Improving exchange-correlation potentials of standard density-functionals with the optimized-effective potential method for higher accuracy of excitation energies

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Overview

1. **Optimized effective potential method and Kohn-Sham inversion**
   - Basic equations
   - Exact conditions, preprocessing of basis sets
   - Self-consistent random phase approximation, σ-functionals
   - Quality of electron densities

2. **Improving exchange-correlation potentials of standard KS methods**
   - OEP for semilocal and hybrid functionals
   - TDDFT with improved input orbitals

3. **Symmetrized KS methods and TDDFT**
   - Symmetrized KS formalism
   - TDDFT based on symmetrized KS methods

4. **Summary & Literature**

Kohn-Sham formalism

$$\begin{tikzcd}
\hat{T}+\hat{V}_{\mathsf{ee}}+\hat{v} \arrow[r] & \Psi_0, E_0 \arrow[r] & \rho_0 \arrow[ll, bend right, "\mathsf{HK}"'] \arrow[rr, bend left, "\mathsf{HK}"] & \Phi_0, \phi_{\mathsf{s}}, \epsilon_{\mathsf{s}} \arrow[l] & \hat{T}+\hat{v}_{\mathsf{s}} \arrow[l]
\end{tikzcd}$$

- ρ_0 connects KS model system of noninteracting 'electrons' with real physical electron system
- v_{s}, N can be used as basic variables as well as ρ_0
- KS orbitals ϕ_{s} and eigenvalues ϵ_{s} can be used to construct exchange-correlation functionals

Optimized effective potential (OEP) method: exact treatment of KS exchange

Exchange energy

$$E_{\mathsf{x}} = -\frac{1}{2}\sum_{i,j}^{\text{occ.}}\langle\phi_i\phi_j|\phi_j\phi_i\rangle$$

Exchange potential $v_{\mathsf{x}}(\vec{r}) = \dfrac{\delta E_{\mathsf{x}}[\{\phi_i\}]}{\delta\rho(\vec{r})}$

$$\int d\mathbf{r}'\,\frac{\delta E_{\mathsf{x}}}{\delta\rho(\mathbf{r}')}\,\frac{\delta\rho(\mathbf{r}')}{\delta v_{\mathsf{s}}(\mathbf{r})} = \int d\mathbf{r}'\,\sum_{i}^{\text{occ.}}\,\frac{\delta E_{\mathsf{x}}}{\delta\phi_i(\mathbf{r}')}\,\frac{\delta\phi_i(\mathbf{r}')}{\delta v_{\mathsf{s}}(\mathbf{r})}$$

$$\int d\mathbf{r}'\;\chi_0(\mathbf{r},\mathbf{r}')\;v_{\mathsf{x}}(\mathbf{r}')\;=\;t_{\mathsf{x}}(\mathbf{r})$$

KS response function $\chi_0(\mathbf{r},\mathbf{r}') = \displaystyle\sum_i^{\text{occ.}}\sum_a^{\text{unocc.}}\frac{\phi_i(\mathbf{r})\phi_a(\mathbf{r})\phi_a(\mathbf{r}')\phi_i(\mathbf{r}')}{\varepsilon_i-\varepsilon_a} + \text{c.c.}$

$$t_{\mathsf{x}}(\mathbf{r}) = \sum_i^{\text{occ.}}\sum_a^{\text{unocc.}}\frac{\phi_i(\mathbf{r})\phi_a(\mathbf{r})\,\left\langle a|\hat{v}_{\mathsf{x}}^{\mathsf{NL}}|i\right\rangle}{\epsilon_i-\epsilon_a} + \text{c.c.}$$

Plane wave methods for solids

Gaussian basis set methods for molecules

Gaussian basis set OEP methods I

Exchange-correlation charge density ρ_{xc}

$$v_{\mathsf{xc}}(\mathbf{r}) = \int \mathrm{d}\mathbf{r}' \, \frac{\rho_{\mathsf{xc}}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

Charge conditions

$$\int \mathrm{d}\mathbf{r} \, \rho_{\mathsf{x}}(\mathbf{r}) = -1 \qquad \int \mathrm{d}\mathbf{r} \, \rho_{\mathsf{c}}(\mathbf{r}) = 0$$

HOMO condition

$$\langle \phi_{\mathsf{HOMO}} | v_{\mathsf{x}} | \phi_{\mathsf{HOMO}} \rangle = \langle \phi_{\mathsf{HOMO}} | \hat{v}_{\mathsf{x}}^{\mathsf{NL}} | \phi_{\mathsf{HOMO}} \rangle$$

Phys. Rev. Lett. **83**, 5459 (1999)

Gaussian basis set OEP methods II

$$\rho_{\mathsf{xc}}(\mathbf{r}) = \sum_{\mu} v_{\mathsf{xc},\mu}\, f_{\mu}(\mathbf{r}) \qquad\qquad v_{\mathsf{xc}}(\mathbf{r}) = \sum_{\mu} v_{\mathsf{xc},\mu} \int \mathrm{d}\mathbf{r}'\, \frac{f_{\mu}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

OEP matrix equation

$$\mathbf{X}_{\mathsf{s}}\, \mathbf{v}_{\mathsf{xc}} = \mathbf{t}_{\mathsf{xc}}$$

Enforce charge and HOMO conditions and balance orbital and auxiliary basis sets by preprocessing of auxiliary basis set

J. Chem. Phys. **155**, 054109 (2021)

Gaussian basis set KS inversion

Determine $\hat{v}_{\mathsf{xc}}$ for given reference density ρ^{ref}

Starting KS Hamiltonian

$$\hat{H}^0 = \hat{T} + \hat{v}_{\mathsf{ext}} + \hat{v}_{\mathsf{H}}\left[\rho^{\mathsf{ref}}\right] + \hat{v}^0_{\mathsf{xc}}$$

