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Density Functionals for Atoms Under Extreme External Specifications

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Some Themes – Insight

Numerical Methods for Scientists and Engineers

Richard Wesley Hamming (1915-1998)

2nd Edition, McGraw-Hill, 1973, (1st edition, 1962)

Section 1.1, page 1: "Numerical methods use numbers to simulate mathematical processes, which in turn usually simulate real-world situations. This implies that there is a *purpose* behind the computing. To cite the motto of the book, "The Purpose of Computing is Insight, Not Numbers" .

"This motto is often thought to mean that the numbers from the computing machine should be read and used, but there is much more to the motto. The choice of a particular formula, or algorithm influences not only the computing, but also how we are to understand the results when they are obtained. … *Thus computing is, or at least should be, intimately bound up with both the source of the problem and the use that is going to be made of the answers - it is not a step to be taken in isolation from reality*."

Antecedent: "Nothing is more terrible than activity without insight."
- Thomas Carlyle (1795-1881)

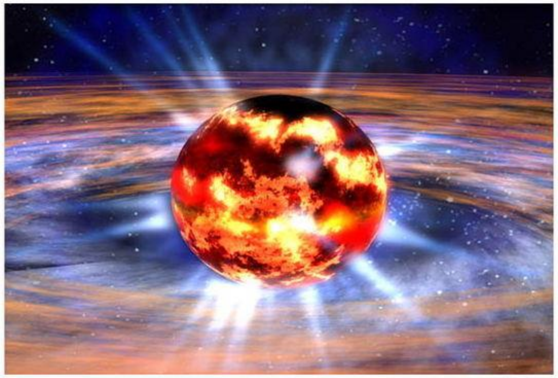
Some Themes – Realism

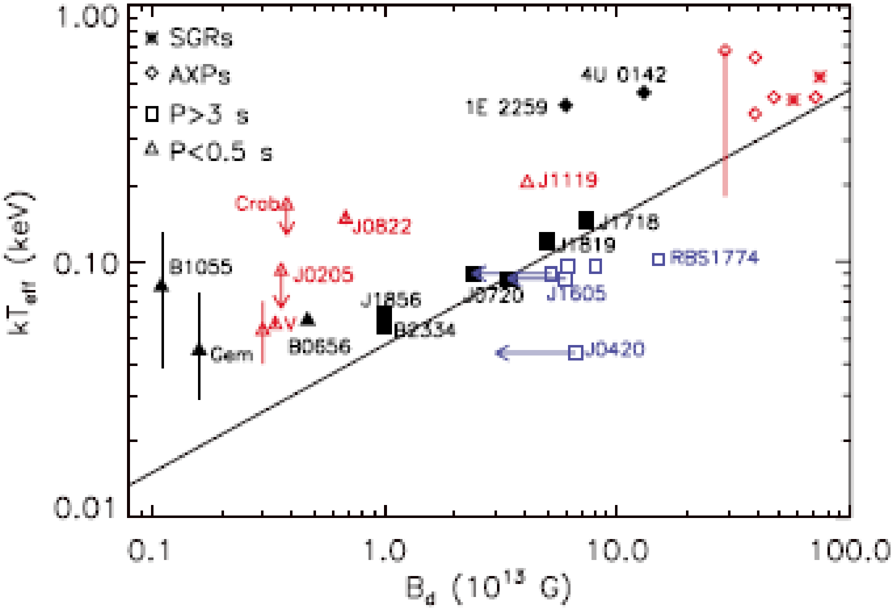
Again from Hamming, ***Numerical Methods for Scientists and Engineers***
2nd Edition, McGraw-Hill, 1973, (1st edition, 1962)

Page 504, the motto
"The Purpose of Computing is Insight, Not Numbers"
is quoted again, with a footnote.

Footnote:
"It is sometimes suggested that the motto be revised to
'the purpose of computing is not yet in sight'."

A motivating physical problem - Atoms near neutron stars





Effective Temp vs. Field in 10^{13} G = 10^9 Tesla for various types of neutron stars. *Pons et al. Phys. Rev. Lett.* *98* *071101 (2007)* **NOTE: B = 1 a.u. = 2.3505 x 10^5 Tesla. Neutron star fields easily are in the range 400 ≤ B ≤ 4000 a.u. or higher.**

This matters for atomic physics of light elements! Extreme compression changes ground state configuration. That changes the spectroscopy – and the chemistry.

