Harmonium: a model to study approximations in TDDFT

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Model systems in quantum mechanics 2024

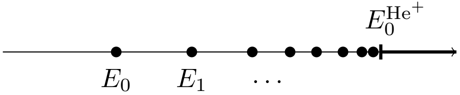
Harmonium/Hooke's atom

Nonrelatisvistic Helium atom

$$\mathcal{H}_{\mathrm{He}} = -\frac{1}{2}\Delta_{r_1} - \frac{1}{2}\Delta_{r_2} - \frac{Z}{|r_1|} - \frac{Z}{|r_2|} + \frac{1}{|r_1 - r_2|},$$

acting on $L^2(\mathbb{R}^3 \times \{\uparrow,\downarrow\}) \bigwedge L^2(\mathbb{R}^3 \times \{\uparrow,\downarrow\})$ with domain $H^2((\mathbb{R}^3 \times \{\uparrow,\downarrow\})^2)$ $(Z = 2)$.

Drawback ground-state not explicitly known



Spectrum of $\mathcal{H}_{\mathrm{He}}$

Harmonium or Hooke's atom

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Properties

- for some values of k, the ground-state is explicit
- $\mathcal{H}_{\mathrm{harm}}$ has only a discrete spectrum with eigenvalues $E_k \to \infty$ (potential tends to ∞)

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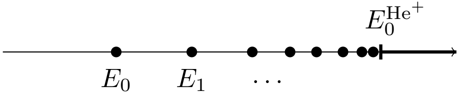

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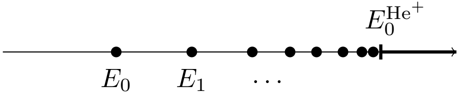

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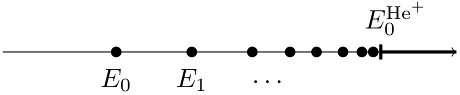

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Calculation of the ground-state

Change of variables $R = \frac{1}{2}(r_1 + r_2)$ and $u = r_2 - r_1$

- separation of variables: $\mathcal{H}_{\text{harm}} = \mathcal{H}_{\text{c}}(u) + \mathcal{H}_{\text{ho}}(R)$ with $\begin{cases} \mathcal{H}_{\text{ho}}(R) = -\frac{1}{4}\Delta_R + k|R|^2, \\ \mathcal{H}_{\text{c}}(u) = -\Delta + \frac{k}{4}|u|^2 + \frac{1}{|u|}. \end{cases}$
- eigenfunctions: $\Psi(r_1, r_2) = \chi(\frac{r_1+r_2}{2})\Phi(r_2 - r_1)$ with $\mathcal{H}_{\text{ho}}\chi = E_{\text{ho}}\chi$ and $\mathcal{H}_{\text{c}}\Phi = E_{\text{c}}\Phi$
- eigenvalues $E = E_{\text{ho}} + E_{\text{c}}$.

Calculation of Φ

- $\frac{k}{4}|u|^2 + \frac{1}{|u|}$ is a central potential so $\Phi(u) = R_\ell(|u|)Y_{\ell m}(\hat{u})$
- look for $R_\ell(u) = \sum_{j=0}^{\infty} a_j u^j \exp(-\frac{\sqrt{k}}{4}u^2)$
- for $k = \frac{1}{4}$, $\sum_{j=0}^{\infty} a_j u^j = 1 + \frac{u}{2}$

Ground-state of the Harmonium ($k = \frac{1}{4}$)

$$\Psi(r_1, r_2) = \frac{1}{2\sqrt{8\pi^{5/2} + 5\pi^3}}\Big(1 + \frac{1}{2}|r_1 - r_2|\Big)\exp\Big(-\frac{|r_1|^2 + |r_2|^2}{4}\Big).$$

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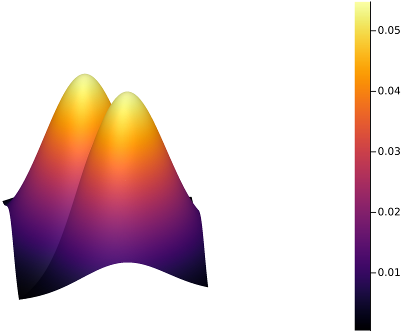
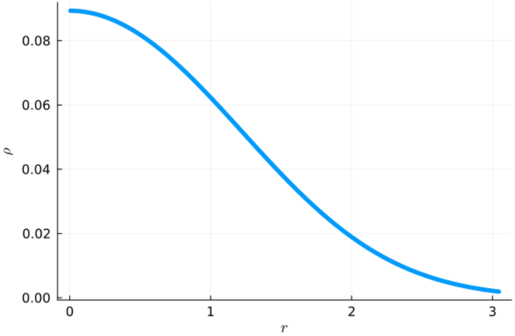
Plots of the ground-state and the electronic density



(a) Wave function $\Psi(r_1, r_2)$



(b) Electronic density ρ

Remarks

- electron-electron cusp in the Harmonium wave function
- no nucleus-electron cusp in the wave function or the electronic density

Linear response TDDFT

LR TDDFT "theorem"

There is an xc-kernel f_{xc} such that the many-body one-body linear response function χ is given by

$$\widehat{\chi}(\omega) = \widehat{\chi_0}(\omega) + \widehat{\chi_0}(\omega)\widehat{f_{\mathrm{xc}}}(\omega)\widehat{\chi}(\omega),$$

where χ_0 is the linear response function of the noninteracting Kohn-Sham Hamiltonian.

