Exchange-Correlation Functional

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

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

Vacuum

with the Hamiltonian operator

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

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

Physicist's notation

Chemist's notation

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

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

Preliminary: Second Quantization (3)

- **Hamiltonian operator in the coordinate representation**

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

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

- **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**

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

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

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

Fock operator

$$\left\{ \begin{aligned} J_j(\mathbf{r})\phi(\mathbf{r}) &= \int d\mathbf{r}' \frac{e^2}{|\mathbf{r}-\mathbf{r}'|} \phi_j^*(\mathbf{r}')\phi_j(\mathbf{r}')\phi(\mathbf{r}) \\ K_j(\mathbf{r})\phi(\mathbf{r}) &= \int d\mathbf{r}' \frac{e^2}{|\mathbf{r}-\mathbf{r}'|} \phi_j^*(\mathbf{r}')\,\phi(\mathbf{r}')\phi_j(\mathbf{r}) \end{aligned} \right.$$

- **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

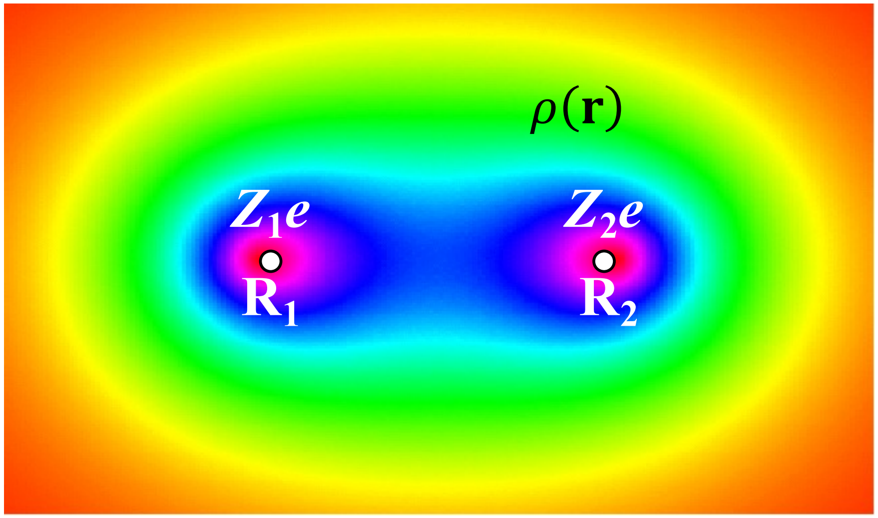
$$E[\rho(\mathbf{r})] = T_s[\rho(\mathbf{r})] + \int d\mathbf{r}\, v(\mathbf{r})\rho(\mathbf{r}) + \frac{1}{2}\int d\mathbf{r}\, d\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + E_{xc}[\rho(\mathbf{r})]$$

