

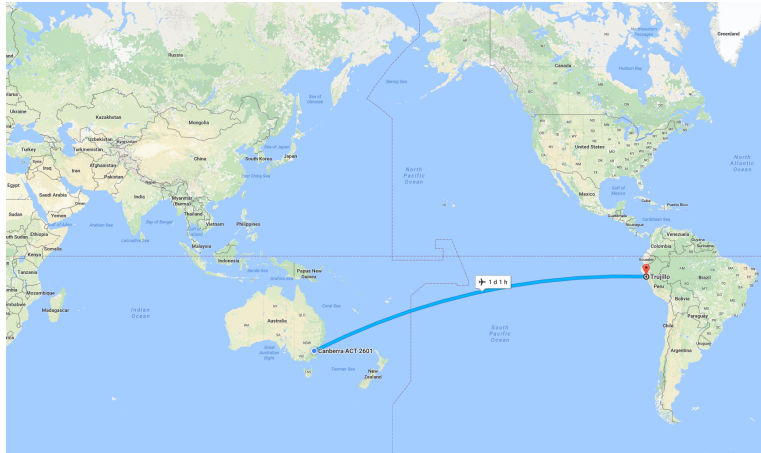
Finite Uniform Electron Gases

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Some basic geography

Lecture Idea #1

$$\begin{aligned}
 [(\mathbf{a} + \mathbf{1}_i)\mathbf{bcd}]^{(l,m,n)} &= \frac{\delta(D_i - A_i)}{\alpha + \delta} [\mathbf{abcd}]^{(l,m,n)} + \frac{2\delta P_i}{\alpha + \delta} [\mathbf{abcd}]^{(l+1,m,n)} \\
 &+ \frac{Q_i}{\alpha + \delta} [\mathbf{abcd}]^{(l,m+1,n)} + \frac{P_i + 2\delta Q_i}{2(\alpha + \delta)} [\mathbf{abcd}]^{(l,m,n+1)} \\
 &+ \frac{a_i}{2(\alpha + \delta)} [(\mathbf{a} - \mathbf{1}_i)\mathbf{bcd}]^{(l,m,n)} + \frac{2a_i\delta^2}{(\alpha + \delta)^2} [(\mathbf{a} - \mathbf{1}_i)\mathbf{bcd}]^{(l+1,m,n)} \\
 &+ \frac{a_i}{2(\alpha + \delta)^2} [(\mathbf{a} - \mathbf{1}_i)\mathbf{bcd}]^{(l,m+1,n)} + \frac{a_i\delta}{(\alpha + \delta)^2} [(\mathbf{a} - \mathbf{1}_i)\mathbf{bcd}]^{(l,m,n+1)} \\
 &+ \frac{2b_i\gamma\delta}{(\alpha + \delta)(\beta + \gamma)} [\mathbf{a}(\mathbf{b} - \mathbf{1}_i)\mathbf{cd}]^{(l+1,m,n)} - \frac{b_i}{2(\alpha + \delta)(\beta + \gamma)} [\mathbf{a}(\mathbf{b} - \mathbf{1}_i)\mathbf{cd}]^{(l,m+1,n)} \\
 &+ \frac{b_i(\gamma - \delta)}{2(\alpha + \delta)(\beta + \gamma)} [\mathbf{a}(\mathbf{b} - \mathbf{1}_i)\mathbf{cd}]^{(l,m,n+1)} - \frac{2c_i\beta\delta}{(\alpha + \delta)(\beta + \gamma)} [\mathbf{ab}(\mathbf{c} - \mathbf{1}_i)\mathbf{d}]^{(l+1,m,n)} \\
 &- \frac{c_i}{2(\alpha + \delta)(\beta + \gamma)} [\mathbf{ab}(\mathbf{c} - \mathbf{1}_i)\mathbf{d}]^{(l,m+1,n)} - \frac{c_i(\beta + \delta)}{2(\alpha + \delta)(\beta + \gamma)} [\mathbf{ab}(\mathbf{c} - \mathbf{1}_i)\mathbf{d}]^{(l,m,n+1)} \\
 &+ \frac{d_i}{2(\alpha + \delta)} [\mathbf{abc}(\mathbf{d} - \mathbf{1}_i)]^{(l,m,n)} - \frac{2d_i\alpha\delta}{(\alpha + \delta)^2} [\mathbf{abc}(\mathbf{d} - \mathbf{1}_i)]^{(l+1,m,n)} \\
 &+ \frac{d_i}{2(\alpha + \delta)^2} [\mathbf{abc}(\mathbf{d} - \mathbf{1}_i)]^{(l,m+1,n)} + \frac{d_i(\delta - \alpha)}{2(\alpha + \delta)^2} [\mathbf{abc}(\mathbf{d} - \mathbf{1}_i)]^{(l,m,n+1)}
 \end{aligned}$$