Current Density Functional Theory – DFT in a B field

Hamiltonian:

$$\hat{H}_{tot} = \sum_i \left[\frac{1}{2}\left(\frac{\nabla_i}{i} + \mathbf{A}(\mathbf{r}_i) \right)^2 + \upsilon(\mathbf{r}_i) \right] + \frac{1}{2}\sum_{i\neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

Kohn-Sham eq.:

$$\left[\frac{1}{2}\left(\frac{\nabla}{i} + \mathbf{A}_{eff}(\mathbf{r}) \right)^2 + \upsilon_{eff}^{cdft}(\mathbf{r}) \right] \varphi_i(\mathbf{r}) = \varepsilon_i \varphi_i(\mathbf{r})$$

KS orbitals generate the same electron density and same paramagnetic current density as in the real system: $n(\mathbf{r})$ $\mathbf{j}_p(\mathbf{r})$

Paramag. current density in terms of field opeators:

$$\mathbf{j}_p(\mathbf{r}) = <\Psi(\mathbf{r}_1,\mathbf{r}_2,\cdots,\mathbf{r}_N) | \mathbf{J}_p^{op}(\mathbf{r}) | \Psi(\mathbf{r}_1,\mathbf{r}_2,\cdots,\mathbf{r}_N) >$$

$$\mathbf{J}_p^{op}(\mathbf{r}) = \frac{1}{2i}\left[\hat{\Psi}^\dagger(\mathbf{r})\nabla\hat{\Psi}(\mathbf{r}) - \hat{\Psi}(\mathbf{r})\nabla\hat{\Psi}^\dagger(\mathbf{r}) \right]$$

Ordinary DFT vs CDFT

	DFT	CDFT
Hamiltonian	$\hat{H} = -\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2 + \sum_{i=1}^{N}\upsilon(\mathbf{r}_i) + \frac{1}{2}\sum_{\substack{i,j=1\\ i\neq j}}^{N}\frac{1}{\lvert\mathbf{r}_i-\mathbf{r}_j\rvert}$	$\hat{H}_{tot} = \sum_i\left[\frac{1}{2}\left(\frac{\nabla_i}{i}+\mathbf{A}(\mathbf{r}_i)\right)^2 + \upsilon(\mathbf{r}_i)\right] + \frac{1}{2}\sum_{i\neq j}\frac{1}{\lvert\mathbf{r}_i-\mathbf{r}_j\rvert}$
Basic variables	**electron density** n	n **and** $\mathbf{j}_p$ **paramagnetic current density**
Total energy	$E[n] = T_s[n] + J + \int d\mathbf{r}\,\upsilon(\mathbf{r})n(\mathbf{r}) + E_{xc}[n]$	$E[n,\mathbf{j}_p] = T_s[n,\mathbf{j}_p] + J + \int d\mathbf{r}\left(\upsilon(\mathbf{r}) + \frac{1}{2}\mathbf{A}^2(\mathbf{r})\right)$ $+ \int d\mathbf{r}\mathbf{A}(\mathbf{r})\cdot\mathbf{j}_p(\mathbf{r}) + E_{xc}^{cdft}[n,\mathbf{j}_p]$
KS equation	$\left[-\frac{\nabla^2}{2} + \upsilon_s(\mathbf{r})\right]\varphi_i(\mathbf{r}) = \varepsilon_i\varphi_i(\mathbf{r})$ $\upsilon_s(\mathbf{r}) = \upsilon(\mathbf{r}) + \upsilon_H(\mathbf{r}) + \upsilon_{xc}^{dft}(\mathbf{r})$ $\upsilon_H(\mathbf{r}) = \int d\mathbf{r}'\frac{n(\mathbf{r})}{\lvert\mathbf{r}-\mathbf{r}'\rvert}$	$\left[\frac{1}{2}\left(\frac{\nabla}{i} + \mathbf{A}_{eff}(\mathbf{r})\right)^2 + \upsilon_{eff}^{cdft}(\mathbf{r})\right]\varphi_i(\mathbf{r}) = \varepsilon_i\varphi_i(\mathbf{r})$ $\mathbf{A}_{eff}(\mathbf{r}) = \mathbf{A}(\mathbf{r}) + \mathbf{A}_{xc}(\mathbf{r})$ $\upsilon_{eff}^{cdft}(\mathbf{r}) = \left[\upsilon(\mathbf{r}) + \upsilon_H(\mathbf{r}) + \upsilon_{xc}^{cdft}(\mathbf{r})\right] + \frac{1}{2}\left[\mathbf{A}^2(\mathbf{r}) - \mathbf{A}_{eff}^2(\mathbf{r})\right]$
XC potentials	$\upsilon_{xc}^{dft}(\mathbf{r}) = \frac{\delta E_{xc}[n(\mathbf{r})]}{\delta n(\mathbf{r})}$	$\mathbf{A}_{xc}(\mathbf{r}) = \left.\frac{\delta E_{xc}^{cdft}\left[n(\mathbf{r}),\mathbf{j}_p(\mathbf{r})\right]}{\delta\mathbf{j}_p(\mathbf{r})}\right\rvert_{n(\mathbf{r})}$ $\upsilon_{xc}^{cdft}(\mathbf{r}) = \left.\frac{\delta E_{xc}^{cdft}\left[n(\mathbf{r}),\mathbf{j}_p(\mathbf{r})\right]}{\delta n(\mathbf{r})}\right\rvert_{\mathbf{j}_p(\mathbf{r})}$

