Exchange-Correlation Functional

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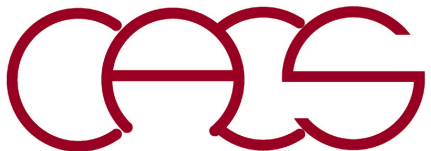*Department of Computer Science*
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How to incorporate many-electron correlations into effective single-electron (Kohn-Sham) equations?

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

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

Vacuum

with the Hamiltonian operator

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

$$\langle m|h|n\rangle = \int d\mathbf{r}\,\psi_m^*(\mathbf{r})h(\mathbf{r})\,\psi_n(\mathbf{r})$$

$$\langle mn|u|pq\rangle = \int d\mathbf{r}\,d\mathbf{r}'\,\psi_m^*(\mathbf{r})\psi_n^*(\mathbf{r}')u(\mathbf{r},\mathbf{r}')\psi_p(\mathbf{r})\psi_q(\mathbf{r}') = [m^*p|u|n^*q]$$

Physicist's notation   Chemist's notation

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

$$\begin{cases} \{\hat{a}_\kappa, \hat{a}_{\kappa'}^\dagger\} = \delta_{\kappa,\kappa'} \\ \{\hat{a}_\kappa, \hat{a}_{\kappa'}\} = \{\hat{a}_\kappa^\dagger, \hat{a}_{\kappa'}^\dagger\} = 0 \end{cases}$$

Preliminary: Second Quantization (3)

- **Hamiltonian operator in the coordinate representation**

$$\widehat{H} = \widehat{T} + \widehat{V} + \widehat{U}$$

$$\widehat{T} = \frac{\hbar^2}{2m} \int d\mathbf{r} \nabla \widehat{\psi}^\dagger(\mathbf{r}) \bullet \nabla \widehat{\psi}(\mathbf{r})$$

$$\widehat{V} = \int d\mathbf{r} \widehat{\psi}^\dagger(\mathbf{r}) v(\mathbf{r}) \widehat{\psi}(\mathbf{r}) = \int d\mathbf{r} \widehat{\rho}(\mathbf{r}) v(\mathbf{r})$$

$$\widehat{U} = \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \widehat{\psi}^\dagger(\mathbf{r}) \widehat{\psi}^\dagger(\mathbf{r}') \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \widehat{\psi}(\mathbf{r}') \widehat{\psi}(\mathbf{r})$$

- **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

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

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

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

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

- **See note on** Hartree-Fock approximation

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

Energy Functional

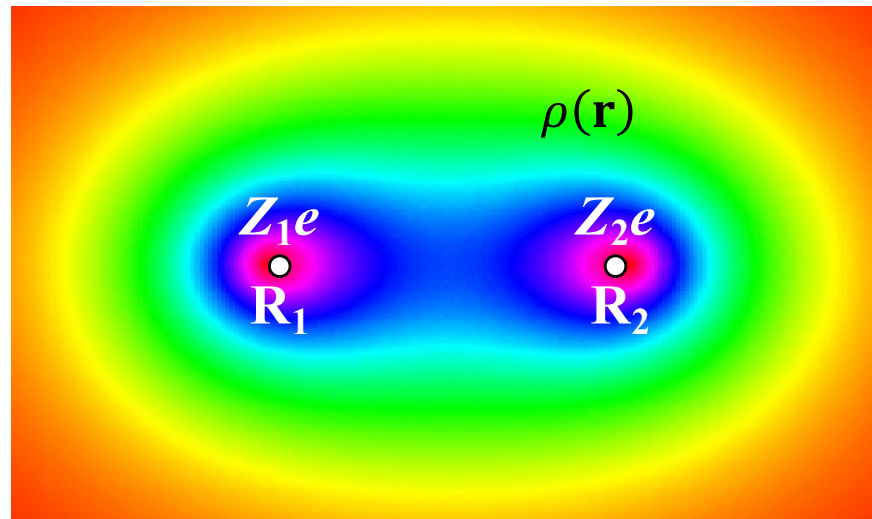**Exchange-correlation (xc) functional *via* Kohn-Sham decomposition**

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

Kinetic energy of non-interacting electrons

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

Exchange-correlation energy

External potential

Electron-Electron Interaction Energy

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

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

Two-body density matrix   Creation operator   Annihilation operator $e = \hbar = 1$

