



**Short Course on Density Functional Theory
and Applications**

**IX. Brief Mentions: GW Method,
Kinetic Energy Density Functionals**

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GW Method for Excitations

Strictly, the **GW** method is not a part of DFT. As generally formulated and practiced, however, GW is a practical realization of the relatively little-noticed third Hohenberg-Kohn-Sham theorem. It is this. The one-particle QM Green's function is a unique functional of the density alone which attains the correct physical one-particle spectrum at the ground state density n_0 . [L.J. Sham and W. Kohn, Phys. Rev. 145, 561 (1966)]

Brief reminder: For a system of a finite number of electrons, the electron ionization energies and electron affinities are found most generally from the one-electron QM Green's function or propagator. The basic structure is

$$G(\mathbf{x}, t; \mathbf{x}', t') = \langle 0 | \mathcal{T} \{ \hat{\Psi}(\mathbf{x}, t) \hat{\Psi}^\dagger(\mathbf{x}', t') \} | 0 \rangle$$

\mathcal{T} = time ordering operator; $\hat{\Psi}(\mathbf{x}, t)$ = electron creation operator

$$\hat{\Psi}(\mathbf{x}, t) = e^{i\hat{H}t} \hat{\Psi}(\mathbf{x}) e^{-i\hat{H}t}; \quad \hat{\Psi}(\mathbf{x}) = \sum_j \varphi_j(\mathbf{x}) \hat{a}_j$$

$$[\hat{a}_i^\dagger, \hat{a}_j]_+ = \delta_{ij}; \quad [\hat{a}_i^\dagger, \hat{a}_j^\dagger]_+ = [\hat{a}_i, \hat{a}_j]_+ = 0$$

$\{\varphi_j(\mathbf{x})\}$ = complete 1-electron basis set

$$\Rightarrow G(\mathbf{x}, t; \mathbf{x}', t') = \sum_{ij} g_{ij}(t, t') \langle 0 | \hat{a}_i \hat{a}_j^\dagger | 0 \rangle$$

A sum of ground state expectation values.

GW (cont'd.) - Photoelectron Excitation and Quasi-particle states

Consider

$|N_e\rangle := N_e$ particle ground state with total energy $E(N_e)$

$|N_e - 1, j\rangle := N_e - 1$ particle excited state "j"

$E(N_e - 1, j)$ = total energy for excited state "j"

Electron removal Dyson orbitals and energies (photoemission):

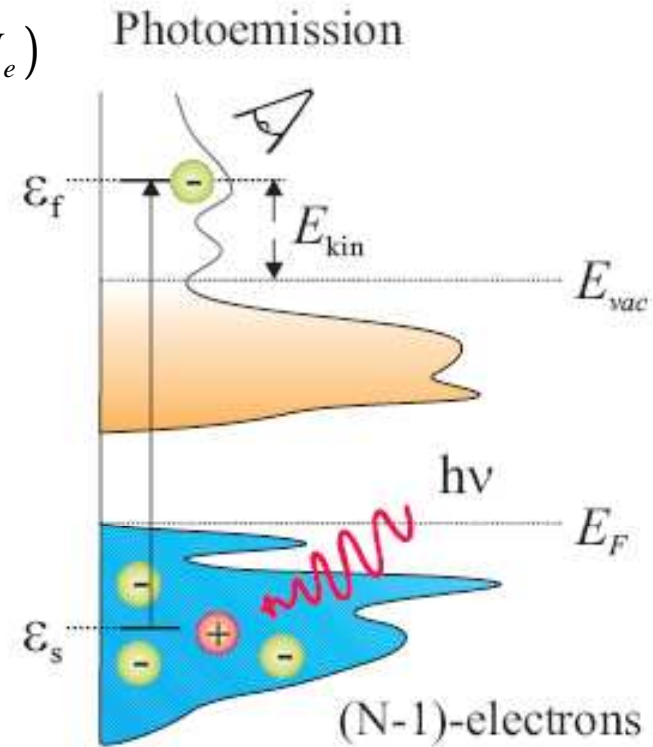
$$\chi_j[\mathbf{x}] = \langle N_e - 1, j | \hat{\Psi}(\mathbf{x}) | N_e \rangle$$

$$\varepsilon_j = E(N_e) - E(N_e - 1, j)$$

Electron addition Dyson orbitals and energies (inverse photoemission):

$$\chi_j[\mathbf{x}] = \langle N_e, j | \hat{\Psi}(\mathbf{x}) | N_e + 1 \rangle$$

$$\varepsilon_j = E(N_e + 1) - E(N_e, j)$$



Credit: Patrick Rinke.

GW (cont'd.) -

The Dyson orbitals obey the one-body equation

$$[-\frac{1}{2}\nabla^2 + V_H(\mathbf{r}) + V_{ext}(\mathbf{r})]\chi_j[\mathcal{E}, \mathbf{x}] + \int d\mathbf{x}'\Sigma[\mathbf{x}, \mathbf{x}', \mathcal{E}]\chi_j[\mathcal{E}, \mathbf{x}'] = \varepsilon_j\chi_j[\mathcal{E}, \mathbf{x}]$$

which requires self-consistency in the energy $\mathcal{E}=\varepsilon_j$. The self-energy operator Σ is defined in terms of the Green's function

$$[\mathcal{E} + \frac{1}{2}\nabla^2 - V_H(\mathbf{r}) - V_{ext}(\mathbf{r})]G[\mathbf{x}, \mathbf{x}', \mathcal{E}] - \int d\mathbf{z}\Sigma[\mathbf{x}, \mathbf{z}, \mathcal{E}]G[\mathbf{z}, \mathbf{x}', \mathcal{E}] = \delta(\mathbf{x} - \mathbf{x}')$$

The self-energy operator takes account of the energy response of the electron population that the quasi-particle experiences due to its own presence in that population.