CDFT for Single Atom in Uniform External Field

Vector potential: $\mathbf{A}(\mathbf{r}) = \frac{1}{2}\mathbf{B}\times\mathbf{r}$ ***with*** $\mathbf{B} = B\mathbf{e}_z$

Many-electron atomic Hamiltonian (Hartree atomic units)

$$\hat{H} = \sum_{i=1}^{N}\left[-\frac{1}{2}\nabla_i^2 - \frac{Z}{r_i} + \frac{B^2}{8}\left(x_i^2 + y_i^2\right) + \frac{B}{2}\left(m_i + 2m_{s,i}\right)\right] + \frac{1}{2}\sum_{\substack{i,j=1\\ i\neq j}}^{N}\frac{1}{\left|\mathbf{r}_i - \mathbf{r}_j\right|}$$

Zeroth-order CDFT approximation reduces to ordinary DFT with B

(naive B-DFT, *or* DFT + B)

$$E_{xc}^{cdft}\left[n,\mathbf{j}_p\right] = E_{xc}^{dft}\left[n\right] \quad\Leftrightarrow\quad \mathbf{A}_{xc}(\mathbf{r}) = 0$$

CDFT for Single Atom in Uniform External Field

Vector potential: $\mathbf{A}(\mathbf{r}) = \frac{1}{2}\mathbf{B}\times\mathbf{r}$ **with** $\mathbf{B} = B\mathbf{e}_z$

Many-electron atomic Hamiltonian (Hartree atomic units)

$$\hat{H} = \sum_{i=1}^{N}\left[-\frac{1}{2}\nabla_i^2 - \frac{Z}{r_i} + \frac{B^2}{8}\left(x_i^2 + y_i^2\right) + \frac{B}{2}\left(m_i + 2m_{s,i}\right)\right] + \frac{1}{2}\sum_{\substack{i,j=1\\ i\neq j}}^{N}\frac{1}{\left|\mathbf{r}_i - \mathbf{r}_j\right|}$$

CDFT approximation - LDA+ Vignale-Rasolt-Geldart (VRG)

$$\mathbf{A}_{xc}(\vec{r}) = \frac{1}{n(\mathbf{r})}\left(\nabla\times\left.\frac{\delta E_{xc}^{cdft}[n,\vec{v}]}{\delta\vec{v}(\mathbf{r})}\right|_{n(\mathbf{r})}\right) = \frac{2}{n(\mathbf{r})}\nabla\times\left[g\left(n(\mathbf{r})\right)\vec{v}(\mathbf{r})\right]$$

$$\upsilon_{xc}^{cdft}(\mathbf{r}) = \upsilon_{xc}^{dft}(\mathbf{r}) + \frac{dg(n)}{dn}\left|\vec{v}(\mathbf{r})\right|^2 - \mathbf{A}_{xc}(\mathbf{r})\cdot\frac{\mathbf{j}_p(\mathbf{r})}{n(\mathbf{r})} \qquad \vec{v}(\mathbf{r}) \equiv \nabla\times\frac{\mathbf{j}_p(\mathbf{r})}{n(\mathbf{r})}$$

