

# Exchange-Correlation Functional

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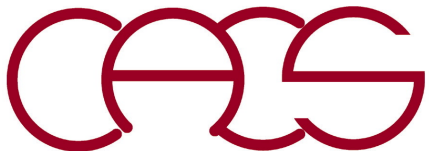
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**How to incorporate many-electron correlations into effective single-electron (Kohn-Sham) equations?**



# Preliminary: Second Quantization (1)

- Consider a system of  $N$  electrons with the Hamiltonian

$$H = \sum_{i=1}^N h(\mathbf{r}_i) + \frac{1}{2} \sum_{i \neq j} u(\mathbf{r}_i, \mathbf{r}_j)$$
$$h(\mathbf{r}) = -\frac{\hbar^2}{2m} \nabla^2 + v(\mathbf{r}); \quad u(\mathbf{r}, \mathbf{r}') = \frac{e^2}{|\mathbf{r} - \mathbf{r}'|}$$

- Occupation-number representation:** An antisymmetric Fermionic wave function can be expanded as a linear combination of Slater determinants

$$\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N) = \sum_{n_1, \dots, n_\infty \in \{0,1\}} f(n_1, \dots, n_\infty) \Phi_{n_1, \dots, n_\infty}(\mathbf{r}_1, \dots, \mathbf{r}_N)$$

where  $n_\kappa$  is the occupation number of the  $\kappa$ -th single-electron state  $\psi_\kappa(\mathbf{r})$ , with the constraint  $\sum_\kappa n_\kappa = N$ , and each Slater determinant (which occupies states  $\kappa_1 < \kappa_2 < \dots < \kappa_N$ ) is

$$\Phi_{\kappa_1, \dots, \kappa_N}(\mathbf{r}_1, \dots, \mathbf{r}_N) = \frac{1}{\sqrt{N!}} \begin{bmatrix} \psi_{\kappa_1}(\mathbf{r}_1) & \cdots & \psi_{\kappa_1}(\mathbf{r}_N) \\ \vdots & \ddots & \vdots \\ \psi_{\kappa_N}(\mathbf{r}_1) & \cdots & \psi_{\kappa_N}(\mathbf{r}_N) \end{bmatrix}$$
$$= \frac{1}{\sqrt{N!}} \sum_P (-1)^P \psi_{\kappa_{P(1)}}(\mathbf{r}_1) \cdots \psi_{\kappa_{P(N)}}(\mathbf{r}_N)$$

Permutation

# Preliminary: Second Quantization (2)

- The quantum-dynamical system is identical to

$$\Psi = \sum_{n_1, \dots, n_\infty \in \{0,1\}} f(n_1, \dots, n_\infty) (\hat{a}_1^\dagger)^{n_1} \dots (\hat{a}_\infty^\dagger)^{n_\infty} |0\rangle$$

Vacuum

with the Hamiltonian operator

$$\hat{H} = \sum_{m,n} \hat{a}_m^\dagger \langle m|h|n\rangle \hat{a}_n + \frac{1}{2} \sum_{m,n,p,q} \hat{a}_m^\dagger \hat{a}_n^\dagger \langle mn|u|pq\rangle \hat{a}_q \hat{a}_p$$

$$\left\{ \begin{array}{l} \langle m|h|n\rangle = \int d\mathbf{r} \psi_m^*(\mathbf{r}) h(\mathbf{r}) \psi_n(\mathbf{r}) \\ \langle mn|u|pq\rangle = \int d\mathbf{r} d\mathbf{r}' \psi_m^*(\mathbf{r}) \psi_n^*(\mathbf{r}') u(\mathbf{r}, \mathbf{r}') \psi_p(\mathbf{r}) \psi_q(\mathbf{r}') = [m^*p|u|n^*q] \end{array} \right.$$

Physicist's notation

Chemist's notation

and the creation ( $\hat{a}_m^\dagger$ ) & annihilation ( $\hat{a}_p$ ) operators anticommute

$$\left\{ \begin{array}{l} \{\hat{a}_\kappa, \hat{a}_{\kappa'}^\dagger\} \equiv \hat{a}_\kappa \hat{a}_{\kappa'}^\dagger + \hat{a}_{\kappa'}^\dagger \hat{a}_\kappa = \delta_{\kappa, \kappa'} \\ \{\hat{a}_\kappa, \hat{a}_{\kappa'}\} = \{\hat{a}_\kappa^\dagger, \hat{a}_{\kappa'}^\dagger\} = 0 \end{array} \right.$$

