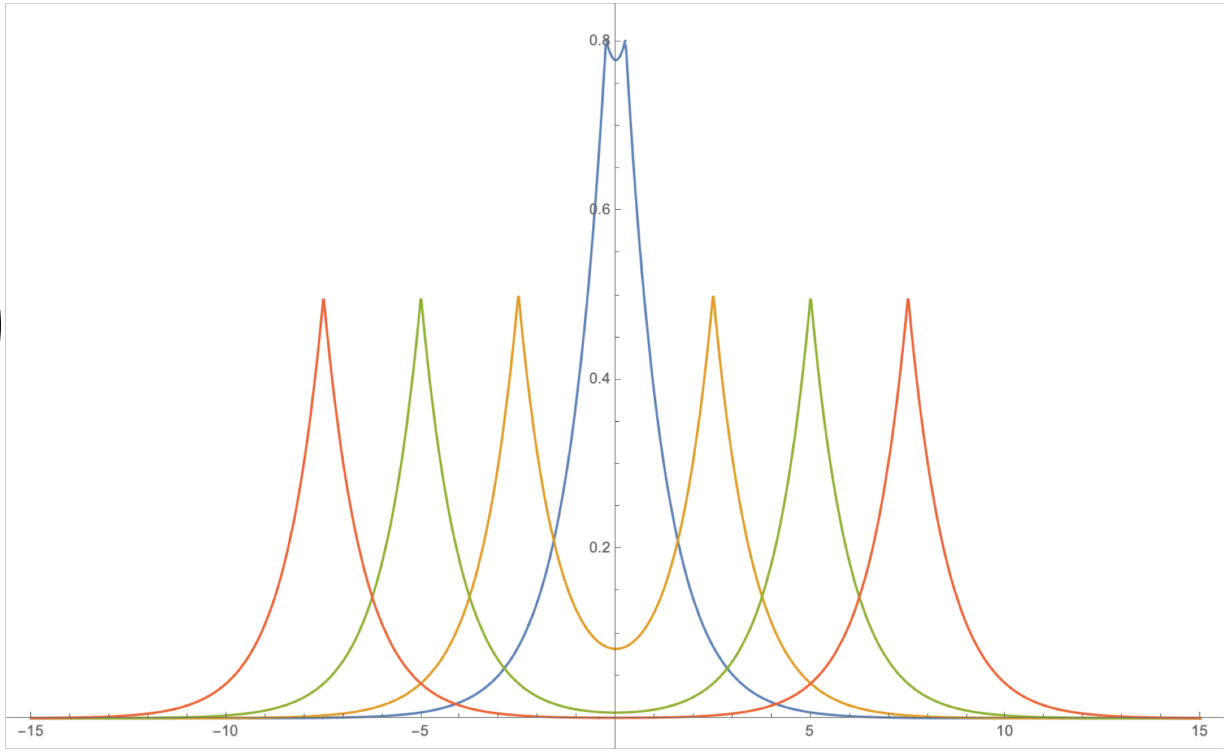
$$F^{\rm ZPE}[\rho+\epsilon\phi]-F^{\rm ZPE}[\rho]\sim\epsilon\int \mathrm{d}x\,\frac{\delta F^{\rm ZPE}[\rho]}{\delta\rho(x)}\phi(x)\qquad \epsilon\ll 1.$$