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

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

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

Two-body density matrix

Creation operator

Annihilation operator

$e = \hbar = 1$

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

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

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

One-body density matrix

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

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

- **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

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

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

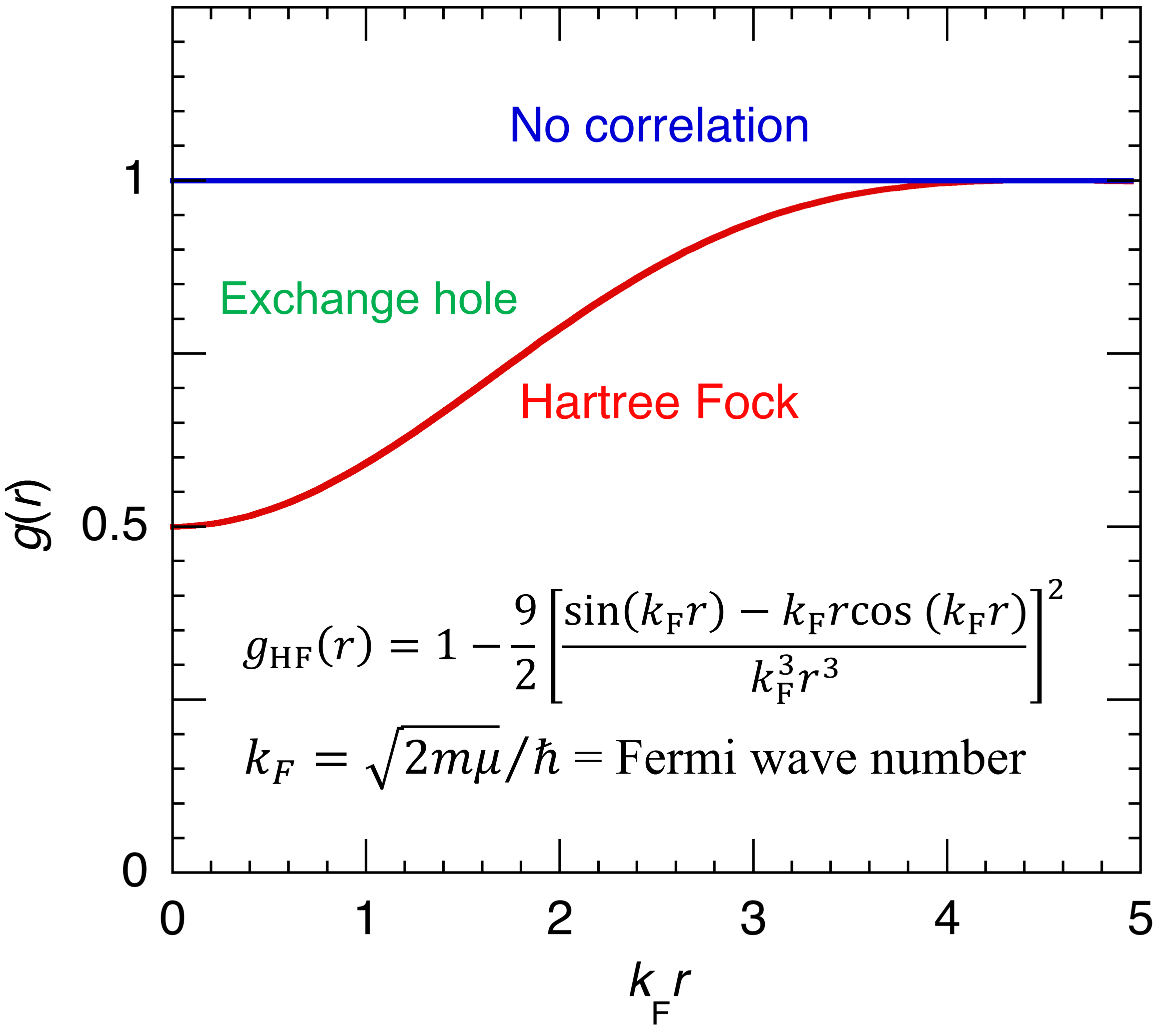
$$\begin{aligned} \chi(\mathbf{r}-\mathbf{r}', t-t') &\equiv \frac{\delta\langle\hat{\rho}(\mathbf{r},t)\rangle}{\delta v(\mathbf{r}',t')} \\ &= -\frac{i}{\hbar}\Theta(t-t')\langle\Psi_0|[\hat{\rho}_{\mathrm{H}}(\mathbf{r},t),\hat{\rho}_{\mathrm{H}}(\mathbf{r}',t')]|\Psi_0\rangle \\ &= -\frac{i}{\hbar}\Theta(t-t')\left\langle\Psi_0\left|\left[\hat{\psi}_{\mathrm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

