2007 Summer School on Computational Materials Science

Quantum Monte Carlo: From Minerals and Materials to Molecules

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Introduction to Density Functional Theory

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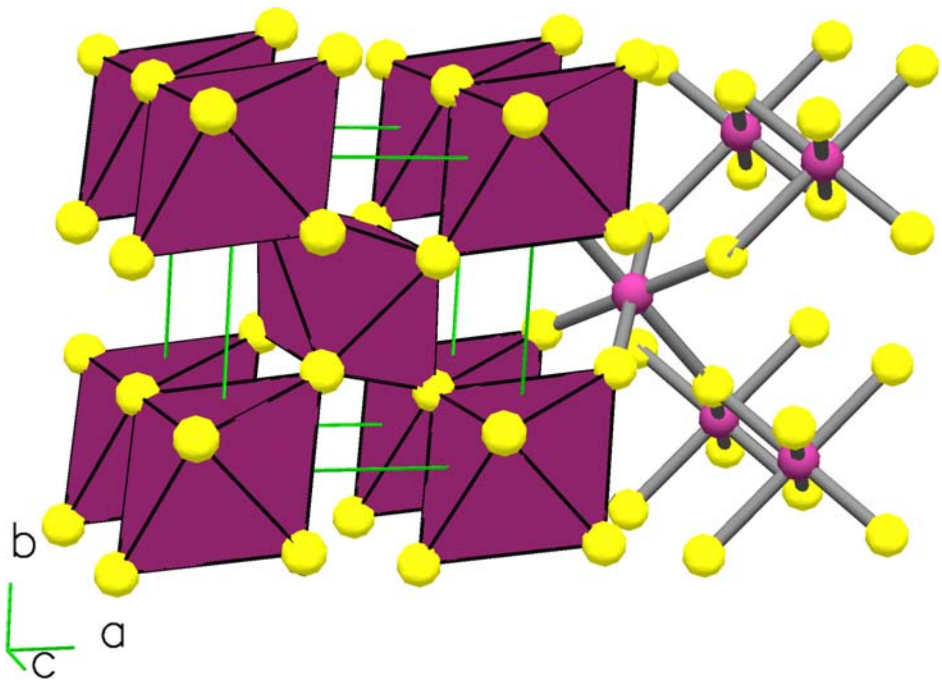
What is Density Functional Theory?

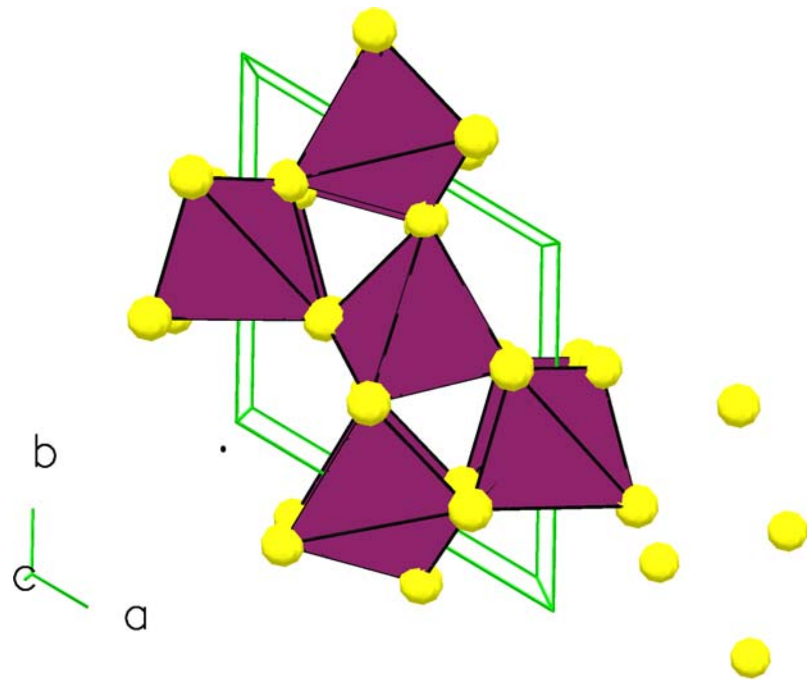
- DFT is an exact many-body theory for the ground state properties of an electronic system.
  - Atoms, molecules, surfaces, nanosystems, crystals
- Although DFT is formally exact, the exact functional is unknown.
- The exact functional probably does not have a closed form, and would be extremely non-local.
- 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.

Outline

- Motivation: an example—Quartz and Stishovite, DFT versus QMC
- What is DFT used for in QMC studies?
- The steps for Diffusion Monte Carlo.
- Density Functional Theory
  - What is a functional?
  - Hohenburg Kohn Theorems
  - Kohn–Sham method
  - Local Density Approximation (LDA)
  - Total energy calculations
  - Typical Errors
  - What is known about exchange and correlation functionals?
  - The exchange correlation hole and coupling constant integration
  - LDA and GGA (more)
  - Band theory
  - Self-consistency
  - A new GGA (WC) and the poential for more accurate density functionals

Quartz and Stishovite





Stishovite (rutile) structure

Dense

octahedrally coordinated Silicon

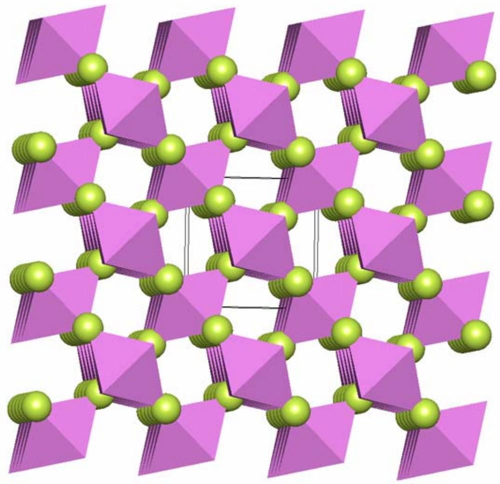
Quartz structure

Open structure

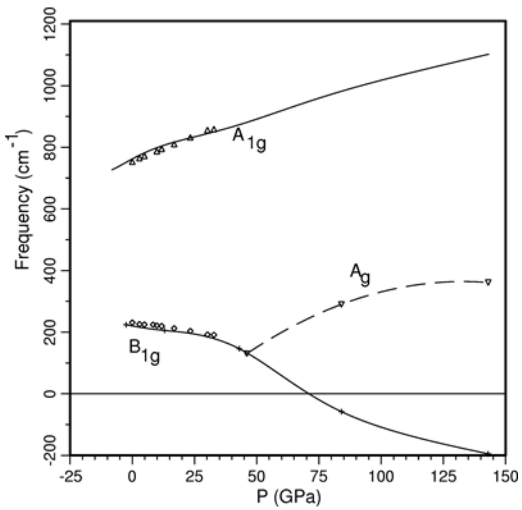
tetrahedrally coordinated Silicon

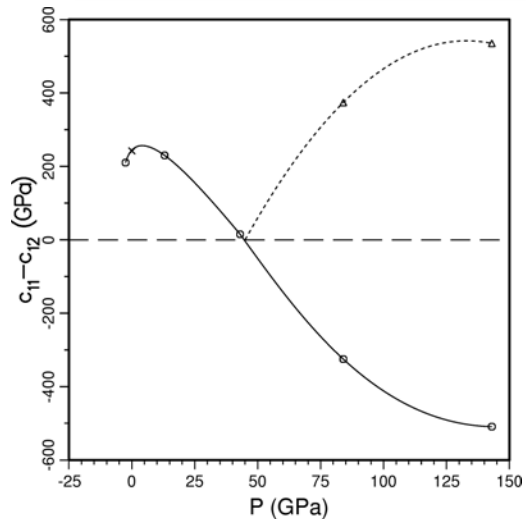
$CaCl_2$ transition in SiO2

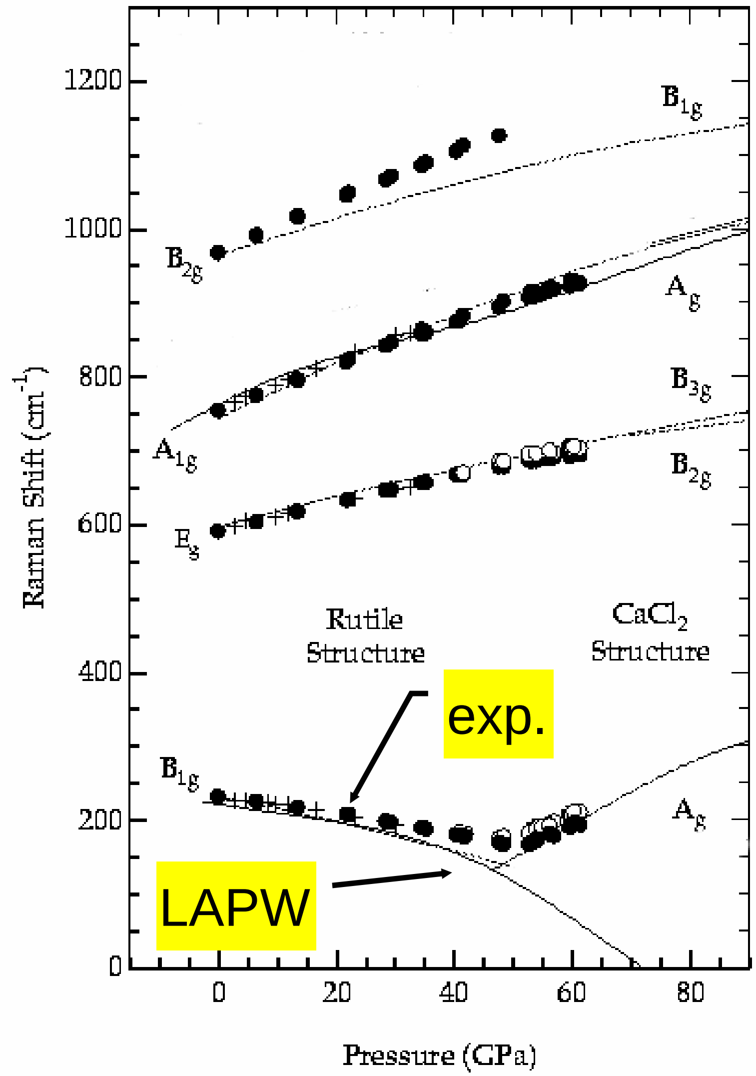
Prediction: A_{1g} Raman mode in stishovite decreases until phase transition to $CaCl_2$ structure, then increases. Does NOT go to zero at transition.