Casida [Phys. Rev. A 51, 2005-13 (1995)] has proved that, in a certain well-defined sense (Klein's energy minimization principle), the KS potential is the best *local approximation* to the non-local self-energy operator Σ .

High precision numerical studies of exact KS eigenvalue differences for simple systems are consistent with this interpretation. [C.J. Umrigar, A. Savin, and X. Gonze in *Electronic Density Functional Theory: Recent Progress and New Directions* J.F. Dobson, G. Vignale, and M.P. Das eds. (Plenum, 1998), pp 167-76].

GW (cont'd.) -

Solution of the Dyson equation involves a nest of equations, written here in a common short hand $\mathbf{x}_1\mathbf{t}_1 \rightarrow \mathbf{1}$, and with some carelessness about time-ordering

$$W(\mathbf{12}) = \int d\mathbf{3}g(\mathbf{13})\epsilon^{-1}(\mathbf{32}) \quad \text{Screened Coulomb interaction}$$

$$\epsilon(\mathbf{12}) = \delta(\mathbf{12}) - \int d\mathbf{3}g(\mathbf{13})\mathcal{P}(\mathbf{32}) \quad \text{Microscopic dielectric function}$$

$$\mathcal{P}(\mathbf{12}) = -i \int d\mathbf{3}d\mathbf{4}G(\mathbf{23})G(\mathbf{42})\Gamma(\mathbf{34};\mathbf{1}) \quad \text{Irreducible polarization}$$

$$\Gamma(\mathbf{12};\mathbf{3}) = \delta(\mathbf{12})\delta(\mathbf{13}) + \int d\mathbf{4}d\mathbf{5}d\mathbf{6}d\mathbf{7} \frac{\delta\Sigma(\mathbf{12})}{\delta G(\mathbf{45})} G(\mathbf{46})G(\mathbf{75})\Gamma(\mathbf{67};\mathbf{3}) \quad \text{Vertex function}$$

$$\Sigma(\mathbf{12}) = i \int d\mathbf{3}d\mathbf{4}W(\mathbf{13})G(\mathbf{14})\Gamma(\mathbf{42};\mathbf{3}) \quad \text{Self-energy operator}$$

The GW approximation is $\Gamma(\mathbf{34};\mathbf{1}) \approx \delta(\mathbf{34})\delta(\mathbf{31})$

which simplifies the equations to

$$\Sigma(\mathbf{12}) \approx iG(\mathbf{12})W(\mathbf{12})$$

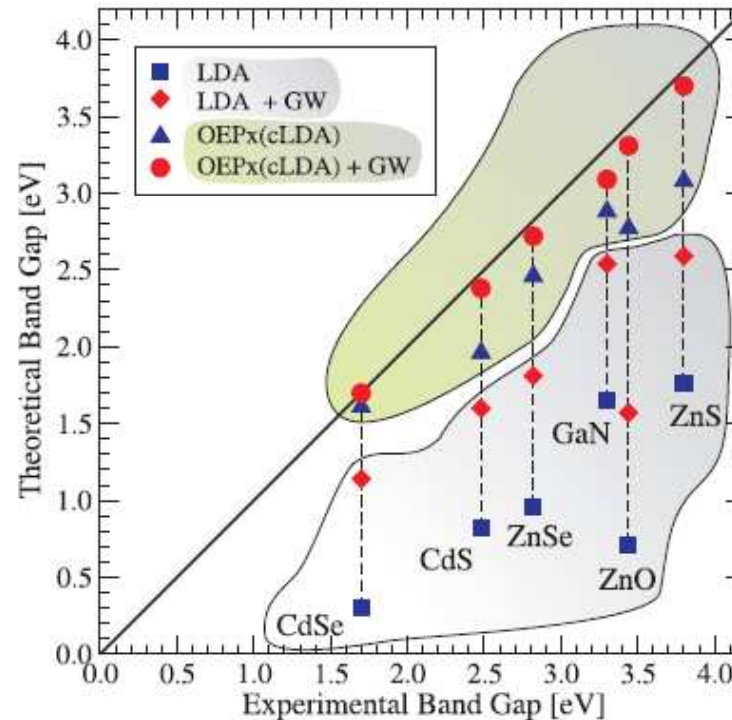
$$\mathcal{P}(\mathbf{12}) \approx -iG(\mathbf{21})G(\mathbf{12})$$

$$W(\mathbf{12}) = \int d\mathbf{3}g(\mathbf{13})\epsilon^{-1}(\mathbf{32})$$

$$\epsilon(\mathbf{12}) \approx \delta(\mathbf{12}) + i \int d\mathbf{3}g(\mathbf{13})G(\mathbf{32})G(\mathbf{23})$$

GW (cont'd.) -

Even with the GW simplification, solution of the Dyson equation is a demanding problem. Often models of the dielectric function are used, non-iterative solutions are done, etc. The connection with DFT is that the orbitals and eigenvalues of a DFT calculation often (almost always) are used as the starting approximations. Especially when combined with OPE X, the results are very good for semiconductor band gaps [P. Rinke et al. New J. Phys. 7, 126 (2005)]:



GW (cont'd.) -

Basic references in GW:

1. **L. Hedin and H. Lundqvist, Solid State Phys. 23, 1 (1969)**
2. **F. Aryasetiawan and O. Gunnarsson, Rep. Prog. Phys. 61, 237 (1998)**
3. **W.G. Aulbur, L. Jönsson, and J.W. Wilkins, Solid State Phys. 54, 1 (2000)**
4. **G. Onida, L. Reining, and A. Rubio, Rev. Mod. Phys. 74, 601 (2002)**

Molecular Dynamics and the Born-Oppenheimer Potential Energy Surface

As remarked at the end of Lect. VII, Molecular Dynamics (MD) is at the heart of much of materials physics and biomolecular simulation. At base, it is just Newton's 2nd Principle.

$$m_I \ddot{\mathbf{R}}_I = -\vec{\nabla}_I V_{inter-particle}(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_N)$$

$V_{inter-particle}(\{\mathbf{R}\})$ is the potential energy for all “particle” coordinates.