Cutoff for $g(n)$, $g_{cutoff} = \frac{k_F}{24\pi^2}\left(c_1 + c_2 r_s\right)e^{-a_{cutoff}\, r_s}$

c_1 and c_2 determined by smooth connection

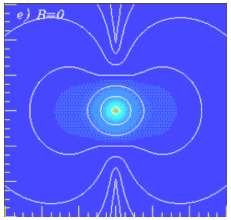
$$g_{cutoff}\left(n_{cutoff}\right) = g_{LCH}\left(n_{cutoff}\right), \quad \left.\frac{dg_{cutoff}}{dn}\right|_{n_{cutoff}} = \left.\frac{dg_{LCH/OMC}}{dn}\right|_{n_{cutoff}}$$

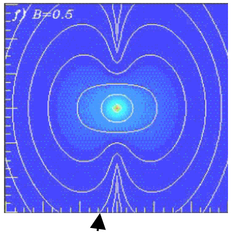
$$E_{xc}^{cdft}\left[n, \mathbf{j}_p\right] = E_{xc}^{dft}[n,0] + \Delta E_{xc}^{VRG}\left[n,\vec{\nu}\right]$$

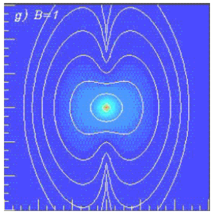
$$\Delta E_{xc}^{VRG}\left[n,\vec{v}\right] = \int d\mathbf{r}\, g\left(n(\mathbf{r})\right)\left|\vec{v}(\mathbf{r})\right|^2$$

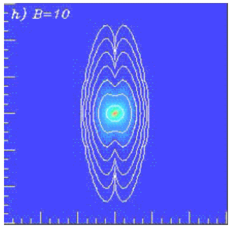
Anisotropic Confinement

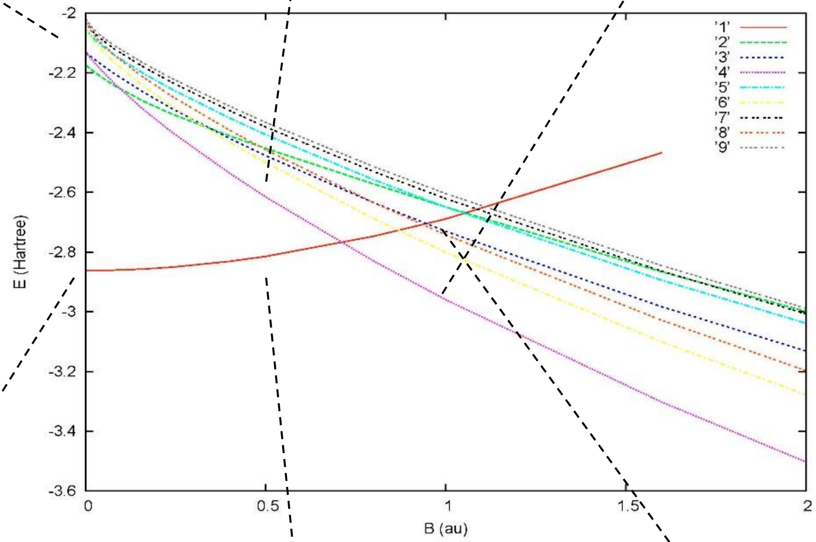
$1s2p_{-1}$











UHF E_{tot} for two electronic states of the He atom in B fields. Curves 1 to 9 are for configurations $1s^2$, $1s2s$, $1s2p_0$, $1s2p_{-1}$, $1s3d_{-1}$, $1s3d_{-2}$, $1s4f_{-2}$, $1s4pf_{-3}$, and $1s5g_{-3}$, respectively.

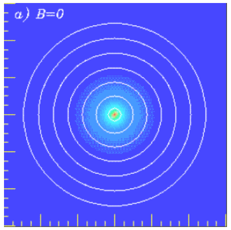
$B = 0$

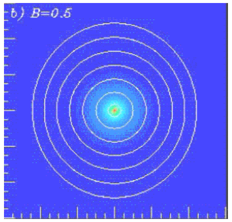
$B = 0.5$ au

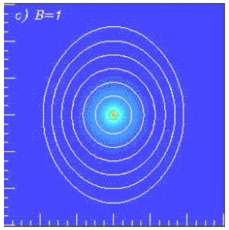
$B = 1$ au

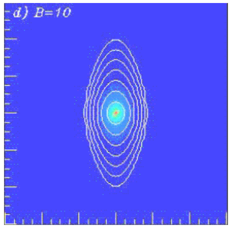
$B = 10$ au

$1s^2$









Basis Sets for Atoms in large B

Anisotropic-GTO (AGTO)