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

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

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

One-body density matrix

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

- **See note on** second quantization

Electron Correlation *vs.* Density Response

- **Information on two-body correlation is encoded in the density response function χ through fluctuation-dissipation theorem; see note on** time-dependent perturbation
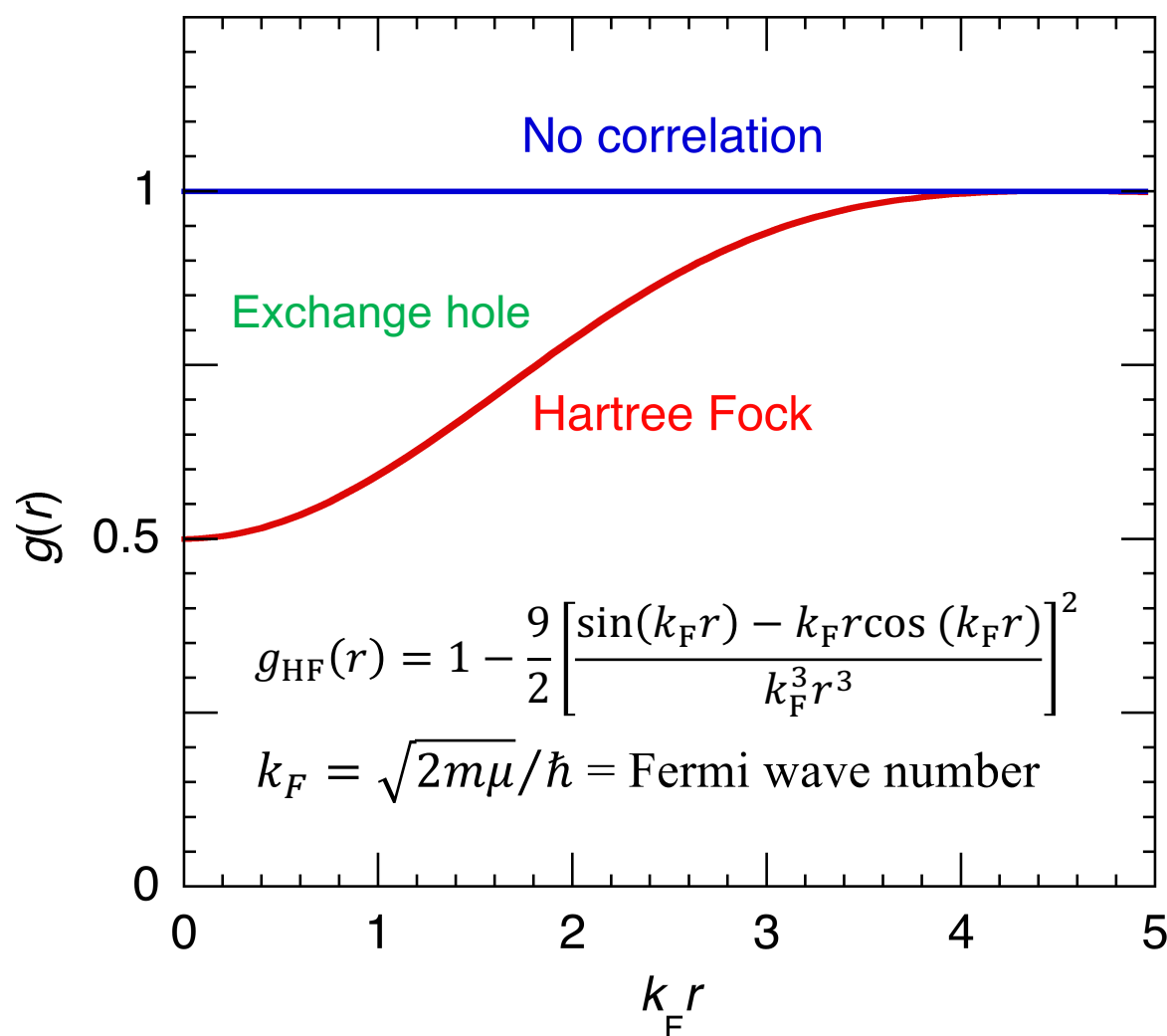
$$\widehat{H}_{\text{tot}} = \widehat{H} + \widehat{V}(t)$$