A “particle” is a fixed, rigid object that can be identified with a point location. For simplicity, just think of point nuclei.

In principle, the inter-particle potential is the Born-Oppenheimer energy surface

$$V_{inter-particle}(\{\mathbf{R}\}) = E_0(\{\mathbf{R}\}) + E_{NN}(\{\mathbf{R}\})$$

where $E_0(\{\mathbf{R}\})$ is the ground state *electronic* total energy and E_{NN} is the nuclear-nuclear repulsion.

In practice $V_{inter-particle}(\{\mathbf{R}\})$ often is represented by parameterization of a classical potential function to some set QM calculations or by an empirically calibrated “force field”. For bond-breaking, fracture, etc. this is not good enough. The real B-O surface is needed.

B-O Forces from DFT

- The KS eigenvalue form of the DFT ground state energy illustrates the computational barrier to using ordinary KS DFT to provide the B-O forces (“gradients” in quantum chemistry jargon) at every MD step:

$$E_0(\{\mathbf{R}\}) = \sum_k \varepsilon_k - \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + E_{xc}[n] - \int d\mathbf{r} [n(\mathbf{r})v_{xc}(\mathbf{r})]$$

$$n(\mathbf{r}) = \sum_k n_k |\phi_k(\mathbf{r})|^2$$

$$\hat{h}^{KS} \phi_k(\mathbf{r}) = \varepsilon_k \phi_k(\mathbf{r}); \quad \hat{h} = -\frac{1}{2} \nabla^2 + v_{KS}(\mathbf{r}); \quad v_{KS}(\mathbf{r}) = v_{ext}(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc}(\mathbf{r})$$

This eigenvalue approach is slow. There are “order- N ” approximate methods but they introduce additional assumptions (e.g. about basis locality, etc.).

Challenge: to get the content of KS DFT *without* doing the KS eigenvalue problem, yet accurately enough to do physics and chemistry studies on realistically available computer clusters.

Orbital-free DFT: Motivation

- ◇ Most DFT methods, even so-called order- N , are focused on determining the Kohn-Sham orbitals in a basis.
- ◇ But in DFT, $E[n]$ is **fundamental**, the eigenvalues $\epsilon_j[\phi_{\text{K-S}}[n]]$ are **not**.

The KS construction does a very good thing. It separates the KE into a tractable part T_S and a remainder which goes into E_{xc} , recall II-6:

$$E_{v_{ext}}[n] = T_S[n] + E_{ee}[n] + E_{xc}[n] + E_{ext}[n]$$

$$T_S[n] := -\frac{1}{2} \sum_j n_j \int d\mathbf{r} \varphi_j(\mathbf{r}) \nabla^2 \varphi_j(\mathbf{r})$$

Unfortunately, KS also introduces an **orbital eigenvalue problem** to calculate T_S . This is a computational bottleneck. What we need instead is an **explicit density functional** for the KS KE:

$$T_S[n] = -\frac{1}{2} \sum_i n_i \int d\mathbf{r} \varphi_i^*(\mathbf{r}) \nabla^2 \varphi_i(\mathbf{r}) \equiv \int d\mathbf{r} t_S[n(\mathbf{r})]$$

Orbital-free DFT: General Structure

Were we to have the K-S KE density kernel, and a good density-dependent (NOT orbitally dependent) E_{XC} , then DFT B-O forces would be simple:

$$E[n] = T_s[n] + E_{ee}[n] + E_{xc}[n] + E_{Ne}[n]$$

$$T_s[n] = \int d\mathbf{r} t_s[n(\mathbf{r})]$$

$$\frac{\delta}{\delta n} \left\{ E[n] - \mu \int d\mathbf{r} n(\mathbf{r}) \right\} = 0 \quad \Rightarrow \quad \frac{\delta T_s}{\delta n} + V_{KS}[n(\mathbf{r})] = \mu \quad \leftarrow \text{“Hydrodynamic” Form of DFT}$$

$$V_{KS}[n(\mathbf{r})] = \frac{\delta}{\delta n} \left\{ E_{ee}[n] + E_{xc}[n] + E_{Ne}[n] \right\}$$

$$\mathbf{F}_I = -\nabla_I E^{OF-DFT}[n] = -\nabla_I E_{NN} - \int d\mathbf{r} n(\mathbf{r}) \nabla_I v_{Ne}(\mathbf{r}) - \int d\mathbf{r} \left[\frac{\delta T_s}{\delta n} + V_{KS}[n(\mathbf{r})] \right] \nabla_I n(\mathbf{r})$$

Electronic contributions to forces become easy

- Is this goal realistic?

