

2007 Summer School on Computational Materials Science

Quantum Monte Carlo: From Minerals and Materials to Molecules

July 9 –19, 2007 • University of Illinois at Urbana–Champaign

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Introduction to Density Functional Theory

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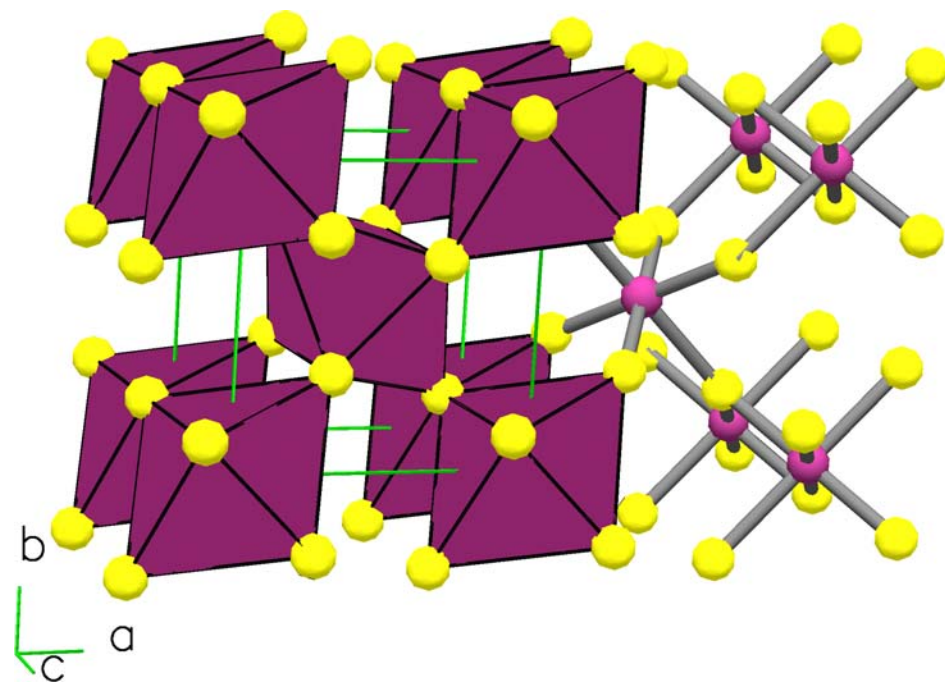
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What is Density Functional Theory?

- DFT is an exact many-body theory for the ground state properties of an electronic system.
 - Atoms, molecules, surfaces, nanosystems, crystals
- Although DFT is formally exact, the exact functional is unknown.
- The exact functional probably does not have a closed form, and would be extremely non-local.
- Nevertheless, very good approximations are known which work well for many systems.
- In practice, DFT is good for structural stability, vibrational properties, elasticity, and equations of state.
- There are known problems with DFT, and accuracy is limited--there is no way to increase convergence or some parameter to obtain a more exact result. In other words there are uncontrolled approximations in all known functionals.
- Some systems are treated quite poorly by standard DFT.



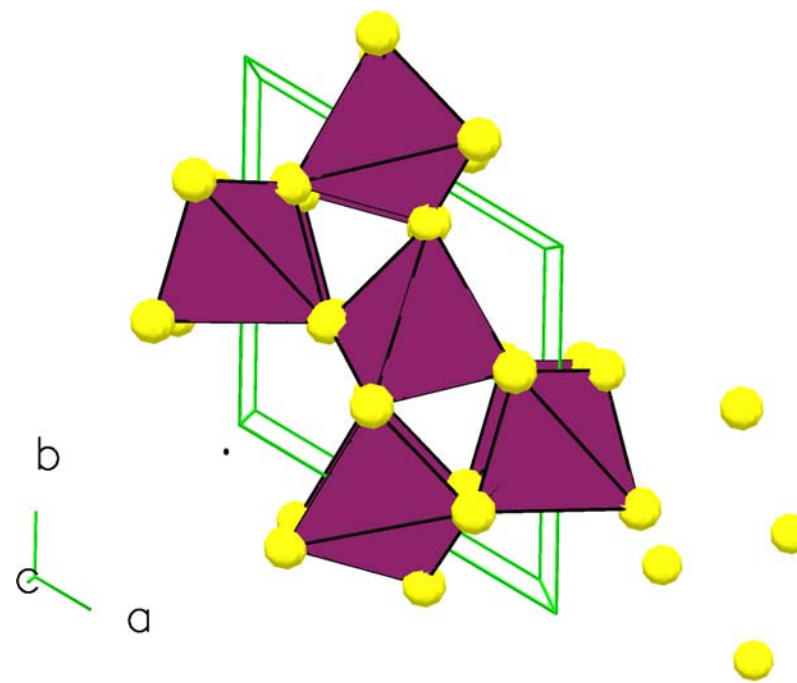
Quartz and Stishovite



Stishovite (rutile) structure

Dense

octahedrally coordinated Silicon



Quartz structure

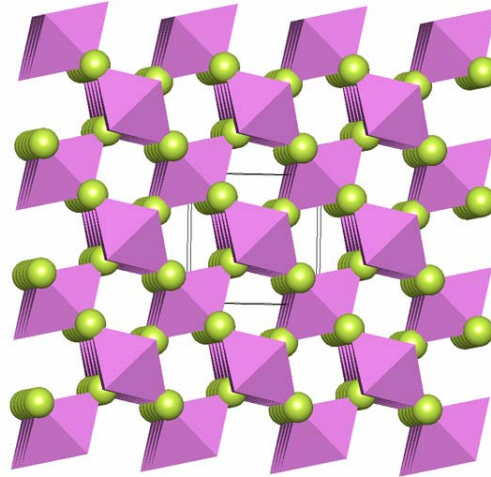
Open structure

tetrahedrally coordinated Silicon

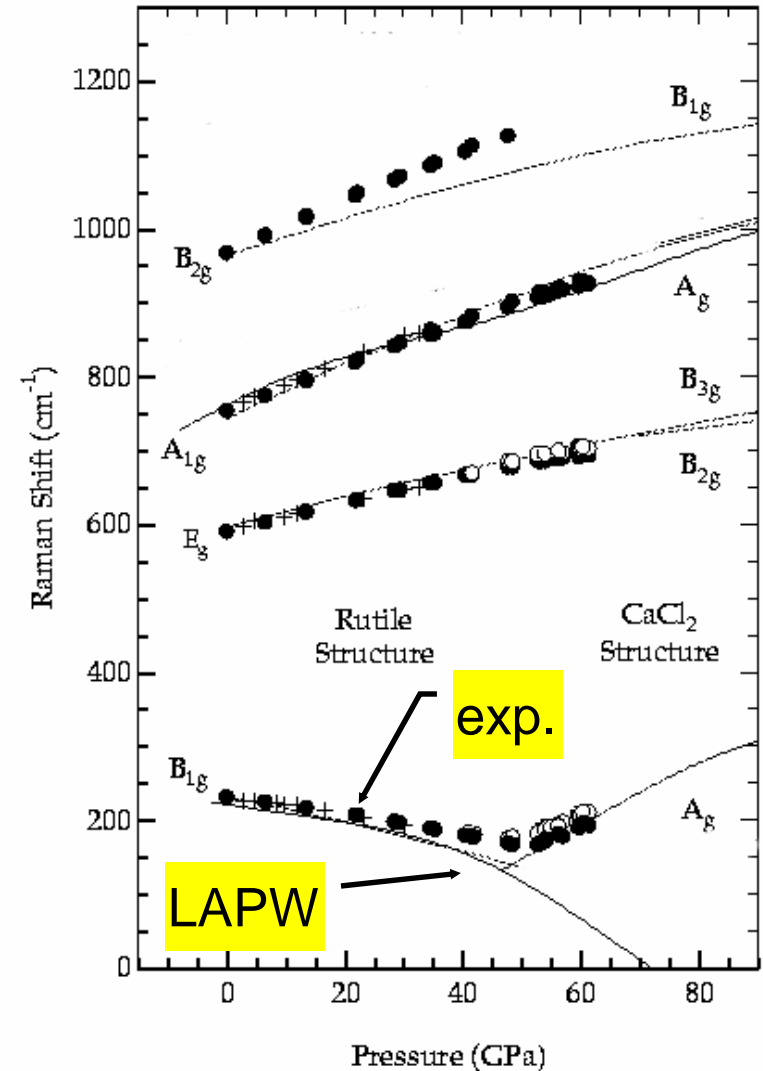
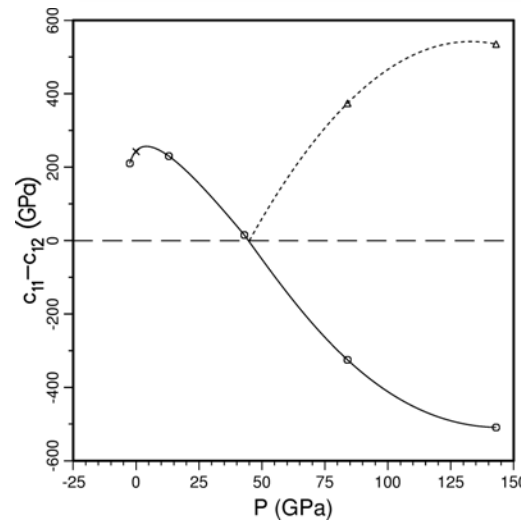
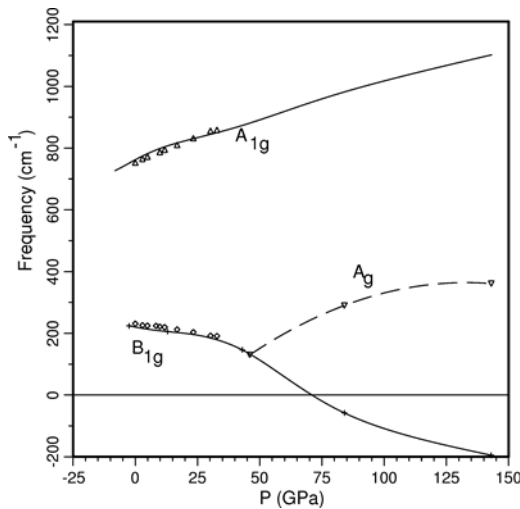
CaCl₂ transition in SiO₂



Prediction: A_{1g} Raman mode in stishovite decreases until phase transition to CaCl₂ structure, then increases. Does NOT go to zero at transition.



Prediction: C₁₁-C₁₂ decreases until phase transition to CaCl₂ structure, then increases. Does go to zero at transition -> superplasticity



Predicted transition (Cohen, 1991) was found by Raman (Kingma et al., Nature 1995).

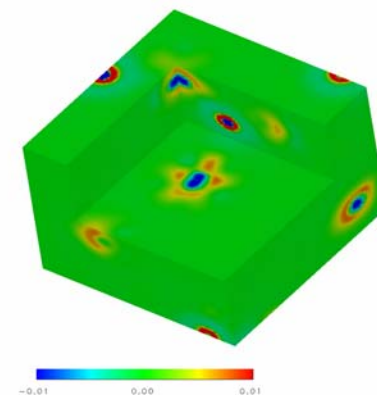
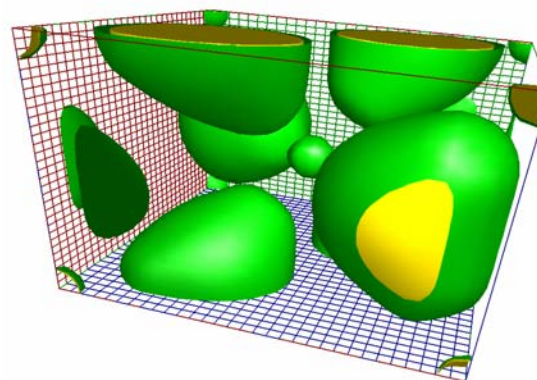
LDA works for stishovite/CaCl₂.