# Preliminary: Second Quantization (3)

- Hamiltonian operator in the coordinate representation

$$\begin{cases} \hat{H} = \hat{T} + \hat{V} + \hat{U} \\ \hat{T} = \frac{\hbar^2}{2m} \int d\mathbf{r} \nabla \hat{\psi}^\dagger(\mathbf{r}) \cdot \nabla \hat{\psi}(\mathbf{r}) \\ \hat{V} = \int d\mathbf{r} \hat{\psi}^\dagger(\mathbf{r}) v(\mathbf{r}) \hat{\psi}(\mathbf{r}) = \int d\mathbf{r} \hat{\rho}(\mathbf{r}) v(\mathbf{r}) \\ \hat{U} = \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \hat{\psi}^\dagger(\mathbf{r}) \hat{\psi}^\dagger(\mathbf{r}') \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \hat{\psi}(\mathbf{r}') \hat{\psi}(\mathbf{r}) \end{cases}$$

- See note on [second quantization](#)

A. L. Fetter & J. D. Walecka, *Quantum Theory of Many-Particle Systems* (McGraw-Hill, '71)

A. Szabo & N. S. Ostlund, *Modern Quantum Chemistry* (McMillan, '82)

# Preliminary: Hartree-Fock Approximation

- **Hartree-Fock approximation** determines the “best single Slater determinant” that minimizes the energy

$$\Phi = \frac{1}{\sqrt{N!}} \sum_P (-1)^P \phi_{P(1)}(\mathbf{r}_1) \cdots \phi_{P(N)}(\mathbf{r}_N)$$

$$\hat{f}(\mathbf{r})\phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r})$$

$h(\mathbf{r}) + \sum_{j=1}^N (J_j(\mathbf{r}) - K_j(\mathbf{r}))$  Fock operator

$$\begin{cases} J_j(\mathbf{r})\phi(\mathbf{r}) = \int d\mathbf{r}' \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \phi_j^*(\mathbf{r}') \phi_j(\mathbf{r}') \phi(\mathbf{r}) \\ K_j(\mathbf{r})\phi(\mathbf{r}) = \int d\mathbf{r}' \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \phi_j^*(\mathbf{r}') \phi(\mathbf{r}') \phi_j(\mathbf{r}) \end{cases}$$

- See note on [Hartree-Fock approximation](#)

# Energy Functional

## Exchange-correlation (xc) functional *via* Kohn-Sham decomposition

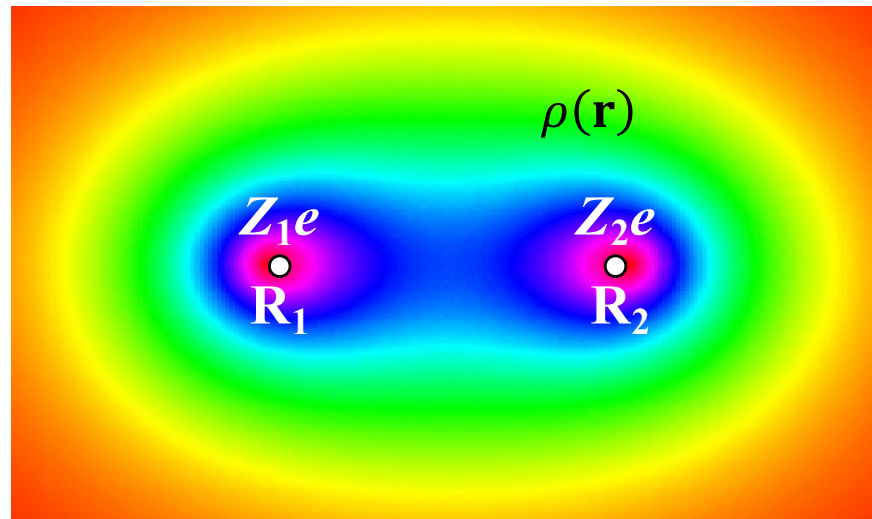
$$E[\rho(\mathbf{r})] = T_s[\rho(\mathbf{r})] + \int d\mathbf{r} v(\mathbf{r})\rho(\mathbf{r}) + \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{xc}[\rho(\mathbf{r})]$$

Kinetic energy of  
non-interacting  
electrons

External potential

Hartree energy (mean-  
field approximation to  
the electron-electron  
interaction energy)

Exchange-correlation  
energy



# Electron-Electron Interaction Energy

$$U = \frac{1}{2} \sum_{i=1}^N \sum_{j \neq i}^N \langle \Psi | \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} | \Psi \rangle = \int d\mathbf{r} \int d\mathbf{r}' \frac{\rho_2(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

$$\rho_2(\mathbf{r}, \mathbf{r}') = \frac{1}{2} \sum_{\sigma, \sigma'} \langle \Psi | \hat{\psi}_{\sigma}^{\dagger}(\mathbf{r}) \hat{\psi}_{\sigma'}^{\dagger}(\mathbf{r}') \hat{\psi}_{\sigma'}(\mathbf{r}') \hat{\psi}_{\sigma}(\mathbf{r}) | \Psi \rangle$$