Prediction: C_{11}-C_{12} decreases until phase transition to $CaCl_2$ structure, then increases. Does go to zero at transition-> superplacticity





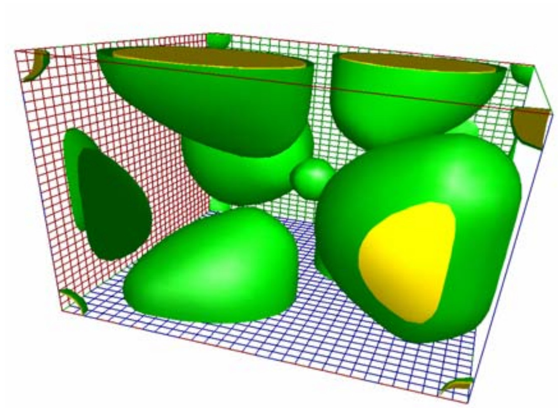


Predicted transition (Cohen, 1991) was found by Raman (Kingma et al., Nature 1995).

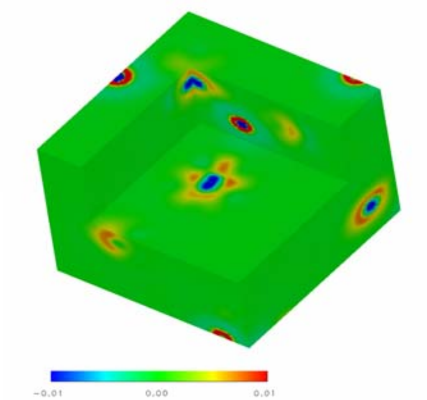
LDA works for stishovite/$CaCl_2$.

Silica

stishovite valence density



Simple close shelled electronic structure, yet problems with DFT



difference in GGA and LDA valence density

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Generalized Gradient Theory for Silica Phase Transitions

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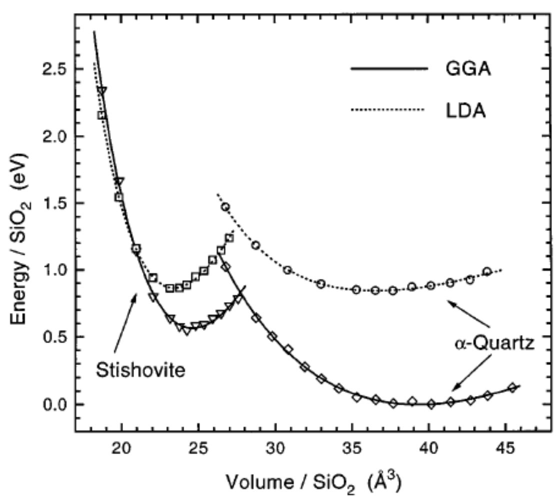
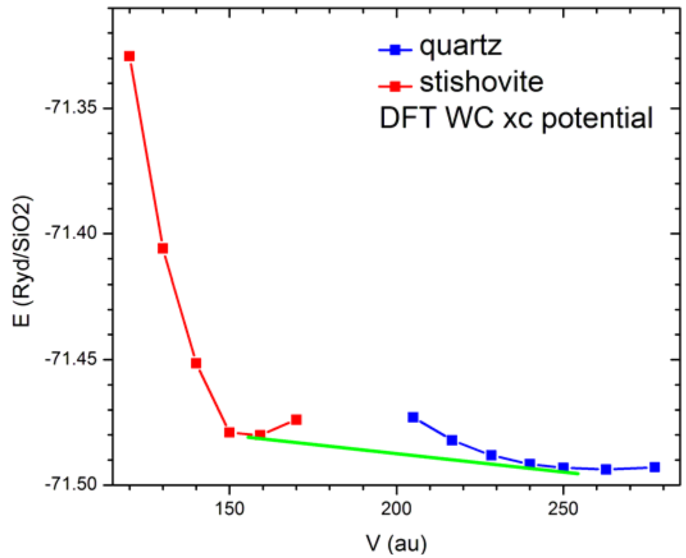
(Received 16 October 1995)

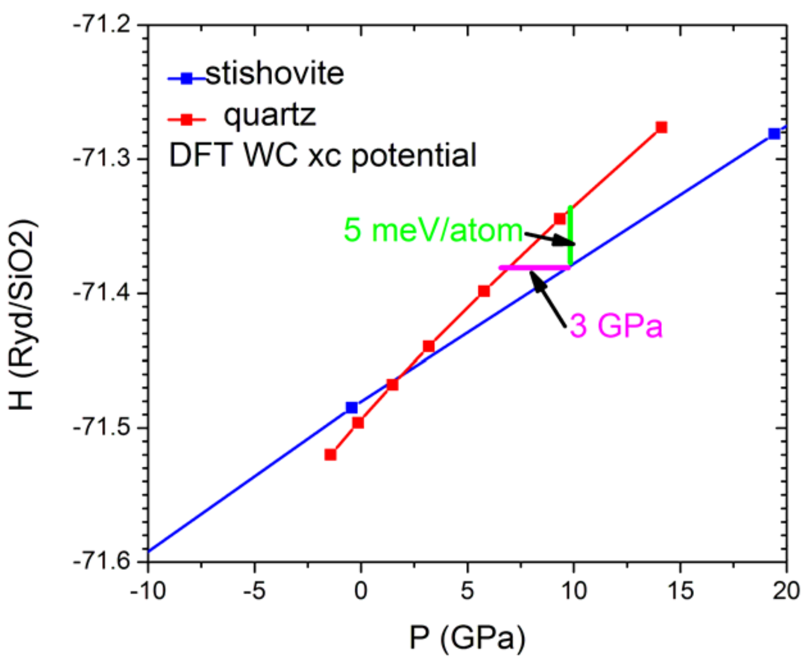


	LDA	PBE*	WC**	Exp.
ΔE (eV)	-0.05	0.5	0.2	0.5
P_{tr}	<0	6.2	2.6	7.5
V_{qz}	244	266	261	254
K_{qz}	35	44	29	38
V_{st}	155	163	159	157
K_{st}	303	257	330	313

*Zupan, Blaha, Schwarz, and Perdew, Phys. Rev. B **58**, 11266 (1998).
Wu and R. E. Cohen, Phys. Rev. B **73**, 235116 (2006).

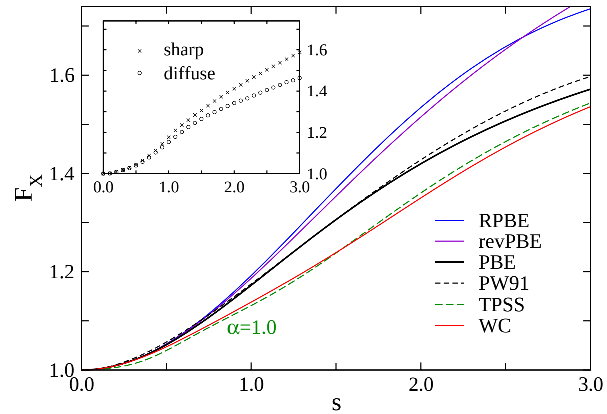
DFT (WC) energies for quartz and stishovite





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.

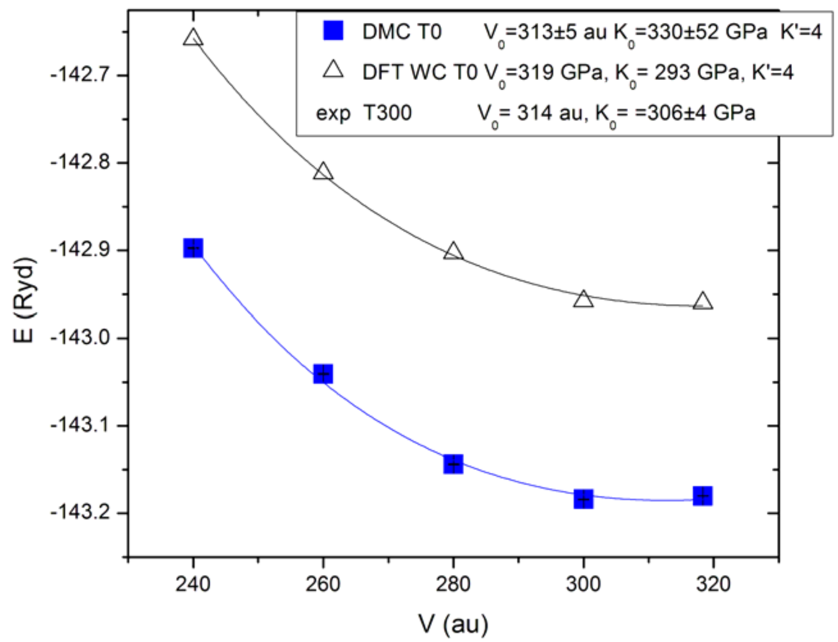
	LDA	PBE	WC	TPSS	PKZB
a_0	1.74	1.30	0.29	0.83	1.65
B_0	12.9	9.9	3.6	7.6	8.0

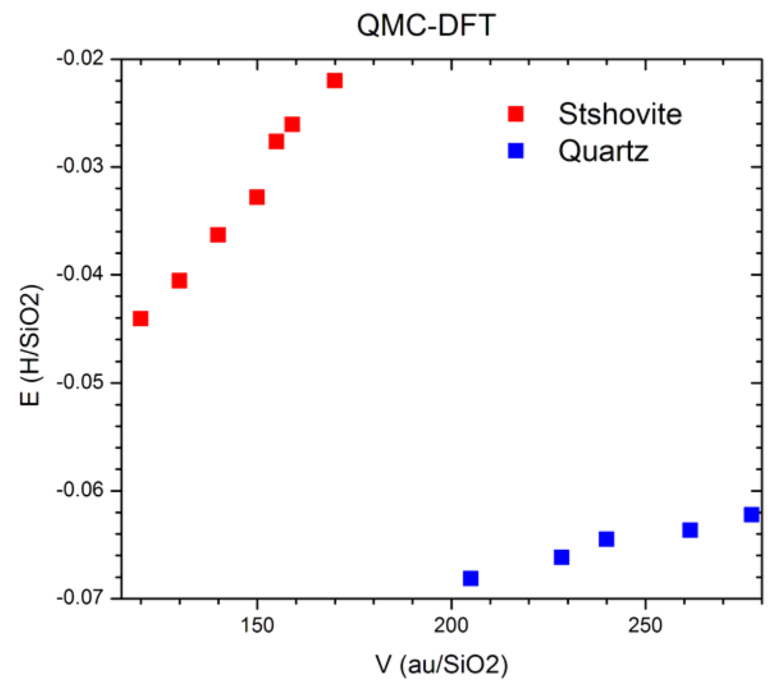
TPSS and PKZB results: Staroverov, *et al*. PRB **69**, 075102