Silica

stishovite valence density

Simple close shelled electronic structure, yet problems with DFT



VOLUME 76, NUMBER 4

PHYSICAL REVIEW LETTERS

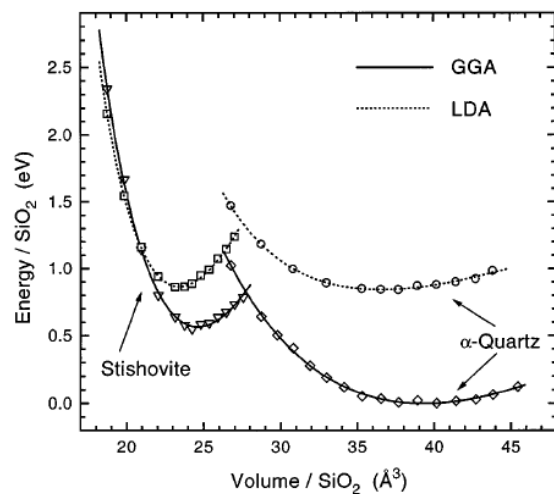
22 JANUARY 1996

Generalized Gradient Theory for Silica Phase Transitions

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(Received 16 October 1995)



difference in GGA and LDA valence density

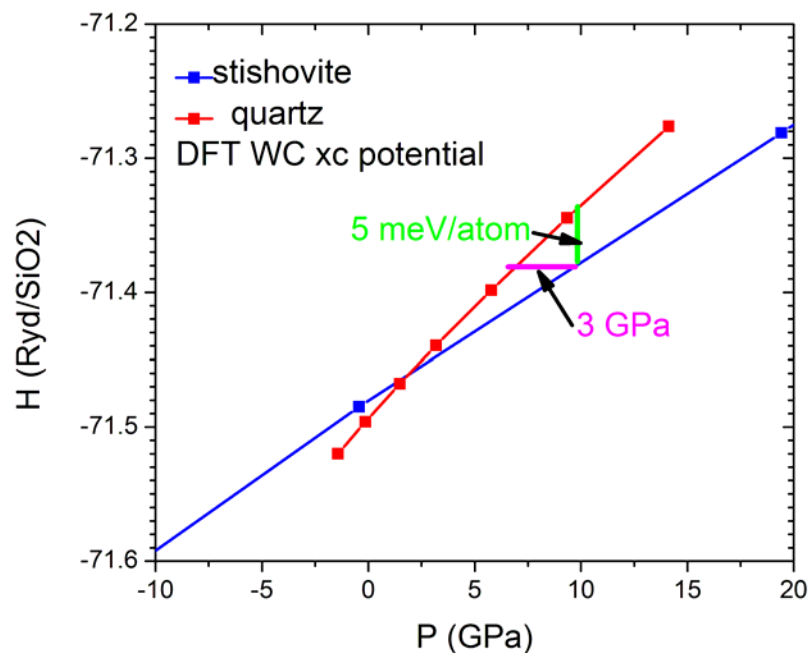
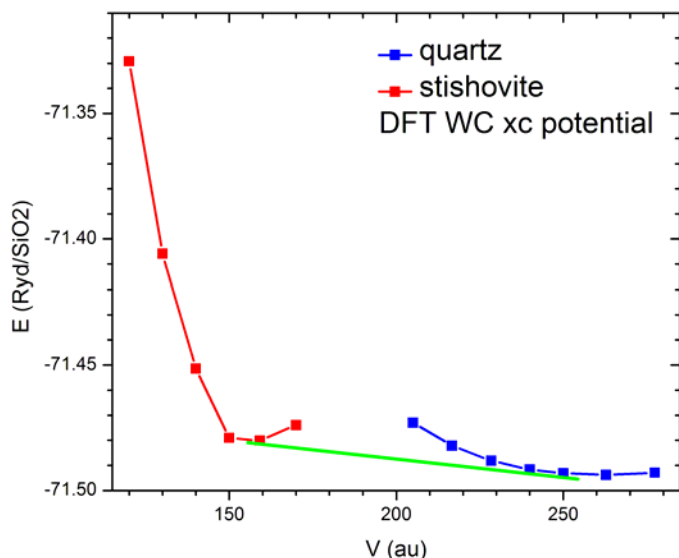
	LDA	PBE*	WC**	Exp.
ΔE (eV)	-0.05	0.5	0.2	0.5
P_{tr}	<0	6.2	2.6	7.5
V_{qz}	244	266	261	254
K_{qz}	35	44	29	38
V_{st}	155	163	159	157
K_{st}	303	257	330	313

*Zupan, Blaha, Schwarz, and Perdew, Phys. Rev. B **58**, 11266 (1998).

Wu and R. E. Cohen, Phys. Rev. B **73**, 235116 (2006).

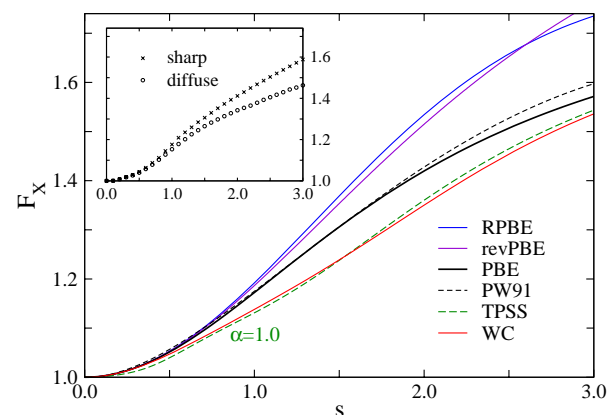


DFT (WC) energies for quartz and stishovite



Z. Wu and R. E. Cohen, Phys. Rev. B **73**, 235116 (2006).

A diffuse cut-off for the exchange fits low and slowly varying densities. F_x agrees well with advanced DFTs with simple GGA functional.



- We tested the following 18 solids: Li, Na, K, Al, C, Si, SiC, Ge, GaAs, NaCl, NaF, LiCl, LiF, MgO, Ru, Rh, Pd, Ag.
- The new GGA is much better than other approximations. Mean errors (%) of calculated equilibrium lattice constants a_0 and bulk moduli B_0 at 0K.

	LDA	PBE	WC	TPS S	PKZB
a_0	1.74	1.30	0.29	0.83	1.65
B_0	12.9	9.9	3.6	7.6	8.0



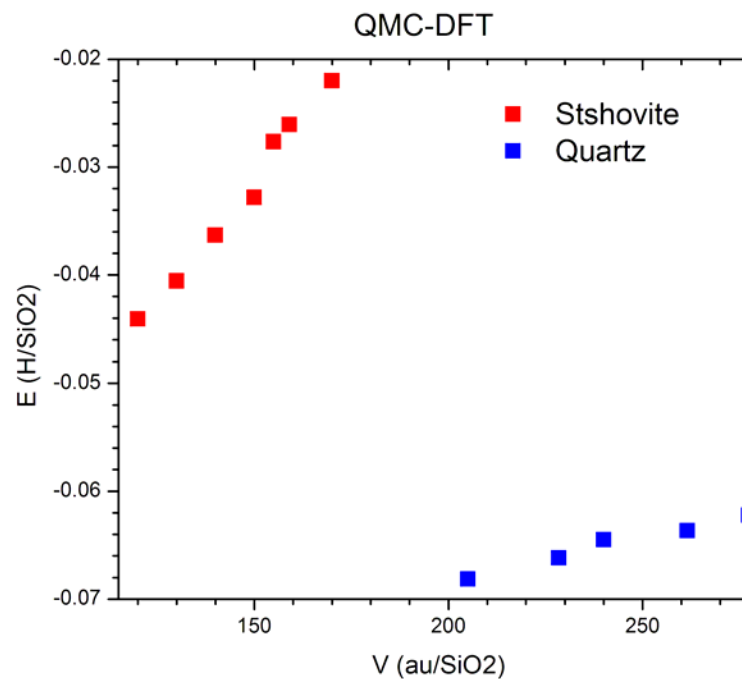
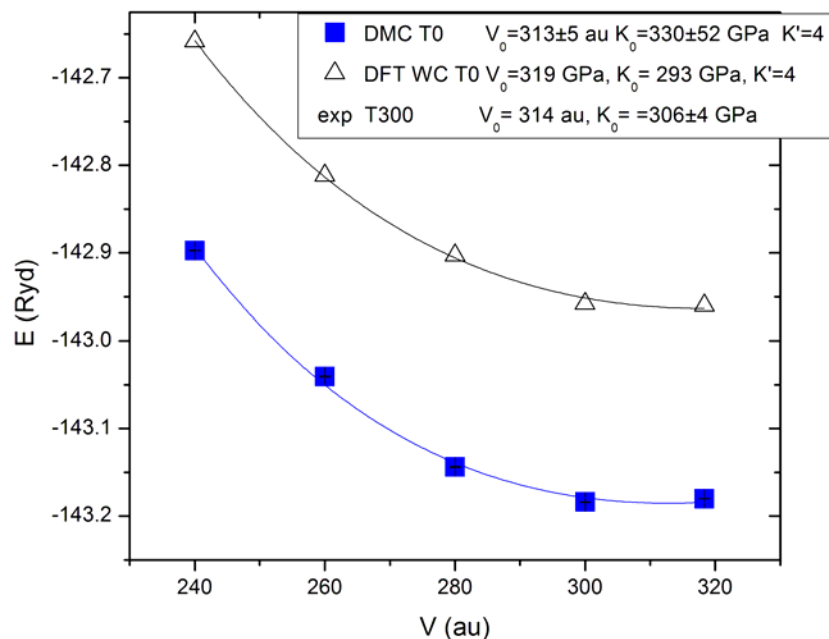
QMC results CASINO

(at DFT WC minimum)

	Quartz (H)	Stishovite (H)	ΔE (eV/fu)
Exp.			0.5
LDA			-0.05
PBE			0.5
WC	-35.7466	-35.7397	0.2
DMC MPC	-35.8071	-35.7912	0.43
stish 3x3x3			
qz 2x2x2			
No finite size corrections			



Comparison of QMC and DFT (WC xc)

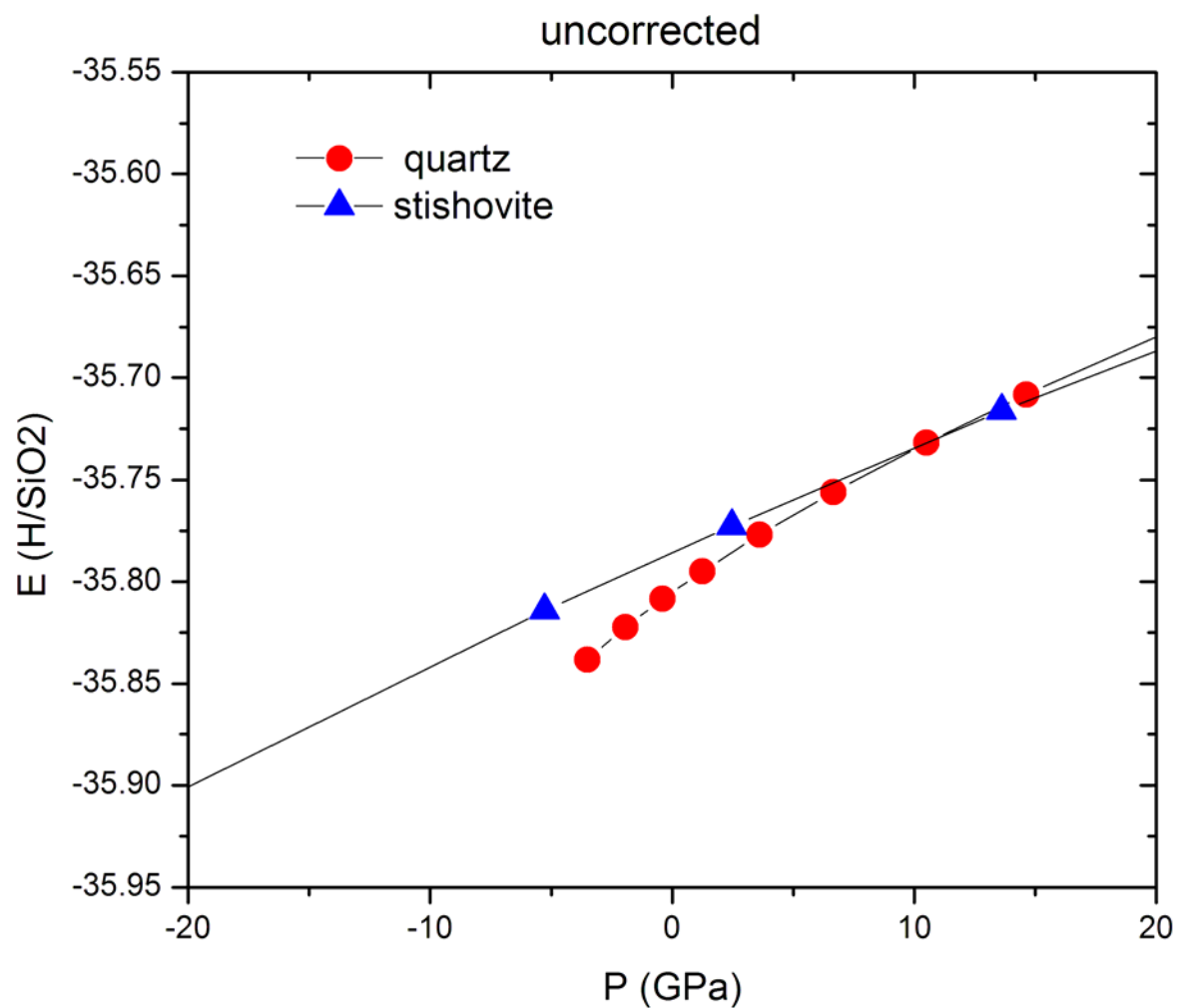


Shifts in energy and pressure from DFT (WC) to QMC (QMC-DFT)