Two-body  
density matrix

Creation operator

Annihilation operator

$e = \hbar = 1$

- **Two-body correlation function**  $g(\mathbf{r}, \mathbf{r}')$

$$\rho_2(\mathbf{r}, \mathbf{r}') = \frac{1}{2} \rho(\mathbf{r}) \rho(\mathbf{r}') g(\mathbf{r}, \mathbf{r}')$$

$$\rho(\mathbf{r}) = \rho_1(\mathbf{r}, \mathbf{r}) \quad \rho_1(\mathbf{r}, \mathbf{r}') = \sum_{\sigma} \langle \Psi | \hat{\psi}_{\sigma}^{\dagger}(\mathbf{r}) \hat{\psi}_{\sigma}(\mathbf{r}') | \Psi \rangle$$

One-body density matrix

$$U = \overbrace{\int d\mathbf{r} \int d\mathbf{r}' \frac{\rho(\mathbf{r}) \rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}}^{E_H} + \overbrace{\int d\mathbf{r} \int d\mathbf{r}' \frac{\rho(\mathbf{r}) \rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} [g(\mathbf{r}, \mathbf{r}') - 1]}^{E_{xc}}$$

- See note on [second quantization](#)

Deviation of  $g(r)$  from 1 signifies exchange-correlation

# Electron Correlation vs. Density Response

- Information on two-body correlation is encoded in the density response function  $\chi$  through fluctuation-dissipation theorem; see note on [time-dependent perturbation](#)

$$\hat{H}_{\text{tot}} = \hat{H} + \hat{V}(t)$$

$$\left\{ \begin{array}{l} \hat{H} = \hat{T} + \hat{U} = \frac{\hbar^2}{2m} \int d\mathbf{r} \nabla \hat{\psi}^\dagger(\mathbf{r}) \cdot \nabla \hat{\psi}(\mathbf{r}) + \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \hat{\psi}^\dagger(\mathbf{r}) \hat{\psi}^\dagger(\mathbf{r}') \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \hat{\psi}(\mathbf{r}') \hat{\psi}(\mathbf{r}) \\ \hat{V}(t) = \int d\mathbf{r} \hat{\psi}^\dagger(\mathbf{r}) v(\mathbf{r}, t) \hat{\psi}(\mathbf{r}) = \int d\mathbf{r} \hat{\rho}(\mathbf{r}) v(\mathbf{r}, t) \end{array} \right.$$