Iteration steps

$$\hat{H}^n \varphi_i^n = \epsilon_i\, \varphi_i^n \longrightarrow \rho^n \longrightarrow \Delta\rho^n = \rho^{\mathsf{ref}} - \rho^n$$

$$X_{\mathsf{s}}^n\, \Delta v_{\mathsf{xc}}^n = \Delta\rho^n \longrightarrow v_{\mathsf{xc}}^{n+1} = v_{\mathsf{xc}}^n + \Delta v_{\mathsf{xc}}^n$$

Gaussian basis set representation

$$\mathbf{X}_{\mathsf{s}}^n\, \Delta\mathbf{v}_{\mathsf{xc}}^n = \Delta\boldsymbol{\rho}^n$$

Preprocessing of auxiliary basis set like in OEP with HOMO condition $\epsilon_{\mathsf{HOMO}} = -\mathsf{IP}$

J. Chem. Phys. **156**, 204124 (2022)

Adiabatic-connection fluctuation-dissipation theorem for KS correlation energy

$$E_{\mathsf{c}} = \frac{-1}{2\pi}\int_0^1 d\alpha \int d\mathbf{r}d\mathbf{r}'\,\frac{1}{|\mathbf{r}-\mathbf{r}'|}\int_0^\infty d\omega\left[\chi_\alpha(\mathbf{r},\mathbf{r}',\mathrm{i}\omega) - \chi_0(\mathbf{r},\mathbf{r}',\mathrm{i}\omega)\right]$$

KS response function $\chi_0(\mathbf{r},\mathbf{r}',\mathrm{i}\omega)$

$$\chi_0(\mathbf{r},\mathbf{r}',\mathrm{i}\omega) = -4\sum_i^{\mathrm{occ}}\sum_a^{\mathrm{unocc}}\frac{\epsilon_{ai}}{\epsilon_{ai}^2+\omega^2}\,\varphi_i(\mathbf{r})\varphi_a(\mathbf{r})\varphi_a(\mathbf{r}')\varphi_i(\mathbf{r}')$$

Introduction of RI basis set orthonormalized with respect to Coulomb norm

$$E_{\mathsf{c}} = \frac{-1}{2\pi}\int_0^\infty d\omega\int_0^1 d\alpha\,\mathsf{Tr}\left\{\left[\mathbf{X}_\alpha(\mathrm{i}\omega) - \mathbf{X}_0(\mathrm{i}\omega)\right]\mathbf{F}_{\mathsf{H}}\right\}$$

Response matrix $\mathbf{X}_\alpha(\mathrm{i}\omega)$ from TDDFT

$$\mathbf{X}_\alpha = [\mathbf{1} - \mathbf{X}_0\,\mathbf{F}^\alpha_{\mathsf{Hxc}}]^{-1}\,\mathbf{X}_0$$

$$E_{\mathsf{c}} = \frac{-1}{2\pi}\int_0^\infty d\omega\int_0^1 d\alpha\,\mathsf{Tr}\left\{\left(\left[\mathbf{1}-\mathbf{X}_0\mathbf{F}^\alpha_{\mathsf{Hxc}}\right]^{-1} - \mathbf{1}\right)\mathbf{X}_0\mathbf{F}_{\mathsf{H}}\right\}$$

Mol. Phys. **109**, 2473 (2011)

Random phase approximation and σ-functionals

$$E_{\mathrm{c}}^{\mathrm{dRPA}} = \frac{-1}{2\pi}\int_0^\infty d\omega \int_0^1 d\alpha\,\mathrm{Tr}\left\{\left(\left[\mathbf{1}-\alpha\mathbf{X}_0\mathbf{F}_{\mathrm{H}}\right]^{-1}-\mathbf{1}\right)\mathbf{X}_0\mathbf{F}_{\mathrm{H}}\right\}$$

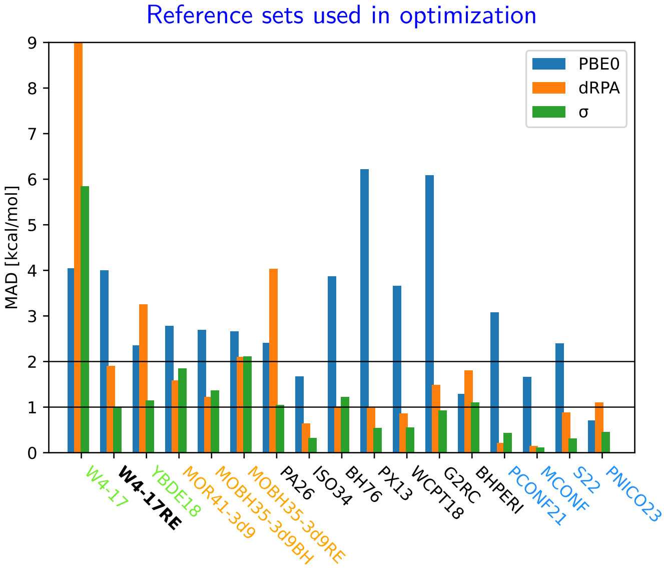
$$-\mathbf{X}_0\mathbf{F}_{\mathrm{H}} = \mathbf{V}\boldsymbol{\sigma}\mathbf{V}^{\mathsf{T}}$$

$$\begin{aligned} E_{\mathrm{c}}^{\mathrm{dRPA}} &= \frac{-1}{2\pi}\int_0^\infty d\omega \int_0^1 d\alpha\,\mathrm{Tr}\left\{\left[-\left(\mathbf{1}+\alpha\boldsymbol{\sigma}\right)^{-1}+\mathbf{1}\right]\boldsymbol{\sigma}\right\} \\ &= \frac{-1}{2\pi}\int_0^\infty d\omega\,\mathrm{Tr}\left\{-\ln\left[\mathbf{1}+\boldsymbol{\sigma}\right]+\boldsymbol{\sigma}\right\} \\ &= \frac{-1}{2\pi}\int_0^\infty d\omega\,\mathrm{Tr}\left\{H^{\mathrm{dRPA}}(\boldsymbol{\sigma}(\omega))\right\} \end{aligned}$$

$$E_{\mathrm{c}}^{\sigma f} = \frac{-1}{2\pi}\int_0^\infty d\omega\,\mathrm{Tr}\left\{H^{\mathrm{dRPA}}(\boldsymbol{\sigma}(\omega)) + H(\boldsymbol{\sigma}(\omega))\right\}$$