Lecture Idea #2

Molecule	Basis 1	Basis 2	A	B	C	D	E	F	G	H
PCl ₅	6-31G(d)	cc-pVTZ	170	28	0.3	—	—	—	2.3	0.37
	6-31G(2d)	cc-pVTZ	142	24	0.8	—	—	—	0.3	0.44
	rcc-pVTZ	cc-pVTZ	15	2.5	5.4	1.3	0.2	0.71	0.2	0.85
Morphine	6-31G(d)	cc-pVTZ	204	5.1	0.3	—	—	—	1.2	0.35
	rcc-pVTZ	cc-pVTZ	24	0.6	3.1	1.9	0.5	0.39	0.2	0.90
Porphine	6-31G(d)	cc-pVTZ	202	5.3	0.2	—	—	—	1.1	0.26
	rcc-pVTZ	cc-pVTZ	32	0.9	4.0	2.5	0.7	0.57	0.3	0.77
Vitamin B2	6-31G(d)	cc-pVTZ	307	6.5	0.3	—	—	—	1.8	0.34
	rcc-pVTZ	cc-pVTZ	36	0.8	3.3	2.8	0.6	0.39	0.3	0.81
Ala ₈	6-31G(d)	cc-pVTZ	445	5.4	0.3	—	—	—	2.4	0.26
	rcc-pVTZ	cc-pVTZ	49	0.6	2.9	3.8	0.5	0.34	0.4	0.73
PCl ₅	cc-pVDZ	cc-pVQZ	91	15	0.4	—	—	—	1.7	0.26
	6-31G(2d)	cc-pVQZ	158	26	0.3	—	—	—	0.4	0.27
	rcc-pVQZ	cc-pVQZ	17	2.8	0.5	1.6	0.3	0.22	0.3	0.41
Morphine	cc-pVDZ	cc-pVQZ	191	4.8	0.5	—	—	—	1.5	0.23
	rcc-pVQZ	cc-pVQZ	26	0.7	0.5	1.9	0.5	0.13	0.2	0.39
Porphine	cc-pVDZ	cc-pVQZ	186	4.9	0.3	—	—	—	0.9	0.10
	rcc-pVQZ	cc-pVQZ	32	0.8	0.8	2.1	0.5	0.15	0.4	0.21
Vitamin B2	cc-pVDZ	cc-pVQZ	284	6.0	0.6	—	—	—	2.2	0.23
	rcc-pVQZ	cc-pVQZ	39	0.8	0.6	2.7	0.6	0.12	0.2	0.35
β -Carotene	STO-3G	6-31G(d)	714	122	0.5	—	—	—	53	0.34
	6-4G	6-31G(d)	750	7.8	1.6	145	1.5	0.29	37	0.51
	6-31G	6-31G(d)	358	3.7	2.6	53	0.6	0.36	10	0.75

Lecture Idea #3



Outline

- 1 Introduction
 - History of DFT
 - Foundations of DFT
 - Problems of DFT
- 2 Electrons on Spheres
 - Spherium atoms
 - Glomium atoms
 - Exact solutions
- 3 Improved DFT
 - A disturbing claim
 - Incontrovertible evidence
 - A modest proposal

Introduction

A Brief History of DFT

1926	Thomas & Fermi	Kinetic energy of the uniform electron gas
1930	Dirac	Exchange energy of the UEG
1951	Slater	Used Dirac's work to approximate HF
1964	Hohenberg & Kohn	Proved universal density functional exists
1965	Kohn & Sham	Introduced Kohn-Sham DFT
1985	Perdew & others	Gradient-corrected functionals
1993	Becke	Hybrid (exact exchange) functionals