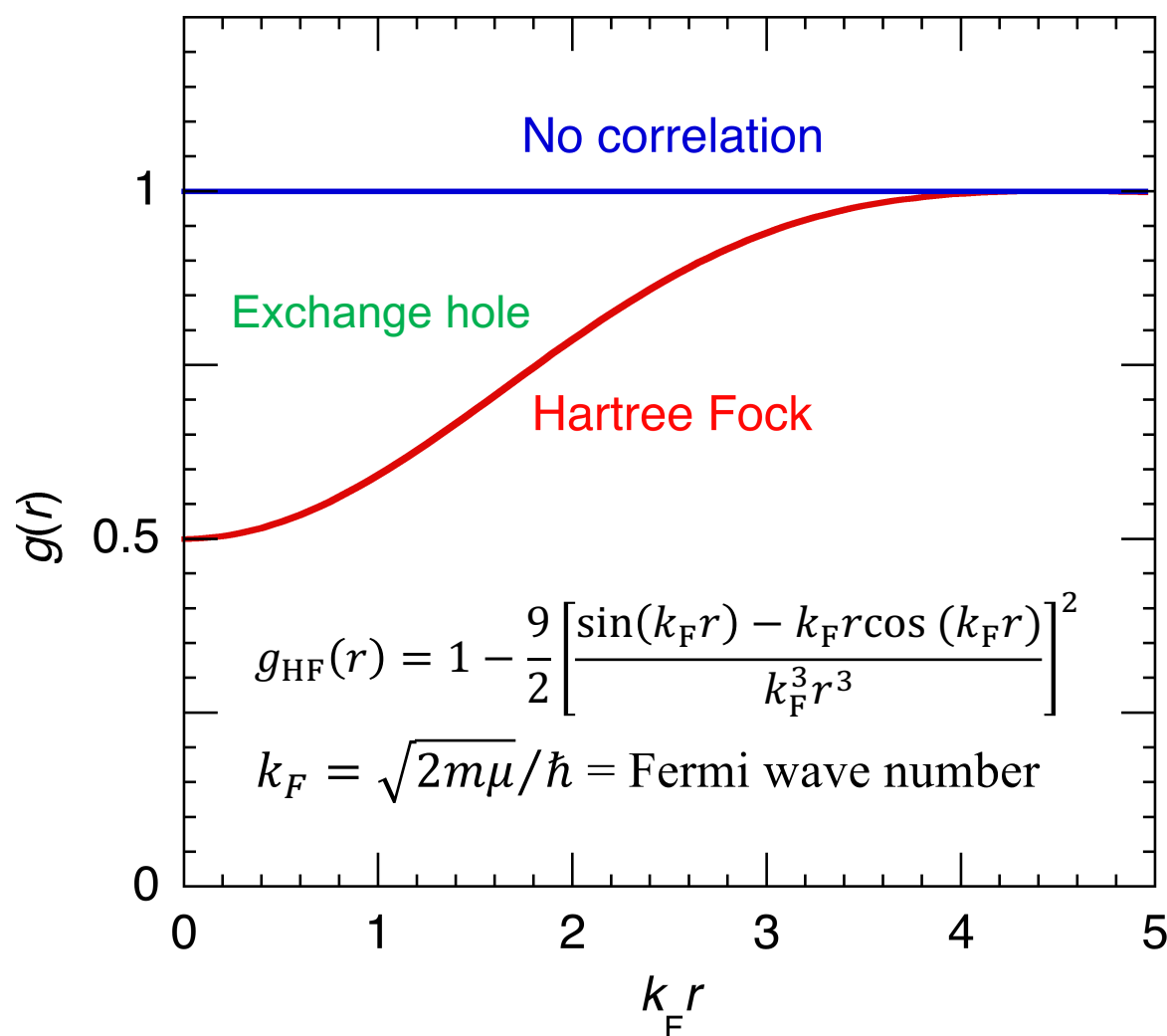
$$\begin{aligned} \chi(\mathbf{r} - \mathbf{r}', t - t') &\equiv \frac{\delta \langle \hat{\rho}(\mathbf{r}, t) \rangle}{\delta v(\mathbf{r}', t')} \\ &= -\frac{i}{\hbar} \Theta(t - t') \langle \Psi_0 | [\hat{\rho}_H(\mathbf{r}, t), \hat{\rho}_H(\mathbf{r}', t')] | \Psi_0 \rangle \\ &= -\frac{i}{\hbar} \Theta(t - t') \langle \Psi_0 | [\hat{\psi}_H^\dagger(\mathbf{r}, t) \hat{\psi}_H(\mathbf{r}, t), \hat{\psi}_H^\dagger(\mathbf{r}', t') \hat{\psi}_H(\mathbf{r}', t')] | \Psi_0 \rangle \end{aligned}$$

- Equation-of-motion & functional derivative to derive approximate  $\chi$ ; see A. Nakano & S. Ichimaru, [Phys. Rev. B \*\*39\*\*, 4930 \('89\)](#); *ibid.* **39**, 4938 ('89)



# Pair Correlation: Exchange Hole

- Radial distribution function  $g(|\mathbf{r} - \mathbf{r}'|)$  in a homogeneous system
- **Hartree-Fock (HF) approximation:** Ground state is a Slater determinant of plane waves occupied up to the chemical potential  $\mu$
- $g(r)$  is analytically calculated for homogeneous electron gas with HF