Orbital-free DFT – Considerations that shape approaches

Remark: The QM Coulomb virial theorem reinforces our focus on $T_S[n]$ rather than the full $T[n]$:

$$\mathcal{E}_0[n_0] = T[n_0] + E_{total\ potential}[n_0]$$

$$-2T[n_0] / E_{total\ potential}[n_0] = 1 \quad \leftarrow \text{Coulomb Virial Theorem}$$

$$\Rightarrow E_{total\ potential}[n_0] = -2T[n_0]$$

$$\Rightarrow \mathcal{E}_0[n_0] = -T[n_0]$$

- **Implication:** Seeking the full $T[n]$ would be roughly equivalent to seeking the exact, universal HKS functional
- **Clearly this is far too challenging a goal!**

Orbital-free DFT: History as Guidance

Search for OF-KE has a long history of big names and big difficulties:

□ Thomas-Fermi-Dirac:
$$T_{TF}[n] = c_0 \int dr n^{5/3}(\mathbf{r})$$

Teller's **non-binding** theorem (1962)
$$c_0 = \frac{3}{10} (3\pi^2)^{2/3}$$

[E. Lieb, Rev. Mod. Phys. 53, 603-41 (1981)]

□ Thomas-Fermi-von Weizsäcker:

$$T_{TFvW}[n] = T_{TF} + T_{vW} = T_{TF} + \frac{1}{8} \int dr \frac{|\nabla n|^2}{n(\mathbf{r})}$$

When combined with $E_{Ne}[n] + E_{ee}[n] + E_{NN}$: binds neutrals, has negative ions.

But **not accurately**.

Orbital-free KE: More Problems (for guidance)

□ Thomas-Fermi-von Weizäcker used in OFDT:

$$E_{TFvW}[n] = T_{TFvW}[n] + E_{ee}[n] + E_{xc}[n] + E_{ne}[n]$$

$E_{TFvW}[n_0] < E_{KS}[n_0]$ Variational treatment – or evaluation with the actual KS n_0 for a given XC – can lead to **disaster**

Paul Ayers (Sanibel 2007): “An *ab initio* quantum chemist will wonder- “Is an N -representability constraint missing?”

“If so, should we surrender? N -representability problems are very difficult”

Orbital-free KE: Fermion N -representability (constraint)

Defⁿ: A KS kinetic energy functional $T_{KS}[n]$ is N -representable iff for each proper density n , there exists a proper N -fermion state (or ensemble) which has the same KS kinetic energy for that density.

Remark – there are infinitely many N -fermion states associated with each proper n .

Consider the constrained search definition of the K-S KE:

$$T_s[n] = \min_{\Psi \rightarrow n} \int \Psi^*(\mathbf{r}_1 \sigma_1, \dots, \mathbf{r}_N \sigma_N) \left(\sum_j \frac{-\nabla_j^2}{2} \right) \Psi(\mathbf{r}_1 \sigma_1, \dots, \mathbf{r}_N \sigma_N) d\mathbf{r}_1 d\sigma_1 \dots d\mathbf{r}_N d\sigma_N$$

Implications:

1. An approximate KE functional which delivers a value below the KS KE T_s for any system is NOT N -representable.
2. Any non- N -representable KE functional will give a value below the KS KE for at least one system.

Observation – the risks of non- N -representability are serious.

Credit: Paul Ayers



Orbital-free KE: TF-vW anyway

Nevertheless, calculations with Thomas-Fermi-von Weizäcker in OFDFT continue to appear. Some very clever finite element techniques for NON-periodic systems and some interesting results for electronic structure of defects in Al are in, for example, V. Gavini *et al.* [J. Mech. Phys. Solids 55, 6987-718 (2007)]

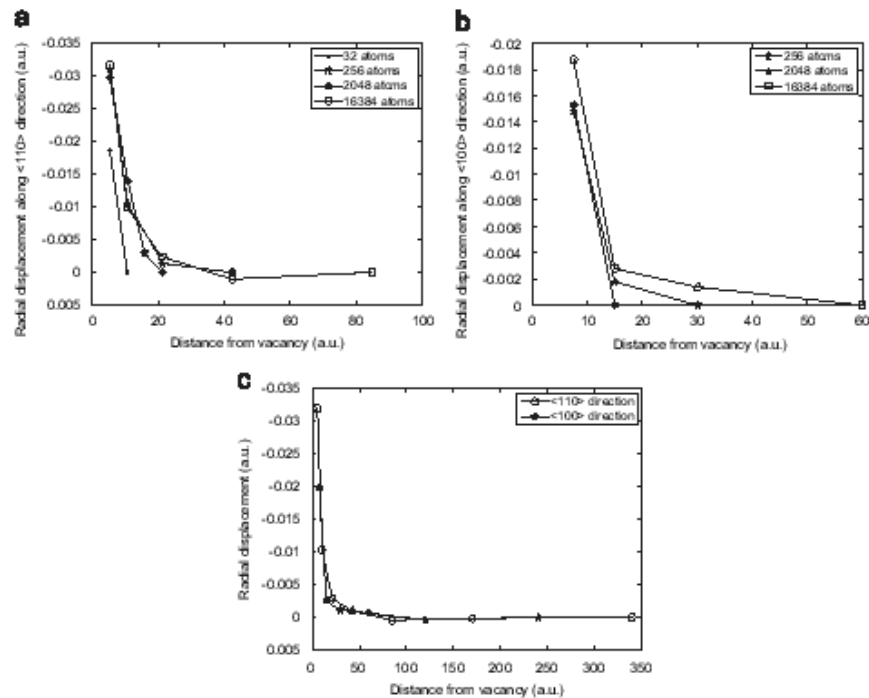


Fig. 8. (a) Radial displacement of atoms along $\langle 110 \rangle$ direction; (b) radial displacement of atoms along $\langle 100 \rangle$ direction; (c) radial displacement of atoms along $\langle 110 \rangle$ and $\langle 100 \rangle$ directions in a million atom sample. The distance from vacancy is listed in atomic units.