$[A,B] \equiv AB - BA$

- **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**



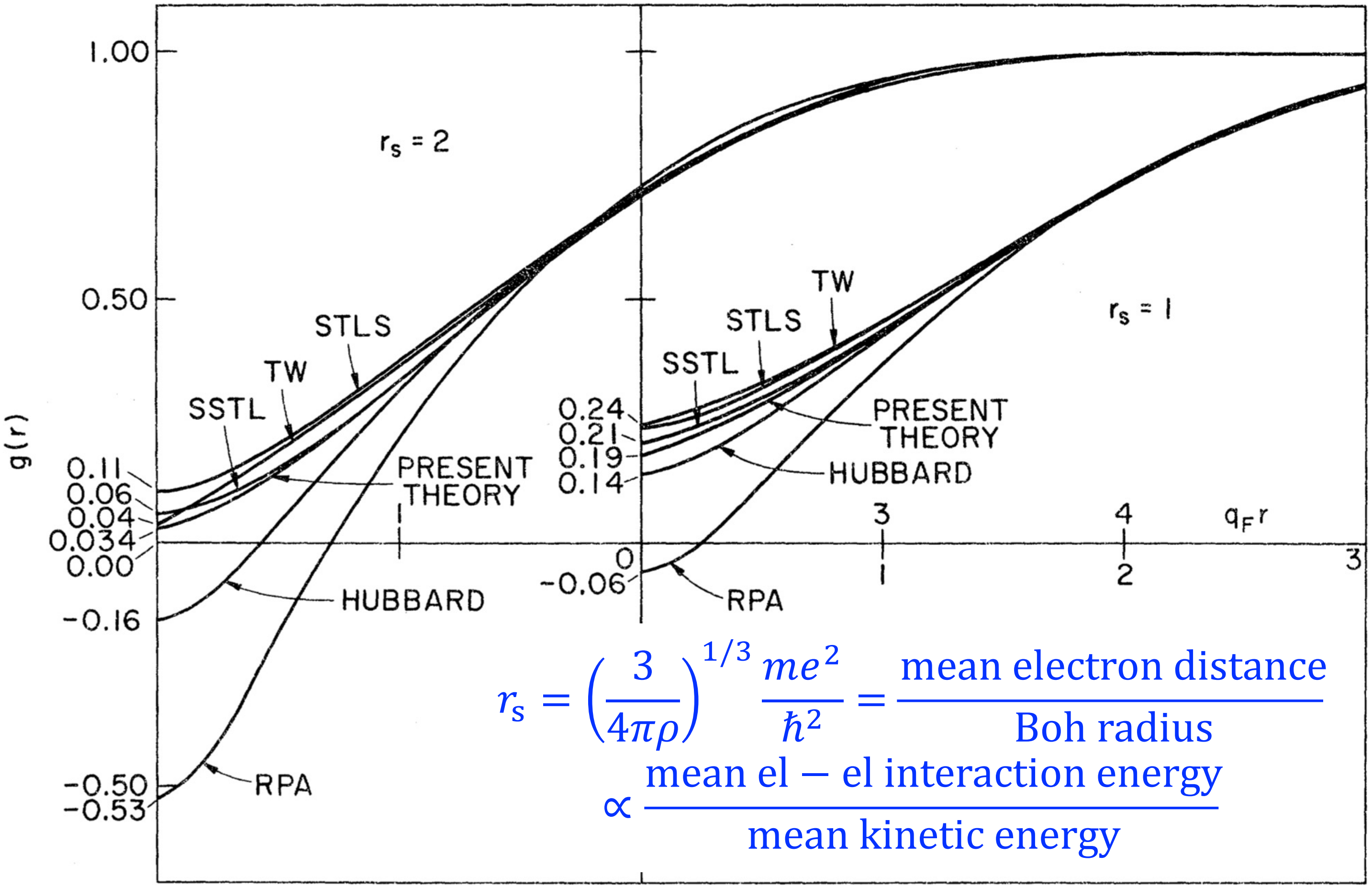
$$g_{\mathrm{HF}}(r) = 1 - \frac{9}{2}\left[\frac{\sin(k_{\mathrm{F}}r) - k_{\mathrm{F}}r\cos(k_{\mathrm{F}}r)}{k_{\mathrm{F}}^3 r^3}\right]^2$$