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 stish 3x3x3 qz 2x2x2 **No finite size corrections**	-35.8071	-35.7912	0.43

Comparison of QMC and DFT (WC xc)

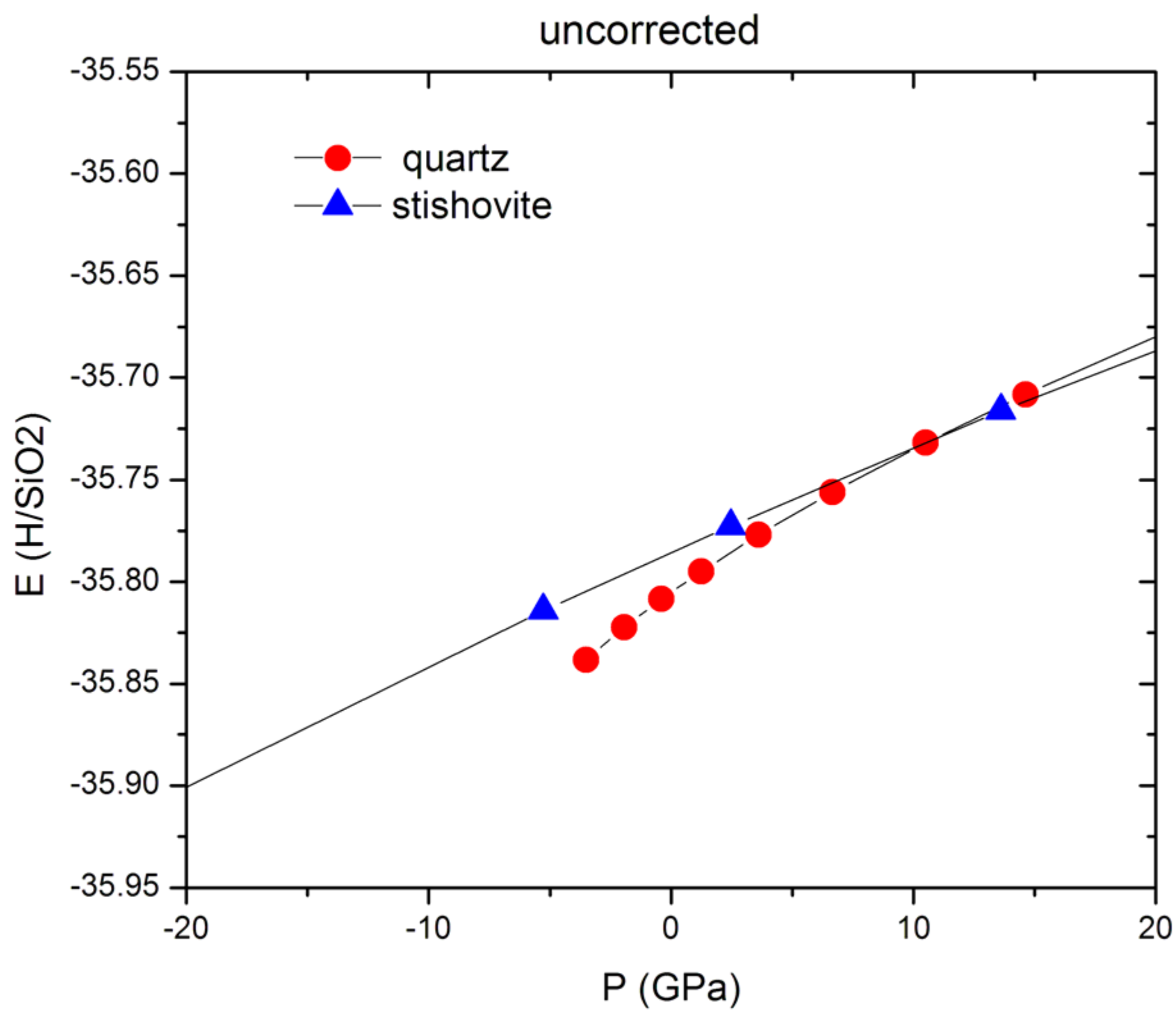




	stishovite	quartz
E_0 eV/SiO_2	-0.77	-1.76
P GPa	-4.6	-8.0

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

Quartz to stishovite transition

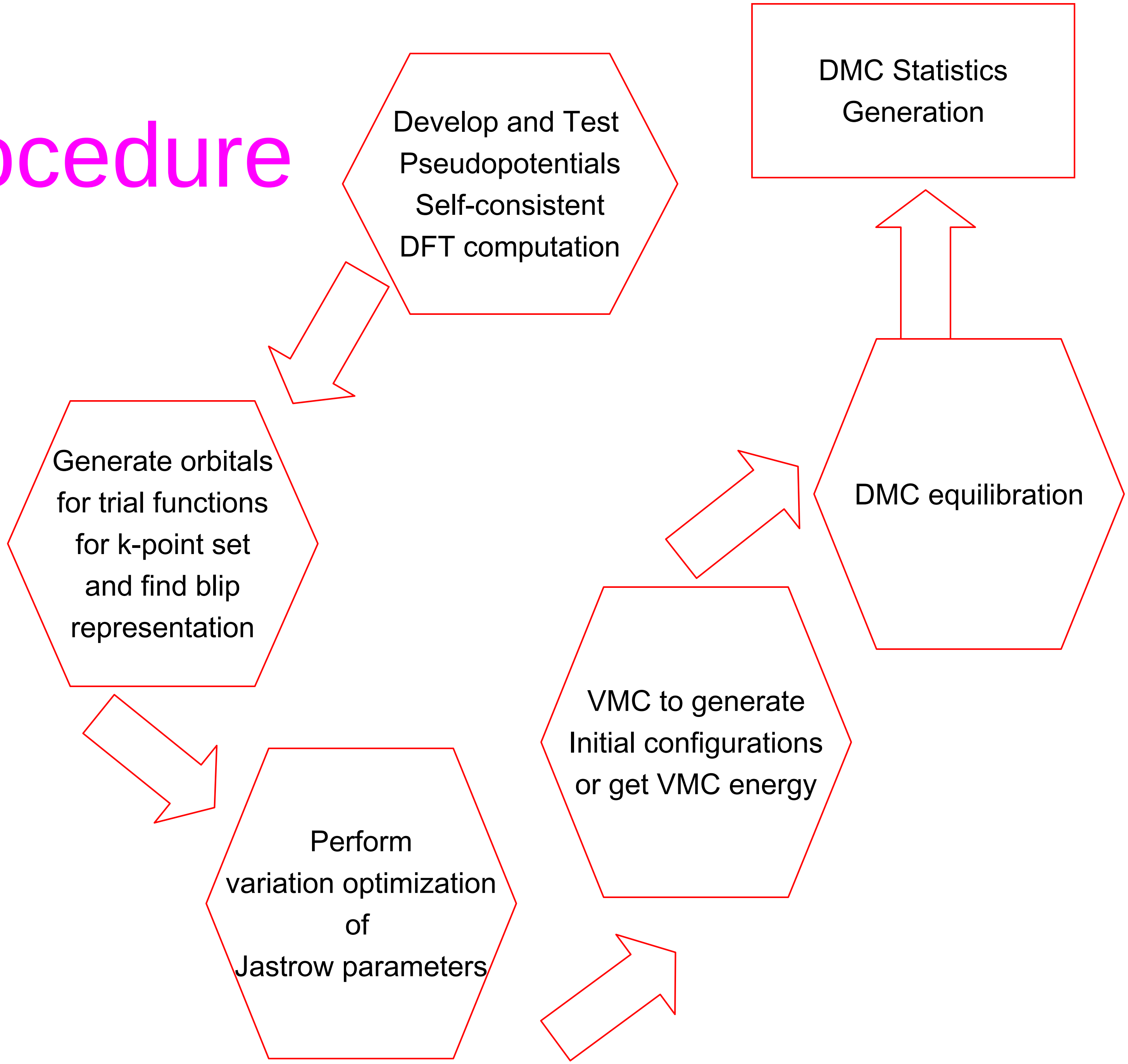


	qz	st
V_0 (au)	247	156
V_0 (exp)	254	157
K_0 (GPa)	39	309
K_0 (exp)	38	313

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



Develop and Test Pseudopotentials Self-consistent DFT computation
Generate orbitals for trial functions for k-point set and find blip representation
Perform variation optimization of Jastrow parameters
VMC to generate Initial configurations or get VMC energy
DMC equilibration
DMC Statistics Generation

Functionals + Functional Derivatives

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

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

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

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

(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

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

where

$$\frac{\delta F[g_0]}{\delta g(x)} = F_1(x) + 2\int dx_1\, g_0(x_1)\, F_2(x_1, x) + 3\int dx_1 \int dx_2\, g_0(x_1)\, g_0(x_2)\, F_3(x_1, x_2, x) + \cdots \qquad (4)$$

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) :

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

$$+ \frac{1}{2} \int dx \int dx' \; \frac{\delta^2 F[g_0]}{\delta g(x)\,\delta g(x')} \; \Delta g(x)\,\Delta g(x')$$

$$+ O(\Delta g)^3 \qquad (5)$$

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

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

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

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

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

Examples of Functional Derivatives

$$I[f] = \int w(x) f(x)\, dx$$

$$\frac{\delta I}{\delta f} = w(x)$$

$$J[g] = \int (g(x))^{\alpha}\, dx$$

$$\frac{\delta J}{\delta g} = \alpha (g(x))^{\alpha - 1}$$

$$E = \int g\left(f(\vec{r}), |\nabla f(r)|\right) d^3r$$

$$\delta E = \int \left[\frac{\delta g}{\delta f} \delta f(r) + \frac{\delta g}{\delta |\nabla f|} \delta |\nabla f| \right] d^3r$$

$$\delta E = \int \left\{ \frac{\delta g}{\delta f} - \nabla \cdot \left[\frac{\delta g}{\delta |\nabla f|} \frac{\nabla f(r)}{|\nabla f(r)|} \right] \right\} \delta f(r)\, dr$$

Density Functional Theory

$$\Psi \longleftrightarrow V \longleftrightarrow \rho$$

exact many-body wavefunction

external potential (nuclei)

ground state charge density

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

Density Functional Theory

Hohenberg-Kohn Theorem

Exact:

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

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

Ψ exact many body wave function

Hohenberg-Kohn Theorem

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

$v(r) - v'(r) \neq$ constant

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

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

$$E' = \langle \Psi' | H' | \Psi' \rangle < \langle \Psi | H' | \Psi \rangle$$

$$= \langle \Psi | H + v' - v | \Psi \rangle$$

$$= \langle \Psi | H | \Psi \rangle + \langle \Psi | v' - v | \Psi \rangle$$

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

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

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

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

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

Add (1) and (2): $E + E' < E + E'$ Contradiction!