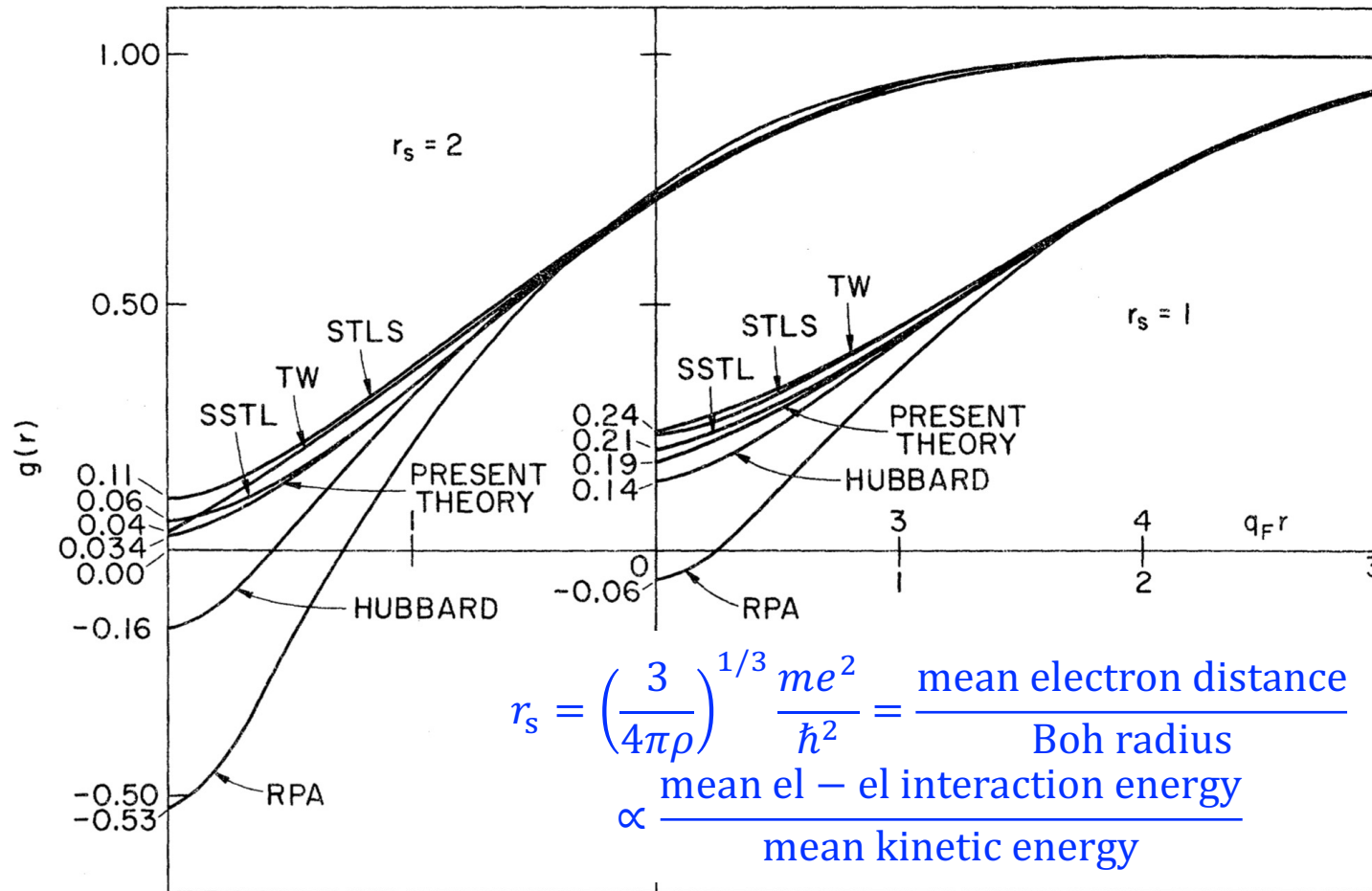


- $g_{\text{HF}}(r)$  represents Pauli exclusion principle between same-spin electrons embodied in the antisymmetric Slater determinant

- See note on [Hartree-Fock approximation](#)

# Exchange & Coulomb Holes

- $g(r)$  of homogeneous electron liquid with various approximations for incorporating the correlation effect, which represents additional Coulomb (or correlation) hole



P. Vashishta & K. S. Singwi, "Electron correlation at metallic densities. V," *Phys. Rev. B* **6**, 875 ('72)

# Exchange-Correlation Functional

- **Universal functional (of density) that describes many-body effects beyond the mean-field approximation**

$$v_{\text{Hxc}}(\mathbf{r}) = \int d\mathbf{r}' \frac{e^2 \rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + v_{\text{xc}}(\mathbf{r}) \quad v_{\text{xc}}(\mathbf{r}) = \frac{\delta E_{\text{xc}}}{\delta \rho(\mathbf{r})}$$

potential energy due to electron-electron interaction      Hartree (mean-field) potential      exchange-correlation potential

- **Some commonly used exchange-correlation functionals**
  - > **LDA (local density approximation):**  $E_{\text{xc}} = \int d\mathbf{r} \rho(\mathbf{r}) \epsilon_{\text{xc}}(\rho(\mathbf{r}))$
  - > **LSDA (local spin density approximation):**  $\epsilon_{\text{xc}}(\rho_{\uparrow}(\mathbf{r}), \rho_{\downarrow}(\mathbf{r}))$
  - > **GGA (generalized gradient approximation):**  $\epsilon_{\text{xc}}(\rho(\mathbf{r}), |\nabla \rho(\mathbf{r})|)$   
**PBE:** Perdew, Burke & Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 ('96)
  - > **MetaGGA: functional of kinetic-energy density**  
 $\tau_{\sigma}(\mathbf{r}) = \frac{1}{2} \sum_{n \in \{\text{occupied}\}} |\nabla \psi_{n\sigma}(\mathbf{r})|^2$   
**SCAN:** Sun, Ruzsinszky & Perdew, *Phys. Rev. Lett.* **115**, 036402 ('15)