$$
\begin{cases}
\widehat{H} = \widehat{T} + \widehat{U} = \dfrac{\hbar^2}{2m} \int d\mathbf{r} \nabla \widehat{\psi}^\dagger(\mathbf{r}) \bullet \nabla \widehat{\psi}(\mathbf{r}) + \dfrac{1}{2} \int d\mathbf{r} d\mathbf{r}' \widehat{\psi}^\dagger(\mathbf{r}) \widehat{\psi}^\dagger(\mathbf{r}') \dfrac{e^2}{|\mathbf{r} - \mathbf{r}'|} \widehat{\psi}(\mathbf{r}') \widehat{\psi}(\mathbf{r}) \\[2em]
\widehat{V}(t) = \displaystyle\int d\mathbf{r} \widehat{\psi}^\dagger(\mathbf{r}) v(\mathbf{r}, t) \widehat{\psi}(\mathbf{r}) = \int d\mathbf{r} \widehat{\rho}(\mathbf{r}) v(\mathbf{r}, t)
\end{cases}
$$

$$\chi(\mathbf{r} - \mathbf{r}', t - t') \equiv \frac{\delta \langle \widehat{\rho}(\mathbf{r}, t) \rangle}{\delta v(\mathbf{r}', t')}$$

$$= -\frac{i}{\hbar} \Theta(t - t') \langle \Psi_0 | [\widehat{\rho}_{\text{H}}(\mathbf{r}, t), \widehat{\rho}_{\text{H}}(\mathbf{r}', t')] | \Psi_0 \rangle$$

$$= -\frac{i}{\hbar} \Theta(t - t') \langle \Psi_0 | [\widehat{\psi}_{\text{H}}^\dagger(\mathbf{r}, t) \widehat{\psi}_{\text{H}}(\mathbf{r}, t), \widehat{\psi}_{\text{H}}^\dagger(\mathbf{r}', t') \widehat{\psi}_{\text{H}}(\mathbf{r}', t')] | \Psi_0 \rangle$$

- **Equation-of-motion & functional derivative to derive approximate χ; 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** μ
- $g(r)$ **is analytically calculated for homogeneous electron gas with HF**

$$g_{HF}(r) = 1 - \frac{9}{2}\left[\frac{\sin(k_F r) - k_F r\cos(k_F r)}{k_F^3 r^3}\right]^2$$

$$k_F = \sqrt{2m\mu}/\hbar = \text{Fermi wave number}$$
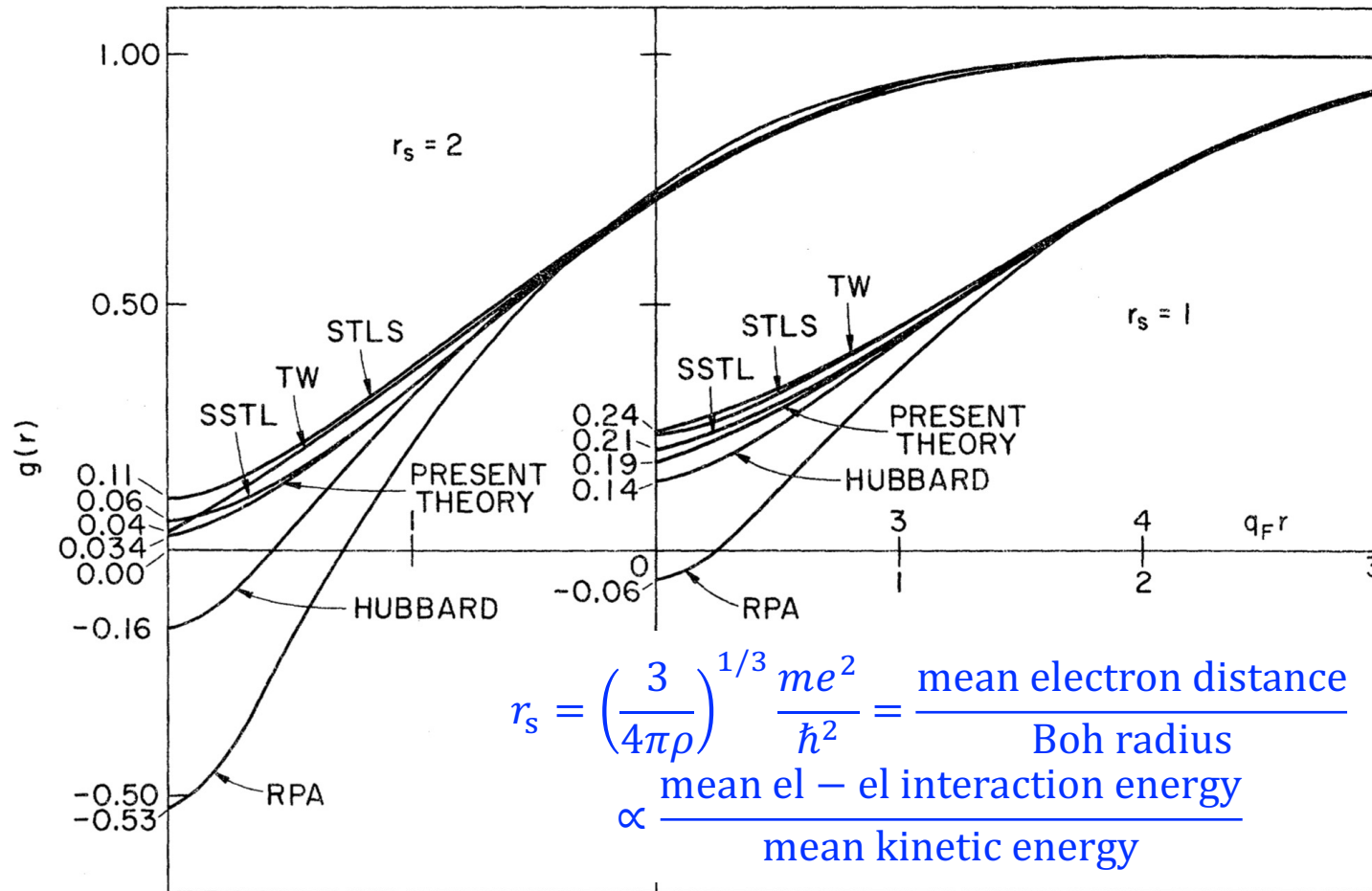
- $g_{HF}(r)$ **represents Pauli exclusion principle between same-spin electrons embodied in the antisymmetric Slater determinant**