$k_F = \sqrt{2m\mu}/\hbar$ = Fermi wave number

- **$g_{\mathrm{HF}}(r)$ 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**

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

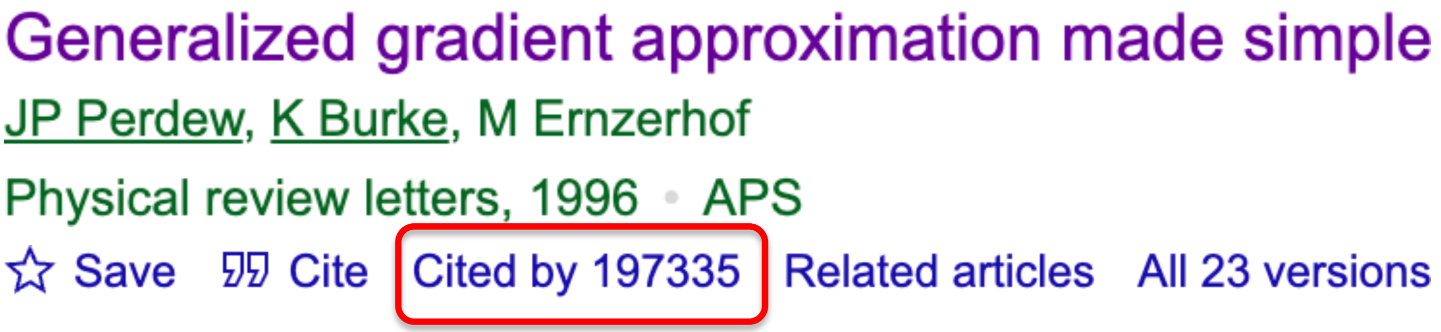
potential energy
due to electron-electron
interaction

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**
    $\tau_\sigma(\mathbf{r}) = \frac{1}{2}\sum_{n\in\{\mathrm{occupied}\}} |\nabla\psi_{n\sigma}(\mathbf{r})|^2$
    SCAN: Sun, Ruzsinszky & Perdew, *Phys. Rev. Lett*. **115**, 036402 ('15)

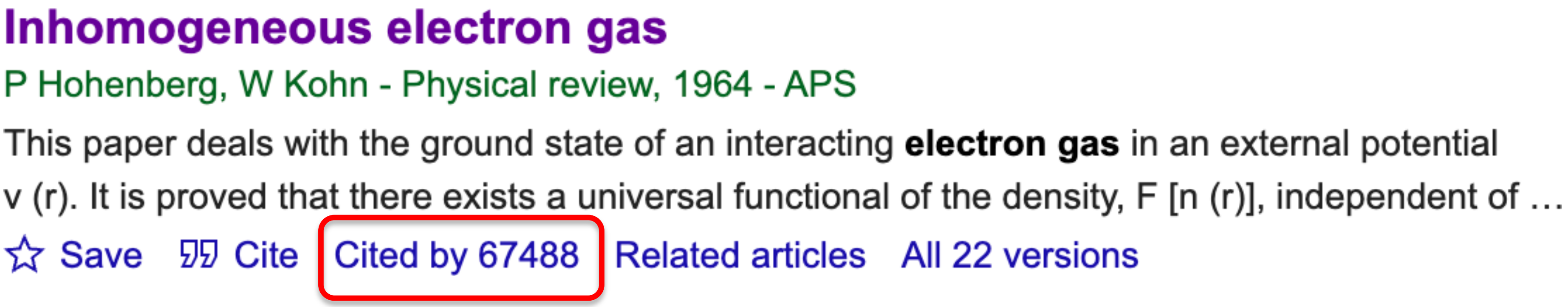
HK *vs.* PBE



Generalized gradient approximation made simple

JP Perdew, K Burke, M Ernzerhof

Physical review letters, 1996 • APS



Inhomogeneous electron gas

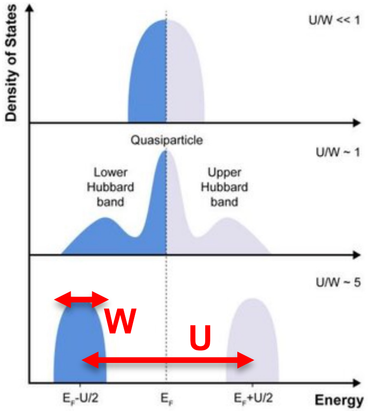
P Hohenberg, W Kohn - Physical review, 1964 - APS

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 …

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

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

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

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

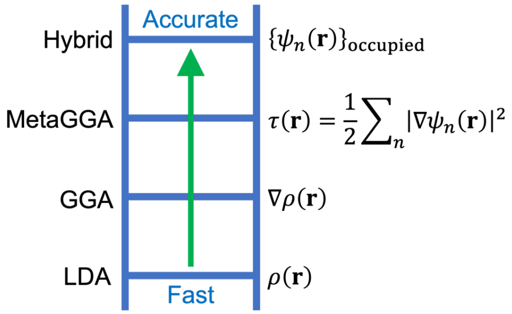
$$E_{\mathrm{disp}} = -s_6 \sum_{i<j} \frac{C_{ij}}{R_{ij}^6} f_{\mathrm{damp}}\,(R_{ij})$$