# HK vs. PBE

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## Generalized gradient approximation made simple

JP Perdew, K Burke, M Ernzerhof

Physical review letters, 1996 • APS

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## Inhomogeneous electron gas

P Hohenberg, W Kohn - Physical review, 1964 - APS

This paper deals with the ground state of an interacting **electron gas** in an external potential  $v(r)$ . It is proved that there exists a universal functional of the density,  $F[n(r)]$ , independent of ...

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**Lesson:** Publish something simple that others can use

# Other Exchange-Correlation Functionals

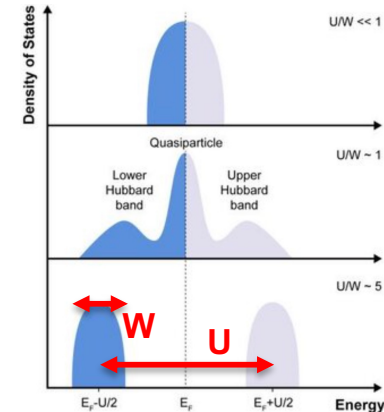
- Select an appropriate functional for the purpose & target system of the QMD simulation

## > LDA+U method for transition metals

$$\delta E_{\text{LDA+U}} / \delta n_i = \epsilon_{\text{LDA}} + U \left( \frac{1}{2} - n_i \right)$$

Occupation of  $i$ -th orbital

Anisimov et al., *Phys. Rev. B* **44**, 943 ('91)



## > DFT-D: van der Waals (vdW) functional for molecular crystals & layered materials

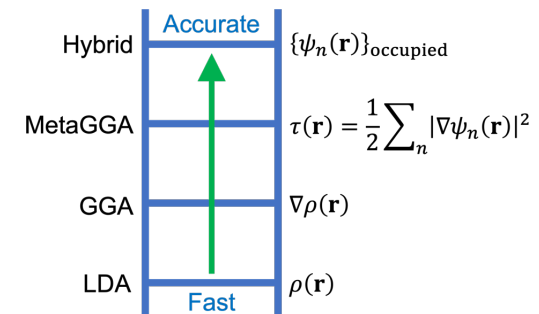
$$E_{\text{disp}} = -s_6 \sum_{i < j} \frac{c_{ij}}{R_{ij}^6} f_{\text{damp}}(R_{ij})$$

Grimme, *J. Comput. Chem.* **25**, 1463 ('04); *J. Chem. Phys.* **132**, 154104 ('10)

## > Nonlocal correlation functional

$$E_c^{\text{nl}} = \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \rho(\mathbf{r}) \phi(\mathbf{r}, \mathbf{r}') \rho(\mathbf{r}')$$

Dion et al., *Phys. Rev. Lett.* **92**, 246401 ('04)