Introduction

Foundations of DFT

- **In principle:**
 - The Hohenberg-Kohn theorem
- **In practice:**
 - The similarity of molecular densities to the **UEG**
 - The Local Density Approximation (LDA)
 - Discover the properties of the **UEG**
 - Treat a molecular density as a sum of tiny chunks of **UEG**

Introduction

The Good News

The properties of the UEG (jellium) are quite well known:

- 1 **Quantum Monte Carlo** calculations (Ceperley & Alder, etc.)
- 2 **Many-body theory** (Wigner, Gell-Mann, Brueckner, etc.)
- 3 **Implemented** in many quantum chemistry software packages

Introduction

The Bad News

Jellium has an **infinite** number of electrons in an **infinite** volume

- 1 Unboundedness of jellium is **mathematically difficult**
- 2 Jellium is **infinite** : molecules are **finite**
- 3 **LDA overbinds** \implies many chemists concluded that DFT is useless

The Better News

Many clever people have found ways to **correct the jellium ansatz**

- 1 Gradient-corrected functionals
- 2 Hybrid (“exact exchange”) functionals
- 3 Meta-GGA functionals
- 4 ... and the functional zoo continues to grow

Introduction

Some of the contemporary problems of DFT

Large systems	Curtiss <i>et al.</i> , JCP 112, 7374	(2000)
Conjugated molecules	Woodcock <i>et al.</i> , JPCA 106, 11923	(2002)
CT excited states	Dreuw & Head-Gordon, JACS 126, 4007	(2004)
Dispersive systems	Wodrich <i>et al.</i> , Org Lett 8, 3631	(2006)
Fractional spin/charge	Cohen <i>et al.</i> , Science 321, 792	(2008)
Isodesmic reactions	Brittain <i>et al.</i> , PCCP 11, 1138	(2009)

Introduction

What is the origin of the problems in DFT?

- Do these many failures mean that DFT is basically bad?

No! In principle, DFT is an exact theory

- How can an exact theory give bad results?

Because our favourite functionals are imperfect

- How did this happen?

Because most are based on the UEG and corrections to it

- Does this mean that we should abandon the UEG?

No. The UEG is a good model, but we used it incorrectly.

Introduction

A house built on a rock



A house built on sand



Electrons on Spheres



Hand with Reflecting Sphere (M.C. Escher, 1935)

Electrons on Spheres

An Electron on a Sphere



Wavefunctions & Energies

$$\mathbf{H} = -\frac{\nabla^2}{2} \quad (r = R)$$

$$\Psi_{\ell,m}(\mathbf{r}) = Y_{\ell,m}(\theta, \phi)$$

$$E_{\ell,m} = \frac{\ell(\ell + 1)}{2R^2}$$

Electrons on Spheres

Two Electrons on a Sphere



Wavefunctions & Energies

$$\mathbf{H} = -\frac{\nabla_1^2}{2} - \frac{\nabla_2^2}{2} + \frac{1}{r_{12}}$$

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = ???$$

$$E = ???$$

Electrons on Spheres

Spheres and Spherium

- What is a “**sphere**”?

A sphere is the **2-dimensional** surface of a 3-dimensional ball

The system consisting of n electrons on a sphere is “**spherium**”

Glomes and Glomium

- What is a “**glome**”?

A glome is the **3-dimensional** surface of a 4-dimensional ball

The system consisting of n electrons on a glome is “**glomium**”