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

> **Nonlocal correlation functional**

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

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



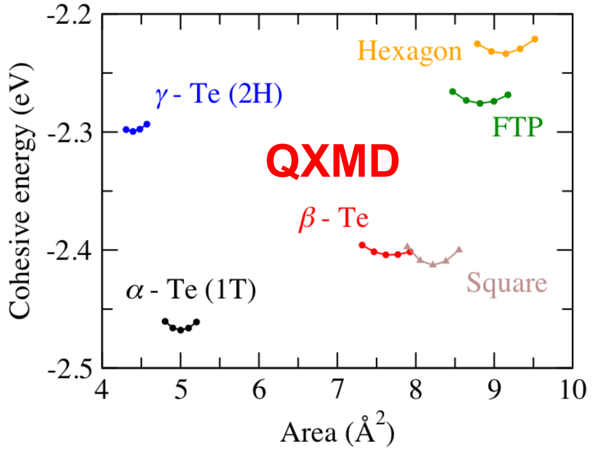
For comparison of DFT-D & nonlocal correlation functionals, see

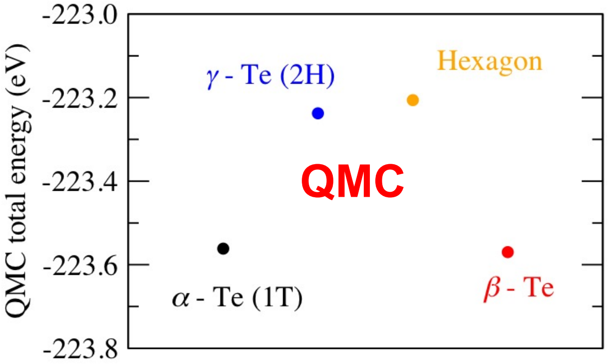
Shimojo *et al*., *J. Chem. Phys*. **132**, 094106 ('10)

Validation of XC Functional

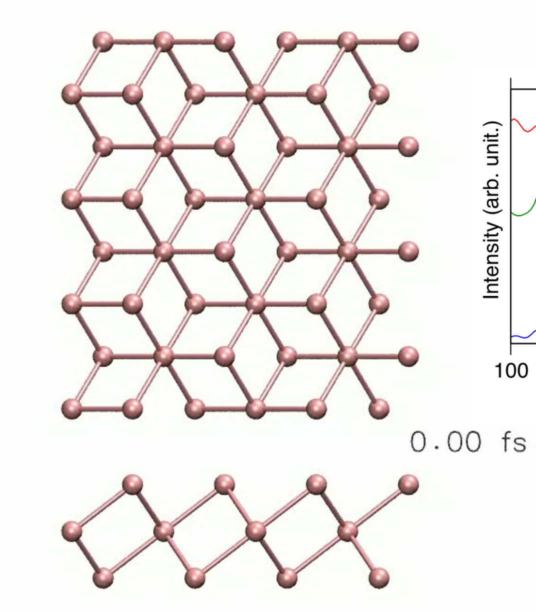
- **Comparison with high accuracy methods, such as quantum Monte Carlo (QMC), high-accuracy quantum chemistry, & experimental data**
- **Sensitivity analysis among different exchange-correlation (xc) functionals**
- **Consistency of the obtained result with the level of approximation**

Example: Atomically thin tellurium (tellurene)

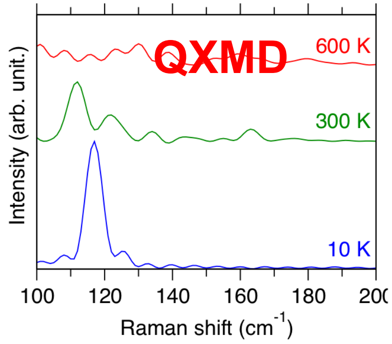


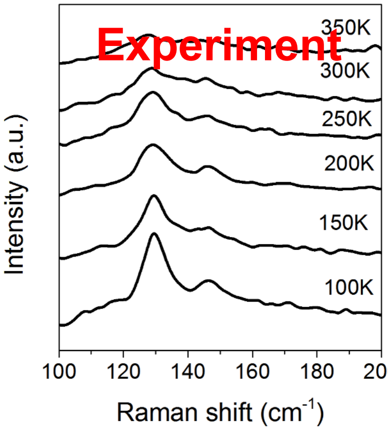


Casino QMC (https://vallico.net/casinoqmc)