$$\chi_j(\rho, z, \varphi) = N_j \rho^{n_{\rho j}} z^{n_{zj}} e^{-\alpha_j \rho^2 - \beta_j z^2} e^{i m_j \varphi} \qquad j = 1, 2, 3, \cdots$$

where

$$n_{\rho_j} = |m_j| + 2k_j, \quad k_j = 0, 1, \cdots \quad m_j = \cdots, -2, -1, 0, 1, 2, \cdots$$

$$n_{z_j} = \pi_{z_j} + 2l_j, \quad l_j = 0, 1, \cdots \quad \pi_{z_j} = 0, 1.$$

Orbitals expanded in AGTOs $\phi_i(\vec{r}\sigma) = \sum_j b_{ij}^{\sigma} \chi_j(\rho, z, \varphi) |\sigma\rangle$

How should the exponents α_j and β_j be chosen?

B does not change confinement in the z direction,

$$\beta_j = pq^j, \qquad j = 1, 2, \cdots N_b.$$

For α_j ,

1. Jones-Ortiz-Ceperley (JOC) basis set: (Helium atom)

$$\alpha_j = \beta_j, \quad 2\beta_j, \quad 4\beta_j, \quad 8\beta_j, \quad \cdots$$

First, second, third, fourth, … sequences

2. Kravchenko-Liberman (KL) basis set: (Hydrogen atom)

$$\alpha_j = \beta_j + B\Delta_{KL}, \beta_j + 1.2B\Delta_{KL}, \beta_j + 0.8B\Delta_{KL}, \beta_j + 1.4B\Delta_{KL}, \beta_j + 0.6B\Delta_{KL}$$

Basis Sets for Atoms in large B *(continued)*

Reminder

$$\cdots e^{-\alpha_j \rho^2 - \beta_j z^2} \cdots$$

3. Present basis set: $\alpha_j = \beta_j + \frac{B}{20}\left\{4\left[1+\frac{4}{b(\gamma)}\frac{\beta_j}{B}\right]^{-2} + \left[1+\frac{4}{b(\gamma)}\frac{\beta_j}{B}\right]^{-1/2}\right\} = \beta_j + \Delta_j$

where $b(\gamma) = -0.16\left[\tan^{-1}(\gamma)\right]^2 + 0.77\tan^{-1}(\gamma) + 0.74$

$\gamma = B/Z^2$ is the reduced field strength.

$$\alpha_j = \beta_j + \Delta_j,\ \beta_j + 1.2\Delta_j,\ \beta_j + 0.8\Delta_j,\ \beta_j + 1.4\Delta_j,\ \beta_j + 0.6\Delta_j$$

"Comparative Studies of Density Functional Approximations for Light Atoms in Strong Magnetic Fields", W. Zhu, L. Zhang, and S.B. Trickey, Phys. Rev. A **90**, 022504 (2014)

Basis Set Error Comparison - Light Atoms in large B

Hartree-Fock energies for atoms in B *= 10 au : (energies in Hartree)*

Atom	G.S. Configuration	HF Energy (Hartree)	Reference
H	1s	- 1.747 797 163 714	PRA 54, 287 (1996)
C	$1s^2 2p_{-1} 3d_{-2} 4f_{-3} 5g_{-4}$	- 44.387 2	PRA 60, 3558 (1999)

Basis set errors in ground state HF energies of the Hydrogen and Carbon atoms; B *= 10 au. (energies in Hartree)*