So $v = v'$ if $\rho = \rho'$ $\quad \Psi \Leftrightarrow v \Leftrightarrow \rho$

Hohenberg-Kohn Theorem #2: Minimum principle

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

Define $F[\rho] \equiv \langle \Psi | T + U | \Psi \rangle$

where T: Kinetic energy $= \sum -\frac{p_i^2}{2}$

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

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: $\mathcal{E}_v[\Psi] = \langle \Psi | T + V + U | \Psi \rangle$

$\delta \mathcal{E}_v[\Psi] \big|_{\langle \Psi^* \Psi \rangle = 1, N} = 0$ Ground state energy $\mathcal{E}_v$

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

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

So: $E_v[\rho'] > E_v[\rho]$

Hohenberg-Kohn, Second Proof
(Levy Constrained Search)

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

First consider:

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

because $v(r)$ implies Ψ and thus ρ !

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

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

$$E = \min_{\rho} E_v[\rho] = \min_{\rho} \left\{ F[\rho] + \int d^3r\, v(r)\rho(r) \right.$$

Use Lagrange multiplier to fix N:

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

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

$\rho(r)$ - N-representable $\qquad$ any Ψ?

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

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

Define: $T_s[\rho]$ = Kinetic energy of a non interacting system with density $\rho(r)$

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

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

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

Use a Lagrange multiplier:

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

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

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

If $\dfrac{\delta T_s}{\delta\rho}$ 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:

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

for a non-interacting system:

$$\left[-\nabla^2 + v_0(r)\right]\psi_i = \varepsilon_i \psi_i$$

$$\rho(r) = \sum_{i=1}^{occ} \psi_i^*(r)\,\psi_i(r)$$

lowest N eigenvectors
ψ_i single particle orbitals

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

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

Local Density Approximation
LDA

$$E_{xc}[\rho] = \int d^3r\, \rho(r)\, \varepsilon_{xc}(\rho(r))$$ Local ε_{xc}

Exchange correlation functional : $v_{xc} \equiv \frac{\delta E_{xc}}{\delta \rho}$ $\qquad \varepsilon_{xc} = E - T_s - \cancel{U}^{\,0}$

Local Exchange Correlation Functional

Total energy for electron gas

kinetic energy for noninteracting electron gas

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

$$E_{xc}[\rho + \delta\rho] - E_{xc}[\rho] = \int d^3r\, \delta\rho \frac{\delta E_{xc}}{\delta \rho} + O(\delta\rho^2) = \boxed{\int d^3r\, \delta\rho\, v_{xc}} + O(\delta\rho^2)$$

$$= \int d^3r \left[(\rho + \delta\rho)\, \varepsilon_{xc}(\rho + \delta\rho) - \rho\, \varepsilon_{xc}[\rho] \right]$$

$$= \int d^3r \left[\rho \left(\cancel{\varepsilon_{xc}(\rho)} + \delta\rho\, \varepsilon'_{xc}[\rho] + \dots \right) + \delta\rho \left(\varepsilon_{xc}(\rho) + \dots \right) - \cancel{\rho\, \varepsilon_{xc}} \right]$$

$$\boxed{= \int d^3r \left[\delta\rho\, \rho\, \varepsilon'_{xc}[\rho] + \delta\rho\, \varepsilon_{xc}(\rho) \right]} + O(\delta\rho^2)$$

So we see $v_{xc}^{LDA} = \frac{d}{d\rho}\left(\rho\, \varepsilon_{xc}(\rho) \right)$ ✱✱

$$E_x^{LDA}[\rho] = A_x \int d^3r\, \rho(r)^{4/3} \qquad \varepsilon_x(\rho) = A\rho^{1/3}$$

$$\boxed{\frac{\delta E_x}{\delta \rho} = v_x = A_x \frac{4}{3} \rho^{\frac{1}{3}}}$$

Total Energy Calculation

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

Now

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

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

So!

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

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)

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

$\boxed{\text{Exact}}$ Exchange

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

single slater determinant of ground state orbitals

(like Hartree-Fock)

e-e interaction $= \frac{1}{|r_1 - r_2|}$

Hartree energy

$$\iint \frac{\rho(r)\rho(r')}{|r_1 - r_2|} d^3r\, d^3r'$$

Note that: $\langle \Phi_\rho^{min} | T + V_{ee} | \Phi_\rho^{min} \rangle$

$$= T_s[\rho] + U[\rho] + E_x[\rho]$$

Correlation

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

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

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

$E_c[\rho] \leq 0$

positive KE part, negative PE part

Scaling Properties

Consider first the Hartree energy:

$$U[\rho] = \frac{1}{2}\int d^3r \int d^3r' \frac{\rho(r)\rho(r')}{|r-r'|}$$

scale r, r' by γ:

$$U[\rho_\gamma] = \frac{1}{2}\int d^3(\gamma r)\int d^3(\gamma r') \frac{\rho(\gamma r)\,\rho(\gamma r')}{|r-r'|}$$

$$= \gamma \frac{1}{2}\int d^3r \int d^3r' \frac{\rho(r)\rho(r')}{|r-r'|} = \gamma U[\rho]$$

Similarly: $E_x[\rho_\gamma] = \gamma E_x[\rho]$

Kinetic energy:

$$\Psi_\gamma(r_1, r_2, \ldots, r_N) = \gamma^{3N/2}\Psi(\gamma r_1, \gamma r_2 \cdots \gamma r_N)$$

$$\rho_\gamma(r) = \gamma^3 \rho(\gamma r)$$

$$\langle \Psi_\gamma | \underset{\substack{\updownarrow \\ T}}{\nabla^2} | \Psi_\gamma \rangle = \gamma^2 \langle \Psi | \underset{\substack{\updownarrow \\ T'}}{\nabla^2} | \Psi \rangle$$

so: $T_s[\rho_\gamma] = \gamma^2 T_s[\rho]$

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

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

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

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

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

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

Exchange and Correlation Hole

Joint probability function

$$n(r,\sigma;r',\sigma') = n(r,\sigma)\,n(r',\sigma') + \Delta n(r,\sigma;r',\sigma')$$

Exact Exchange hole

$$\Delta n_x = \Delta n_{HF}(r,\sigma;r'\sigma')$$

$$= -\delta_{\sigma\sigma'}\left|\sum_i \psi_i^{\sigma *}(r)\,\psi_i^{\sigma'}(r')\right|^2$$

$$= -\delta_{\sigma\sigma'}\left|\rho_\sigma(r,r')\right|^2$$

Cancels self-interaction in Hartree term:

$$E_H = \frac{1}{2}\sum_{\sigma\sigma'}\int d^3r\,d^3r'\,\frac{n(r)\,n(r')}{|r-r'|}$$

$$E = \left[\langle V_{int}\rangle - E_H\right]_{HF} = \frac{1}{2}\sum_{\sigma\sigma'}\int d^3r\,d^3r'\,\frac{\Delta n_x}{|r-r'|}$$

$$\int d^3r'\,\Delta n_x(r,\sigma;r'\sigma') = -1$$

Exchange Correlation Hole

$$\Delta n_{xc}(r,\sigma;r',\sigma') = n_x + n_c$$

$$\int d^3r'\, n_c = 0$$

Coupling Constant Integration

Vary electron charge from 0 to e

Then

$$E_{xc}[n] = \int_0^{e^2} d\lambda \left\langle \psi_\lambda \left| \frac{dV_{int}}{d\lambda} \right| \psi_\lambda \right\rangle - E_H$$

$$= \frac{1}{2}\int d^3r\, d^3r' \frac{n(r)\,\bar{n}_{xc}(r,r')}{|r-r'|}$$

Where

$$\bar{n}_{xc}(r,r') = \int_0^1 d\lambda\, n_{xc}^{\lambda}(r,r')$$

Summary of DFT

HK1 $\quad \Psi \longleftrightarrow V \longleftrightarrow \rho$

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

KS $\quad H\psi_\alpha = \varepsilon_\alpha \psi_\alpha \qquad \rho = \sum^{occ} \psi_\alpha^* \psi_\alpha$

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

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

v: external potential (nuclei)

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

$v_{xc} = \frac{\delta E_{xc}}{\delta \rho}$ $\qquad$ Solve Self-consistently

Total Energy:

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

$T_s = \sum^{occ} \langle \psi_\alpha | -\frac{1}{2}\nabla^2 | \psi_\alpha \rangle$

OR:

$$E = \sum^{occ} \varepsilon_\alpha - U(\rho) - \int d^3r\, \rho(r)\, v_{xc}(r) + E_{xc}$$

Summary of LDA

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

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

See this from definition:

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

$$\begin{aligned}
E_{xc}[\rho + \Delta\rho] &= \int e_{xc}(\rho + \Delta\rho)(\rho + \Delta\rho)\, d^3r \\
&= \int e_{xc}(\rho + \Delta\rho)\, \rho \, d^3r + \int d^3r \; e_{xc}(\rho + \Delta\rho)\, \Delta\rho \\
&= \int d^3r \, \rho \left(e_{xc}(\rho) + e'_{xc}(\rho)\Delta\rho + \dots \right) + \int d^3r \; e_{xc}(\rho + \Delta\rho)\, \Delta\rho \\
&= E_{xc}[\rho] + \int d^3r \, \Delta\rho \left(\rho e'_{xc} + e_{xc}(\rho) + e'\Delta\rho \right)\Big|_{\Delta\rho \to 0} \\
&= E_{xc}[\rho] + \int d^3r \, \Delta\rho \, \underbrace{\left(\rho e'_{xc} + e_{xc} \right)}
\end{aligned}$$

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

Explicit LDA Functionals

Free Electron Gas

Exchange:

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

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

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

Correlation:

high density: $r_s \to 0$

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

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

$$e_c \to -\frac{d_0}{r_s} + \frac{d_1}{r_s^{3/2}} + \cdots$$

Perdew + Wang, PRB 45, 13244 (1992) fit Monte Carlo Results of Ceperley + Alder, PRL 45, 566 (1980):