	stishovite	quartz
E_0 eV/SiO ₂	-0.77	-1.76
P GPa	-4.6	-8.0



Quartz to stishovite transition



	qz	st
V_0 (au)	247	156
V_0 (exp)	254	157
K_0 (GPa)	39	309
K_0 (exp)	38	313

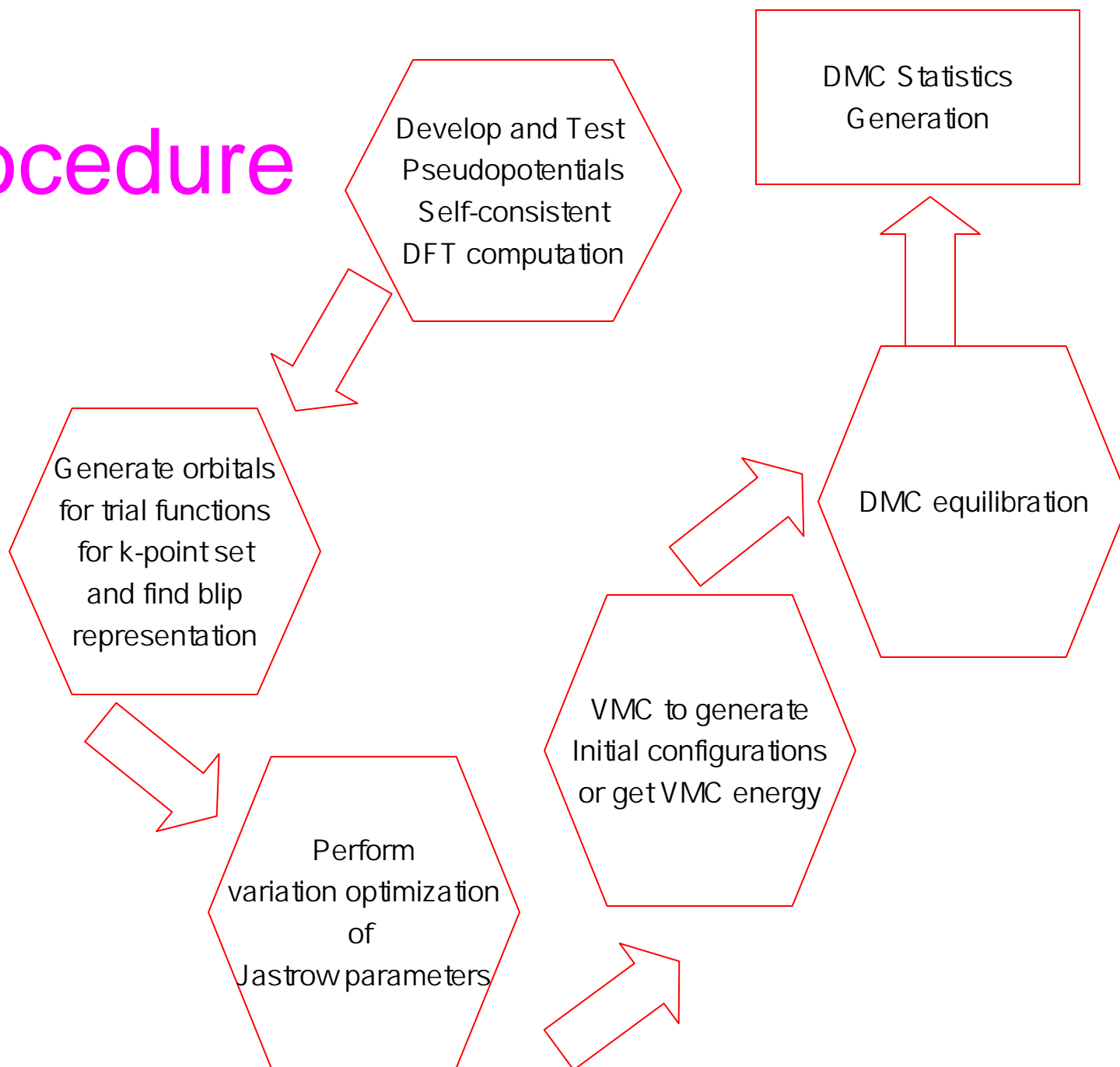
What is DFT used for in QMC?

- DFT is used to relax ground state structures, since QMC relaxation is not yet tractable for crystals.
- DFT is used to compute phonons to obtain quasiharmonic estimates of zero point and thermal contributions to the free energy.
- DFT is used to generate trial wavefunctions for QMC.
- Sometimes DFT is used to estimate finite size corrections to QMC.





Procedure



Functionals + Functional Derivatives

Functionals are mappings from function spaces to the real (or complex) numbers. A general representation for a functional F is

$$\begin{aligned}
 F[g] = & F_0 + \int dx F_1(x) g(x) + \\
 & + \int dx_1 \int dx_2 F_2(x_1, x_2) g(x_1) g(x_2) \\
 & + \int dx_1 \int dx_2 \int dx_3 F_3(x_1, x_2, x_3) g(x_1) g(x_2) g(x_3) + \dots
 \end{aligned} \tag{1}$$

where the kernels F_i may themselves be either ordinary functions or generalized functions containing, for example, the delta function and its derivatives.

Now let $g = g_0 + \Delta g$. To linear order in Δg we have

$$\begin{aligned}
 F[g] = & F[g_0] + \int dx F_1(x) \Delta g(x) + \\
 & + 2 \int dx_1 \int dx F_2(x_1, x) g_0(x_1) \Delta g(x) \\
 & + 3 \int dx_1 \int dx_2 \int dx F_3(x_1, x_2, x) g_0(x_1) g_0(x_2) \Delta g(x) + \dots
 \end{aligned} \tag{2}$$

(To obtain (2) I have assumed the kernels F_i are symmetric functions of their arguments; This clearly does not restrict the generality of (1))

We can rewrite (2) as

$$F[g_0 + \Delta g] = F[g_0] + \int dx \frac{\delta F[g_0]}{\delta g(x)} \Delta g(x) \quad (3)$$

where

$$\begin{aligned} \frac{\delta F[g_0]}{\delta g(x)} = & F_1(x) + 2 \int dx_1 g_0(x_1) F_2(x_1, x) \\ & + 3 \int dx_1 \int dx_2 g_0(x_1) g_0(x_2) F_3(x_1, x_2, x) \\ & + \dots \end{aligned} \quad (4)$$

Alternatively, when (as is often the case) we do not have an explicit representation such as (1) for F , equation (3) serves to define the functional derivative $\frac{\delta F}{\delta g(x)}$.

The higher functional derivatives are defined by

analogy to (3) :

$$\begin{aligned}
F[g_0 + \Delta g] &= F[g_0] + \int dx \frac{\delta F[g_0]}{\delta g(x)} \Delta g(x) \\
&+ \frac{1}{2} \int dx \int dx' \frac{\delta^2 F[g_0]}{\delta g(x) \delta g(x')} \Delta g(x) \Delta g(x') \\
&+ O(\Delta g)^3
\end{aligned}
\tag{5}$$

From (1) we find an explicit representation for $\delta^2 F / \delta g(x) \delta g(x')$:

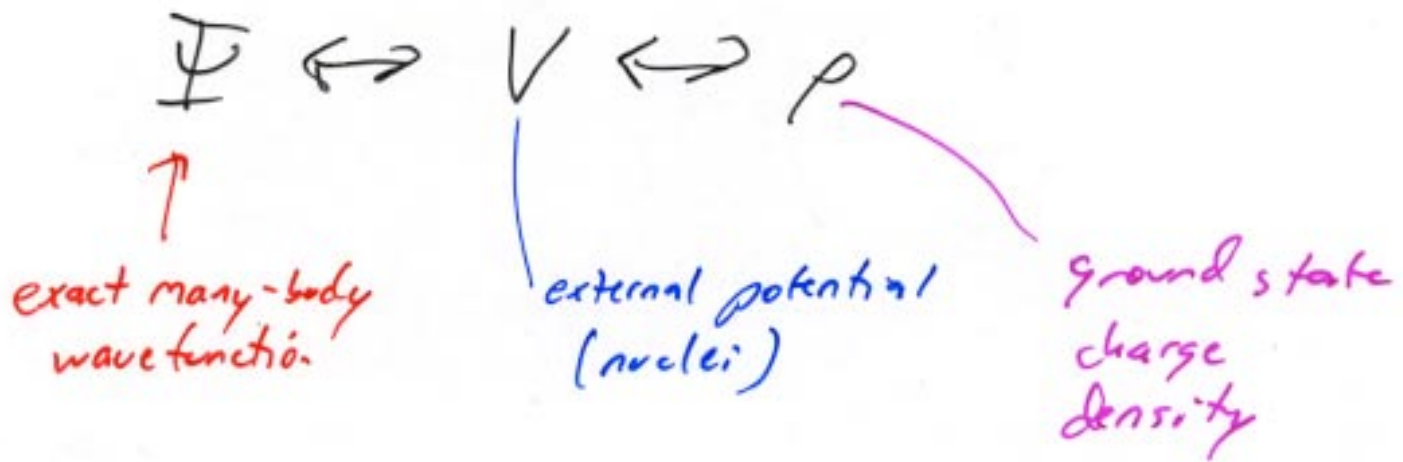
$$\frac{\delta^2 F[g_0]}{\delta g(x) \delta g(x')} = 2F_2(x, x') + 6 \int dx_1 g_0(x_1) F_3(x_1, x, x') + \dots
\tag{6}$$

Example: The Coulomb energy of a charge distribution $n(r)$ is given by a functional $U[n]$, with

$$U_0 = 0, \quad U_1 = 0, \quad U_2(\vec{r}_1, \vec{r}'_1) = \frac{e^2}{2} \frac{1}{|\vec{r}_1 - \vec{r}'_1|}, \quad U_{n \geq 2} = 0$$

$$\frac{\delta U[n_0]}{\delta n(r)} = e^2 \int d^3 r_1 \frac{n_0(\vec{r}_1)}{|\vec{r} - \vec{r}_1|}, \quad \frac{\delta^2 U[n_0]}{\delta n(r) \delta n(r')} = \frac{e^2}{|\vec{r} - \vec{r}'|}$$

Density Functional Theory



All properties of the system are functionals of the charge density, iff there is a one to one correspondence between ρ and V !

Density Functional theory

Hohenberg - Kohn Theorem

Exact:

$$H = \sum_{i=1}^N -\nabla_i^2 + \sum_i v(r_i) + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|r_i - r_j|}$$

$$\underbrace{\hspace{10em}}_{KE} \quad \underbrace{\hspace{10em}}_V \quad \underbrace{\hspace{10em}}_U$$

$$H\Psi = E\Psi \quad \rho(r) = \langle \Psi^* \Psi \rangle$$

Ψ exact many body wave function

Hohenberg-Kohn Theorem

(1) Can two different v 's give the same charge density $\rho(r)$?

$$v(r) - v'(r) \neq \text{constant}$$

Assume: $\rho'(r) = \rho(r)$

$\Psi' \neq \Psi$ since they solve different Schrödinger's equations

$$\begin{aligned} E' &= \langle \Psi' | H' | \Psi' \rangle < \langle \Psi | H' | \Psi \rangle \\ &= \langle \Psi | H + v' - v | \Psi \rangle \\ &= \langle \Psi | H | \Psi \rangle + \langle \Psi | v' - v | \Psi \rangle \\ &= E + \int d^3r [v'(r) - v(r)] \rho(r) \end{aligned}$$

$$\text{So } \boxed{E' < E + \int d^3r [v'(r) - v(r)] \rho(r)} \quad (1)$$

Now do: $E = \langle \Psi | H | \Psi \rangle < \langle \Psi' | H' | \Psi' \rangle$

$$= E' + \int d^3r [v(r) - v'(r)] \rho(r)$$

$$\boxed{E < E' + \int d^3r [v(r) - v'(r)] \rho(r)} \quad (2)$$

Add (1) and (2): $E + E' < E + E'$ Contradiction!
So $v = v'$ if $\rho = \rho'$ $\Psi \leftrightarrow v \leftrightarrow \rho$

Hohenberg-Kohn Theorem #2: Minimum principle

The calculated ground state energy is a minimum for the ground state density $\rho(r)$:

$$\text{Define } F[\Psi] \equiv \langle \Psi | T + U | \Psi \rangle$$

where T :

$$\text{Kinetic energy} = \sum \frac{-\hbar^2 \nabla^2}{2}$$

$$U: \text{Hartree energy} = \frac{1}{2} \sum_{i,j} \frac{e^2}{|r_i - r_j|}$$

since $\Psi = \Psi[\rho]$, $F = F[\rho]$

$$E_v[\rho] \equiv \int d^3r v(r)\rho(r) + F[\rho]$$

v : external potential

$E_v[\rho]$ is the ground state energy for external potential v for the correct density $\rho(r)$.

We know that: $E_v[\Psi] = \langle \Psi | T + V + U | \Psi \rangle$
 $\delta E_v[\Psi] = 0$ (Grandstate energy E_v)
 $\langle \Psi | \Psi \rangle = 1, N$

$$E_v[\Psi'] \equiv \int v(r)\rho'(r)d^3r + F[\rho'] \leftrightarrow E_v[\rho']$$

$$> E_v[\Psi] \equiv \int v(r)\rho(r)d^3r + F[\rho] \leftrightarrow E_v[\rho]$$

$$\text{So: } E_v[\rho'] > E_v[\rho]$$

Hohenberg-Kohn, Second Proof (Levy Constrained Search)

$$E = \min_{\Psi} \langle \Psi | H | \Psi \rangle$$

First consider:

$$\min_{\Psi \rightarrow \rho} \langle \Psi | H | \Psi \rangle = \min_{\Psi \rightarrow \rho} \langle \Psi | T + V_{ee} | \Psi \rangle + \int d^3r v(r) \rho(r)$$

because $v(r)$ implies Ψ and thus ρ !

Define: $F[\rho] \equiv \min_{\Psi \rightarrow \rho} \langle \Psi | T + V_{ee} | \Psi \rangle = \langle \Psi^{\min} | T + V_{ee} | \Psi^{\min} \rangle$

Now minimize over all N -electron densities $\rho(r)$

$$E = \min_{\rho} E_{\text{ex}}[\rho] = \min_{\rho} \left\{ F[\rho] + \int d^3r v(r) \rho(r) \right\}$$

Use Lagrange multiplier to fix N :

$$\delta \left\{ F[\rho] + \int d^3r v(r) \rho(r) - \mu \left(\int d^3r \rho(r) \right) \right\} = 0$$

$$\frac{\delta}{\delta \rho(r)} \rightarrow \frac{\delta F[\rho]}{\delta \rho(r)} + v(r) = \mu \quad \text{So } v(r) \leftrightarrow \rho(r)$$

$\rho(r)$ - N -representable any Ψ ?