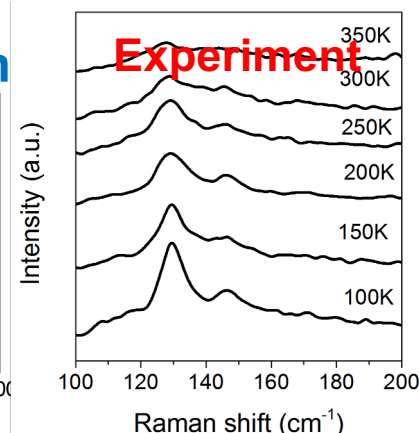
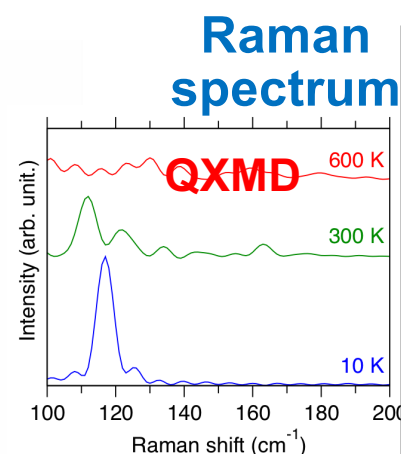
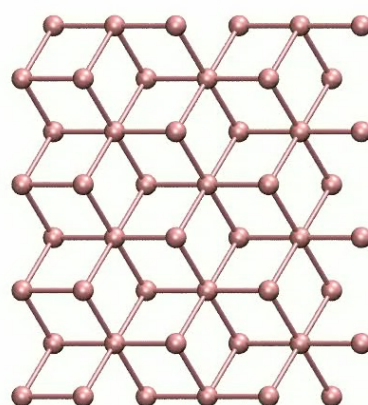
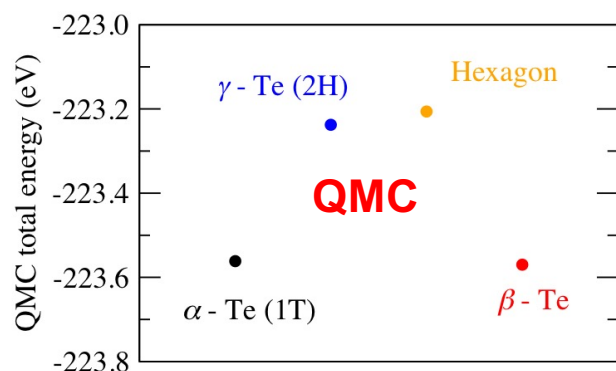
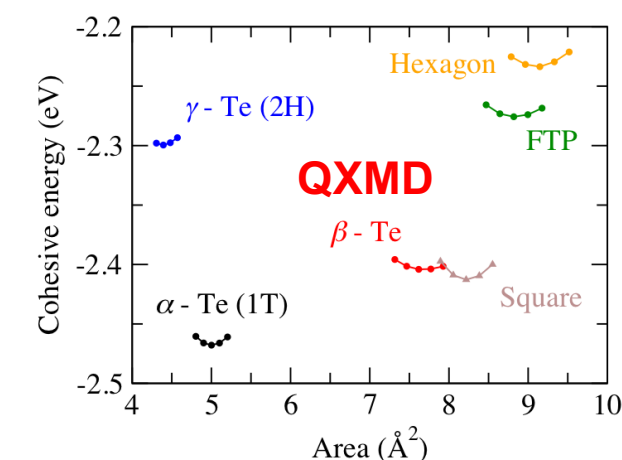
**For comparison of DFT-D & nonlocal correlation functionals, see**

Shimojo et al., *J. Chem. Phys.* **132**, 094106 ('10)

# Validation of XC Functional

- Comparison with high accuracy methods, such as quantum Monte Carlo (QMC), high-accuracy quantum chemistry, & experimental data
- Sensitivity analysis among different exchange-correlation (xc) functionals
- Consistency of the obtained result with the level of approximation

## Example: Atomically thin tellurium (tellurene)



	$a$ ( $\text{\AA}$ )	$B$ (N/m)
GGA	4.26	23.2138
GGA-D	4.17	28.6845
Spin GGA	4.26	22.1372
Hybrid HSE	-	23.8448
Hybrid HSE with GGA-D	-	29.7649

$a$ : Lattice constant  
 $B$ : Bulk modulus

# Band-Gap Problem

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- Janak's theorem equates the ionization potential (IP) & electron affinity (EA) with the Kohn-Sham (KS) eigenenergies of the highest occupied molecular orbital (HOMO) & lowest unoccupied molecular orbital (LUMO), respectively
- Band gap,  $E_{\text{gap}} = \text{IP} - \text{EA}$ , is usually underestimated with GGA-type exchange-correlation (xc) functional
- This is partly due to self interaction: Note the Hartree potential  $v_{\text{H}}(\mathbf{r}) = \int d\mathbf{r}' e^2 \rho(\mathbf{r}') / |\mathbf{r} - \mathbf{r}'|$  includes repulsive interaction of an occupied electron with itself (artifact), but not for an unoccupied electron
- **Self-interaction correction (SIC):** A quick fix subtracts the self-interaction of each KS orbital,  $v_{\text{H},n\sigma}(\mathbf{r}) = \int d\mathbf{r}' e^2 [\rho(\mathbf{r}') - |\psi_{n\sigma}|^2] / |\mathbf{r} - \mathbf{r}'|$ , which introduces an orbital-dependent KS potential (expensive & deviates from the DFT principle)

Perdew & Zunger, *Phys. Rev. B* **23**, 5048 ('81)

- Thorough analysis of the band-gap problem focuses on the discreteness of an electron

Cohen *et al.*, *Science* **321**, 792 ('08)

Mori-Sanchez *et al.*, *Phys. Rev. Lett.* **100**, 146401 ('08)

# Hybrid Exact Exchange Functional

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- Hartree-Fock (HF) approximation, with the underlying antisymmetric Slater determinant, is free from self interaction
- Hybrid exact-exchange functional incorporates part of the exact exchange using HF approximation & the rest with other xc functional (it is not strictly DFT)