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

Local Spin Density Approximation
LSDA

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

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

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

α_c "spin stiffness"

Lepeley & Alder
QMC

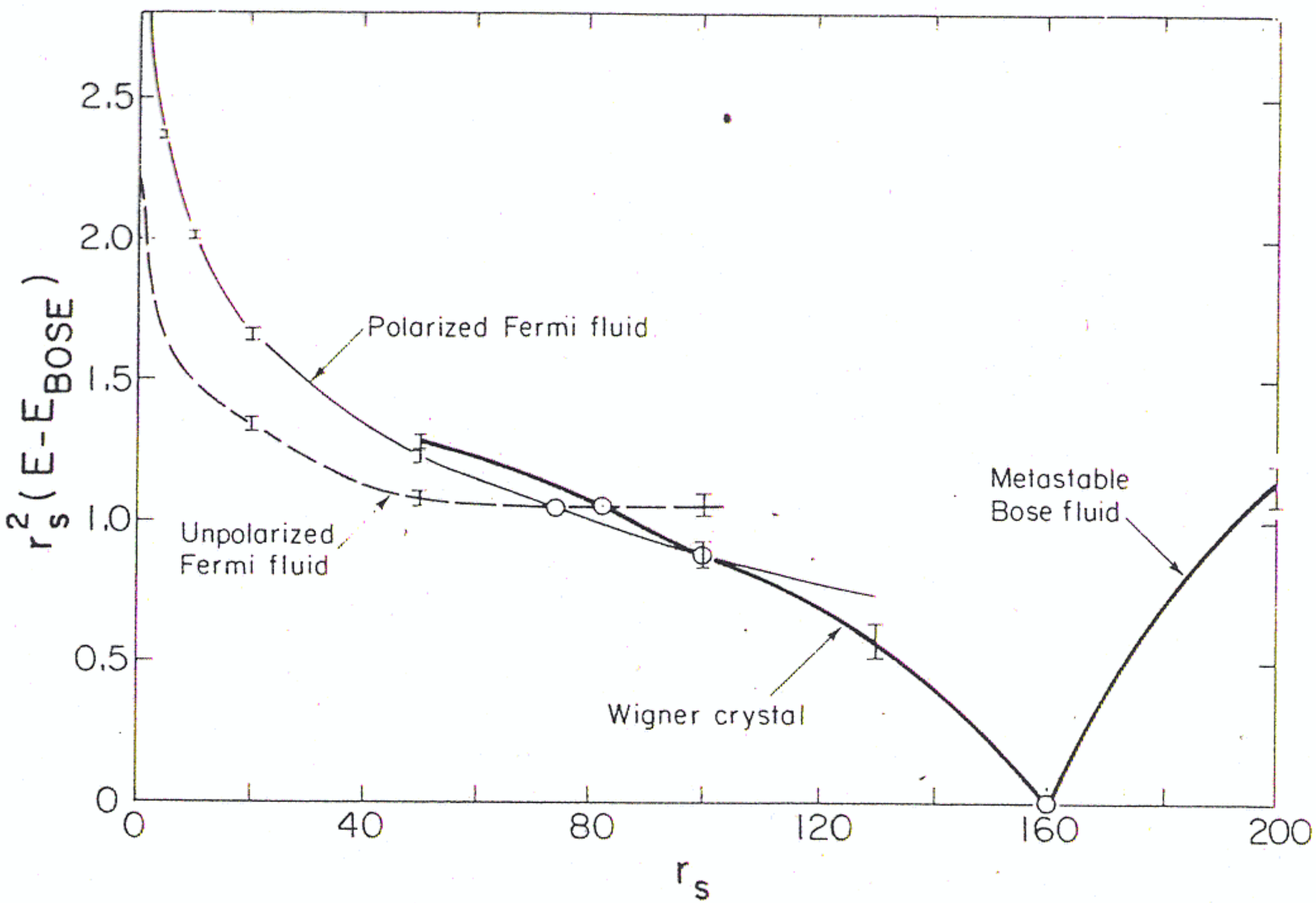


FIG. 2. The energy of the four phases studied relative to that of the lowest boson state times r_s^2 in rydbergs vs r_s in Bohr radii. Below $r_s = 160$ the Bose fluid is the most stable phase, while above, the Wigner crystal is most stable. The energies of the polarized and unpolarized Fermi fluid are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

Free Electron Gas II

Thomas-Fermi Kinetic Energy

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

(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:

$$k_\alpha = \frac{2\pi n_\alpha}{L_\alpha}$$ are the allowed values of k, n_α integers

Allowed wavenumbers, 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 $\int \frac{-\hbar^2}{2m}\nabla^2 \psi_i \psi_i^* = \frac{\hbar^2 k^2}{2m}$

So fill states in a sphere up to k_F

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

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

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

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

Self-consistent LDA (GGA)

1. initial guess for potential or density

   ↓

   Compute potential

2. Solve $H\psi_i = \varepsilon_i \psi_i$

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

   $V_{eff} = V_{(e-n)} + V_H + V_{xc}$

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

4. Compute potential:

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

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

   c) V_{xc}

5. Check for self-consistency — Yes — Compute total E and output results.

6. Mix input + output density

7. compute potential

What are the eigenvalues in DFT?

They are not excitation energies.

One can show (Perdew + Zunger, 1981) that

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

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 $E_g = \left(E(N+1) - E(N)\right) - \left(E(N) - E(N-1)\right)$ ☆

$$E_g = E^N_{\substack{\text{conduction}\\ \text{band}\\ \text{minimum}}} - E^N_{\substack{\text{valence}\\ \text{band}\\ \text{max}}} + \Delta V_{xc}$$

$$E_g = \varepsilon_{N+1}(N+1) - \varepsilon_N(N)$$

$$\neq \varepsilon_{N+1}(N) - \varepsilon_N(N)$$

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

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

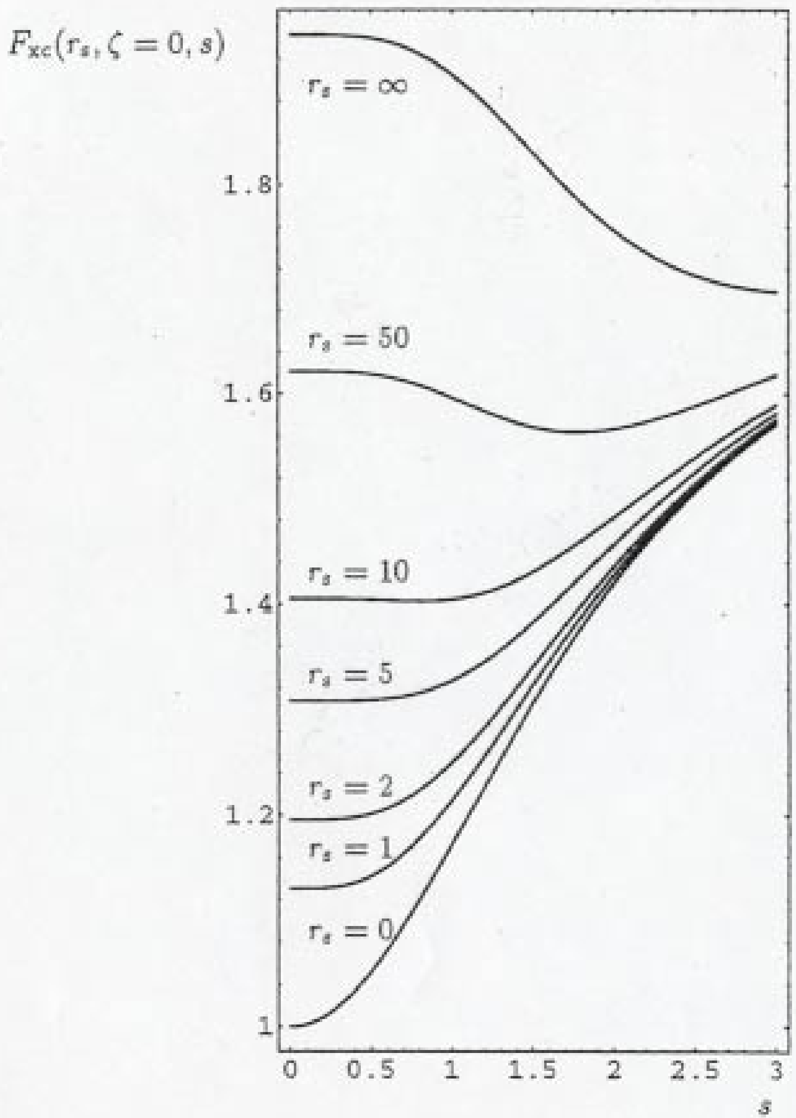
B) reduce to LSDA for $\nabla\rho \to 0$

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

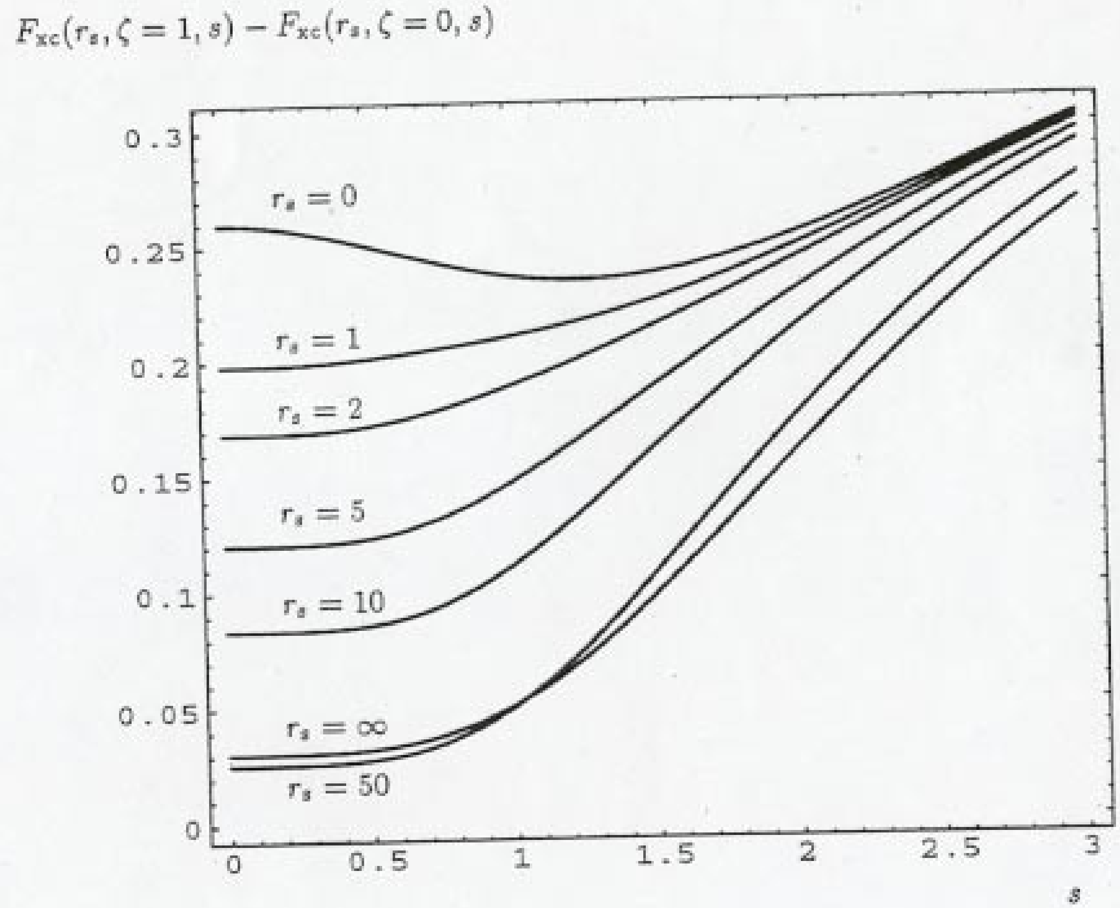
$$r_s = \left(\frac{4}{3}\pi\rho\right)^{\frac{1}{3}}$$ avg dist between electrons