Tests on a one-dimensional Harmonium

$$\mathcal{H} = -\frac{1}{2}\frac{\partial^2}{\partial x^2} - \frac{1}{2}\frac{\partial^2}{\partial y^2} + \frac{1}{2}k(x^2+y^2) - |x-y|,$$

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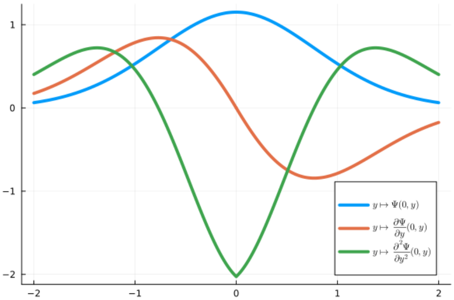
Properties

- spectrum of $\mathcal{H}$ is only discrete
- all the eigenfunctions are explicit (via the Whittaker function U)
- electron-electron cusp in the 2nd derivative



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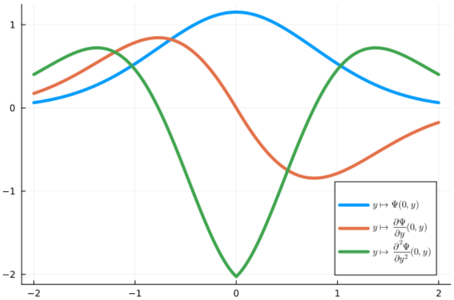

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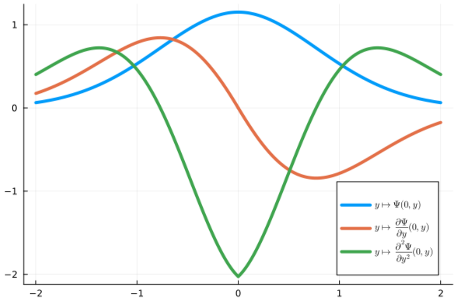

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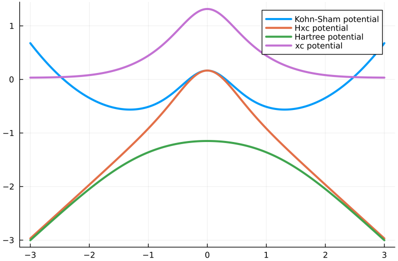
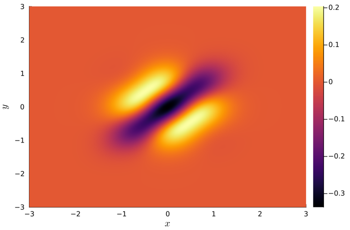
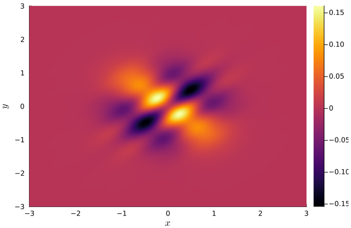


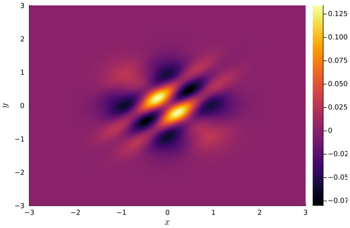
Kohn-Sham and other potentials



Exact linear response function $\widehat{\chi}(x, y; 0)$



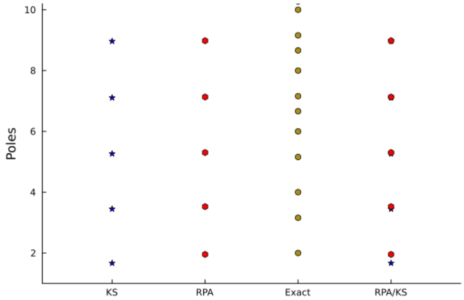
Difference $\widehat{\chi}(x, y; 0) - \widehat{\chi_0}(x, y; 0)$



Difference $\widehat{\chi}(x, y; 0) - \widehat{\chi}^{\mathrm{RPA}}(x, y; 0)$

Poles of the linear response function $\widehat{\chi}$ == excited energies $E_k - E_0$ $(k \geq 1)$

- **TDDFT Dyson equation**: correction to the KS eigenvalues



Poles of the Kohn-Sham LRF $\widehat{\chi_0}$, the RPA LRF $\widehat{\chi}^{\mathrm{RPA}}$ and the exact LRF $\widehat{\chi}$

Observations

- many more poles in the exact than RPA/KS linear response functions (failure of adiabatic xc kernels)
- RPA poles smaller than KS poles (positivity of the xc kernel)

Reference for RPA pole shifting

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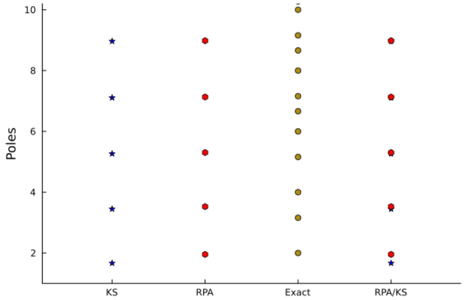

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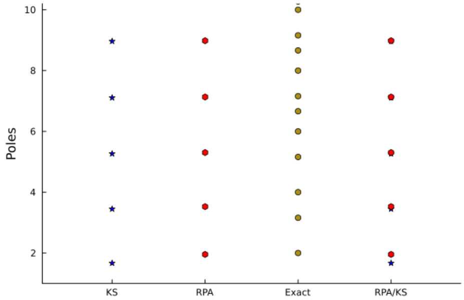

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