- **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**

$$r_s = \left(\frac{3}{4\pi\rho}\right)^{1/3}\frac{me^2}{\hbar^2} = \frac{\text{mean electron distance}}{\text{Boh radius}}$$

$$\propto \frac{\text{mean el} - \text{el interaction energy}}{\text{mean kinetic energy}}$$

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**

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

potential energy due to electron-electron interaction

Hartree (mean-field) potential

exchange-correlation potential

- **Some commonly used exchange-correlation functionals**

> **LDA (local density approximation):** $E_{\mathrm{xc}} = \int d\mathbf{r}\, \rho(\mathbf{r}) \epsilon_{xc}(\rho(\mathbf{r}))$

> **LSDA (local spin density approximation):** $\epsilon_{xc}(\rho_\uparrow(\mathbf{r}), \rho_\downarrow(\mathbf{r}))$

> **GGA (generalized gradient approximation):** $\epsilon_{xc}(\rho(\mathbf{r}), |\nabla \rho(\mathbf{r})|)$
> **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

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
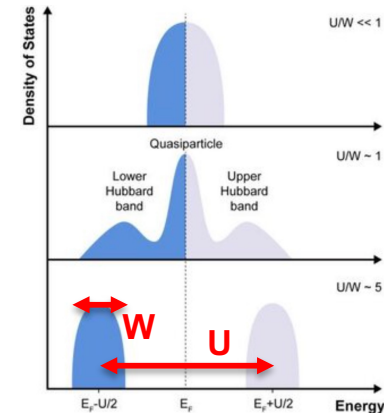
Other Exchange-Correlation Functionals

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

  > **LDA+U method for transition metals**

  Occupation of *i*-th orbital

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

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

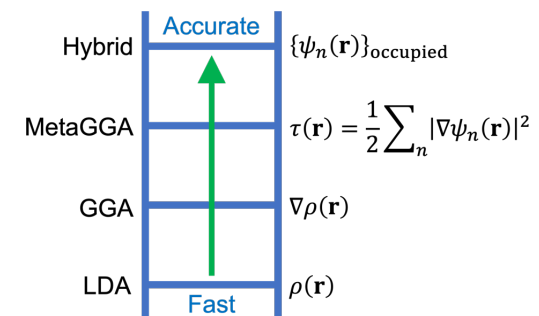 > **DFT-D: van der Waals (vDW) functional for molecular crystals & layered materials**