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

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



$F_{xc}(r_s, \zeta = 0, s)$
$r_s = \infty$
$r_s = 50$
$r_s = 10$
$r_s = 5$
$r_s = 2$
$r_s = 1$
$r_s = 0$
1.8
1.6
1.4
1.2
1
0 0.5 1 1.5 2 2.5 3
s



$F_{xc}(r_s, \zeta = 1, s) - F_{xc}(r_s, \zeta = 0, s)$
$r_s = 0$
$r_s = 1$
$r_s = 2$
$r_s = 5$
$r_s = 10$
$r_s = \infty$
$r_s = 50$
0.3
0.25
0.2
0.15
0.1
0.05
0
0 0.5 1 1.5 2 2.5 3
s

Pfrommer & Louie 1998

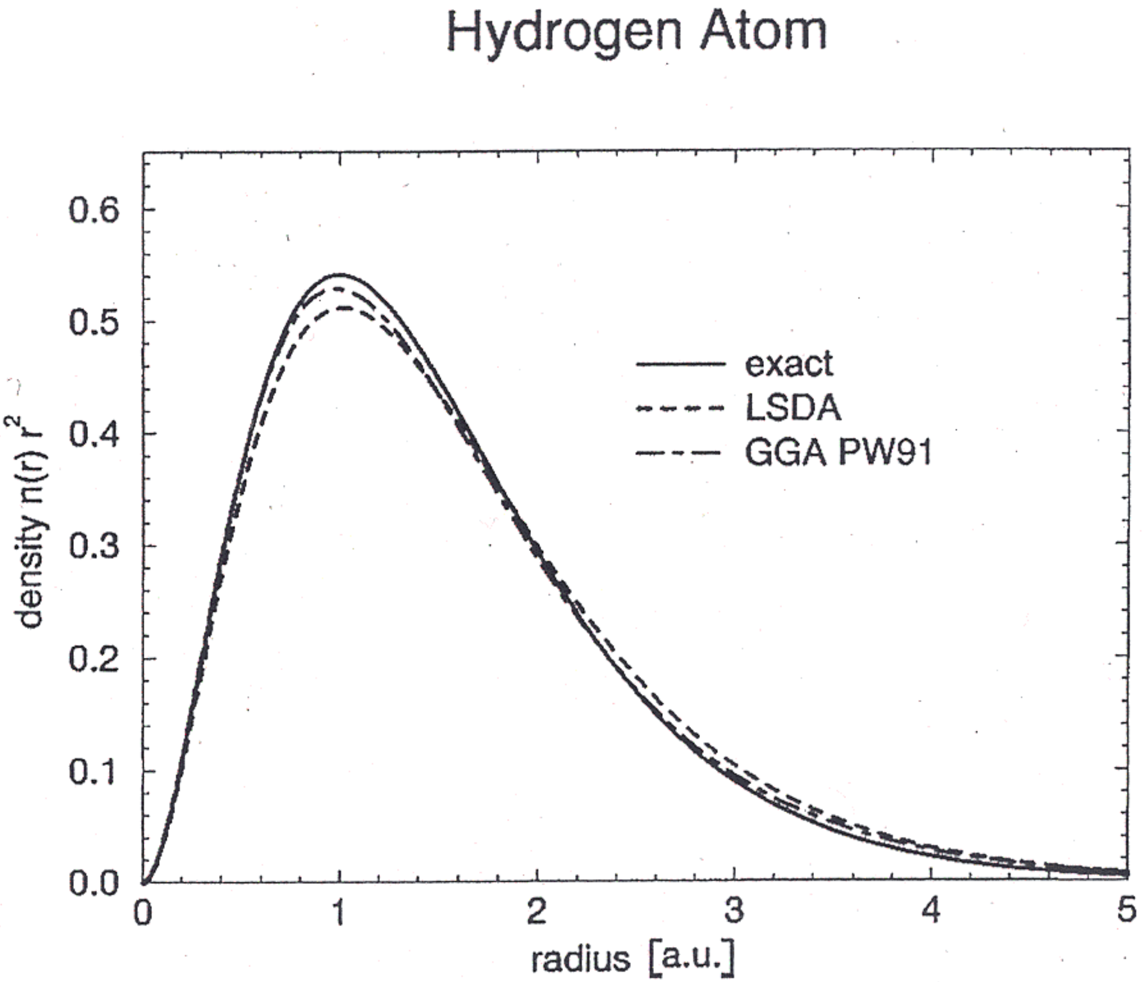
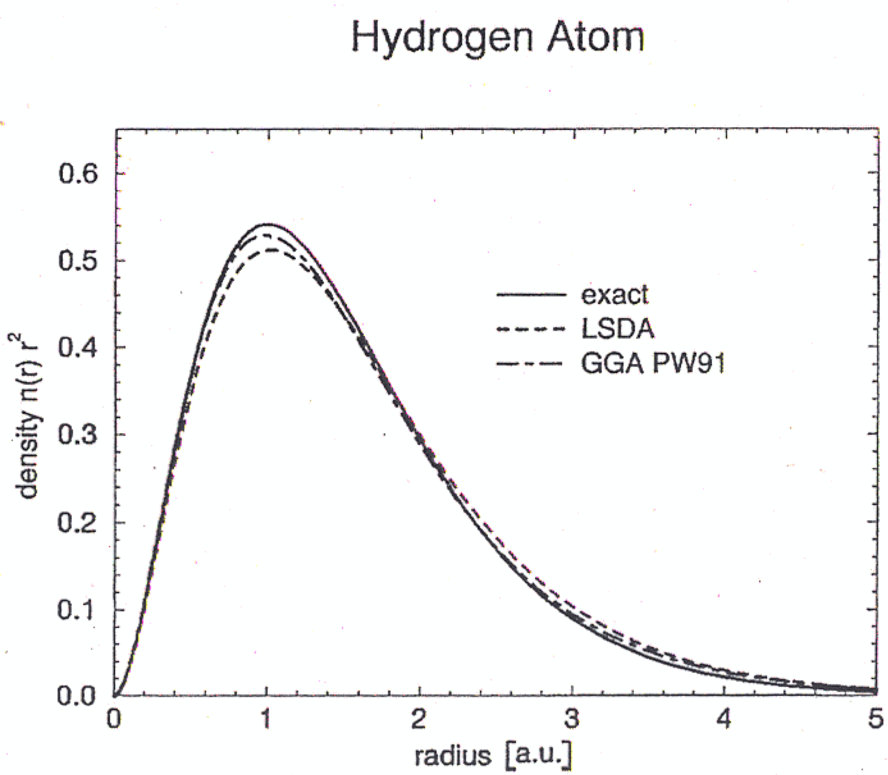


FIG. 1. Electron number density *n(r)* of the hydrogen atom as a function of the radius. Shown are the exact density (solid line), and the self-consistent densities in LSDA (dashed line) and GGA PW91 (dot-dashed line).

Pfrommer + Louie 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



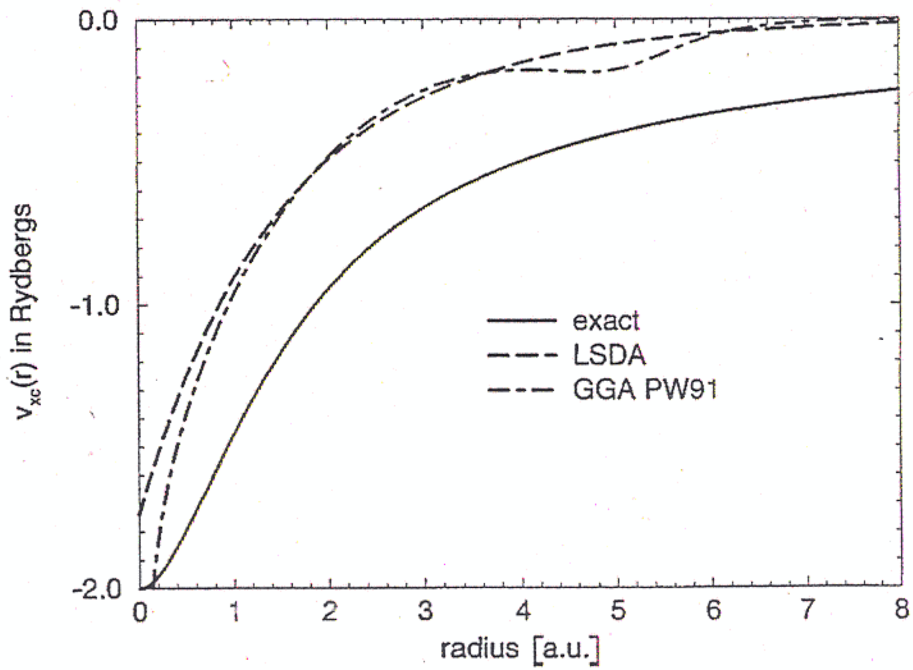


FIG. 2. Exchange-correlation potential $v_{\mathrm{xc}}(r)$ in Rydbergs for the hydrogen atom as a function of the radius. Shown are the exact v_{xc} (solid line), and the self-consistent v_{xc} in LSDA (dashed line) and GGA PW91 (dot-dashed line).