Kinetic peaks in the xc correlation potential: the case of a 1D dimer

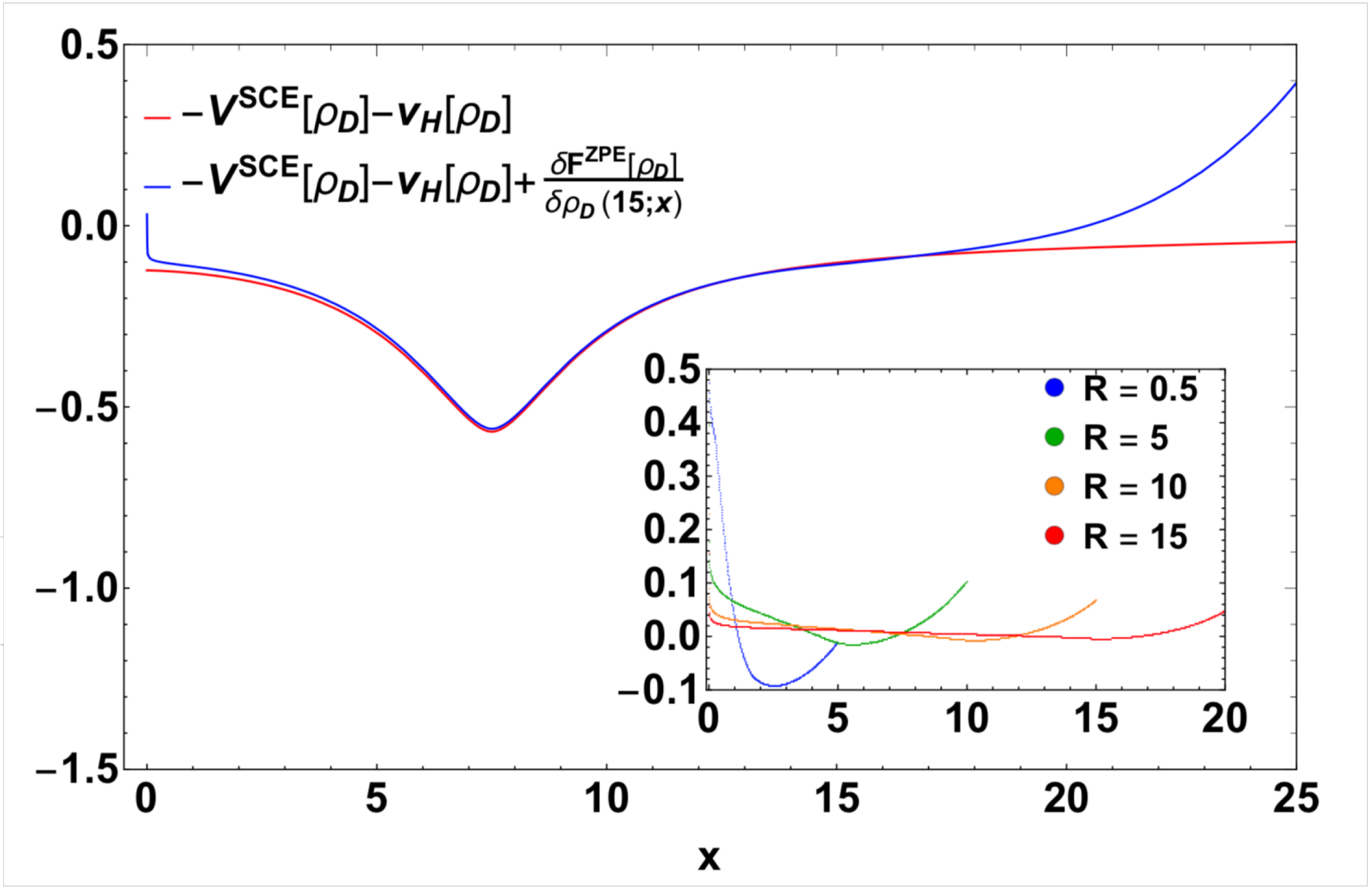
$$\rho_D(R;x) = \frac{1}{2}\left(e^{-|x-\frac{R}{2}|} + e^{-|x+\frac{R}{2}|}\right)$$



Kinetic peaks in the xc correlation potential: the case of a 1D dimer

$$v_{\rm xc}[\rho](\mathbf{r}) \sim -v^{\rm SCE}(\mathbf{r}) - v_{\rm H}(\mathbf{r}) + \frac{\delta F^{\rm ZPE}[\rho]}{\delta\rho(x)}$$

$$\frac{\delta F^{\rm ZPE}[\rho_D]}{\delta\rho_D(R;x)} \sim \frac{(8x)^{-1/2}}{(1+|R+\log(1+{\rm e}^{-R})-\log(2x)|)^{3/2}}.$$



Wrap up…and Conclusions

- $v^{\lambda}[\rho](x) \in L^{3/2} + L^{\infty}$???
- Competition between the decay of the density and the interaction
- Provides a (infinite) kinetic peak in the midbond region

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Acknowledgements

Michael Seidl

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…Questions!

$$v_{ee}(x) = \frac{1}{1+|x|}$$

$$v_{ee}^{\mathrm{Yuk}}(x) = \frac{\mathrm{e}^{-\alpha|x|}}{1+|x|}$$

$$v_{ee}^{\exp}(x) = A\mathrm{e}^{-\kappa|x|}$$