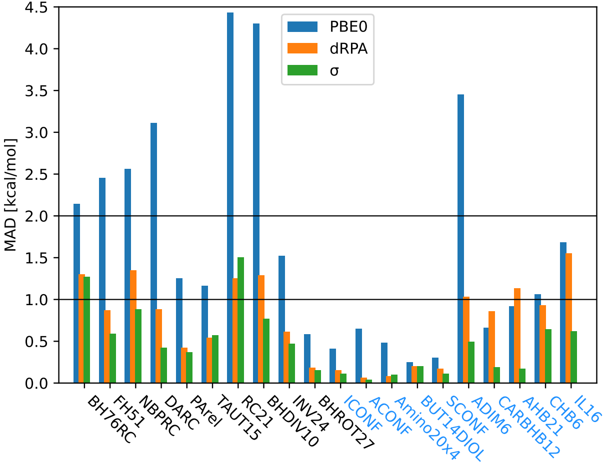
Computational steps:
(i) construct $\mathbf{X}_0$, (ii) diagonalize $-\mathbf{X}_0\mathbf{F}_{\mathrm{H}}$ to obtain $\boldsymbol{\sigma}$, (iii) calculate $E_{\mathrm{c}}^{\mathrm{dRPA}}$, $E_{\mathrm{c}}^{\sigma f}$