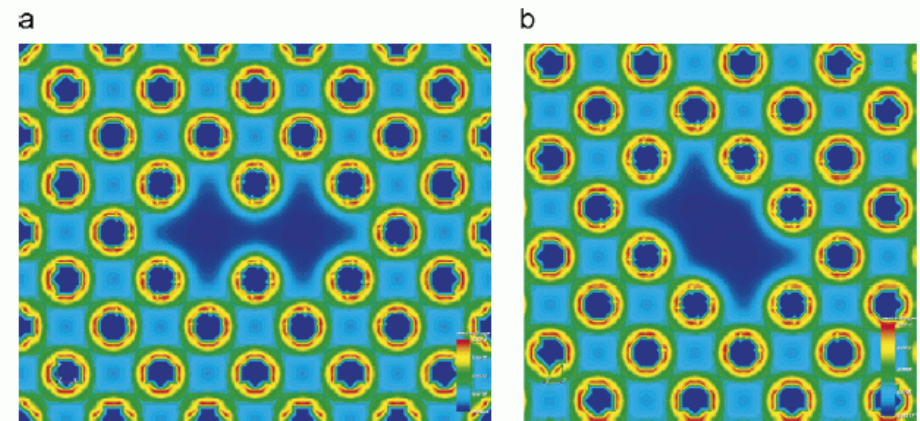


Fig. 9. (a) Contours of electron-density around a di-vacancy complex along $\langle 100 \rangle$; (b) contours of electron-density around a di-vacancy complex along $\langle 110 \rangle$.

Orbital-free KE Approaches – Response Function

Several groups, *e.g.* Madden *et al.*, Carter *et al.*, Teeter, and others, have focused on $T_s[n]$ with a response function strategy for developing OF-KE approximations. Use Carter *et al.*, as an example of much of the literature. [See Y.A. Wang and E.A. Carter in *Theoretical Methods in Condensed Phase Chemistry*, S.D. Schwartz ed. (Kluwer NY 2000) p. 117]

They calibrate their KE density models to linear response on grounds that

1. In atoms and molecules, “shell structure is the barometer” of a good OF-KE
2. “short range [density] oscillations and Friedel oscillations” are the “corresponding physical standard” in solid state physics, and
3. “correct linear response behavior is the key to predicting such oscillations.”

Result is a set of non-local or two-point approximations – work moderately well for metals, not insulators.

Orbital-free KE Approaches – Response Function

Here, in somewhat sloppy translationally invariant notation, is the basic theme of the response function approach

$$\delta n(\mathbf{r}) = \int d\mathbf{r}' \chi(\mathbf{r} - \mathbf{r}') \delta V_{KS}(\mathbf{r}') \Rightarrow \delta n(\mathbf{q}) = \chi(\mathbf{q}) \delta V_{KS}(\mathbf{q})$$

$$\delta(\mathbf{r} - \mathbf{r}') = \int d\mathbf{r}'' \frac{\delta n(\mathbf{r})}{\delta V_{KS}(\mathbf{r}'')} \frac{\delta V_{KS}(\mathbf{r}'')}{\delta n(\mathbf{r}')} \Rightarrow \delta(\mathbf{q} - \mathbf{q}') = \chi(\mathbf{q}) \frac{\delta V_{KS}}{\delta n}(\mathbf{q}, \mathbf{q}')$$

$$\frac{\delta T_s}{\delta n} + V^{KS}[n(\mathbf{r})] = \mu \Rightarrow \delta(\mathbf{q} - \mathbf{q}') = -\chi(\mathbf{q}) \frac{\delta^2 T_s}{\delta n \delta n}(\mathbf{q}, \mathbf{q}')$$

- Outcome of efforts by Carter *et al.*: models based on Average Density Approximation, Weighted Density Approximation, and Nonlocal Approximations.
- Related work by García-Aldea, Alvarellos, Stott, García-Cervera, Ghringhelli, Delle Sitte,

Orbital-free KE Approaches – Response Function

An older example of the Response Function Approach

[Phys. Rev. B 60, 16350 (1999),
Erratum, Phys. Rev. B 64, 089903
(2001)]

The “surface” actually is a slab
and the axis should be “atomic
units” not “arb units”.

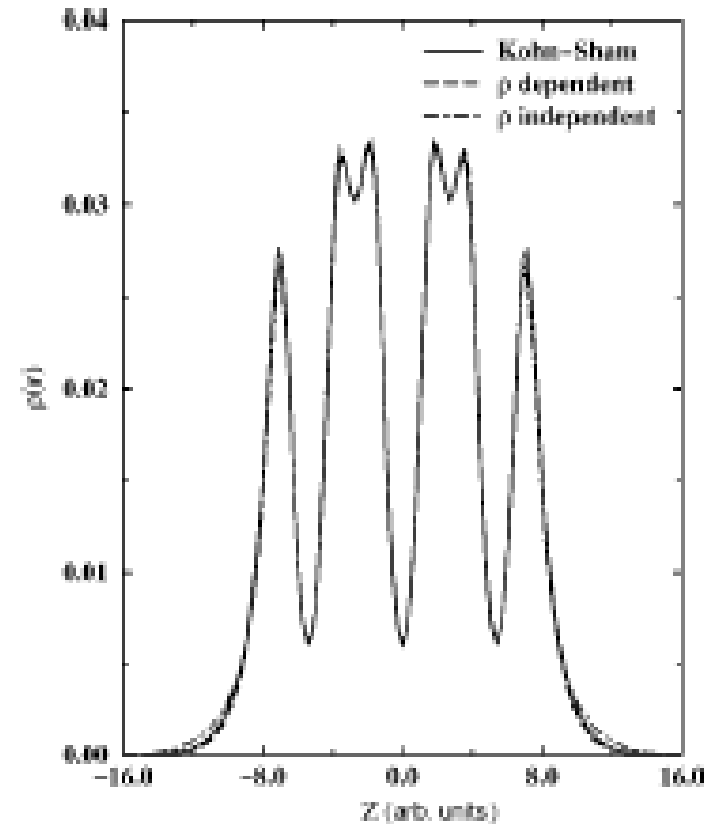


FIG. 4. Density cross section for aluminum fcc-(110) surface. The KEDF is $\gamma^{5.6 \pm 0.6}$ for both nonsolid curves. The long-dashed line is for the density-dependent kernel with $\gamma=2.7$; the dot-dashed line is for the density-independent kernel. $\rho_{\pm} = \rho_0^{\text{bulk}}$.