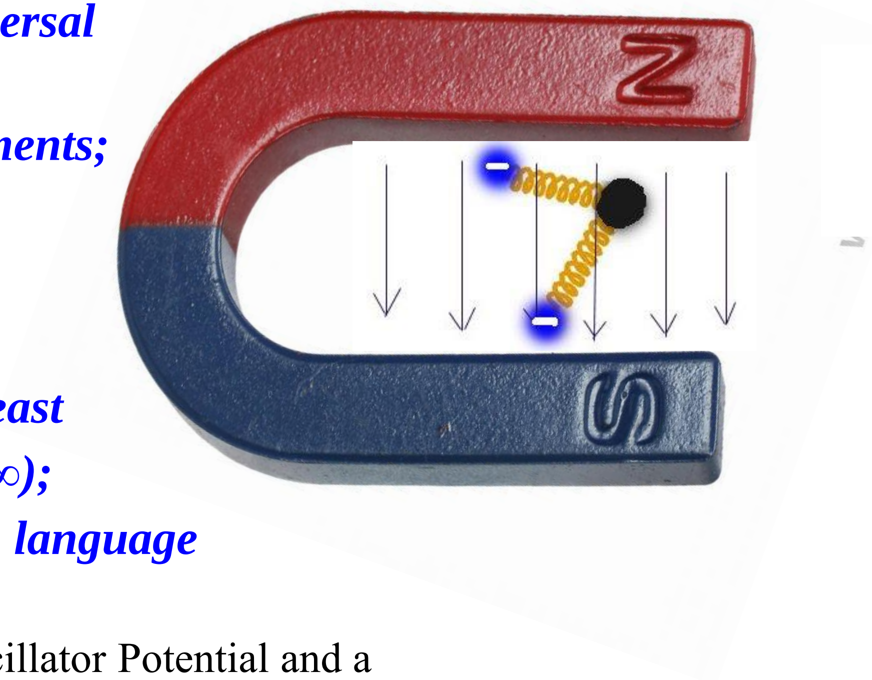
Atom	Sequences	Spherical	JOC Basis Set	KL Basis Set	Present Basis Set
H	1	0.4198 **(16)** *	0.419 787 28 **(16)**	0.003 738 20 **(16)**	0.001 044 51 **(16)**
	2	0.0815 **(32)**	0.027 124 87 **(32)**		
	3	0.0217 **(48)**	0.001 008 57 **(48)**	0.000 005 39 **(32)**	0.000 000 50 **(32)**
	4	0.0081 **(64)**	0.000 075 02 **(64)**		
	5			0.000 001 12 **(40)**	0.000 000 28 **(40)**
C	1			0.2243 **(80)**	0.0013 **(50)** †
	2	0.7715 **(112)**	0.2300 **(160)**	0.0048 **(120)**	0.0002 **(72)** †