Electrons on Spheres

An Electron on a Glome



Wavefunctions & Energies

$$\mathbf{H} = -\frac{\nabla^2}{2} \quad (r = R)$$

$$\Psi_{\ell,m,n}(\mathbf{r}) = Y_{\ell,m,n}(\chi, \theta, \phi)$$

$$E_{\ell,m,n} = \frac{\ell(\ell + 2)}{2R^2}$$

Electrons on Spheres

Two Electrons on a Glome



Wavefunctions & Energies

$$\mathbf{H} = -\frac{\nabla_1^2}{2} - \frac{\nabla_2^2}{2} + \frac{1}{r_{12}}$$

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = ???$$

$$E = ???$$

Electrons on Spheres

Exact solutions for TWO electrons on a D -dimensional sphere

State	D	R	E	$\Psi(\mathbf{r}_1, \mathbf{r}_2)$
$^1S^e$	2	$\sqrt{3}/2$	1	$1 + r_{12}$
	3	$\sqrt{10}/2$	1/2	$1 + r_{12}/2$
	4	$\sqrt{21}/2$	1/3	$1 + r_{12}/3$
$^3P^o$	2	$\sqrt{15}/2$	1/3	$(1 + r_{12}/3)(\cos \theta_1 - \cos \theta_2)$
	3	$\sqrt{28}/2$	1/4	$(1 + r_{12}/4)(\cos \theta_1 - \cos \theta_2)$
	4	$\sqrt{45}/2$	1/5	$(1 + r_{12}/5)(\cos \theta_1 - \cos \theta_2)$
$^1P^o$	2	$\sqrt{5}/2$	1	$(1 + r_{12})(\cos \theta_1 + \cos \theta_2)$
	3	$\sqrt{14}/2$	1/2	$(1 + r_{12}/2)(\cos \theta_1 + \cos \theta_2)$
	4	$\sqrt{27}/2$	1/3	$(1 + r_{12}/3)(\cos \theta_1 + \cos \theta_2)$

Loos & Gill, *Phys Rev Lett* 103 (2009) 123008

Loos & Gill, *Mol Phys* 108 (2010) 2527

Loos & Gill, *Phys Rev Lett* 108 (2012) 083002

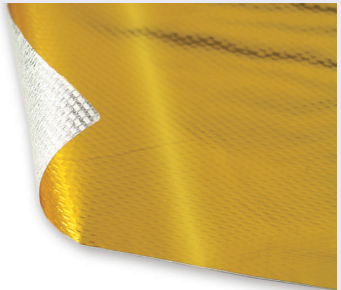
Electrons on Spheres

It is very interesting to compare spherium with 2D jellium ...

Spherium



2D jellium



... and, similarly, one can also compare **glomium** with **3D jellium**

Electrons on Spheres

Exact solutions for MANY electrons on a sphere or in jellium

In the **high-density limit**, the exact energy per electron is

$$E = \frac{\epsilon_{-2}}{r_s^2} + \frac{\epsilon_{-1}}{r_s} + \lambda_0 \ln r_s + \epsilon_0 + \dots$$

System	ϵ_{-2}	ϵ_{-1}	λ_0	ϵ_0
Spherium	$\frac{1}{2}$	$-\frac{4\sqrt{2}}{3\pi}$	0	$\ln 2 - 1 + \beta(2) - \frac{8}{\pi^2}\beta(4)$
2d jellium	$\frac{1}{2}$	$-\frac{4\sqrt{2}}{3\pi}$	0	$\ln 2 - 1 + \beta(2) - \frac{8}{\pi^2}\beta(4)$
Glomium	$\frac{3}{10}(3\pi^2)^{2/3}$	$\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3}$	$(1 - \ln 2)/\pi^2$	-0.0469203
3d jellium	$\frac{3}{10}(3\pi^2)^{2/3}$	$\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3}$	$(1 - \ln 2)/\pi^2$	-0.0469203

Loos & Gill, *Phys Rev B* 83 (2011) 233102

Loos & Gill, *Phys Rev B* 84 (2011) 033103

Electrons on Spheres

New Uniform Electron Gases

Suppose that we fill all orbitals with $0 \leq \ell \leq L$ in spherium and glomium

L	0	1	2	3	4	5	6	7	...
n -spherium	2	8	18	32	50	72	98	128	...
n -glomium	2	10	28	60	110	182	280	408	...

- Each of these systems has a completely uniform electron density
- They are therefore a new family of uniform electron gases (UEGs)
- Unlike jellium, each has a finite number of electrons in a finite volume

Improved DFT

A disturbing claim

The uniform electron gas of density ρ is not unique

or, equivalently, ...

Two uniform electron gases with the same density ρ
can have different energies.

Improved DFT

How can we test this claim?