$\frac{\delta F}{\delta \rho}$ V -representable Ψ and some $v(r)$

Kohn-Sham: Self consistent equations for obtaining the ground state properties

Define: $T_s[\rho]$ = kinetic energy of a noninteracting system with density $\rho(r)$

$$E[\rho] = \int v(r)\rho(r)d^3r + T_s[\rho] + \frac{1}{2} \iint \frac{\rho(r)\rho(r')}{|r-r'|} d^3r + E_{xc}[\rho]$$

$$\text{Define: } \frac{\delta E_{xc}[\rho]}{\delta \rho(r)} \equiv v_{xc}(r)$$

$$\text{Now } \frac{\delta E}{\delta \rho(r)} = 0 \text{ for } N[\rho] = \int \rho(r)d^3r$$

Use a Lagrange multiplier:

$$\frac{\delta}{\delta \rho(r)} \left\{ E[\rho] - \mu N[\rho] \right\} = 0$$

$$\text{Define Hartree potential } v_h \equiv \int d^3r' \frac{\rho(r')}{|r-r'|}$$

Then:

$$\frac{\delta T_s}{\delta \rho(r)} + v(r) + v_h(r) + v_{xc}(r) = \mu$$

If $\frac{\delta T_s}{\delta \rho}$ and v_{xc} were known exactly, and were simple functions of ρ , $\rho(r)$ could be found to satisfy this equation.

Kohn-Sham (cont'd)

Non-interacting system:

We do know how to solve:

$$\frac{\delta T_S[\rho]}{\delta \rho(r)} + v_0(r) = \mu \quad (1)$$

for a non-interacting system:

$$[-\nabla^2 + v_0(r)] \psi_i = \epsilon_i \psi_i$$

$$\rho(r) = \sum_{i=1}^{\text{occ}} \psi_i^*(r) \psi_i(r) \quad \begin{array}{l} \text{lowest } N \text{ eigenvalues} \\ \psi_i \text{ single particle orbitals} \end{array}$$

Since this is the correct ground state density $\rho(r)$, it must satisfy (1).

Interacting system:

We want to solve:

$$\frac{\delta T_S}{\delta \rho(r)} + v(r) + v_h(r) + v_{xc}(r) = \mu$$

for $\rho(r)$, but we do not know $\frac{\delta T_S}{\delta \rho(r)}$

But if $v_0 = v + v_h + v_{xc} = v_{\text{eff}}$, we could solve the non-interacting problem:

$$\frac{\delta T_S}{\delta \rho(r)} + v_{\text{eff}} = \mu$$

Local Density Approximation LDA

$$E_{xc}[\rho] = \int d^3r \rho(r) \epsilon_{xc}(\rho(r)) \quad \text{local } \epsilon_{xc}$$

Exchange correlation functional

$$N_{xc} \equiv \frac{\delta E_{xc}}{\delta \rho}$$

$$\epsilon_{xc} = E - T_s - V \rightarrow 0$$

Local Exchange Correlation Functional

kinetic energy for noninteracting electron gas

Total energy for electron gas

Consider $\delta E_{xc}[\rho]$

$$\begin{aligned} E_{xc}[\rho + \delta\rho] - E_{xc}[\rho] &= \int d^3r \delta\rho \frac{\delta E_{xc}}{\delta \rho} + O(\delta\rho^2) \\ &= \int d^3r \left[(\rho + \delta\rho) \epsilon_{xc}(\rho + \delta\rho) - \rho \epsilon_{xc}(\rho) \right] \\ &= \int d^3r \left[\rho \epsilon_{xc}(\rho) + \delta\rho \epsilon'_{xc}(\rho) + \dots \right] + \delta\rho \left[\epsilon_{xc}(\rho) + \dots \right] - \rho \epsilon_{xc}(\rho) \\ &= \int d^3r \left[\delta\rho \rho \epsilon'_{xc}(\rho) + \delta\rho \epsilon_{xc}(\rho) \right] + O(\delta\rho^2) \end{aligned}$$

So we see $N_{xc}^{LDA} = \frac{d}{d\rho} (\rho \epsilon_{xc}(\rho)) \quad \neq \neq$

$$E_x^{LDA}[\rho] = A_x \int d^3r \rho(r)^{4/3} \quad \epsilon_x(\rho) = A_x \rho^{1/3}$$

$$\frac{\delta E_x}{\delta \rho} = N_x = A_x \frac{4}{3} \rho^{1/3}$$

Total Energy Calculations

$$E[\rho] = \int v(r) \rho(r) d^3r + T_s[\rho] + \frac{1}{2} \iint d^3r d^3r' \frac{\rho(r) \rho(r')}{|r-r'|} + E_{xc}[\rho]$$

Now

$$T_s[\rho] + \int d^3r \rho(r) \left\{ v(r) + \int d^3r' \frac{\rho(r')}{|r-r'|} + v_{xc}(r) \right\} = \sum \epsilon_i$$

Two equivalent expressions for the ground state energy for non-interacting (independent) electrons.

So:

$$E[\rho] = \sum \epsilon_i - \frac{1}{2} \int d^3r \frac{\rho(r) \rho(r')}{|r-r'|} + E_{xc}[\rho] - \int \rho(r) v_{xc}(r) d^3r$$

Note: near nuclei there is a very large kinetic energy density and a very negative potential energy density. Extreme accuracy is required.

say 10^{-9} or smaller.

Typical errors

Perdew + Kurth

Atoms, molecules + solids

	LSD	GGA
E_x	5%	0.5%
E_c	100% (too negative)	5%
bond length	1% (too short)	1% (too long)
structure	close packed	more correct
energy barrier	100% (too low)	30% (too low)

Atomization energy for 20 molecules

Unrestricted Hartree Fock	3.1 eV underbinding
LSD	1.3 eV overbinding
GGA	0.3 eV (mostly over)
"Chemical accuracy"	0.05 eV

Exchange and Correlation Energies (general case)

$$E_{xc}[\rho] = E_x[\rho] + E_c[\rho]$$

Exact

$$E_x[\rho] = \langle \Phi_{\rho}^{\min} | V_{ee} | \Phi_{\rho}^{\min} \rangle - U[\rho]$$

single
slater determinant
of ground state orbitals

(like Hartree-Fock)

$$e-e \text{ interaction} = \frac{1}{|r_i - r_j|}$$

Hartree energy

$$\iint \frac{\rho(r)\rho(r')}{|r-r'|} d^3r d^3r'$$

Note that: $\langle \Phi_{\rho}^{\min} | T + V_{ee} | \Phi_{\rho}^{\min} \rangle$
 $= T_s[\rho] + U[\rho] + E_x[\rho]$

Correlation

$$E_c[\rho] = F[\rho] - \{T_s[\rho] + U[\rho] + E_x[\rho]\}$$

$$= \langle \Phi_{\rho}^{\min} | T + V_{ee} | \Phi_{\rho}^{\min} \rangle$$

$$- \langle \Phi_{\rho}^{\min} | T + V_{ee} | \Phi_{\rho}^{\min} \rangle$$

$$E_c[\rho] \leq 0$$

positive KE part, negative PG part

Scaling continued

Consider any functional $G[\rho]$
and a local density approximation:

$$G[\rho] = \int d^3r g(\rho(r))$$

If $G[\rho_\lambda] = \lambda^p G[\rho]$ then

$$\lambda^{-3} \int d^3(\lambda r) g(\lambda^3 \rho(\lambda r)) = \lambda^p \int d^3r g(\rho(r))$$

$$\text{or: } g(\lambda^3 \rho) = \lambda^{p+3} g(\rho)$$

$$\boxed{g(\rho) \propto \rho^{1+p/3}}$$

$$\text{For } E_x, p=1 \text{ so } E_x^{\text{LOA}}[\rho] = A_x \int d^3r \rho(r)^{4/3}$$

$$T_s, p=2 \text{ so } T_s^{\text{LOA}}[\rho] = A_s \int d^3r \rho(r)^{5/3}$$

Summary of DFT

HK1 $\Psi \leftrightarrow V \leftrightarrow \rho$

HK2 $\delta E[\rho] = 0$

KS $H \Psi_\alpha = \epsilon_\alpha \Psi_\alpha$ $\rho = \sum_{\alpha}^{\text{occ}} \Psi_\alpha^* \Psi_\alpha$

$$H = -\frac{1}{2} \nabla^2 + V_{\text{eff}}$$

$$V_{\text{eff}} = v + U + v_{\text{xc}}$$

v : external potential (nuclei)

U : Hartree potential $U(r) = \int d^3 r' \frac{\rho(r')}{|r-r'|}$

$$v_{\text{xc}} = \frac{\delta E_{\text{xc}}}{\delta \rho}$$

Solve self-consistently

Total Energy:

$$E = T_s + \int d^3 r \rho(r) v(r) + \underbrace{\frac{1}{2} \int d^3 r d^3 r' \frac{\rho(r) \rho(r')}{|r-r'|}}_U + E_{\text{xc}}$$

$$T_s = \sum_{\alpha}^{\text{occ}} \langle \Psi_\alpha | -\frac{1}{2} \nabla^2 | \Psi_\alpha \rangle$$

OR:

$$E = \sum_{\alpha}^{\text{occ}} \epsilon_\alpha - U(\rho) - \int d^3 r \rho(r) v_{\text{xc}}(r) + E_{\text{xc}}$$

Summary of LDA

$$E_{xc} = \int d^3r \rho(r) e_{xc}(r)$$

$$v_{xc} = \frac{\delta E_{xc}}{\delta \rho} = \frac{d}{d\rho} (\rho(r) e_{xc}(r))$$

See this from definition:

$$F[\rho_0 + \Delta\rho] = F[\rho_0] + \int dx \frac{\delta F[\rho_0]}{\delta \rho} \Delta\rho(x)$$

$$E_{xc}[\rho + \Delta\rho] = \int e_{xc}(\rho + \Delta\rho)(\rho + \Delta\rho) d^3r$$

$$= \int e_{xc}(\rho + \Delta\rho) \rho d^3r + \int d^3r e_{xc}(\rho + \Delta\rho) \Delta\rho$$

$$= \int d^3r \rho (e_{xc}(\rho) + e'_{xc}(\rho) \Delta\rho + \dots) + \int d^3r e_{xc}(\rho + \Delta\rho) \Delta\rho$$

$$= E_{xc}[\rho] + \int d^3r \Delta\rho \left(\rho e'_{xc} + e_{xc}(\rho) + e'_{xc} \Delta\rho \right) \Big|_{\Delta\rho \rightarrow 0}$$

$$= E_{xc}[\rho] + \int d^3r \Delta\rho \underbrace{(\rho e'_{xc} + e_{xc})}$$

$$\frac{\delta E_{xc}^{LDA}}{\delta \rho} = \frac{d}{d\rho} (\rho e_{xc})$$

Explicit LDA Functionals

Free Electron Gas

Exchange:

$$e_x(r) = -\frac{3}{4\pi} (3\pi^2 \rho(r))^{1/3}$$

$$\frac{\delta E_x}{\delta \rho} = -\frac{1}{\pi} k_F$$

$$\rho = \frac{k_F^3}{3\pi^2} = \frac{3}{4\pi r_s^3}$$

Correlation:

high density: $r_s \rightarrow 0$

$$e_c = c_0 \ln r_s - c_1 + c_2 r_s \ln r_s - c_3 r_s + \dots$$

low density: $r_s \rightarrow \infty$ Wigner crystal

$$e_c \rightarrow -\frac{d_0}{r_s} + \frac{d_1}{r_s^{3/2}} + \dots$$

Perdew + Wang, PRB 45, 13244 (1992) fit

Monte Carlo results of Ceperley + Alder, PRL 45, 566

(1980):

$$e_c(\rho(r)) = -2c_0(1 + \alpha_1 r_s) \ln \left[1 + \frac{2c_0(\beta_1 r_s^{1/2} + \beta_2 r_s + \beta_3 r_s^{3/2} + \beta_4 r_s^2)}{\beta_4 r_s^2} \right]$$

Local Spin Density Approximation LSDA

Fractional Spin density: $s(r) = \frac{\rho_{\uparrow}(r) - \rho_{\downarrow}(r)}{(\rho_{\uparrow} + \rho_{\downarrow})}$

$$e_x(\rho_{\uparrow}, \rho_{\downarrow}) = e_x(\rho) \frac{[(1+s)^{4/3} + (1-s)^{4/3}]}{2}$$

RPA: $e_c(\rho_{\uparrow}, \rho_{\downarrow}) = e_c(\rho) + \alpha_c(\rho) s^2 + O(s^4)$

α_c "spin stiffness"

Self-consistent LDA (GGA)

1. initial guess for potential or density



Compute potential

→ 2. Solve $H \psi_i = \epsilon_i \psi_i$

for $H = -\frac{1}{2} \nabla^2 + V_{\text{eff}}$.

$$V_{\text{eff}} = V_{\text{e-n}} + V_H + V_{xc}$$

3. Compute $\rho = \sum_{occ} \psi_i^* \psi_i$

4. Compute potential:

a) $V_{\text{e-n}} = \sum_a \int d^3r' \frac{\rho(r') Z_a}{|r - R_a|}$

b) $V_H = \int d^3r' \frac{\rho(r')}{|r' - r|}$

c) V_{xc}

5. Check for self-consistency

Yes

6. Mix input + output density

Compute total E and output results.