**B3LYP:** e.g., Stephens *et al.*, *J. Phys. Chem.* **98**, 11623 ('94)

**PBE0:** Perdew *et al.*, *J. Chem. Phys.* **105**, 9982 ('96)

- Range-separated hybrid exact-exchange mixes HF & other xc functional at different distance

**HSE:** Heyd, Scuseria & Ernzerhof, *J. Chem. Phys.* **118**, 8207 ('03)

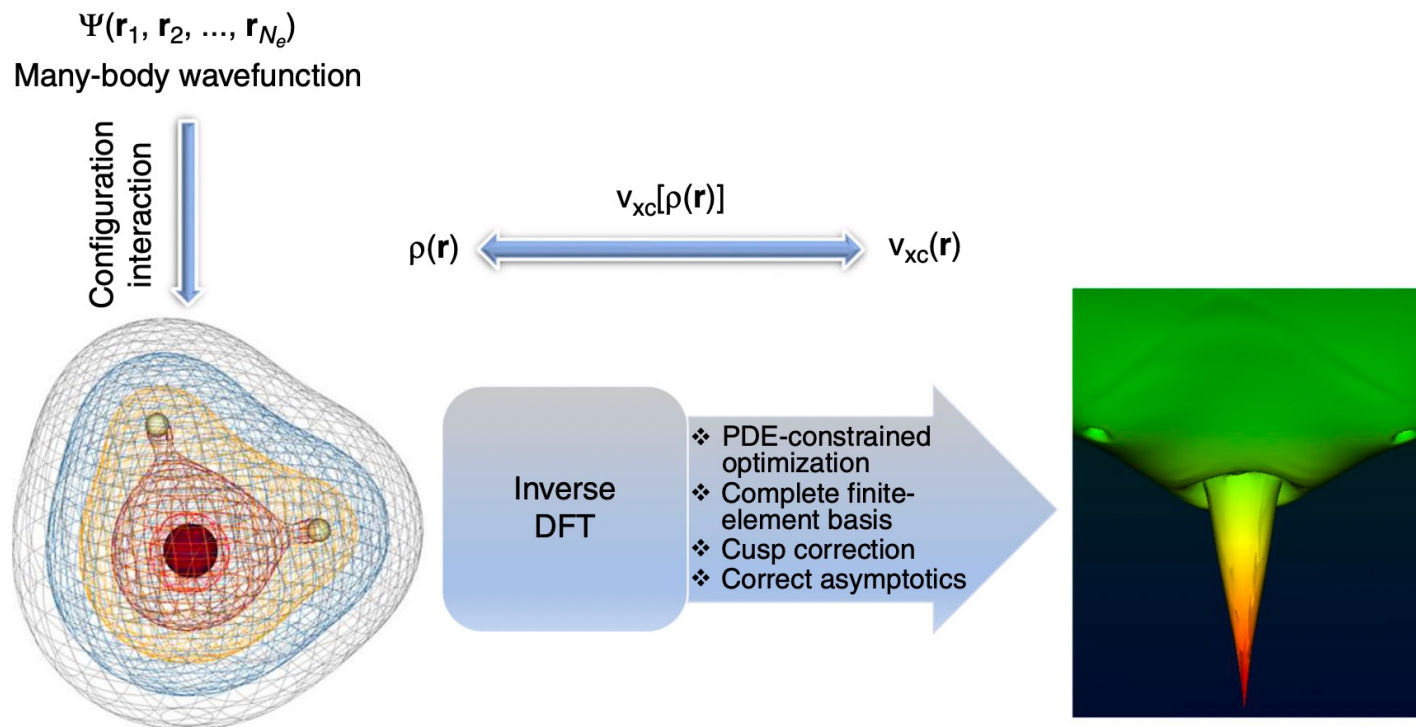
For comparison of LSDA, SIC & HF for a 2-electron problem,  
see Nakano *et al.*, *Phys. Rev. B* **44**, 8121 ('91)

- See note on [Hartree-Fock approximation](#)



# Inverse DFT

- **Inverse DFT problem:** Map the ground-state density (from high-accuracy many-body wave functions) to its exchange-correlation (xc) potential (to be used in DFT calculations) toward achieving “exact” xc potential
- Solve as constrained optimization problem



B. Kanungo *et al.*, *Nat. Commun.* **10**, 4497 ('19); *J. Phys. Chem. Lett.* **14**, 10039 ('23)

**cf. DeepMind's deep-learning xc functional & fractional electron problem** [J. Kirkpatrick *et al.*, *Science* **374**, 1385 ('21)]; **the central role of DFT in the age of AI** [B. Huang *et al.*, *Science* **381**, 170 ('23)]