

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

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D 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
- 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

Summary & Literature



- ρ_0 connects KS model system of noninteracting 'electrons' with real physical electron system
- $v_{\rm s},N$ can be used as basic variables as well as ho_0
- KS orbitals ϕ_s and eigenvalues ϵ_s can be used to construct exchange-correlation functionals





Exchange energy

$$E_{x} = -\frac{1}{2} \sum_{i,j}^{\text{occ.}} \langle \phi_{i} \phi_{j} | \phi_{j} \phi_{i} \rangle$$
Exchange potential $v_{x}(\vec{r}) = \frac{\delta E_{x}[\{\phi_{i}\}]}{\delta \rho(\vec{r})}$

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

$$\int d\mathbf{r}' \chi_{0}(\mathbf{r}, \mathbf{r}') v_{x}(\mathbf{r}') = t_{x}(\mathbf{r})$$

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

$$t_{\mathsf{x}}(\mathbf{r}) = \sum_{i}^{\text{occ. }} \sum_{a}^{\text{unocc. }} \frac{\phi_{i}(\mathbf{r})\phi_{a}(\mathbf{r})\left\langle a|\hat{v}_{\mathsf{x}}^{\mathsf{NL}}|i\right\rangle}{\epsilon_{i}-\epsilon_{a}} + \mathsf{c.c.}$$

Plane wave methods for solids Gaussian basis set methods for molecules

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Exchange-correlation charge density $\rho_{\rm xc}$

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

Charge conditions

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

HOMO condition

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

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

Gaussian basis set OEP methods II

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

OEP matrix equation

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

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

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







Determine $\hat{v}_{\rm xc}$ for given reference density $\rho^{\rm ref}$

Starting KS Hamiltonian

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

Iteration steps

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

$$X^n_{\mathsf{s}}\,\Delta v^n_{\mathsf{x}\mathsf{c}} = \Delta \rho^n \longrightarrow v^{n+1}_{\mathsf{x}\mathsf{c}} = v^n_{\mathsf{x}\mathsf{c}} + \Delta v^n_{\mathsf{x}\mathsf{c}}$$

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 $\epsilon_{HOMO} = -IP$

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



Adiabatic-connection fluctuation-dissipation theorem for KS correlation energy

$$E_{\mathsf{c}} = rac{-1}{2\pi} \int_{0}^{1} dlpha \int d\mathbf{r} d\mathbf{r}' \, rac{1}{|\mathbf{r} - \mathbf{r}'|} \int_{0}^{\infty} d\omega \left[\chi_{lpha}(\mathbf{r}, \mathbf{r}', \mathrm{i}\omega) \, - \, \chi_{0}(\mathbf{r}, \mathbf{r}', \mathrm{i}\omega)
ight]$$

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

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

Introduction of RI basis set orthonormalized with respect to Coulomb norm

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

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

$$\mathbf{X}_{\alpha} = \left[\mathbf{1} - \mathbf{X}_{0} \mathbf{F}_{\mathsf{Hxc}}^{\alpha}\right]^{-1} \mathbf{X}_{0}$$
$$E_{\mathsf{c}} = \frac{-1}{2\pi} \int_{0}^{\infty} d\omega \int_{0}^{1} d\alpha \operatorname{Tr} \left\{ \left(\left[\mathbf{1} - \mathbf{X}_{0} \mathbf{F}_{\mathsf{Hxc}}^{\alpha}\right]^{-1} - \mathbf{1} \right) \mathbf{X}_{0} \mathbf{F}_{\mathsf{H}} \right\}$$

Mol. Phys. 109, 2473 (2011)