7. compute, h potential

Some Details

1. Solve for atomic or atomic-like states on an exponential grid:

$$R_n = R_N \exp(D(n-N)) \quad R_0 = R_N e^{-ND}$$

Then you need R' and chain rule to solve Schrödinger eq.

In this case $R_n = r_p (\exp(nD) - 1)$

$$r_p = \frac{R_N}{\exp(ND)} \quad R_0 = 0$$

And then rewrite:

$$u(j) = v(j) e^{Dn/2}$$

$$\frac{d^2}{dj^2} v(j) - \frac{D^2}{4} v(j) = r_p^2 D^2 e^{2nD} [V(j) - E] v(j)$$

Free Electron Gas II

Thomas-Fermi Kinetic Energy

solutions: $\psi_i = \frac{1}{\sqrt{V}} e^{i\mathbf{k}\cdot\mathbf{r}}$

(in a large box of volume V , and lengths L_x, L_y, L_z)

Solutions must have nodes at boundaries L_x, L_y, L_z :

$$k_\alpha = \frac{2\pi n_\alpha}{L_\alpha} \quad \text{are the allowed values of } k$$

n_α integers

Allowed wave numbers, 1 per $\delta k_x \delta k_y \delta k_z = \frac{2\pi}{L_x} \frac{2\pi}{L_y} \frac{2\pi}{L_z} = \frac{(2\pi)^3}{V}$

Density of states $\frac{V}{(2\pi)^3}$

KE of each state is $\int \frac{\hbar^2 \mathbf{v}^2}{2m} \psi_i^* \psi_i = \frac{\hbar^2 k^2}{2m}$

So fill states in a sphere upto k_F

$$N = \rho V = \frac{4}{3} \pi k_F^3 \cdot 2 \cdot \frac{V}{(2\pi)^3}$$

$$k_F = (3\pi^2 \rho)^{1/3}$$

Average KE: $\left\langle \frac{\hbar^2 k^2}{2m} \right\rangle = \frac{\int_0^{k_F} \frac{\hbar^2 k^2}{2m} 4\pi k^2 dk}{\int_0^{k_F} 4\pi k^2 dk} = \frac{3}{5} \frac{\hbar^2 k_F^2}{2m}$

$$KE_{TF} = \frac{3}{5} \frac{\hbar^2}{2m} (3\pi^2 \rho)^{2/3} \rightarrow \frac{3}{10} (3\pi^2 \rho)^{2/3} \text{ in Hartrees}$$

Hartree Potential

Solve Poisson's equation.

$$\nabla^2 V_H(r) = -4\pi \rho(r)$$

$$U(r) = r V_H(r)$$

$$\frac{d^2}{dr^2} U(r) = -4\pi r \rho(r)$$

If you normalize $\int dr U^2(r) = 1$

$$U''(r) = -\frac{u^2(r)}{r}$$

$$U(0) = 0 \quad V_H'(r_{\max}) = \frac{g_{\max}}{r_{\max}^2}$$

$$g_{\max} = \int_0^{r_{\max}} dr u^2(r)$$

Integrate outward $U(0) = 0 \quad U(h) = h$

Homogeneous solution: $U(r) = \alpha r \quad U''(r) = 0$

So add αr to solution w/ α chosen to
make $U(r_{\max}) = g_{\max}$

What are the eigenvalues in DFT?

They are not excitation energies.

One can show (Perdew + Zunger, 1981) that

$$\epsilon_{\alpha} = \frac{\partial E}{\partial f_{\alpha}}$$

where f_{α} is the occupation of state α .

Band gap problem:

Gaps are too small, and sometimes zero for insulators.

Band gap is the difference in ground state energy for the N -electron and $N+1$ electron system, so it seems the exact DFT should give this energy difference correctly (though not necessarily for the eigenvalues).

(Nevertheless, there is an argument based on defects that the eigenvalues should also give the correct gap.)

Excitation Energies in DFT

Band gap $E_g = E(N+1) - E(N)$

$$E_g = \underbrace{E_{\text{conduction band minimum}}^N}_{\text{conduction band minimum}} - \underbrace{E_{\text{valence band max}}^N}_{\text{valence band max}} + \Delta V_{xc}$$

$$E_g = \epsilon_{N+1}(N+1) - \epsilon_N(N)$$

$$\neq \epsilon_{N+1}(N) - \epsilon_N(N)$$

$$\Delta V_{xc} = \epsilon_{N+1}(N+1) - \epsilon_{N+1}(N)$$

Much more can be said...

Another point: excitation energies can all be obtained by applying a time varying potential and looking for resonances.

Perdew Burke + Ernzerhof (PBE) GGA Generalized Gradient Approximation

- 1) non-empirical
- 2) universality
- 3) simplicity
- 4) accuracy

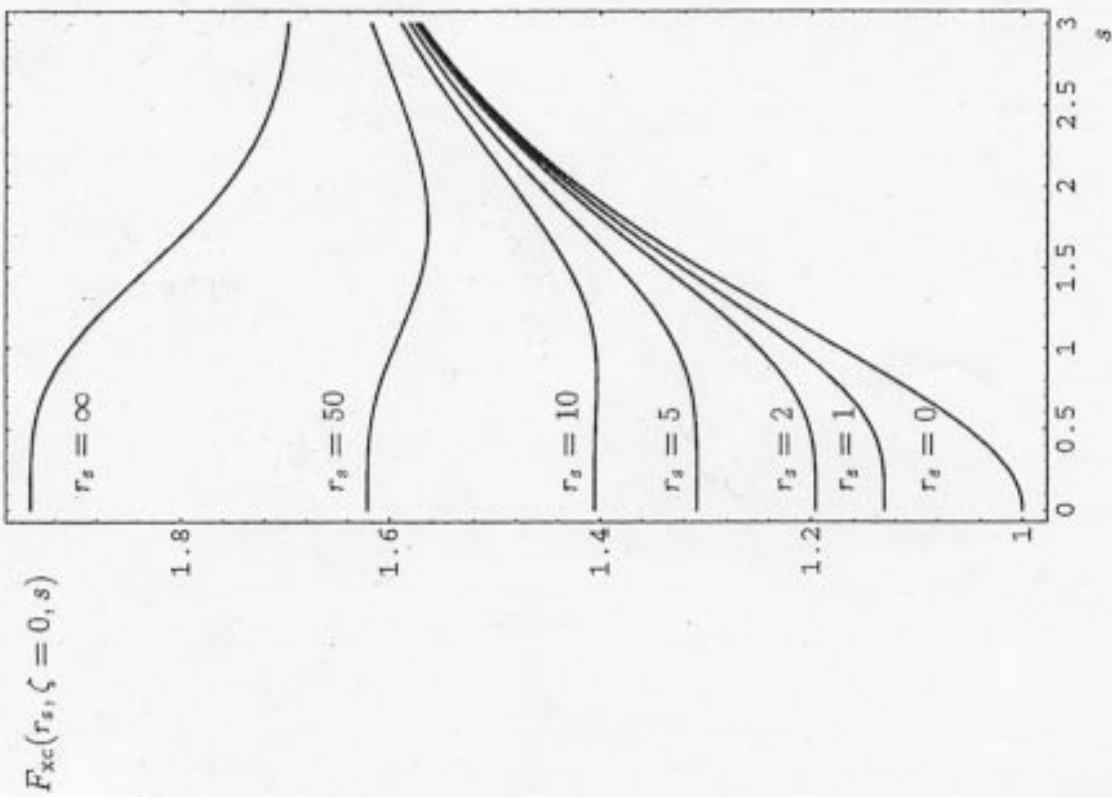
- A) Keep everything that LDA does right.
Scaling, xc hole = -1, bounds, r_s limits
- B) reduce to LDA for $\nabla\rho \rightarrow 0$

$$E_{xc}^{GGA}[\rho_\uparrow, \rho_\downarrow] = \int d^3r \rho e_x F_{xc}(r_s, \zeta, s)$$

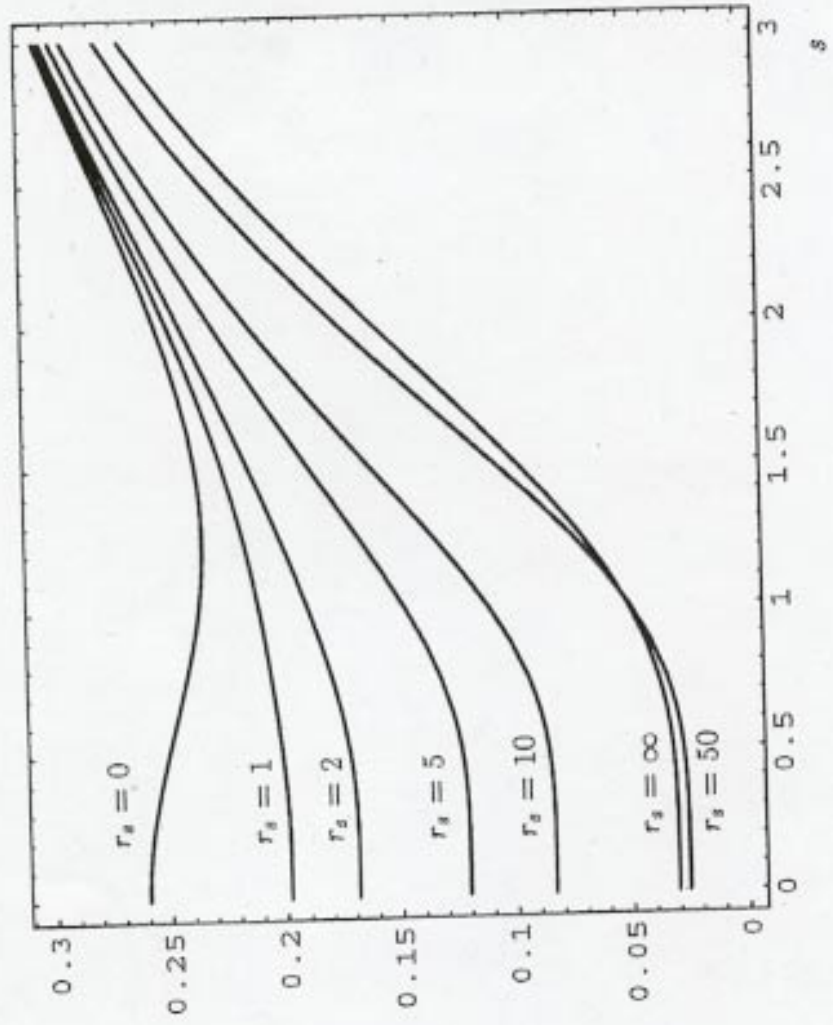
$$r_s = \left(\frac{4}{3}\pi\rho\right)^{-1/3} \quad \text{avg dist between electrons}$$

$$\zeta = \frac{\rho_\uparrow - \rho_\downarrow}{\rho}$$

$$s = \frac{|\nabla\rho|}{2k_F\rho} = \frac{|\nabla\rho|}{2\left(\frac{3\pi}{4}\right)^{1/3}\rho^{4/3}} = \frac{3}{2}\left(\frac{4}{9\pi}\right)^{1/3}|\nabla r_s|$$



$F_{xc}(r_s, \zeta = 1, s) - F_{xc}(r_s, \zeta = 0, s)$



Notes on atomic calculations

Central field approximation (not made in basis set calculations if potential is also represented by $f_{lm}(r)$)

$$\psi_i^{lm}(r) = \frac{u_i^l}{r} Y_{lm}(\theta, \varphi)$$

$$V = V(r) \quad \text{No } m \text{ dependence of } u.$$

(OK for closed shells)

But for open shell systems should have a non-spherical density + potential, and radial part will have m dependence (few implement)

Atoms (more)

Find eigen energies

E, E_{high}, E_{low}

Initial guess input

$$E_{high} = 0$$

$$E_{low} = 10 \times E$$

→ Find classical turning point at E (largest one)
Integrate outward to R_{turn}
Count nodes

Correct # nodes $n - l - 1$?

too many nodes? E too high, bisect E, E_{low}
(set $E_{high} = E$)

too few nodes? E too low, bisect E, E_{high}
(set $E_{low} = E$)

Check log derivative, negative

→ Integrate inward

Difference in log derivative $D = \frac{u'_{out}}{u_{out}} - \frac{u'_{in}}{u_{in}}$
small?