Orbital-free KE Approaches – Orbital Corrections

OFDFT generally gives the “smooth” part of the density, so why not use the OFDFT density as an input to a Harris functional approach? [J. Chem. Phys. **124**, 081107 (2006)]

$$E_{\text{Harris}}(\{\mathbf{R}\}) = \sum_k \varepsilon_k^{(1)} - \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{n_{\text{OF}}(\mathbf{r})n_{\text{OF}}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{\text{xc}}[n_{\text{OF}}(\mathbf{r})] - \int d\mathbf{r} n_{\text{OF}}(\mathbf{r}) V_{\text{xc}}[n_{\text{OF}}(\mathbf{r})]$$

$$E_{\text{HK}}(\{\mathbf{R}\}) = \sum_k \varepsilon_k^{(1)} + \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{n_{\text{OO}}(\mathbf{r})n_{\text{OO}}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{\text{xc}}[n_{\text{OO}}(\mathbf{r})] - \int d\mathbf{r} n_{\text{OO}}(\mathbf{r}) \{V_{\text{Hi}}[n_{\text{OF}}(\mathbf{r})] + V_{\text{xc}}[n_{\text{OF}}(\mathbf{r})]\}$$

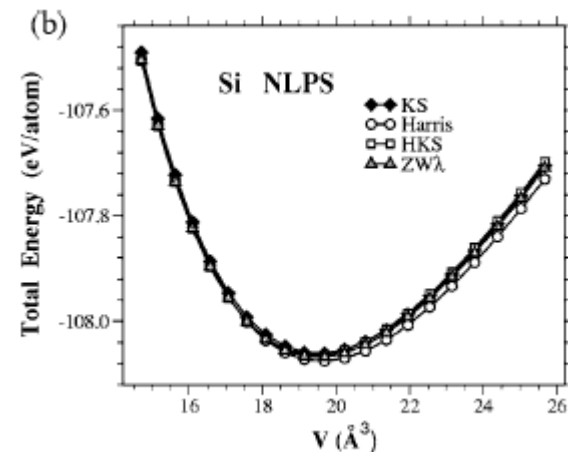
$$h_{\text{KS}}[n_{\text{OF}}(\vec{r})]\phi_k^{(1)} = \varepsilon_k^{(1)} \phi_k^{(1)}$$

$$n_{\text{OO}} = \sum_k n_k \phi_k^{(1)} \phi_k^{(1)}$$

The third line is a “one-shot” diagonalization, not self-consistent. Zhou and Wang propose an interpolated functional “ZW λ ” as being superior. Here’s one example of their results.

The approach is closely related to “Strutinsky” shell corrections

[Yannouleas and Landman, Chem. Phys. Lett. **210**, 437 (1993); Phys. Rev. B **48**, 8376 (1993); Ullmo, Nagano, Tomsovic, and Baranger, Phys. Rev. B **63**, 125339 (2001)]



Orbital-free KE: Constraint-based Approach

- **Models based on Average Density Approximation, Weighted Density Approximation, and Nonlocal Approximations are all two-point.**
- **Too complicated for our (Karasiev, Harris, Jones, and SBT) purposes!**
- **OBJECTIVE: $t_{orb}[n(r)]$ be no more complicated than GGA E_{XC} (depends on gradient of the density) or perhaps those meta-GGAs which depend on Laplacian of the density also.**
- **Assumption: continued progress on *pure* E_{XC} approximations, i.e., NOT hybrids or OEP.**
- **Goal: a workable recipe for $t_s[n]$ primarily for driving MD. Note the wording: we do NOT seek a KE density kernel that will do everything that is in the basic DFT theorems**

Orbital-free KE: Constraint-based Approach (cont'd.)

1) Use “conjointness” [H. Lee, C. Lee, and R.G. Parr, Phys. Rev. A **44**, 768 (1991)] to build the initial model of the functional but not for the parameters. (Note: the conjointness hypothesis itself is false.) Conjointness is:

$$E_x^{GGA}[n] = -c_x \int dr n^{4/3}(r) F_x(s(r)); \quad s(r) = |\nabla n| / \{2(3\pi^2)^{1/3} n^{4/3}\}$$

F_x = exchange enhancement factor

$$\text{Let } T_s^{GGA}[n] = \int dr n^{5/3}(r) F_t(s(r))$$

$F_t(s(r)) \propto F_x(s(r))$ conjoint KE enhancement factor

2) Use **Pauli KE and Pauli potential positivity** [M. Levy and H. Ou-Yang, Phys. Rev. B **38**, 625 (1988); A. Holas and N.H. March, Phys. Rev. A **44**, 5521 (1991); E.V. Ludeña, V.V. Karasiev, R. López-Boada, E. Valderama, and J. Maldonado, J. Comp. Chem. **20**, 155 (1999) and refs. therein]. **An exact decomposition is**

$$T_s[n] = T_w[n] + T_\theta[n], \quad T_\theta[n] \geq 0$$

$$\left(-\frac{1}{2} \nabla^2 + v_{KS}(r) + v_\theta(r) \right) \sqrt{n(r)} = \mu \sqrt{n(r)}$$

$$v_\theta(r) := \delta T_\theta / \delta n \geq 0 \quad \forall r$$

Orbital-free KE: Constraint-based Approach (cont'd.)