Raman spectrum





	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

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 $v_{\mathrm{H}}(\boldsymbol{r}) = \int d\mathbf{r}'\, e^2\rho(\mathbf{r}')/|\mathbf{r}-\mathbf{r}'|$ 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, $v_{\mathrm{H},n\sigma}(\boldsymbol{r}) = \int d\mathbf{r}'\, e^2[\rho(\mathbf{r}') - |\psi_{n\sigma}{}^2|]/|\mathbf{r}-\mathbf{r}'|$, 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**

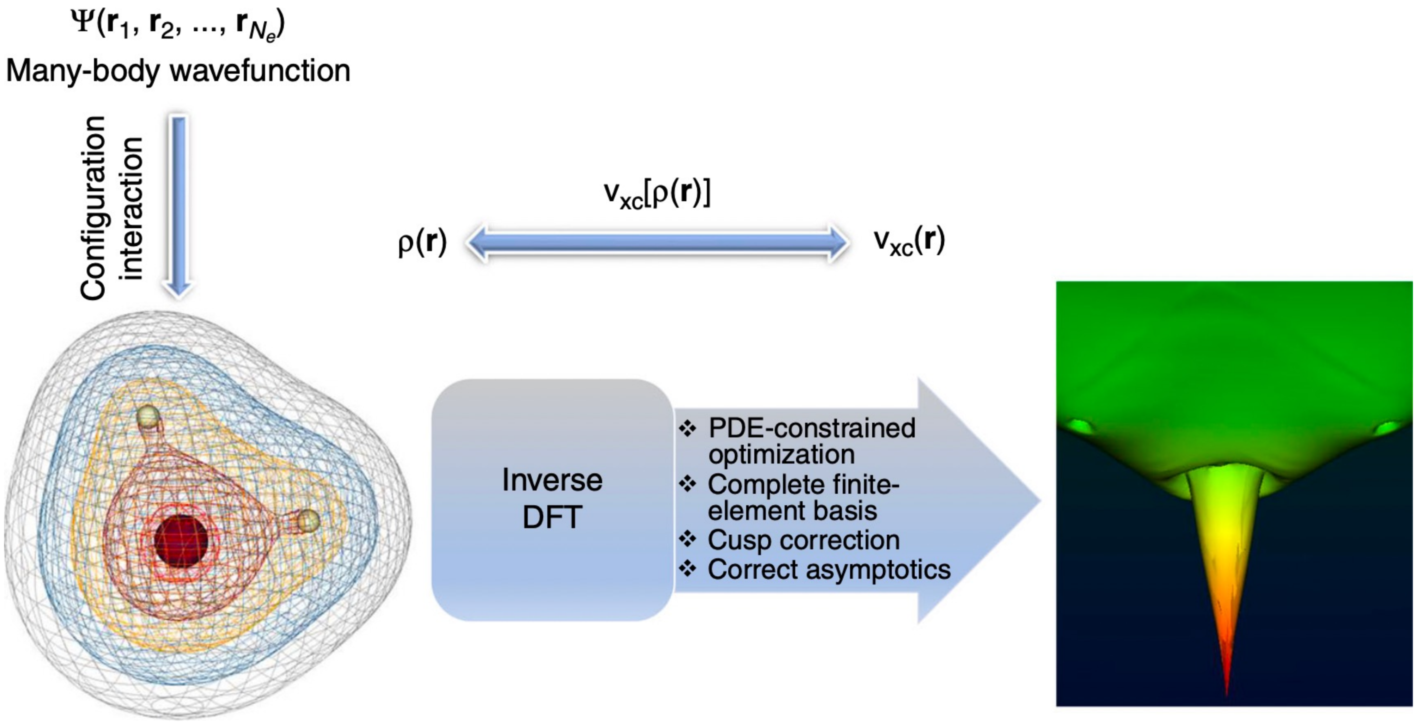
  HSE: Heyd, Scuseria & Ernzerhof, *J. Chem. Phys*. **118**, 8207 ('03)

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**



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)]