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$$E_{c}^{dRPA} = \frac{-1}{2\pi} \int_{0}^{\infty} d\omega \int_{0}^{1} d\alpha \operatorname{Tr} \left\{ \left(\left[\mathbf{1} - \alpha \mathbf{X}_{0} \mathbf{F}_{\mathsf{H}} \right]^{-1} - \mathbf{1} \right) \mathbf{X}_{0} \mathbf{F}_{\mathsf{H}} \right\} - \mathbf{X}_{0} \mathbf{F}_{\mathsf{H}} = \mathbf{V} \boldsymbol{\sigma} \mathbf{V}^{\mathsf{T}}$$
$$E_{c}^{dRPA} = \frac{-1}{2\pi} \int_{0}^{\infty} d\omega \int_{0}^{1} d\alpha \operatorname{Tr} \left\{ \left[-\left(\mathbf{1} + \alpha \boldsymbol{\sigma} \right)^{-1} + \mathbf{1} \right] \boldsymbol{\sigma} \right\} \right\}$$
$$= \frac{-1}{2\pi} \int_{0}^{\infty} d\omega \operatorname{Tr} \left\{ -\ln \left[\mathbf{1} + \boldsymbol{\sigma} \right] + \boldsymbol{\sigma} \right\}$$
$$= \frac{-1}{2\pi} \int_{0}^{\infty} d\omega \operatorname{Tr} \left\{ H^{dRPA}(\boldsymbol{\sigma}(\omega)) \right\}$$

$$E_{\rm c}^{\sigma f} = \ \frac{-1}{2\pi} \int_0^\infty \!\!\! d\omega \ {\rm Tr} \ \big\{ H^{\rm dRPA}(\pmb{\sigma}(\omega)) + H(\pmb{\sigma}(\omega)) \big\} \label{eq:eq:constraint}$$

Computational steps:

(i) construct X_0 , (ii) diagonalize $-X_0F_H$ to obtain σ , (iii) calculate E_c^{dRPA} , $E_c^{\sigma f}$





9 PBE0 8 dRPA σ 7 6 MAD [kcal/mol] 5 4 3 2 1 Ma Ha BORDA 0 ALLS TIME CORPUTING THE CONSTRUCTION AN LAS 50,

Reference sets used in optimization







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





Correlation potentials from scRPA II







Correlation potentials from scRPA III



























Dipole moments







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

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

Why OEP?

$$v_{\rm xc}^{\rm DFA-OEP} = \int d\mathbf{r}' \, \frac{\rho_{\rm xc}^{\rm DFA-OEP}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \qquad \qquad {\rm Phys. \ Rev. \ Lett.} \ \mathbf{83}, \ 5459 \ (1999)$$

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

• enforce HOMO condition J. Chem. Theor. Comput. 21, 1667 (2025)





HOMO condition for exact $v_{\rm x}$

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

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

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

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

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

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

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😽 🍌 🗛 PBE0 IPs from negative HOMO eigenvalues 🐼 sca 🐲 👘







🚱 🍌 FAU Exchange-correlation potentials from OEP II 🐼 SCA 🐲 🚱



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

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

Sources of errors:

- Input orbitals and eigenvalues
- Approximation for $f_{\rm xc}$



Excitation energies with improved input orbitals





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





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)

B
$$[1s^2 \ 2s^2 \ 2p^1] \ ^2P$$

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

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

Phys. Rev. A 47, 2783 (1993)





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

 $B [1s^2 2s^2 2p^1] - ^2P$

$$v_{\text{ext}} \longrightarrow \begin{cases} \Psi_0^{2P}(\frac{1}{2},\pm 1) & \longrightarrow \rho(\frac{1}{2},\pm 1) \\ \Psi_0^{2P}(\frac{1}{2},0) & \longrightarrow \rho(\frac{1}{2},0) \\ \Psi_0^{2P}(-\frac{1}{2},\pm 1) & \longrightarrow \rho(-\frac{1}{2},\pm 1) \\ \Psi_0^{2P}(-\frac{1}{2},0) & \longrightarrow \rho(-\frac{1}{2},0) \end{cases} \longrightarrow \bar{\rho} \to \bar{v}_{\text{s}} \longrightarrow \begin{cases} \Phi_0^{2P}(\frac{1}{2},\pm 1) \\ \Phi_0^{2P}(\frac{1}{2},0) \\ \Phi_0^{2P}(-\frac{1}{2},\pm 1) \\ \Phi_0^{2P}(-\frac{1}{2},0) \end{cases}$$

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

Phys. Rev. A 47, 2783 (1993)





Symmetrized \bar{v}_{Hxc}

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

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

 $\bar{v}_{\rm Hxc}$ 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)





Example B



Spin-symmetrized



Space- and spin-symmetrized



🚱 🍌 🗛 TDDFT on top of symmetrized KS formalism 🚳 🔬 🏀







- 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)
- $\bullet\,$ Self-consistent RPA yields almost exact $v_{\rm xc}$
 - 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