Performance of σ-functionals I



Performance of σ-functionals II

Reference sets **not** used in optimization

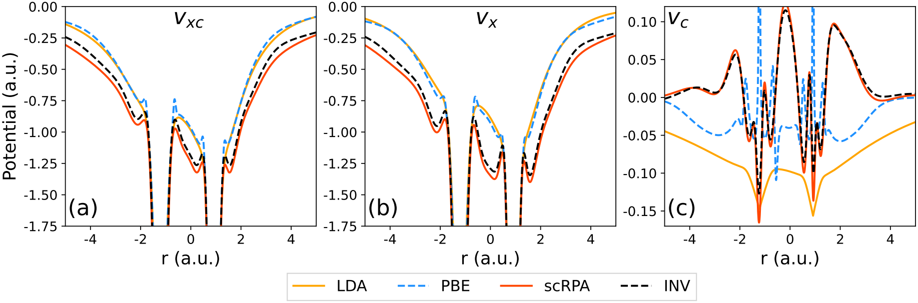


σ-functionals available in Molpro, Turbomole, ADF, PySCF, FermiONs++

J. Chem. Phys. **154**, 014104 (2020); **155**, 134111 (2021); **157**, 114105 (2023)

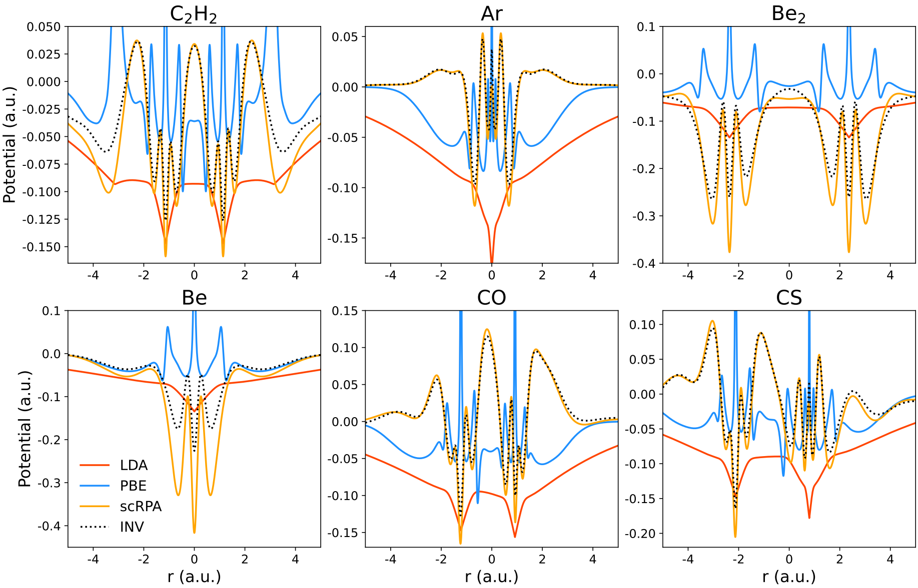
Correlation potentials from scRPA I

Potentials of CO



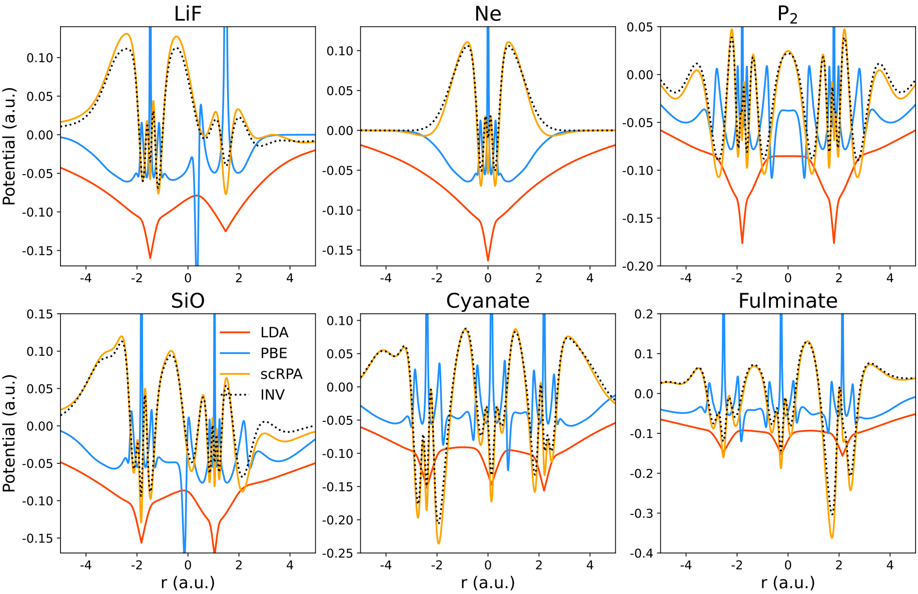
Phys. Rev. Lett. **134**, 016402 (2025)

Correlation potentials from scRPA II

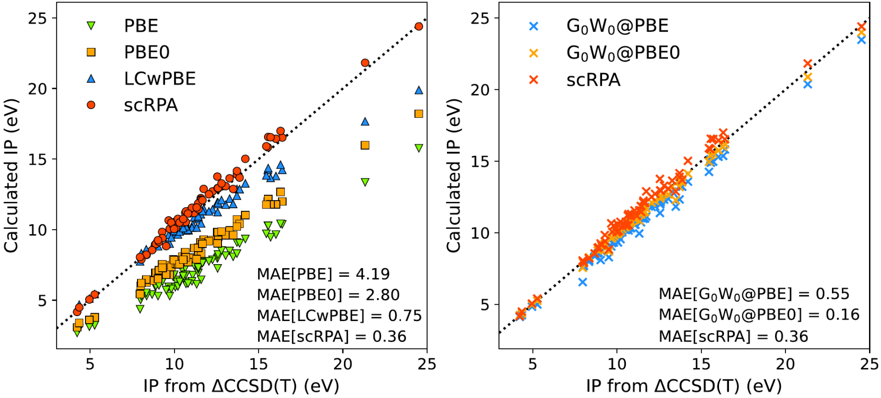


Phys. Rev. Lett. **134**, 016400 (2025)

Correlation potentials from scRPA III

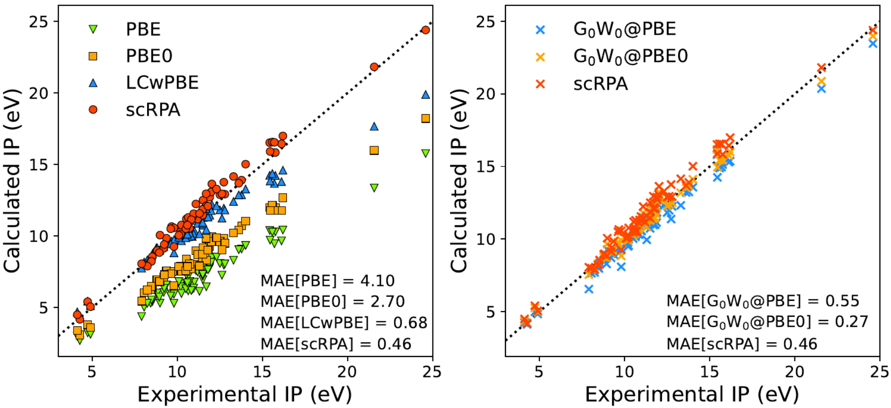


Ionization potentials from scRPA I



Phys. Rev. Lett. **134**, 016402 (2025)

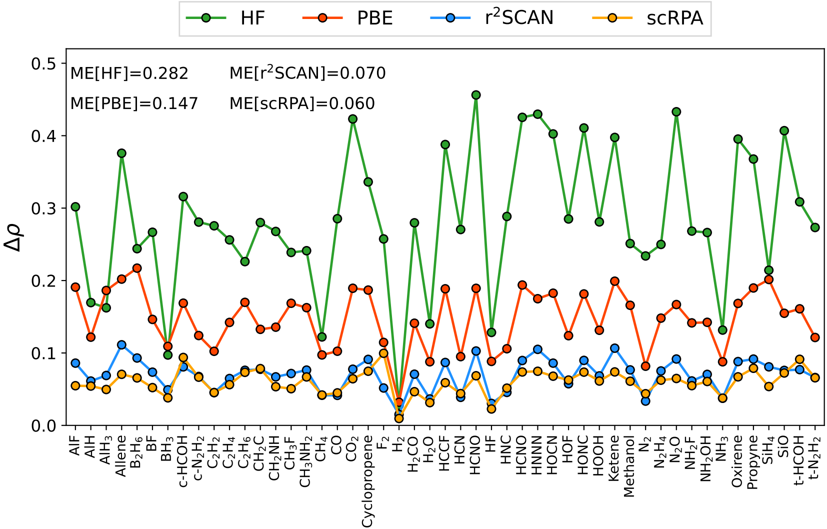
Ionization potentials from scRPA II



Phys. Rev. Lett. **134**, 016402 (2025)