$D > 0$ E is too low $E_{low} = E$

$D < 0$ E is too high $E_{high} = E$

Bisection or secant method for E

Integrate out

→ Do for all states

Atoms (contd)

Compute charge density

compute potential



converged?

total ϵ etc.

$$V(r) \rightarrow -\frac{Z}{r} \text{ as } r \rightarrow 0$$

$$V(r) \rightarrow 0 \text{ as } r \rightarrow \infty$$

Leporelly + Alder
QMC

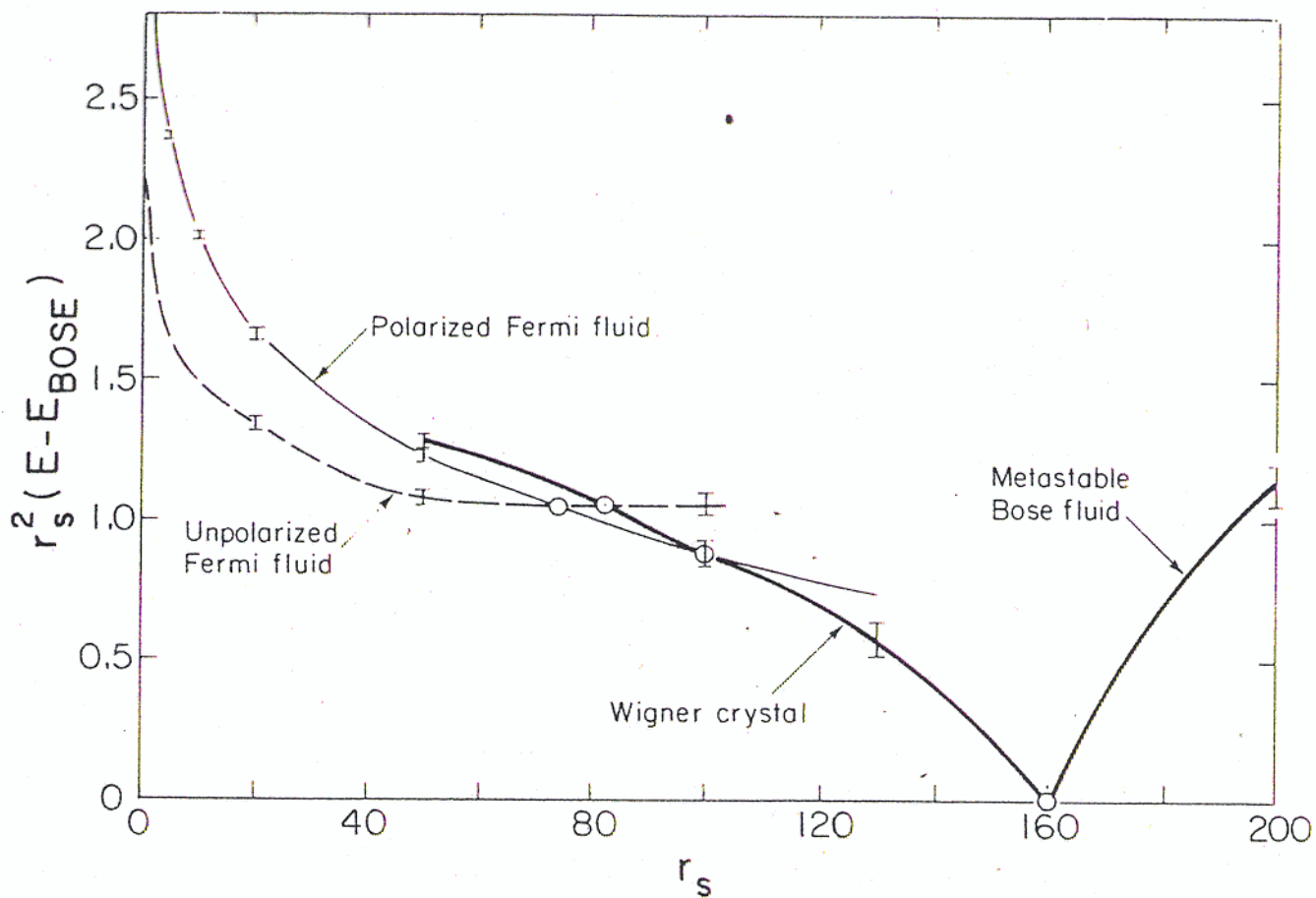


FIG. 2. The energy of the four phases studied relative to that of the lowest boson state times r_s^2 in rydbergs vs r_s in Bohr radii. Below $r_s = 160$ the Bose fluid is the most stable phase, while above, the Wigner crystal is most stable. The energies of the polarized and unpolarized Fermi fluid are seen to intersect at $r_s = 75$. The polarized (ferromagnetic) Fermi fluid is stable between $r_s = 75$ and $r_s = 100$, the Fermi Wigner crystal above $r_s = 100$, and the normal paramagnetic Fermi fluid below $r_s = 75$.

Pfaffner & Louie (1998)

Hydrogen Atom

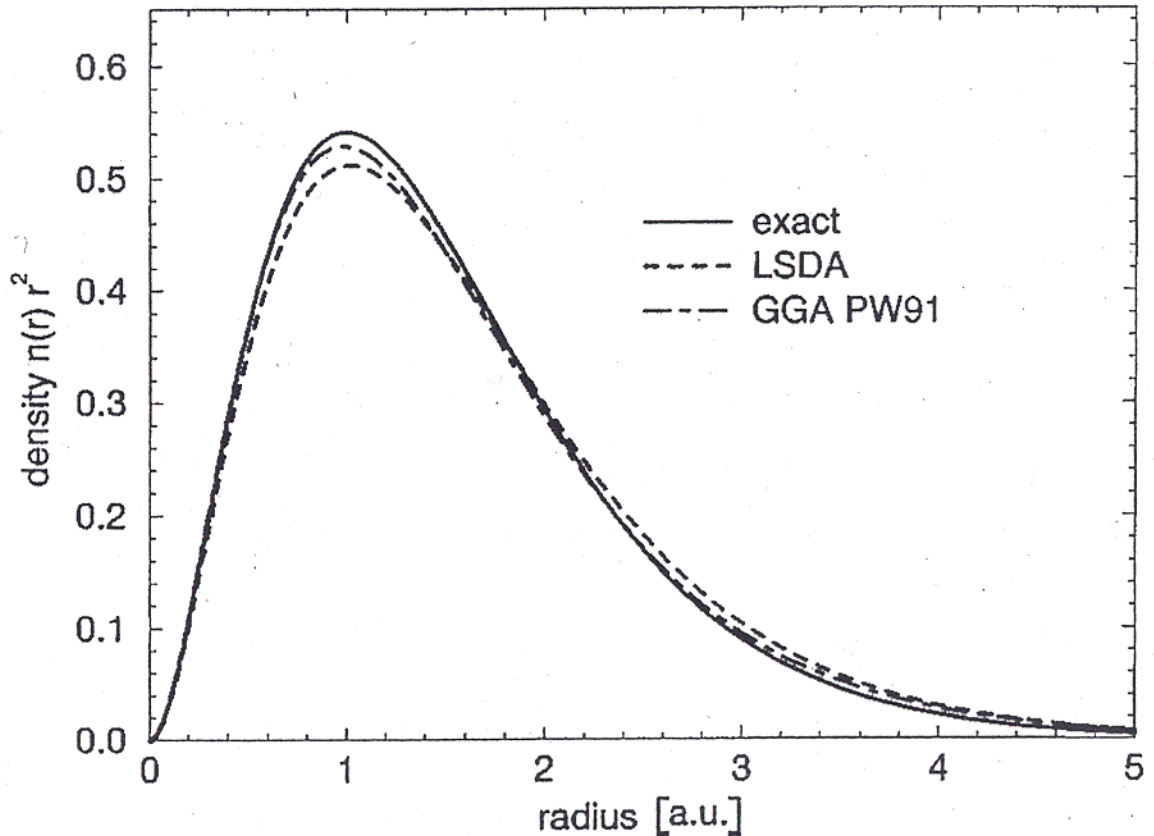


FIG. 1. Electron number density $n(r)$ of the hydrogen atom as a function of the radius. Shown are the exact density (solid line), and the self-consistent densities in LSDA (dashed line) and GGA PW91 (dot-dashed line).

Pfommer
&
Lovic 1998

TABLE I. values (in Rydbergs) for total energy E_{tot} , kinetic energy T , potential energy V , Hartree energy E_H , exchange energy E_x , correlation energy E_c , and exchange-correlation energy E_{xc} . A self-consistent electron density is used for the GGA PW91 functional and the LSDA.

	E_{tot}	T	V	E_H	E_x	E_c	E_{xc}
Exact	-1	1	-2	0.625	-0.625	0	-0.625
LSDA	-0.958	0.933	-1.891	0.597	-0.513	-0.044	-0.557
PW91	-1.003	0.993	-1.991	0.615	-0.606	-0.013	-0.619

Hydrogen Atom

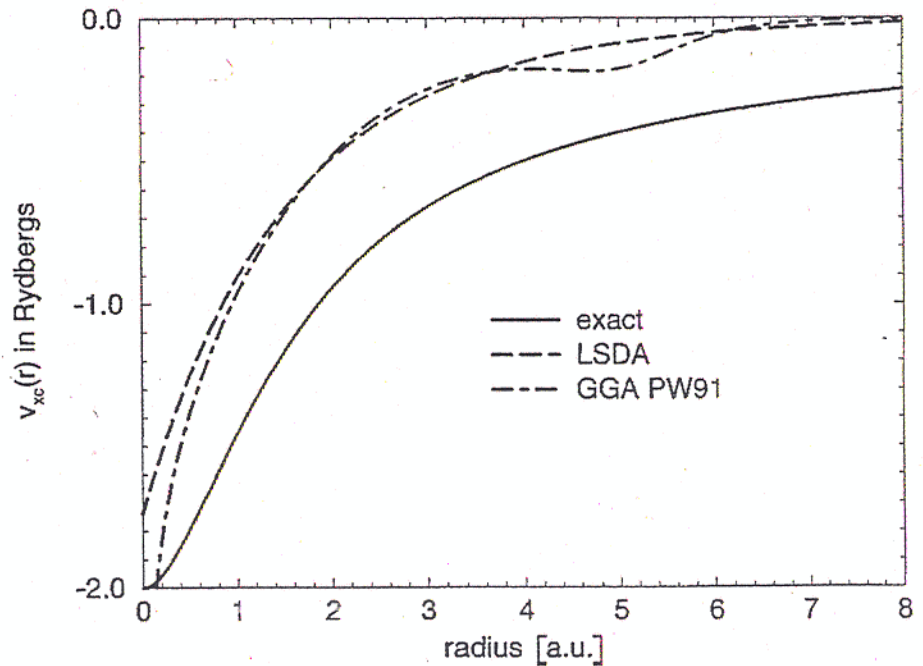
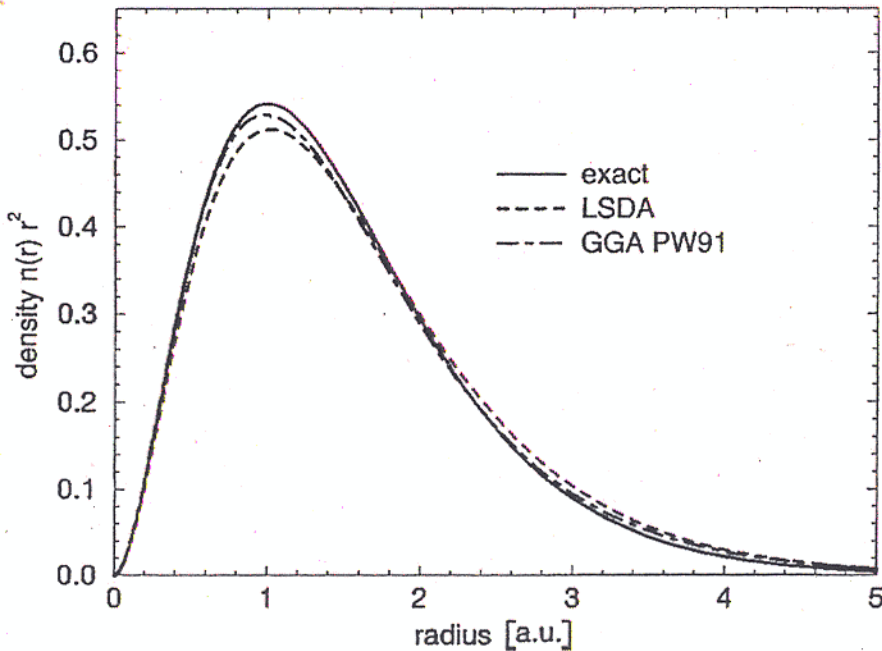


FIG. 2. Exchange-correlation potential $v_{xc}(r)$ in Rydbergs for the hydrogen atom as a function of the radius. Shown are the exact v_{xc} (solid line), and the self-consistent v_{xc} in LSDA (dashed line) and GGA PW91 (dot-dashed line).

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Central field approximation (not made in basis set calculations if potential is also represented by $f_{lm}(r)$)

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(OK for closed shells)

But for open shell systems should have a non-spherical density + potential, and radial part will have m dependence (few implement)

Atoms (more)

Find eigen energies

$E, E_{\text{High}}, E_{\text{Low}}$

Initial guess input

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Integrate outward to R_{turn}
Count nodes

Correct # nodes $n - l - 1$?

too many nodes? E too high, bisection E, E_{Low}
(set $E_{\text{High}} = E$)

too few nodes? E too low, bisection E, E_{High}
(set $E_{\text{Low}} = E$)

Check log derivative, negative

Integrate inward

Difference in log derivatives $D = \frac{u'_{\text{out}}}{u_{\text{out}}} - \frac{u'_{\text{in}}}{u_{\text{in}}}$

small?

$D > 0$ E is too low $E_{\text{Low}} = E$

$D < 0$ E is too high $E_{\text{High}} = E$

Bisection or secant method for E

Integrate out

Do for all states

Atoms (contd.)