- **Jellium** is a uniform electron gas whose **energy $E[\rho]$** is well known
- Let's apply the jellium functional $E[\rho]$ to **L -spherium** or **L -glomium**
- If the resulting **energy is incorrect** \implies the claim is **true**
- If the resulting **energy is correct** \implies the claim may be **false**

Improved DFT

The components of the Kohn-Sham energy

The reduced Kohn-Sham electronic energy of a system can be written

$$E = T_S + E_V + E_J + E_{XC}$$

where

$$T_S = -\frac{1}{2n} \sum_i^n \int \psi_i^*(\mathbf{r}) \nabla^2 \psi_i(\mathbf{r}) d\mathbf{r} \quad (\text{Non-interacting kinetic})$$

$$E_V = +\frac{1}{n} \int \rho(\mathbf{r}) v(\mathbf{r}) d\mathbf{r} \quad (\text{External})$$

$$E_J = +\frac{1}{2n} \iint \rho(\mathbf{r}_1) r_{12}^{-1} \rho(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \quad (\text{Coulomb})$$

and E_{XC} is defined so that the total energy E is correct.

Improved DFT

Incontrovertible evidence

- We chose four of the exactly solvable two-electron systems
- Feeding their electron densities into the jellium functionals yields ...

	$2R$	Jellium-based Kohn-Sham DFT						E	$E_{KS} - E$
		T_S	E_V	E_J	$-E_X$	$-E_C$	E_{KS}		
0-spherium	$\sqrt{3}$	0	0	1.154701	0.490070	0.1028	0.562	1/2	0.062
	$\sqrt{28}$	0	0	0.377964	0.160413	0.0593	0.158	1/7	0.015
0-glomium	$\sqrt{10}$	0	0	0.536845	0.217762	0.0437	0.275	1/4	0.025
	$\sqrt{66}$	0	0	0.208967	0.084764	0.0270	0.097	1/11	0.006

- In each case, the computed Kohn-Sham energy E_{KS} is too high
- This proves, as claimed, that **a UEG of density ρ is not unique.**

Improved DFT

Escaping from the paradox

- UEGs with the same ρ but different $E[\rho]$ exist. Is this a paradox?
- **No. The density parameter ρ does not tell us everything about the UEG.**
- If UEGs have the same one-electron density ρ , how can they differ?
- **They can have different two-electron densities (*i.e.* intracules)**
- Does this mean that a UEG is defined by more than one parameter?
- **Yes. At least two parameters are required. We suggest ρ and η .**

$$\eta = h(\mathbf{r}, \mathbf{r}) \quad \text{where} \quad \rho_2(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{2}\rho(\mathbf{r}_1)\rho(\mathbf{r}_2) [1 + h(\mathbf{r}_1, \mathbf{r}_2)]$$

Improved DFT

A modest proposal

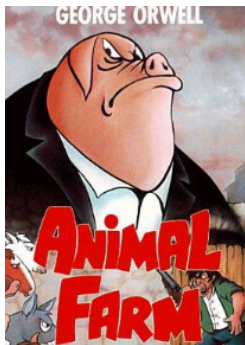
- The “two parameter” discovery has many ramifications for DFT
- E.g., the foundations of the Local Density Approximation must be rebuilt
- Old way: $E_C = \int C(\rho) dr$ Find $C(\rho)$ from jellium
- This required the energies of jellium for various ρ values
- This is an almost solved problem and there is little more to do
- New way: $E_C = \int C(\rho, \eta) dr$ Find $C(\rho, \eta)$ from spherium / glomium
- This requires the energies of L -spherium / glomium for various ρ and η
- This is **an important new project** and there is much to do. Join the game!
CI, MPn, CC, F12, QMC, ICI, *etc.*

Improved DFT

Summary

- 1 n -spherium and n -glomium provide valuable new UEG models
- 2 2-spherium and 2-glomium are exactly solvable two-electron systems
- 3 ∞ -spherium has the same energy as 2D jellium
- 4 ∞ -glomium has the same energy as 3D jellium
- 5 n -spherium and n -glomium with $n < \infty$ differ from jellium
- 6 A UEG is therefore defined by (at least) two parameters, say, ρ and η .
- 7 This will yield a radical new Local Density Approximation $E[\rho, \eta]$
- 8 For more details, see *Theoretical Chemistry Accounts*, 2012, Issue 1

Concluding Remark



“All uniform electron gases are equal, but some uniform electron gases are more equal than others.”