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

  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)
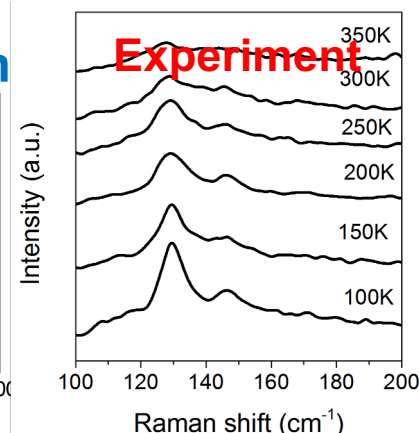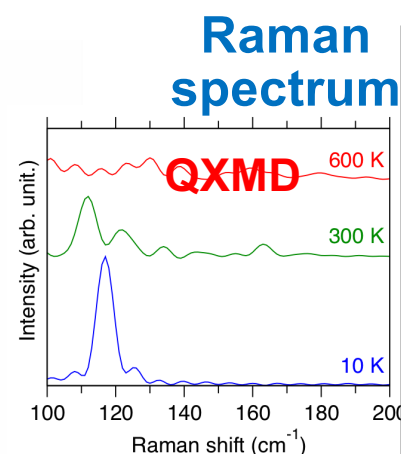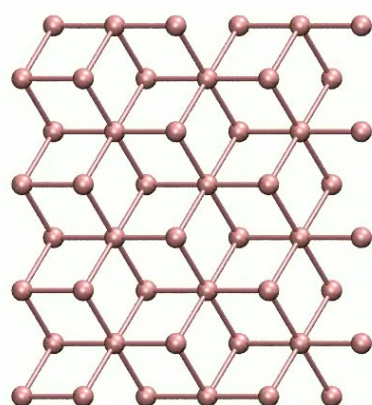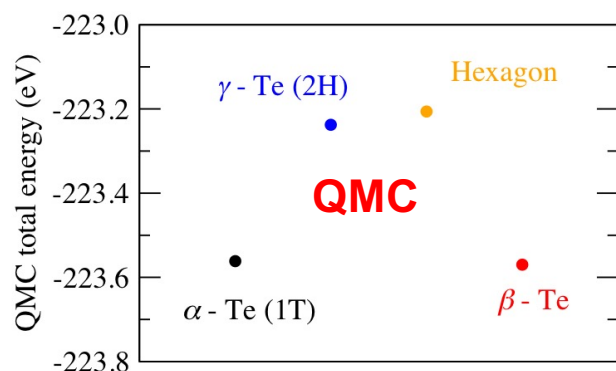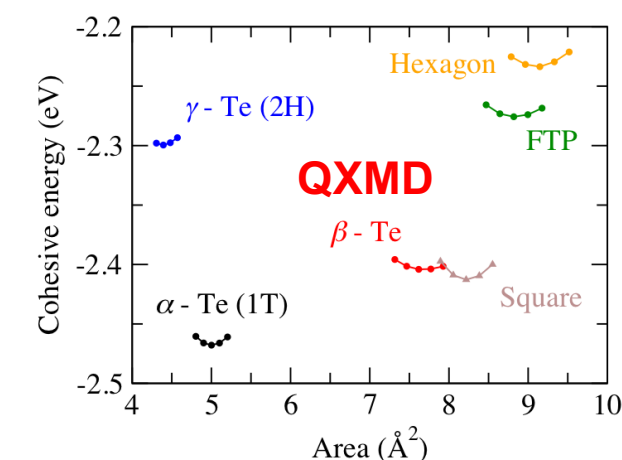
	a (Å)	*B* (N/m)
GGA	4.26	23.2138
GGA-D	4.17	28.6845
Spin GGA	4.26	22.1372
Hybrid HSE	-	23.8448
Hybrid HSE with GGA-D	-	29.7649

a: Lattice constant
B: Bulk modulus

Casino QMC (https://vallico.net/casinoqmc)

Band-Gap Problem

- **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**

  Janak, *Phys. Rev. B* **18**, 7165 ('78)

- **Band gap, E_{gap} = IP – EA, is usually underestimated with GGA-type exchange-correlation (xc) functional**