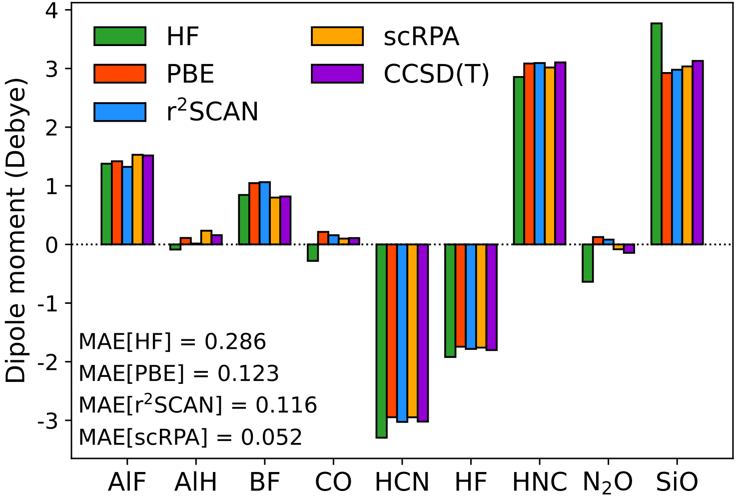
Quality of electron densities I

$$\Delta\rho = \int d\mathbf{r}\, \left|\rho^{\text{app}}(\mathbf{r}) - \rho^{\text{ref}}(\mathbf{r})\right|$$



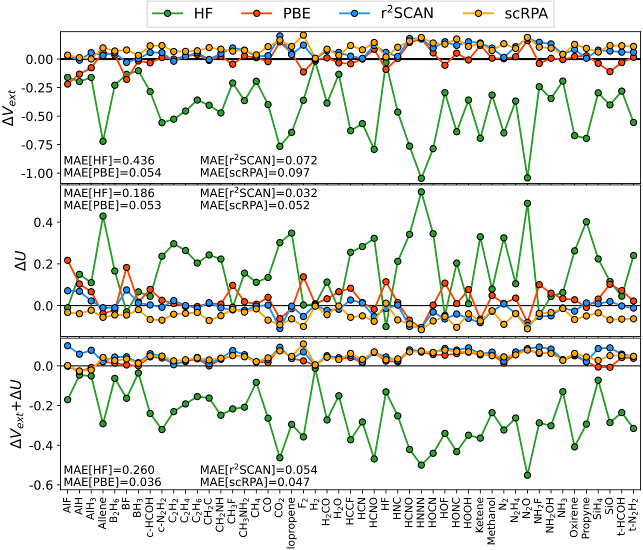
Quality of electron densities II

Dipole moments



Quality of electron densities III

$$\Delta v_{\text{ext}} = \int d\mathbf{r}\; v_{\text{ext}}(\mathbf{r}) \left[\rho^{\text{ref}}(\mathbf{r}) - \rho^{\text{app}}(\mathbf{r})\right] \qquad \Delta U = \int d\mathbf{r}\, \frac{\rho^{\text{ref}}(\mathbf{r})\rho^{\text{ref}}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} - \int d\mathbf{r}\, \frac{\rho^{\text{app}}(\mathbf{r})\rho^{\text{app}}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$



OEP for semilocal and hybrid functionals

$$\int d\mathbf{r}' \chi_{\mathsf{s}}(\mathbf{r},\mathbf{r}') v_{\mathsf{xc}}^{\mathsf{DFA\text{-}OEP}}(\mathbf{r}') = \frac{\delta E_{\mathsf{xc}}^{\mathsf{DFA}}}{\delta v_{\mathsf{s}}(\mathbf{r})} = \int d\mathbf{r}' \frac{\delta E_{\mathsf{xc}}^{\mathsf{DFA}}}{\delta \rho(\mathbf{r}')} \frac{\rho(\mathbf{r}')}{v_{\mathsf{s}}(\mathbf{r})} = \int d\mathbf{r}' \chi_{\mathsf{s}}(\mathbf{r},\mathbf{r}') v_{\mathsf{xc}}^{\mathsf{DFA}}(\mathbf{r}')$$

$$v_{\mathsf{xc}}^{\mathsf{DFA\text{-}OEP}} = v_{\mathsf{xc}}^{\mathsf{DFA}} + C$$

Why OEP?

$$v_{\mathsf{xc}}^{\mathsf{DFA\text{-}OEP}} = \int d\mathbf{r}' \frac{\rho_{\mathsf{xc}}^{\mathsf{DFA\text{-}OEP}}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

Phys. Rev. Lett. **83**, 5459 (1999)

- enforce charge condition $\int d\mathbf{r}\, \rho_{\mathsf{xc}}^{\mathsf{DFA\text{-}OEP}}(\mathbf{r}) = -1$
  N. I. Gidopoulos *et al.* J. Chem. Phys. **136**, 224109 (2012)
- enforce HOMO condition J. Chem. Theor. Comput. **21**, 1667 (2025)

HOMO condition for approximate exchange potentials

HOMO condition for exact v_{x}

$$\langle \phi_{\mathsf{HOMO}} | \hat{v}_{\mathsf{x}} | \phi_{\mathsf{HOMO}} \rangle = \left\langle \phi_{\mathsf{HOMO}} \middle| \hat{v}_{\mathsf{x}}^{\mathsf{NL}} \middle| \phi_{\mathsf{HOMO}} \right\rangle$$

$$\langle \phi_{\mathsf{HOMO}} | \hat{v}_{\mathsf{H}} + \hat{v}_{\mathsf{x}} | \phi_{\mathsf{HOMO}} \rangle = E_{\mathsf{Hx}}(N) - E_{\mathsf{Hx}}^{\mathsf{frz}}(N-1)$$