	3		0.0343 **(240)**	0.0009 **(160)**	<0.0001 **(90)** †

*** Numbers in parenthesis indicate basis set sizes;** † Extremely tight and diffuse basis functions discarded.

Hooke's Atom (HA) in B *– An Instructive Model*

***Two electrons, harmonically confined*.**

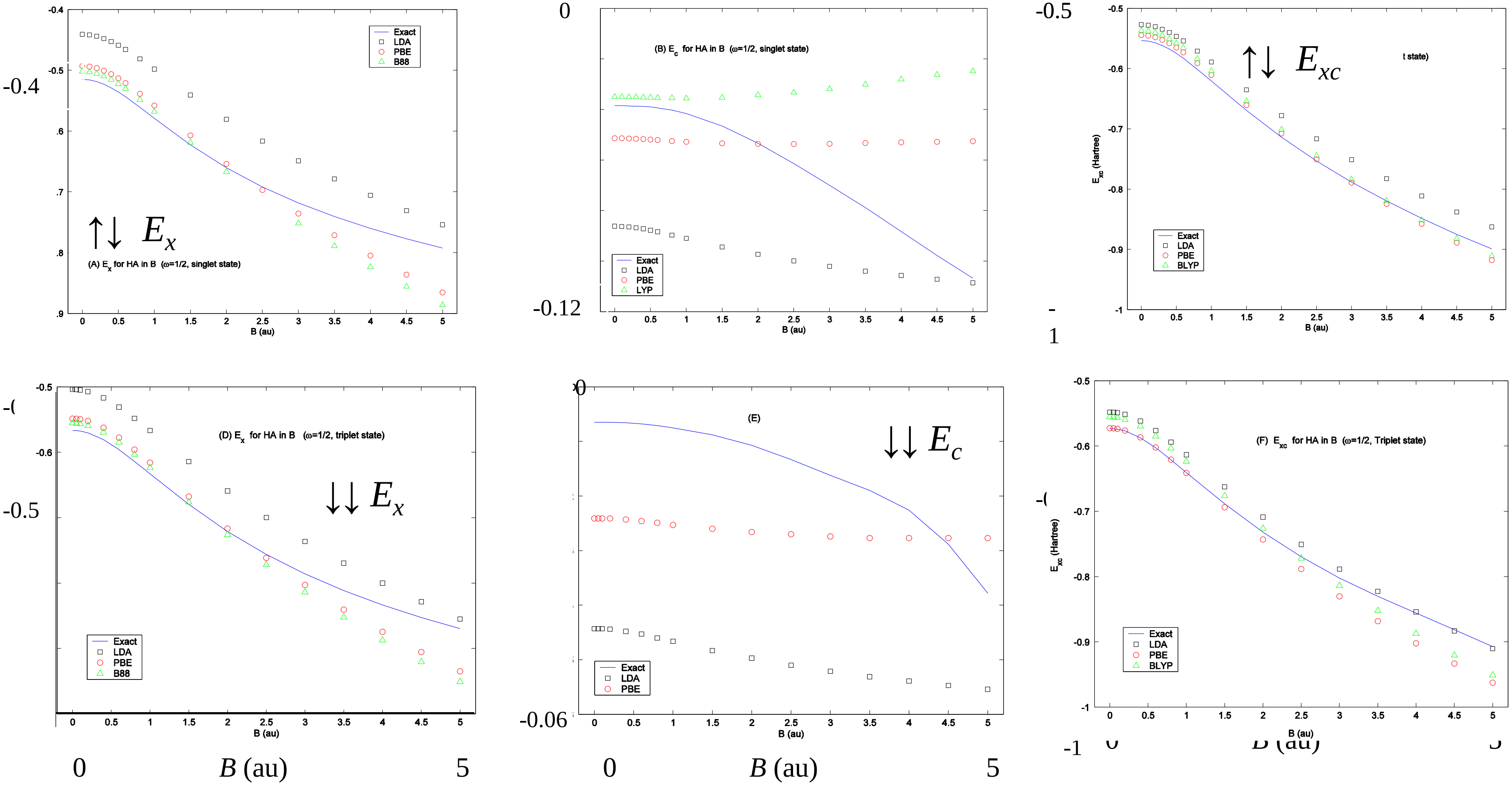
$$\hat{H}_{tot} = \frac{1}{2}\left[\left(\frac{\nabla_1}{i} + \mathbf{A}(\mathbf{r}_1)\right)^2 + \left(\frac{\nabla_2}{i} + \mathbf{A}(\mathbf{r}_2)\right)^2\right] + \frac{\omega^2}{2}(r_1^2 + r_2^2) + \frac{1}{r_{12}} + \hat{H}_{spin}$$