- 3) Use the gradient expansion for $T_\sigma[n]$, but not the expansion coefficients. Instead, choose the coefficients to remove nuclear-site singularities from $v_\sigma[n]$ to a specified order in the expansion.
- 4) Test existing conjoint (or nearly) models of $T_s[n]$ by inputting the density from a conventional KS calculation with a selected E_{xc} approximation.
- 5) Upon step 4) success, use $t_s[n]$ to generate n from Euler equation (in a basis) and compare with n_0 from conventional KS calc. Continue or loop back as required.
- 6) Apply to MD calculation on target system(s) related to training set.
- 7) Replace basis calculation of density with parameterized density model (parameters become dynamical variables in MD).

OF-DFT: Tests of Existing KE Functionals

- Tests of 6 existing functionals, three conjoint; two others close.

PW91: Lacks and Gordon, J.Chem. Phys. **100**, 4446 (1994) [conjoint]

PBE-TW: Tran and Wesolowski, Internat. J. Quantum Chem. **89**, 441 (2002) [conjoint]

GGA-Perdew: Perdew, Phys. Lett. A **165**, 79 (1992) [conjoint]

DPK: DePristo and Kress, Phys. Rev. A **35**, 438 (1987)

Thakkar: Thakkar, Phys. Rev. A **46**, 6920 (1992)

SGA: Second order Gradient Approx. $T_S = T_{TF} + (1/9) T_W$

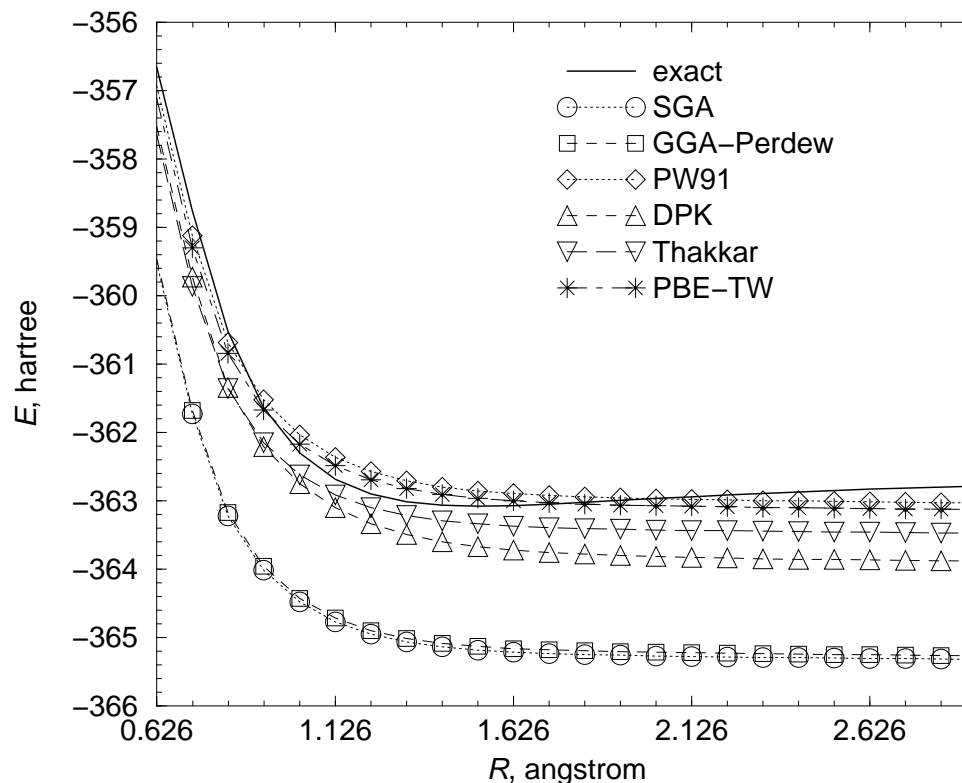
SiO Stretch; Total energy vs.
bond length.

Exact is KS (LDA-VWN).

Input to KE functionals is the
KS density.

All six T_S approximations **fail to bind!** V_θ (not shown) **violates positivity.**

J. Comput. Aided Matl. Design **13**, 111 (2006)



Modified Conjoint GGA OFKE Functionals

Write T_W in GGA-like form and define a shifted enhancement factor

$$T_W[n] = c_0 \int dr n^{5/3}(\mathbf{r}) \left\{ \frac{5}{3} s^2(\mathbf{r}) \right\}; \quad \tilde{F}_t \equiv F_t - \frac{5}{3} s^2(\mathbf{r})$$

Small s (nominally weakly inhomogeneous) limit: $\tilde{F}_t(s(\mathbf{r})) \underset{s \rightarrow 0}{\sim} 1 - \frac{40}{27} s^2$

- **Conjoint** Pauli KE and potential for GGA-level models:

$$T_\theta[n] \approx T_\theta^{GGA}[n] = \int dr t_\theta^{GGA}[n(\mathbf{r})] \equiv c_0 \int dr n^{5/3}(\mathbf{r}) \tilde{F}_t(s(\mathbf{r}))$$

$$v_\theta = \left(\frac{5}{3} \right) c_0 n^{2/3} \tilde{F}_t + c_0 n^{5/3} \frac{\delta \tilde{F}_t}{\delta s} \left(\frac{\delta s}{\delta n} - \frac{5}{3} \frac{\nabla n \cdot \delta s}{n \delta \nabla n} - \nabla \cdot \frac{\delta s}{\delta \nabla n} \right) - c_0 n^{5/3} \frac{\delta^2 \tilde{F}_t}{\delta s^2} \left(\nabla s \cdot \frac{\delta s}{\delta \nabla n} \right)$$