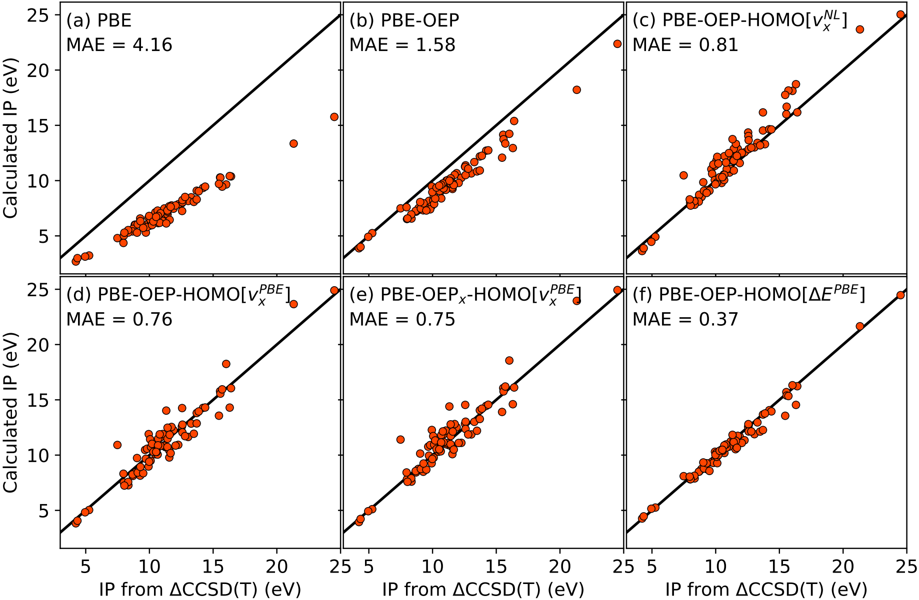
HOMO condition for exact $v_{\mathsf{x}}^{\mathsf{DFA}}$

$$\left\langle \phi_{\mathsf{HOMO}} \middle| \hat{v}_{\mathsf{H}} + \hat{v}_{\mathsf{x}}^{\mathsf{DFA}} \middle| \phi_{\mathsf{HOMO}} \right\rangle = E_{\mathsf{Hx}}(N)^{\mathsf{DFA}} - E_{\mathsf{Hx}}^{\mathsf{DFA,frz}}(N-1)$$

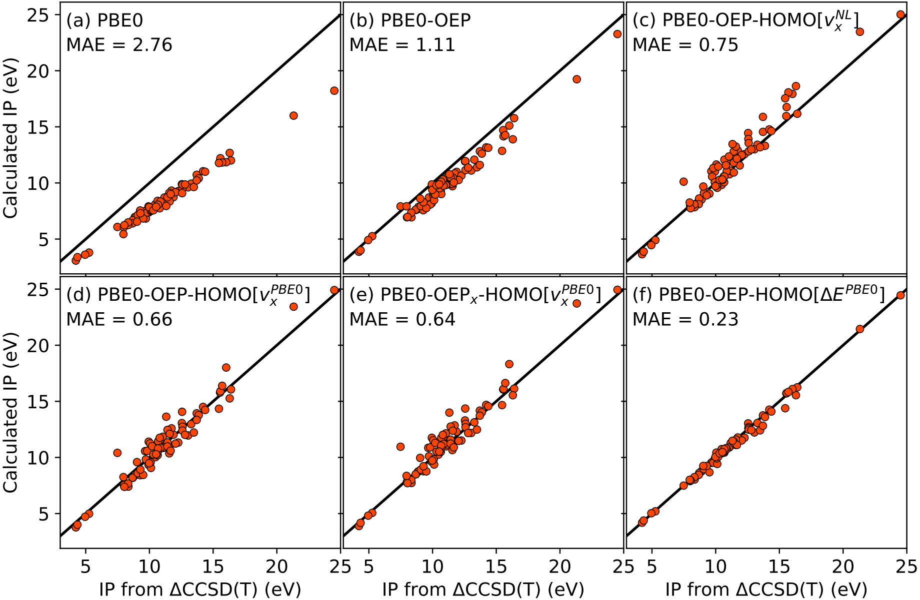
$$\left\langle \phi_{\mathsf{HOMO}} \middle| \hat{v}_{\mathsf{x}}^{\mathsf{DFA}} \middle| \phi_{\mathsf{HOMO}} \right\rangle = -\mathsf{IP}_{\mathsf{x}}^{\mathsf{frz}} - \left\langle \phi_{\mathsf{HOMO}} \middle| -\frac{1}{2}\vec{\nabla}^2 + \hat{v}_{\mathsf{ext}} + \hat{v}_{\mathsf{H}} \middle| \phi_{\mathsf{HOMO}} \right\rangle$$