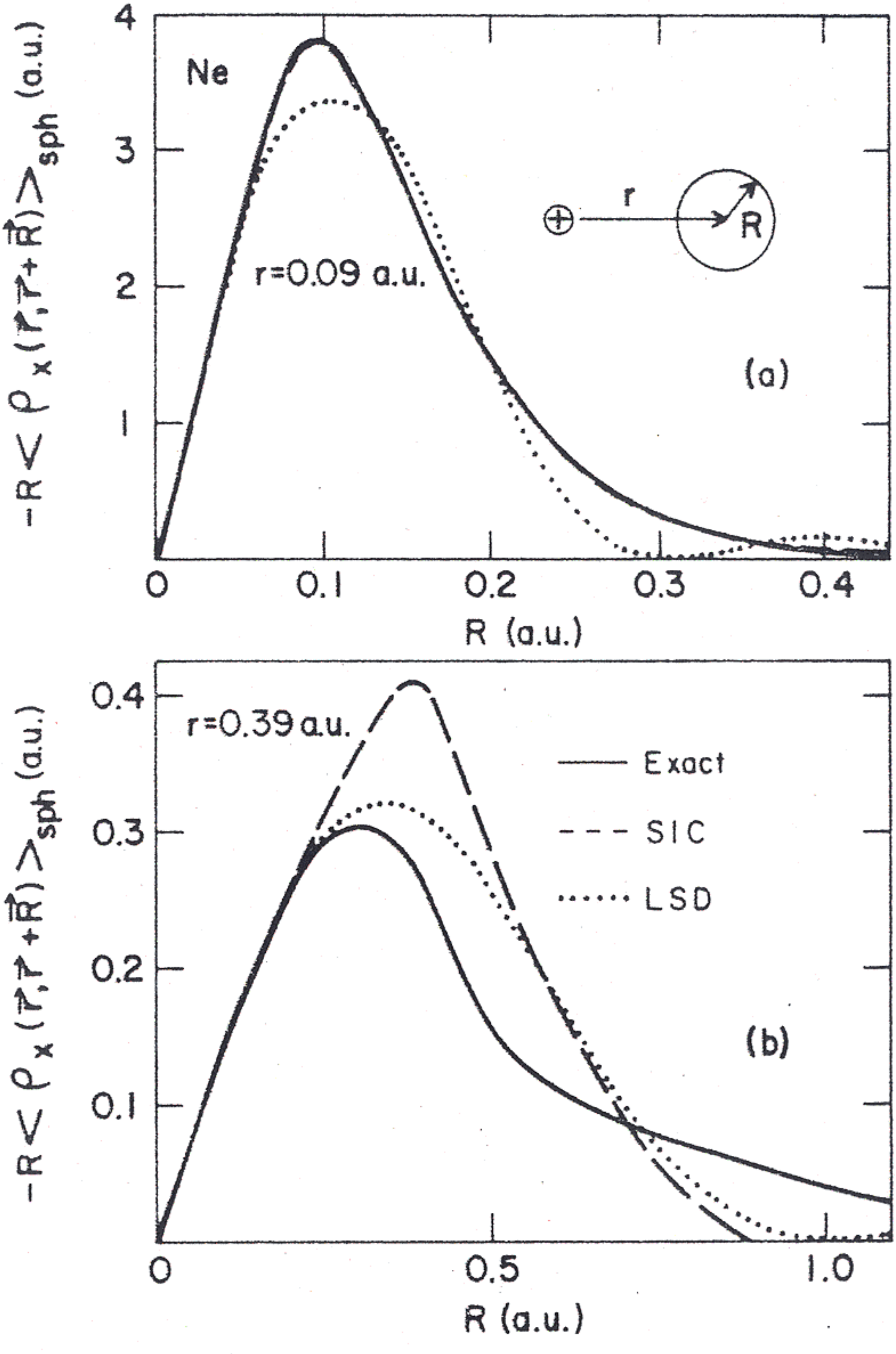


FIG. 2. Spherical average of the neon exchange hole times R for (a) $r = 0.09$ a.u. and (b) $r = 0.39$ a.u. The full, dashed, and dotted curves are the exact, SIC-LSD and LSD results, respectively. In part (a), the SIC-LSD curve is almost indistinguishable from the exact one.

Perdew + Zunger

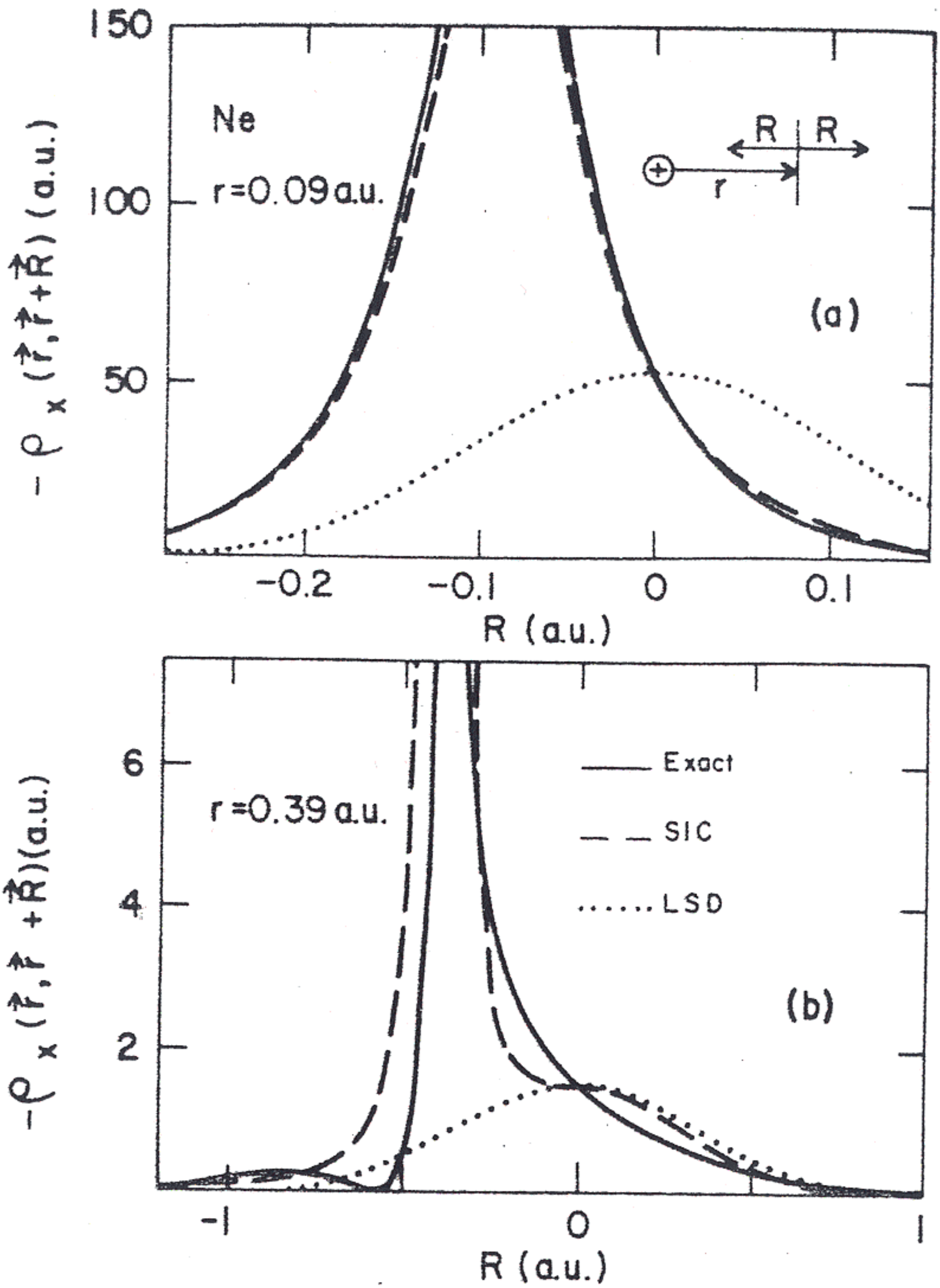


FIG. 1. Exchange hole about an electron located at distance r from the nucleus in the neon atom. The full curves are exact, while the dashed and dotted curves represent the SIC-LSD and LSD approximations,

Perdew + Zunger

Periodic Solids

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

$\vec{a}_{i=1,3}$ 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.

$R \cdot G = 2\pi n$, n integer

$a_i \cdot g_j = 2\pi \delta_{ij}$

$g_j = 2\pi \epsilon_{jkl} \dfrac{a_k \times a_l}{V}$ $\quad V = \vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)$

ϵ_{jkl} +1 even −1 odd

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

k-point

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 $\vec{K} = 2\pi \left(\dfrac{n_1}{L_1}, \dfrac{n_2}{L_2}, \dfrac{n_3}{L_3} \right)$

Band Theory

Consider the Fourier transform of the potential

$$V(r) = \sum_G e^{i\vec{G}\cdot\vec{r}} V_G$$

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

$\vec{G} = 0$ → constant

$|G| = 1$ → 1 period per cell

2 → 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 $\left(-\frac{1}{2}\nabla^2 + V\right)\psi = \varepsilon\psi$

$$-\frac{1}{2}\nabla^2\psi = \frac{1}{2}\sum_K K^2 e^{iK\cdot r} C_K$$

$$V\psi = \left(\sum_G e^{i\vec{G}\cdot\vec{r}} V_G\right)\left(\sum_{\vec{K}} e^{i\vec{K}\cdot\vec{r}} C_K\right)$$

Band Theory (contd)

$$V\psi = \left(\sum_G e^{iG\cdot r} V_G\right)\left(\sum_K e^{iK\cdot r} C_K\right)$$

$$= \sum_{GK} V_G C_K e^{i(K+G)\cdot r} = \sum_{GK'} V_G C_{K'-G} e^{iK'\cdot r}$$

$K' = G+K$

So Schrodinger's eq. becomes:

$K' \to K,\ G \to G'$

$$\sum_K e^{iK\cdot r}\left\{\left(\tfrac{1}{2}K^2 - \varepsilon\right) C_K + \sum_{G'} V_{G'} C_{K-G'}\right\} = 0$$

Now since plane waves are orthogonal, each term must be zero (can also prove by multiplying by $C_{K'}^{*} e^{-iK'\cdot r}$ and integrating)

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

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

$G' \to G' - G$

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

☆ Note $\vec{k}$ vectors are independent. Solve secular equation for each $\vec{k}$, get $\varepsilon_{i\vec{k}}$, $C_{\vec{k}+\vec{G}}$

Bloch's theorem: $\psi_k(r) = \sum_G C_{k-G} e^{i(k-G)\cdot r}$

Band Theory cont'd

Bloch's theorum:

$$\psi_k(r) = \sum_G C_{k-G}\, e^{i(k-G)\cdot r}$$

$$\psi_k(r) = e^{i\vec{k}\cdot\vec{r}} \underbrace{\left(\sum_G C_{\vec{k}-\vec{G}}\, e^{-iG\cdot r} \right)}_{\text{This is a periodic function of } r}$$

$$\psi_k(r) = e^{i\vec{k}\cdot\vec{r}}\, u(\vec{r})$$

Summary: assumption of band theory
periodic external potential.