Compute charge density

compute potential

converged?

total ϵ etc.

$$V(r) \rightarrow -\frac{Z}{r} \text{ as } r \rightarrow 0$$

$$V(r) \rightarrow 0 \text{ as } r \rightarrow \infty$$

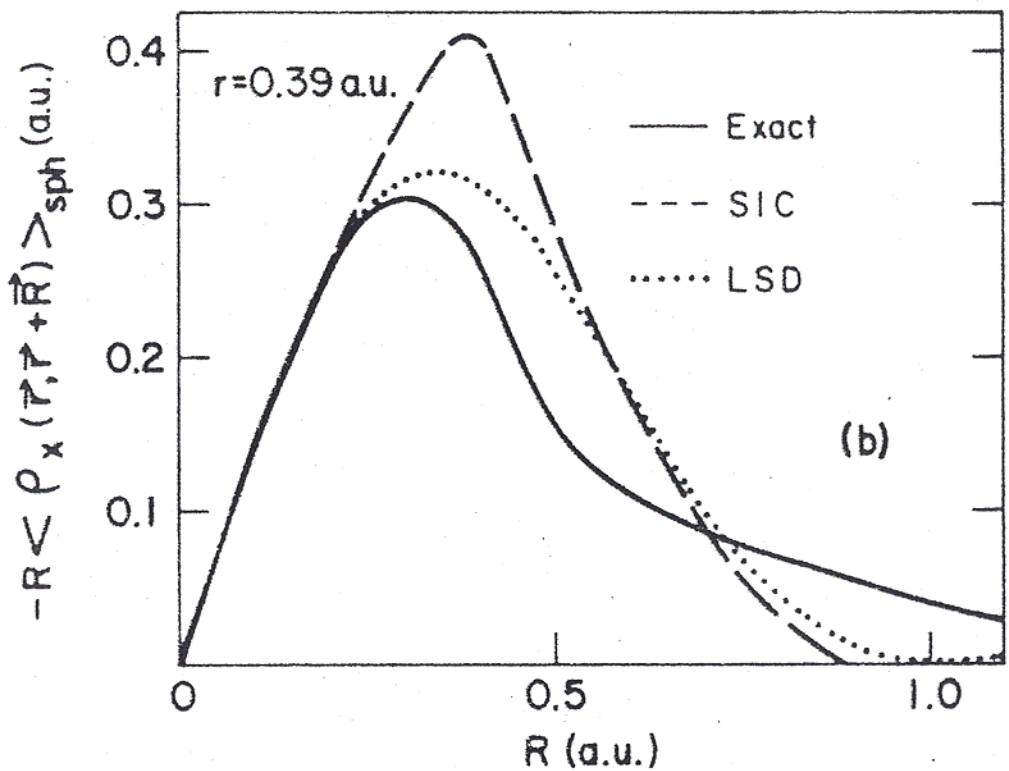
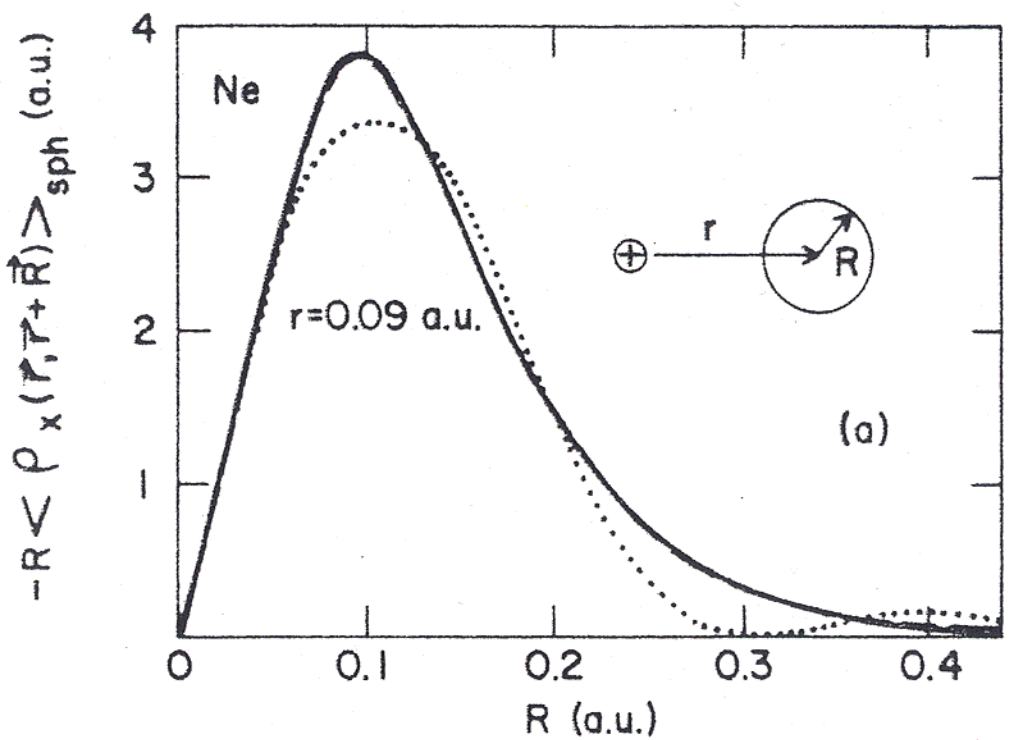


FIG. 2. Spherical average of the neon exchange hole times R for (a) $r = 0.09$ a.u. and (b) $r = 0.39$ a.u. The full, dashed, and dotted curves are the exact, SIC-LSD and LSD results, respectively. In part (a), the SIC-LSD curve is almost indistinguishable from the exact one.

Perdew + Zunger

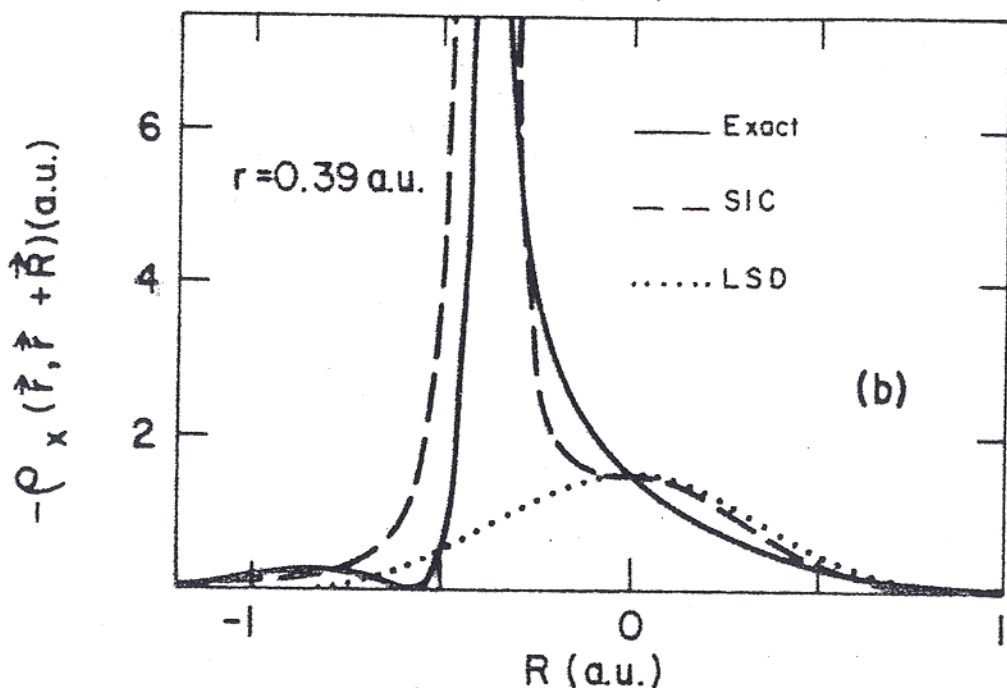
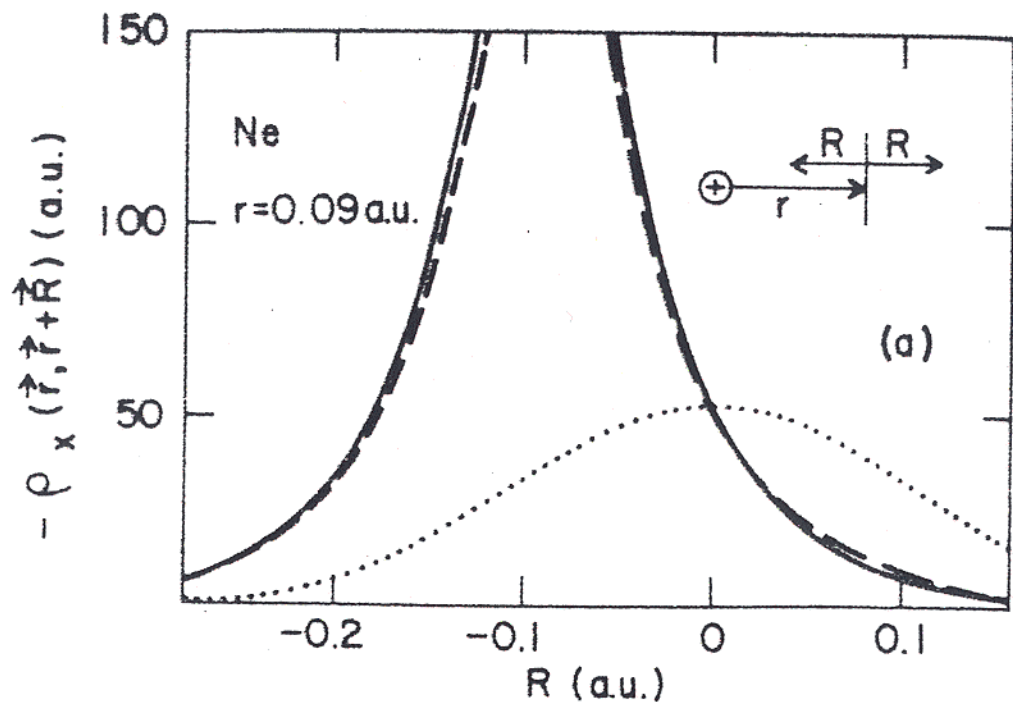


FIG. 1. Exchange hole about an electron located at distance r from the nucleus in the neon atom. The full curves are exact, while the dashed and dotted curves represent the SIC-LSD and LSD approximations,

Perdew + Zunger

Periodic Solids

Nuclei are at $\vec{r}_i = \sum_{i=1}^3 \vec{a}_i n_i + \vec{b}_i$

$\vec{a}_{i=1,2,3}$ lattice vectors

14 Bravais lattices

\vec{b}_i basis vectors

230 Space groups

Lattice: $\vec{R}_{i,j,k} = i\vec{a}_1 + j\vec{a}_2 + k\vec{a}_3$
 i, j, k integers

Reciprocal lattice: $\vec{G}_{h,k,l} = h\vec{g}_1 + k\vec{g}_2 + l\vec{g}_3$
 h, k, l integers.

$$\vec{R} \cdot \vec{G} = 2\pi n, \quad n \text{ integer}$$

$$\vec{a}_i \cdot \vec{g}_j = 2\pi \delta_{ij}$$

$$\vec{g}_j = 2\pi \epsilon_{jkl} \frac{\vec{a}_k \times \vec{a}_l}{V}$$

$$V = \vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)$$

ϵ_{jkl} +1 even -1 odd

$$\vec{K} = \vec{r} + \vec{G}$$

\uparrow
k-point

\nwarrow
reciprocal
lattice
vector

first Brillouin zone:

All points closer to $\vec{K} = 0$
than to any other point \vec{G} .

van Karman boundary conditions (periodic)
allowed $\vec{K} = 2\pi \left(\frac{n_1}{L_1}, \frac{n_2}{L_2}, \frac{n_3}{L_3} \right)$

Band Theory

Consider the Fourier transform of the potential

$$V(r) = \sum_{\vec{G}} e^{i\vec{G}\cdot\vec{r}} V_{\vec{G}}$$

This is a periodic potential with periodicity given by $\vec{G} = h\vec{g}_1 + k\vec{g}_2 + l\vec{g}_3$

$\vec{G} = 0$ \rightarrow 1 period per cell
 $|\vec{G}| = \frac{1}{2}$ \rightarrow 2 periods per cell etc.

The orbitals (wave functions) do not have to have the periodicity of the cell.

$$\psi(r) = \sum_{\vec{k}} e^{i\vec{k}\cdot\vec{r}} C_{\vec{k}}$$

Now $\vec{k} = \vec{k} + \vec{G}$ \vec{k} is not a reciprocal lattice vector.