J. Chem. Theor. Comput. **21**, 1667 (2025)

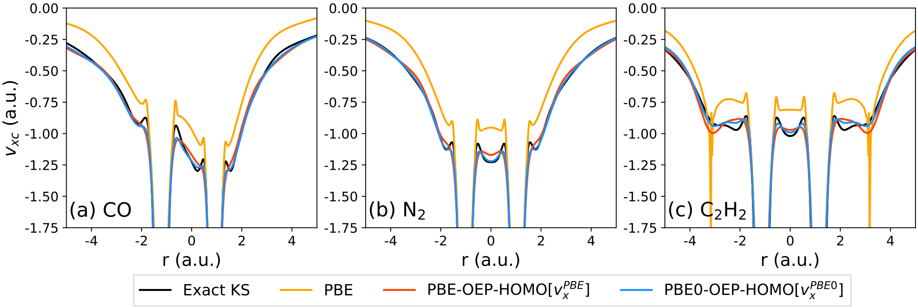
PBE IPs from negative HOMO eigenvalues



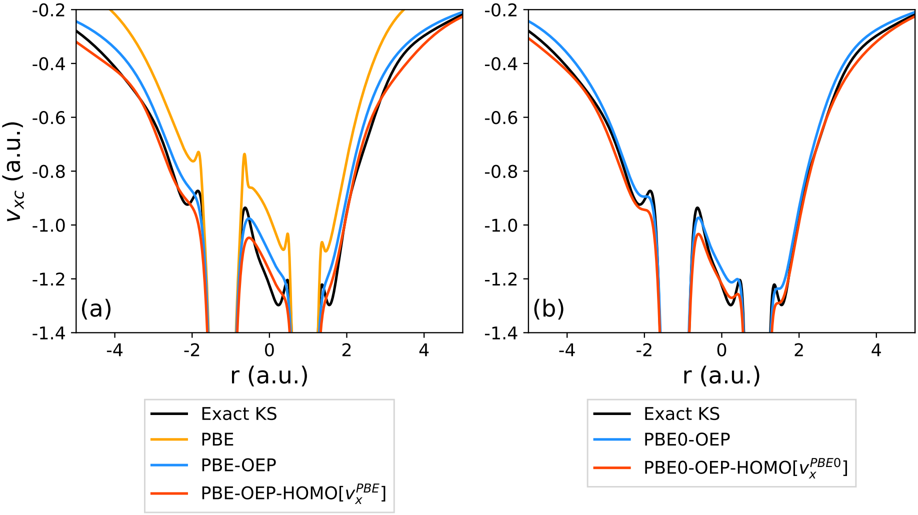
PBE0 IPs from negative HOMO eigenvalues



Exchange-correlation potentials from OEP I



Exchange-correlation potentials from OEP II



J. Chem. Theor. Comput. **21**, 1667 (2025)

Excitation energies from TDDFT in the linear response regime

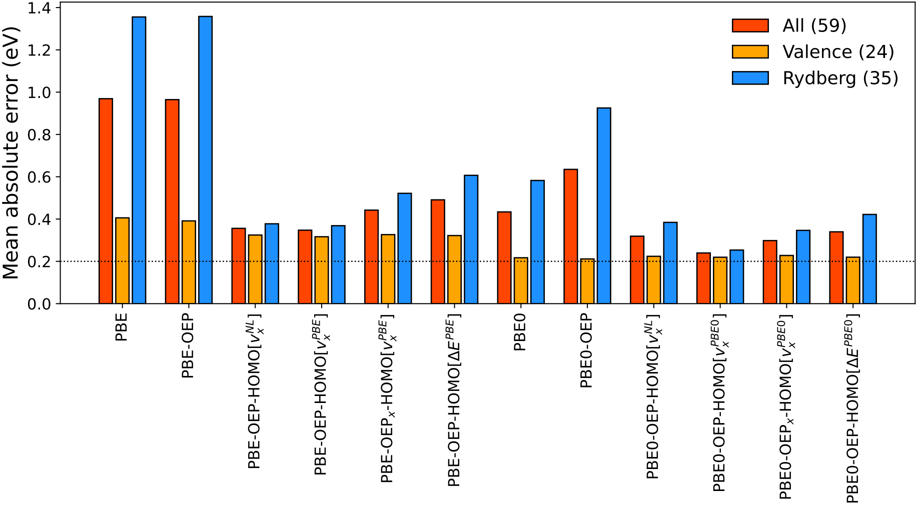
$$\left[\boldsymbol{\epsilon}^2 + 2\boldsymbol{\epsilon}^{\frac{1}{2}}\boldsymbol{\kappa}\boldsymbol{\epsilon}^{\frac{1}{2}}\right]\mathbf{Z} = \Omega^2\mathbf{Z}$$

$$\epsilon_{ia,jb} = \delta_{ia,jb}(\epsilon_a - \epsilon_i) \qquad K_{ia,jb} = \int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'\, \varphi_i(\mathbf{r})\varphi_a(\mathbf{r}) f_{\mathsf{Hxc}}(\mathbf{r},\mathbf{r}')\varphi_j(\mathbf{r}')\varphi_b(\mathbf{r}')$$

Sources of errors:

- Input orbitals and eigenvalues
- Approximation for f_{xc}

Excitation energies with improved input orbitals



J. Chem. Theor. Comput. **21**, 1667 (2025)

Symmetry in the KS formalism

Hohenberg-Kohn theorem

- The ground state electron density determines uniquely external potential
- There is a one-to-one mapping between groundstate densities and potentials (not generally true)

$$\text{B}\ [1s^2\ 2s^2\ 2p^1]\quad {}^2P$$

$$v_{\text{ext}} \longrightarrow \begin{cases} \Psi_0^{{}^2P}(M_S=\frac{1}{2}, M_L=\pm 1) \longrightarrow \boldsymbol{\rho}(M_S=\frac{1}{2}, M_L=\pm 1) \longrightarrow v_{\text{s}}^{1/2} \longrightarrow \Phi_0^{1/2} \\ \Psi_0^{{}^2P}(M_S=\frac{1}{2}, M_L=0) \longrightarrow \boldsymbol{\rho}(M_S=\frac{1}{2}, M_L=0) \longrightarrow v_{\text{s}}^{3} \longrightarrow \Phi_0^{3} \\ \Psi_0^{{}^2P}(M_S=-\frac{1}{2}, M_L=\pm 1) \longrightarrow \boldsymbol{\rho}(M_S=-\frac{1}{2}, M_L=\pm 1) \longrightarrow v_{\text{s}}^{4/5} \longrightarrow \Phi_0^{4/5} \\ \Psi_0^{{}^2P}(M_S=-\frac{1}{2}, M_L=0) \longrightarrow \boldsymbol{\rho}(M_S=-\frac{1}{2}, M_L=0) \longrightarrow v_{\text{s}}^{6} \longrightarrow \Phi_0^{6} \end{cases}$$

- v_{s}^i has symmetry of corresponding spin density $\boldsymbol{\rho}$ and thus lower symmetry than v_{ext}
- Φ_0^i are symmetry broken

Phys. Rev. A **47**, 2783 (1993)