To solve: could form $H_{GG'}$ and diagonalize,
but need too many G's (1 million for Al)
for full potential.

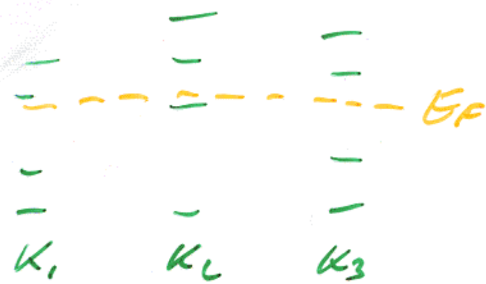
Self-consistent crystalline computations.

Initial ρ

Compute V — V_H, V_N (Poisson's eq.), V_{xc}

Solve KS equations for each k-point

Determine E_F



Compute ρ^{out} $\left(\sum_k \sum_i \psi_{ik}^* \psi_{ik} f(\varepsilon - E_F) w_k\right)$

Compute E

Converged?

No

↓

K-points

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

and $\rho = V \int_{BZ} dk^3 \sum_i \psi_{i,k}^* \psi_{i,k} f(\varepsilon_i - \varepsilon_F)$ $\quad f(\varepsilon_i - \varepsilon_F) = \left(e^{\varepsilon_i - \varepsilon_F / k_B T} + 1\right)^{-1}$

Fermi function

How to accurately integrate over BZ?

$$V \int_{BZ} dk^3 \,\_\_ \rightarrow \sum_k w_k \,\_\_\_\_$$

Two main methods used: Tetrahedron method

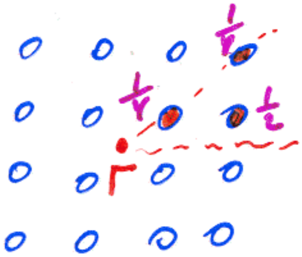
Assume linear between mesh points.

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 of increment
- Use space group operations to rotate all points into the irreducible part of BZ (IBZ)
- Determine weights



3 points rather than 16

Density functional theory (DFT)

- All of the ground state properties of an electronic system are determined by the charge and spin densities.
- DFT is an exact many-body theory, but the exact functional is unknown. However, exact sum-rules are known.

Solve the Kohn-Sham equations:

$$\left[-\nabla^2 + V(\vec{r}) + \varepsilon_i\right]\psi_i = 0$$

$$V(\vec{r}) = V_{\text{electrostatic}} + V_{\text{xc}}$$

Why it works (usually) quite well:

$$E = E_{\text{kinetic}}^{\text{non-interacting}} + E_{\text{electrostatic}} + E_{\text{xc}}$$

$$V_{xc} = \frac{\delta E_{xc}}{\partial \rho}$$

known exactly

Interactions for valence (bonding) electrons are most important

$$E = E_{\text{kinetic}}^{\text{non-interacting}} + E_{\text{electrostatic}} + E_{\text{xc}}$$

known for uniform electron gas and other model systems

Calculation of physical properties from first-principles

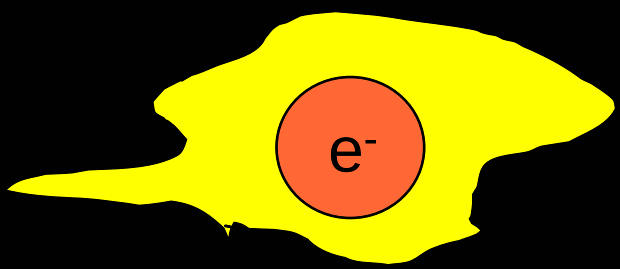
Exact theory is known

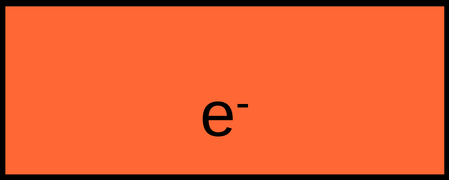
$$H\psi = E\psi$$ Schrödinger's equation

$$H = V(E-N) + V(E-E) + KE$$

Local Density Approximation of DFT

Complicated many-body interactions in material of interest (atom, molecule, crystal…) at each point…





…are like those of homogeneous electron gas with same density as the density at that point.

Becomes more accurate with increasing P

Calculation of physical properties from first-principles

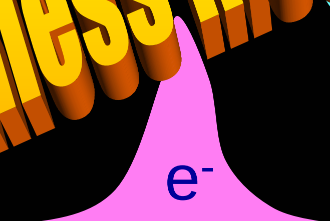
Exact theory is known

$$H\psi = E\psi$$ Schrödinger's equation

$$H = V(E-N) + V(E-E) + KE$$

Generalized Gradient Approximation (GGA)

Complicated many-body interactions in material of interest (atom, molecule, crystal…) at each point…



…are like those of homogeneous electron gas with same density as the density *at that point*, and imposed gradients *at that point*.

A disaster for ferroelectrics unless modified…

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(Å^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:

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

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

- LDA and GGA:

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

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

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

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.

$$F_{\mathrm{x}}^{\mathrm{PBE}} = 1 + \kappa - \kappa / (1 + \mu s^2)$$

$$\text{where } s : \text{reduced gradients}, \kappa = 0.804$$

- 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 than .
  (Perdew et al., PRB **54**, 16533)
- For slowly varying density systems, (Svendsen and von Barth, PRB 54, 17402)

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

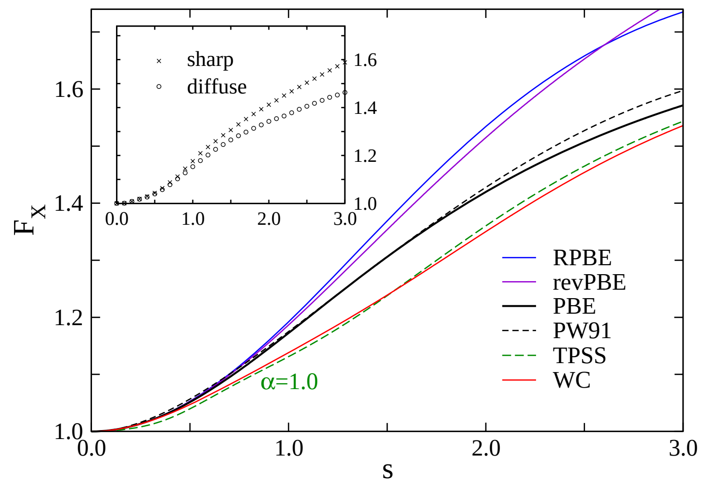
$$\text{where } p = s^2, q : \text{reduced Laplacian.}$$

- A new based on above observations:

$$\boxed{\begin{aligned} &F_x^{WC} = 1 + \kappa - \kappa/(1 + x/\kappa) \\ &\text{and } x = \frac{10}{81} s^2 + (\mu - \frac{10}{81}) s^2 \cdot \exp(-s^2) + \ln(1 + cs^4) \end{aligned}}$$

- and $E_c^{wc} = E_c^{PBE}$

- 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.



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

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

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

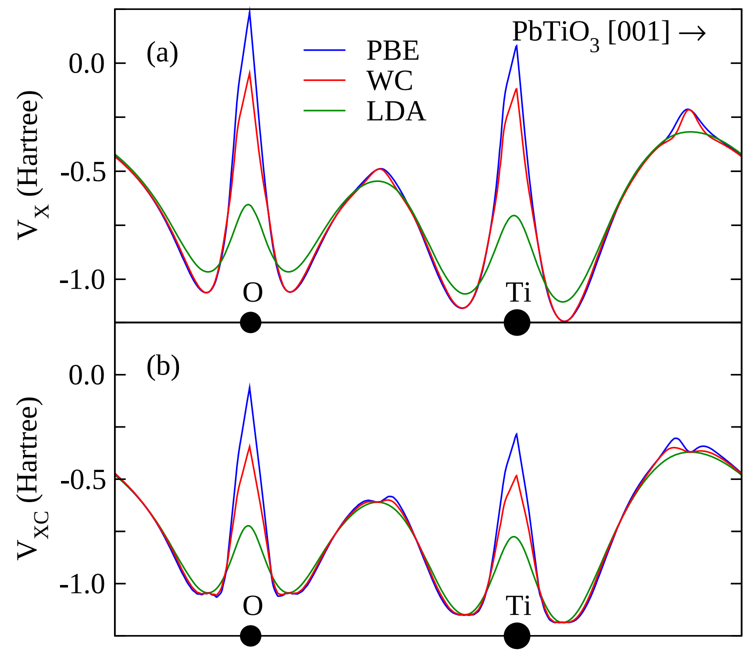
Constants a_0 and bulk moduli B_0 at 0K.

	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 $PbTiO_3$

	LDA	PBE	WC	Expt
V_0(Å^3)	60.37	70.54	63.47	63.09
c/a	1.046	1.239	1.078	1.071
u_z(Pb)	0.0000	0.0000	0.0000	0.000
u_z(Ti)	0.5235	0.5532	0.5324	0.538
$u_z(O_{1,2})$	0.5886	0.6615	0.6106	0.612
$u_z(O_3)$	0.0823	0.1884	0.1083	0.112

R3m $BaTiO_3$

	LDA	PBE	WC	Expt
V_0(Å^3)	61.59	67.47	64.04	64.04
β(°)	89.91	89.65	89.86	89.87
u_z(Pb)	0.0000	0.0000	0.0000	0.0000
u_z(Ti)	0.4901	0.4845	0.4883	0.487
$u_z(O_{1,2})$	0.5092	0.5172	0.5116	0.511
$u_z(O_3)$	0.0150	0.0295	0.0184	0.018

u_z are given in terms of the lattice constants