Consider $(-\frac{1}{2}\nabla^2 + V)\psi = \epsilon\psi$

$$-\frac{1}{2}\nabla^2\psi = \frac{1}{2}\sum_{\vec{k}} k^2 e^{i\vec{k}\cdot\vec{r}} C_{\vec{k}}$$

$$V\psi = \left(\sum_{\vec{G}} e^{i\vec{G}\cdot\vec{r}} V_{\vec{G}}\right) \left(\sum_{\vec{k}} e^{i\vec{k}\cdot\vec{r}} C_{\vec{k}}\right)$$

Band Theory (contd.)

$$\psi = \left(\sum_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}} V_{\mathbf{G}} \right) \left(\sum_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}} C_{\mathbf{k}} \right)$$

$$= \sum_{\mathbf{G}, \mathbf{k}} V_{\mathbf{G}} C_{\mathbf{k}} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} = \sum_{\mathbf{G}, \mathbf{k}'} V_{\mathbf{G}} C_{\mathbf{k}-\mathbf{G}} e^{i\mathbf{k}'\cdot\mathbf{r}}$$

\uparrow
 $\mathbf{k}' = \mathbf{k} + \mathbf{G}$

So Schrodinger's eq. becomes:

$$\sum_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}} \left\{ \left(\frac{1}{2} \mathbf{k}^2 - \epsilon \right) C_{\mathbf{k}} + \sum_{\mathbf{G}'} V_{\mathbf{G}'} C_{\mathbf{k}-\mathbf{G}'} \right\} = 0$$

\downarrow
 $\mathbf{k}' \rightarrow \mathbf{k}, \mathbf{G} \rightarrow \mathbf{G}'$

Now since plane waves are orthogonal, each term must be zero (can also prove by multiplying by $C_{\mathbf{k}'} e^{i\mathbf{k}'\cdot\mathbf{r}}$ and integrate)

Let $\vec{\mathbf{k}} = \vec{\mathbf{k}} + \vec{\mathbf{G}}$ and we get:

$$\left(\frac{1}{2} |\vec{\mathbf{k}} + \vec{\mathbf{G}}|^2 - \epsilon \right) C_{\vec{\mathbf{k}} + \vec{\mathbf{G}}} + \sum_{\mathbf{G}'} V_{\mathbf{G}'} C_{\vec{\mathbf{k}} + \vec{\mathbf{G}} - \mathbf{G}'} = 0$$

$$\mathbf{G}' \rightarrow \mathbf{G}' - \mathbf{G}$$

$$\left(\frac{1}{2} |\vec{\mathbf{k}} + \vec{\mathbf{G}}|^2 - \epsilon \right) C_{\vec{\mathbf{k}} + \vec{\mathbf{G}}} + \sum_{\mathbf{G}'} V_{\mathbf{G}' - \mathbf{G}} C_{\mathbf{k} - \mathbf{G}'} = 0$$

★ Note $\vec{\mathbf{k}}$ vectors are independent. Solve secular equation for each $\vec{\mathbf{k}}$, set $\epsilon_{i\vec{\mathbf{k}}}, C_{\vec{\mathbf{k}} + \vec{\mathbf{G}}}$

Bloch's theorem: $\psi_{\vec{\mathbf{k}}}(\mathbf{r}) = \sum_{\mathbf{G}} C_{\mathbf{k}-\mathbf{G}} e^{i(\mathbf{k}-\mathbf{G})\cdot\mathbf{r}}$

Band Theory contd

Bloch's theorem:

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} C_{\mathbf{k}-\mathbf{G}} e^{i(\mathbf{k}-\mathbf{G}) \cdot \mathbf{r}}$$

$$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\vec{k} \cdot \vec{r}} \left(\sum_{\mathbf{G}} C_{\mathbf{k}-\mathbf{G}} e^{-i\mathbf{G} \cdot \mathbf{r}} \right)$$

This is a periodic function of \mathbf{r}

$$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\vec{k} \cdot \vec{r}} u(\vec{r})$$

Summary: assumption of band theory
periodic external potential.

To solve: could form $H_{\mathbf{G}\mathbf{G}'}$ and diagonalize,
but need too many \mathbf{G} 's (million for \mathbf{A})
for full potential.

Self-consistent crystalline computations.

Initial ρ

Compute V — $\begin{pmatrix} V_A \\ V_N \\ V_C \end{pmatrix}$ (Poisson's eq.)

Solve KS equations for each k -point

Determine E_F



The diagram shows three vertical columns representing energy levels at k_1 , k_2 , and k_3 . Each column has three horizontal lines representing energy bands. A dashed orange horizontal line, labeled E_F , represents the Fermi level. It is positioned between the middle and top bands of each column.

Compute ρ_{out} $\left(\sum_{\mathbf{k}} \sum_{\mathbf{l}} \psi_{i\mathbf{k}}^* \psi_{j\mathbf{l}} t(\mathbf{E} - E_F)_{ij} \right)$

Compute E

No Converged?



K-points

States are labeled by k in the first Brillouin zone (BZ)

and $\rho = V \int_{BZ} d^3k \sum_i \psi_{i,k}^* \psi_{i,k} f(\epsilon_i - \epsilon_F)$

$f(\epsilon_i - \epsilon_F) = (e^{\epsilon_i - \epsilon_F / k_B T} + 1)^{-1}$
Fermi function

How to accurately integrate over BZ?

$$V \int_{BZ} d^3k \longrightarrow \sum_k w_k$$

Two main methods used: Tetrahedron method

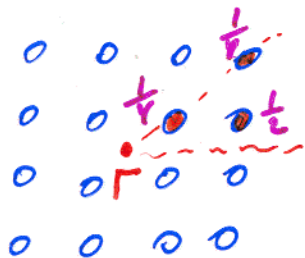
Assume linear between mesh points

Special K-points

Integrates Fourier series exactly
up to some G_{max}

Special Points: Monkhorst & Pack (1976, 1977)

- Generate a uniform grid, displaced by 0.5 π increment
- Use space group operations to rotate all points into the irreducible part of BZ (IBZ)
- Determine weights



3 points rather than 16



LDA or GGA do not work for everything

- LDA and (PBE) GGA provide accurate predictions of many properties at expt. volume.
- However, LDA **underestimates** while (PBE) GGA **overestimates** lattice constant by 1-2%.
- Certain properties, such as ferroelectricity, are very **sensitive to volume**.
- For ground state structures of ferroelectrics with strains, GGAs are particularly bad:

Equilibrium volume and strain of tetragonal PbTiO_3

	LDA	PBE	revPBE	RPBE	WDA*	Expt.
$V_0(\text{\AA}^3)$	60.37	70.58	74.01	75.47	68.48	63.08
c/a	1.046	1.239	1.286	1.301	1.19	1.075

Exchange-Correlation Energy

- Density functional theory (DFT): electron density $n(\vec{r})$ is the basic variable.
- Kohn-sham Equation:

$$\left[-\frac{1}{2}\nabla^2 + v_{\text{ext}}(\vec{r}) + v_{\text{H}}(\vec{r}) + v_{\text{xc}}(\vec{r})\right]\psi_i = \lambda_i\psi_i$$

where $v_{\text{xc}}(\vec{r}) = \frac{\delta E_{\text{xc}}[n(\vec{r})]}{\delta n(\vec{r})}$, $v_{\text{H}}(\vec{r}) = \int \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}'$

- LDA and GGA:

$$E_{\text{xc}}^{\text{LDA}}[n] = \int n(\vec{r}) \varepsilon_{\text{xc}}^{\text{hom}}(n) d\vec{r}$$

$$E_{\text{xc}}^{\text{GGA}}[n] = \int f[n(\vec{r}), \nabla n(\vec{r})] d\vec{r}$$

$$= \int F_{\text{x}} \cdot n(\vec{r}) \varepsilon_{\text{x}}^{\text{hom}}(n) d\vec{r} + E_{\text{c}}^{\text{GGA}}$$

PBE GGA

- Perdew-Burke-Ernzerhof (PBE) formalism is the most widely used GGA. (PRL 77, 3865)
- Correlation correction was derived from the low and high variation limits, plus linear scaling.
- Exchange enhancement factor was derived from a **sharp** cutoff of the exchange hole in real space.

$$F_x^{\text{PBE}} = 1 + \kappa - \kappa / (1 + \mu s^2)$$

where s : reduced gradients, $\kappa = 0.804$

- Here μ is set to 0.21951 to **cancel the correlation** correction for $s \rightarrow 0$.

Construction of a new GGA

- The xc hole in solids can have a **diffuse** tail, not in atoms or small molecules.
- A diffuse cutoff of the exchange hole leads to a smaller E_c than E_c^{PBE} . (Perdew et al., PRB **54**, 16533)
- For slowly varying density systems, (Svendsen and von Barth, PRB **54**, 17402)

$$F_x = 1 + \frac{10}{81} p + \frac{146}{2025} q^2 - \frac{73}{405} pq + O(\nabla^6)$$

where $p = s^2$, q : reduced Laplacian.

- A new F_x^{WC} based on above observations:

$$F_x^{\text{WC}} = 1 + \kappa - \kappa / (1 + x / \kappa)$$

$$\text{and } x = \frac{10}{81} s^2 + \left(\mu - \frac{10}{81}\right) s^2 \cdot \exp(-s^2) + \ln(1 + cs^4)$$

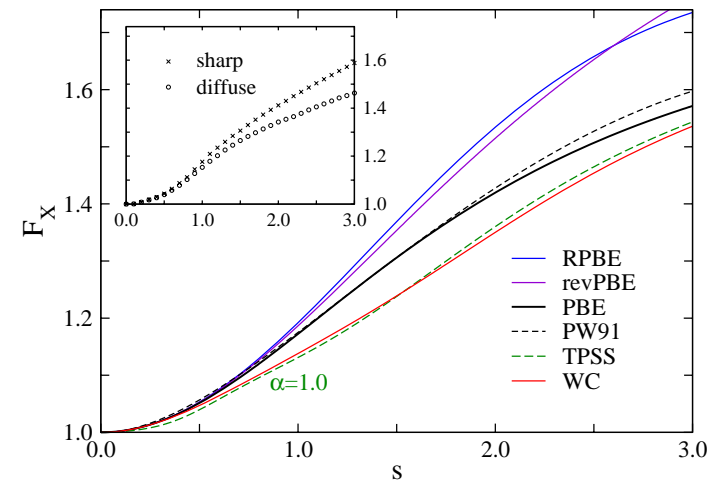
- and $E_c^{\text{WC}} = E_c^{\text{PBE}}$

[1] Perdew, Burke, and Wang, PRB **54**, 16533

[2] Tao et al., PRL **91**, 146401

- Symbols in insert are determined by the real space cutoff procedure [1].

F_x^{WC} matches that of TPSS meta-GGA [2] for the slowly varying limit well.



Simple solids

- We tested the following 18 solids: Li, Na, K, Al, C, Si, SiC, Ge, GaAs, NaCl, NaF, LiCl, LiF, MgO, Ru, Rh, Pd, Ag.
- The new GGA is **much better** than other approximations.

Mean errors (%) of calculated equilibrium lattice Constants a_0 and bulk moduli B_0 at 0K.

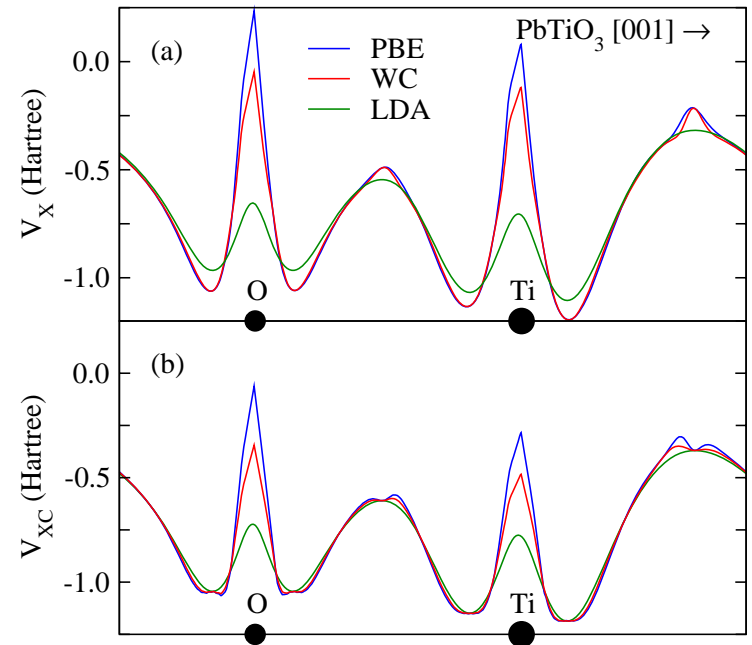
	LDA	PBE	WC	TPSS	PKZB
a_0	1.74	1.30	0.29	0.83	1.65
B_0	12.9	9.9	3.6	7.6	8.0

TPSS and PKZB results: Staroverov, *et al.* PRB **69**, 075102

More accurate E_{xc} for Ferroelectrics

- The new GGA is **very accurate** for the ground state structure of ferroelectrics.
- V_x^{WC} differs from V_x^{PBE} **significantly** only in core regions.
- In bonding regions, the difference V_x^{WC} and V_x^{PBE} is much smaller.

P4mm PbTiO₃



R3m BaTiO₃

	LDA	PBE	WC	Expt
$V_0(\text{\AA}^3)$	60.37	70.54	63.47	63.09
c/a	1.046	1.239	1.078	1.071
$u_z(\text{Pb})$	0.0000	0.0000	0.0000	0.000
$u_z(\text{Ti})$	0.5235	0.5532	0.5324	0.538
$u_z(\text{O}_{1,2})$	0.5886	0.6615	0.6106	0.612
$u_z(\text{O}_3)$	0.0823	0.1884	0.1083	0.112

	LDA	PBE	WC	Expt
$V_0(\text{\AA}^3)$	61.59	67.47	64.04	64.04
$\beta(^{\circ})$	89.91	89.65	89.86	89.87
$u_z(\text{Pb})$	0.0000	0.0000	0.0000	0.0000
$u_z(\text{Ti})$	0.4901	0.4845	0.4883	0.487
$u_z(\text{O}_{1,2})$	0.5092	0.5172	0.5116	0.511
$u_z(\text{O}_3)$	0.0150	0.0295	0.0184	0.018

u_z are given in terms of the lattice constants