- **This is partly due to self interaction: Note the Hartree potential $v_{\text{H}}(r) = \int d\mathbf{r}' \, e^2 \rho(\mathbf{r}')/|\mathbf{r} - \mathbf{r}'|$ 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, $v_{\text{H},n\sigma}(r) = \int d\mathbf{r}' \, e^2 [\rho(\mathbf{r}') - |\psi_{n\sigma}{}^2|]/|\mathbf{r} - \mathbf{r}'|$, 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

- **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)

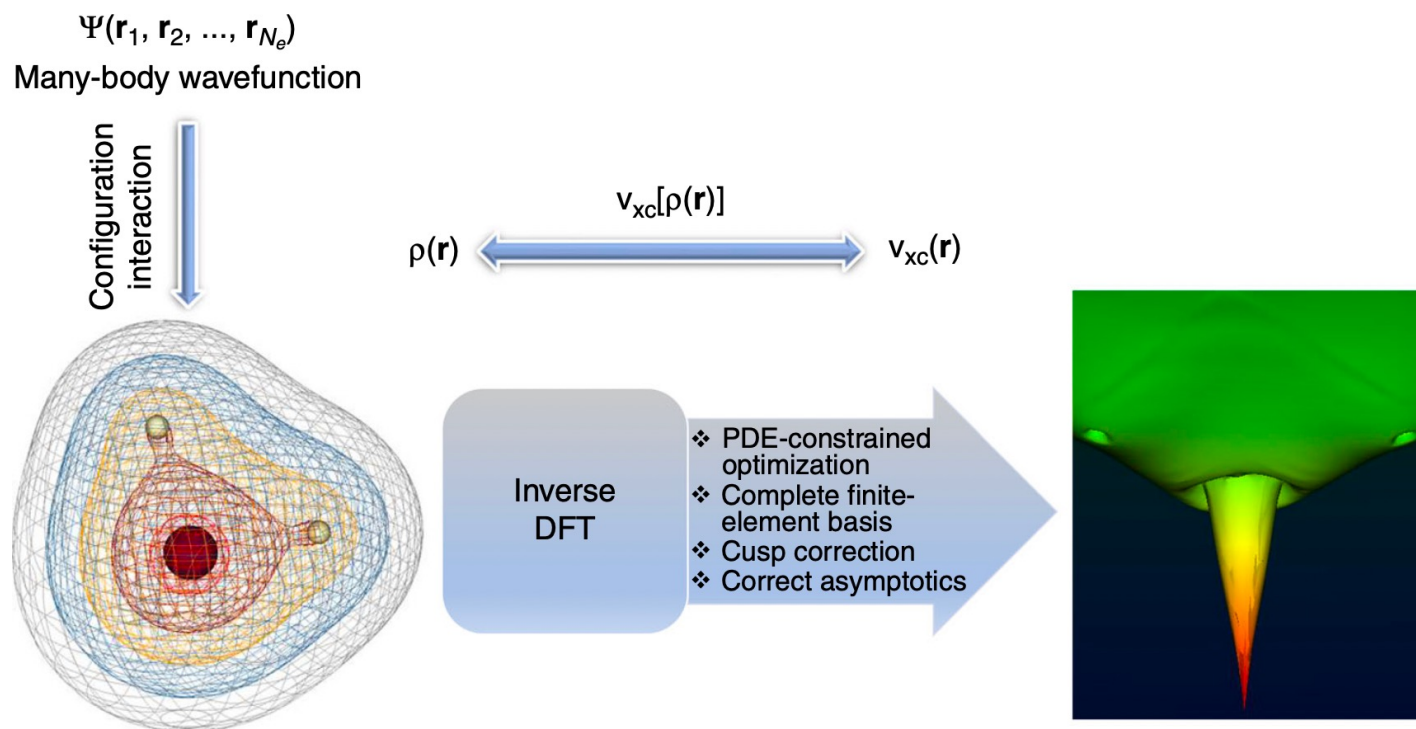- **Range-separated hybrid exact-exchange mixes HF & other xc functional at different distance**

  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

$\Psi(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_{N_e})$
Many-body wavefunction

Configuration interaction

$v_{xc}[\rho(\mathbf{r})]$

$\rho(\mathbf{r})$ ⟷ $v_{xc}(\mathbf{r})$

Inverse DFT

- ❖ PDE-constrained optimization
- ❖ Complete finite-element basis
- ❖ Cusp correction
- ❖ Correct asymptotics

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)]