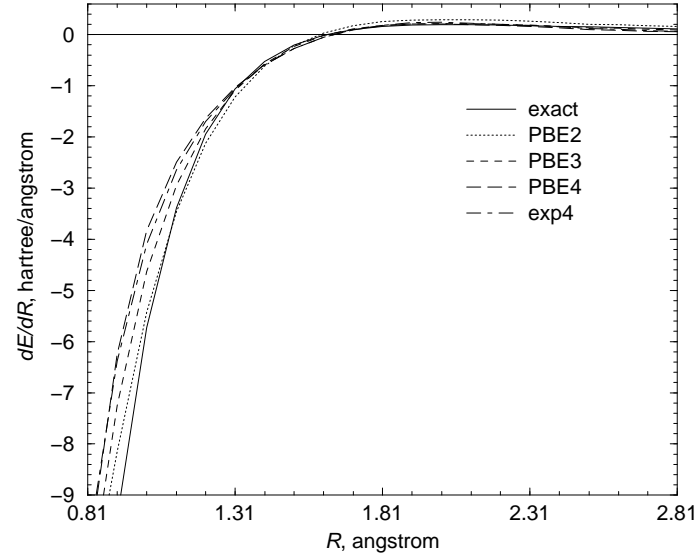
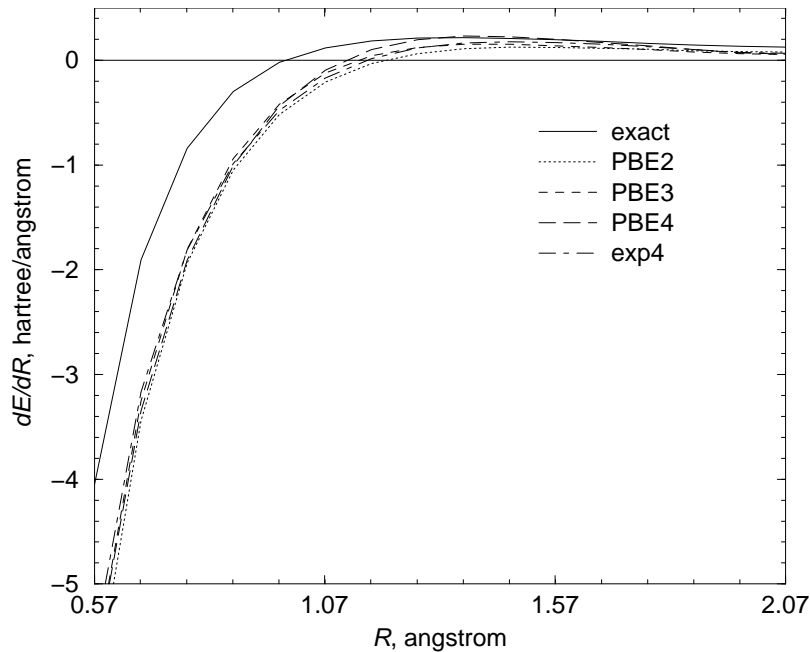
F_t comes from F_X Parameterize to enforce positivity of v_θ

Modified Conjoint GGA OFKE Functionals

Si-O bond stretching gradient in $\text{H}_6\text{Si}_2\text{O}_7$.

→

OF-KE parameters from 3-member training set (SiO , H_4SiO_4 , and $\text{H}_6\text{Si}_2\text{O}_7$) except PBE2 model. Exact is KS (LDA-VWN)



H_2O – gradient for single-bond stretching

←

NO information about H_2O in the training set.

But all the OFKE models give bond lengths that are too long. Problem – positive singularities at nuclei.

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Orbital-free KE: Constraint-based Approach (cont'd.)

Solution to “too positive” a Pauli potential (nuclear site singularities): Analyze the gradient expansion for $T_{\sigma}[n]$ using known (Kato cusp condition) near-nucleus behavior of the density. Determine expansion coefficients through given order that suppress the singularities. [V.V. Karasiev, R.S. Jones, S.B.T. and F.E. Harris, Phys. Rev. B (submitted)]

Comparison of T_{σ} errors at KS equilibrium geometries for the Thakkar, Perdew-Constantin (MGGA) and Karasiev et al.’s new “RDA” OFKE functionals. RDA is generally better than the others - but not always.

TABLE I: KS kinetic energy T_{σ} values (in Hartrees) for selected molecules and differences ($T_{\sigma}^{\text{OF-DFT}} - T_{\sigma}^{\text{KS}}$) calculated using a GGA (Thakkar), MGGA and RDA explicit semi-local approximate functionals. LDA-KS densities for LDA equilibrium geometries (with TZVP basis set) were used as input.

	KS	Thakkar	MGGA	RDA
H ₂	1.080	-0.022	0.103	0.006
LiH	7.784	0.021	0.296	0.063
H ₂ O	75.502	-0.285	0.318	-0.128
FH	99.390	-0.353	0.329	-0.148
N ₂	108.062	-0.340	0.300	-0.041
LiF	106.183	-0.261	0.566	0.086
CO	111.832	-0.333	0.300	-0.074
BF	123.117	-0.273	0.456	0.077
NaF	260.097	-0.348	1.295	0.648
SiH ₄	290.282	0.084	3.112	0.381
SiO	362.441	-0.262	2.825	0.293
SiOH ₄	364.672	-0.163	3.338	0.293
SiO ₄ H ₄	587.801	-0.860	4.133	-0.034
Si ₂ O ₇ H ₆	1100.227	-1.408	7.968	0.086
MAE(14)	-	0.358	1.810	0.168

GW and OFKE - Some Commentary

- **GW is still an active area of research**
- **There has been considerable controversy about the role of the multiple self-consistency requirements in GW and the impact of basis sets.**
- **A simplified, computationally fast, yet basically accurate approximate version of GW would be highly desirable.**
- **OFKE is also an area of active research, though for a smaller community.**
- **There is a strong divergence of approaches between the “response function” (two-point schemes) and the newer, less-well-developed “constraint-based” schemes.**
- **Note that, in all fairness, the response function approach is also “constraint-based”.**