Symmetrized KS formalism I

Use totally symmetric contribution $\bar{\rho}$ instead of spin density as basic variable

$$\text{B}\ [1s^2\ 2s^2\ 2p^1] \quad {}^2P$$

$$v_{\text{ext}} \longrightarrow \left\{ \begin{array}{ll} \Psi_0^{^2P}(\frac{1}{2},\pm 1) & \longrightarrow \boldsymbol{\rho}(\frac{1}{2},\pm 1) \\ \Psi_0^{^2P}(\frac{1}{2},0) & \longrightarrow \boldsymbol{\rho}(\frac{1}{2},0) \\ \Psi_0^{^2P}(-\frac{1}{2},\pm 1) & \longrightarrow \boldsymbol{\rho}(-\frac{1}{2},\pm 1) \\ \Psi_0^{^2P}(-\frac{1}{2},0) & \longrightarrow \boldsymbol{\rho}(-\frac{1}{2},0) \end{array} \right\} \longrightarrow \bar{\boldsymbol{\rho}} \rightarrow \bar{v}_{\text{s}} \longrightarrow \left\{ \begin{array}{l} \Phi_0^{^2P}(\frac{1}{2},\pm 1) \\ \Phi_0^{^2P}(\frac{1}{2},0) \\ \Phi_0^{^2P}(-\frac{1}{2},\pm 1) \\ \Phi_0^{^2P}(-\frac{1}{2},0) \end{array} \right.$$

- $\bar{v}_{\text{s}}$ has symmetry of v_{ext}
- $\Phi_0^{^2P}(M_S, M_L)$ have well-defined symmetry like $\Psi_0^{^2P}(M_S, M_L)$

Phys. Rev. A **47**, 2783 (1993)

Symmetrized KS formalism II

Symmetrized $\bar{v}_{\text{Hxc}}$

$$\bar{v}_{\text{Hxc}}(\mathbf{r}) = \frac{\delta E_{\text{Hxc}}\left[\rho_\alpha, \rho_\beta\right]}{\delta \bar{\rho}(\mathbf{r})} = \int \mathrm{d}\mathbf{r}' \frac{\delta E_{\text{Hxc}}\left[\rho_\alpha, \rho_\beta\right]}{\delta \rho_\alpha(\mathbf{r}')} \frac{\delta \rho_\alpha(\mathbf{r}')}{\delta \bar{\rho}(\mathbf{r})} + \int \mathrm{d}\mathbf{r}' \frac{\delta E_{\text{Hxc}}\left[\rho_\alpha, \rho_\beta\right]}{\delta \rho_\beta(\mathbf{r}')} \frac{\delta \rho_\beta(\mathbf{r}')}{\delta \bar{\rho}(\mathbf{r})}$$

Derivatives $\frac{\delta \rho_\sigma(\mathbf{r}')}{\delta \bar{\rho}(\mathbf{r})}$ not accessible

$\bar{v}_{\text{Hxc}}$ is accessible via OEP with symmetrized auxiliary basis set

Phys. Rev. Lett. **85**, 4229 (2000)

J. Chem. Phys. **159**, 244109 (2023)

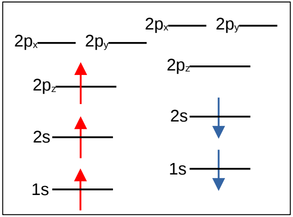
J. Chem. Phys. **162**, 034116 (2025)

J. Chem. Theor. Comput. **21**, 1667 (2025)

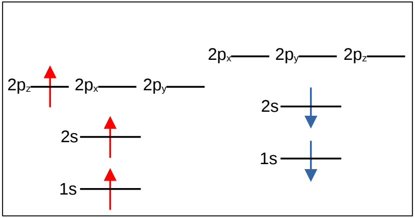
Symmetrized KS formalism III

Example B

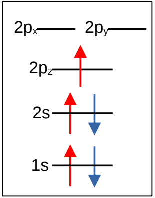
Non-symmetrized



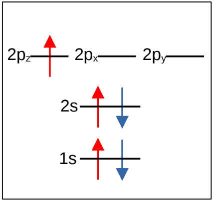
Space-symmetrized



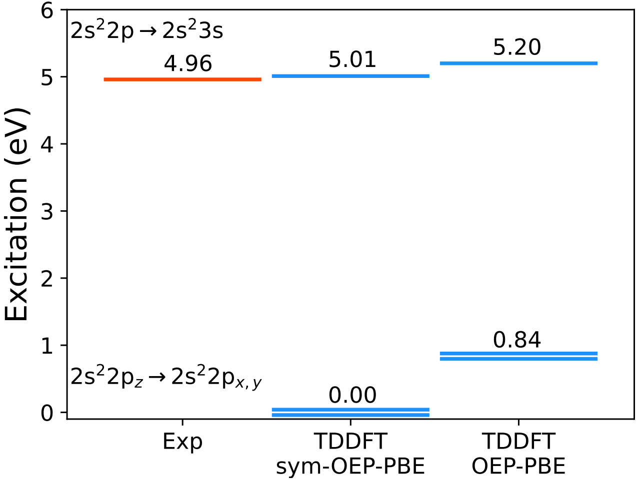
Spin-symmetrized



Space- and spin-symmetrized



TDDFT on top of symmetrized KS formalism



Conclusions

- Efficient, numerically stable Gaussian basis set OEP methods and KS inversion using standard basis sets are available

  J. Chem. Phys. **155**, 054109 (2021)
  J. Chem. Phys. **156**, 204124 (2022)
- Self-consistent RPA yields almost exact v_{xc}

  Phys. Rev. Lett. **134**, 016402 (2025)
- Chemical accuracy with σ-functionals

  J. Chem. Phys. **154**, 014104 (2020)
  J. Chem. Phys. **155**, 134111 (2021)
  J. Chem. Phys. **157**, 114105 (2023)
- OEP for standard (local or hybrid) xc-functionals yields improved orbitals and eigenvalues resulting in more accurate TDDFT excitation energies

  J. Chem. Theor. Comput. **21**, 1667 (2025)
- Symmetrized KS formalism free of symmetry breaking and spin poisoning can be applied in practice by OEP