- ***HA has been useful in ordinary DFT (universal functional)***
- ***Analytical solutions exist for some confinements;***
- ***An exact CDFT functional is desirable;***
- ***Includes both exchange and correlation (N = 2);***
- ***Schrödinger equation can be solved with least effort for the whole range of B field (0 ≤ B < ∞);***
- ***Solutions can be easily cast in Kohn-Sham language***

"Analytic Solutions for Two Electrons in an Oscillator Potential and a Magnetic Field", W. Zhu and S.B. Trickey, Phys. Rev. A **72**, 022501 (2005)

Exac vs. Approx. XC energies for HA in B



HA exact (blue curve) and appro. X (left), C (middle), and XC (right) energies for *ω* = 1/2 in *B* fields. Upper panels – singlets. Lower - triplets. Black squares (□) are LDA, red circles (o) PBE, green triangles (Δ) BLYP.

"Exact Density Functionals for Two Electrons Systems in an Magnetic Field", W. Zhu and S.B. Trickey, J. Chem. Phys. Rev. 1**25**, 094317 (2006)

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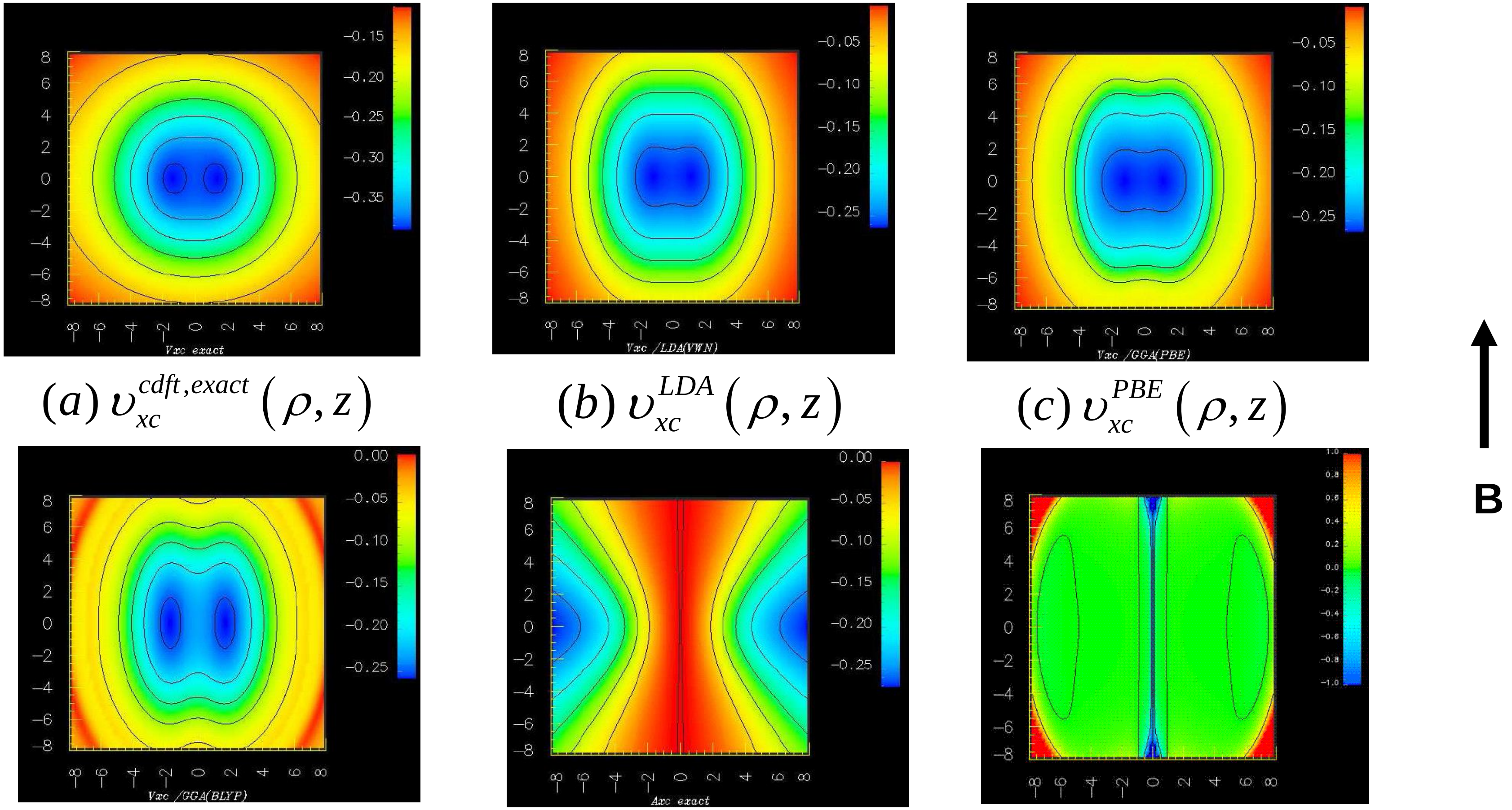
Exact vs. Approx. XC potentials for HA in **B**



$(a)\ \upsilon_{xc}^{cdft,exact}(\rho,z)$ $(b)\ \upsilon_{xc}^{LDA}(\rho,z)$ $(c)\ \upsilon_{xc}^{PBE}(\rho,z)$

$(d)\ \upsilon_{xc}^{BLYP}(\rho,z)$ $(e)\ \mathbf{A}_{xc}(\mathbf{r})=\hat{\varphi}A_{xc}^{cdft,exact}(\rho,z)$ $(f)\ \mathbf{A}_{xc}^{VRG}(\rho,z)$

Cross-sectional views of exact and approximate XC quantities for HA ground state with $\boldsymbol{\omega}$ **= 1/10** ***and*** $B=\sqrt{3}/5\approx 8{,}100\,\text{Tesla}$

XC Hole Densities for HA in B

Exact XC holes

For an electron at $\mathbf{r}'$, $$n_{xc}(\mathbf{r},\mathbf{r}') = \frac{2\left|\Psi\left(\mathbf{r},\mathbf{r}'\right)\right|^2}{n(\mathbf{r}')} - n(\mathbf{r})$$

$$n_{x\sigma}\left(\mathbf{r},\mathbf{r}'\right) = -\frac{\left|\sum_i^{\sigma}\phi_i^*\left(\mathbf{r}'\right)\phi_i\left(\mathbf{r}\right)\right|^2}{n\left(\mathbf{r}\right)} \qquad n_c\left(\mathbf{r},\mathbf{r}'\right) = n_{xc}\left(\mathbf{r},\mathbf{r}'\right) - n_x\left(\mathbf{r},\mathbf{r}'\right)$$

Approximate XC Holes

LDA (PW92), Perdew and Wang, Phys. Rev. B 46, 12947, (1992).

GGA (PBE), Perdew, Burke and Wang, Phys. Rev. B 54, 16533, (1996).

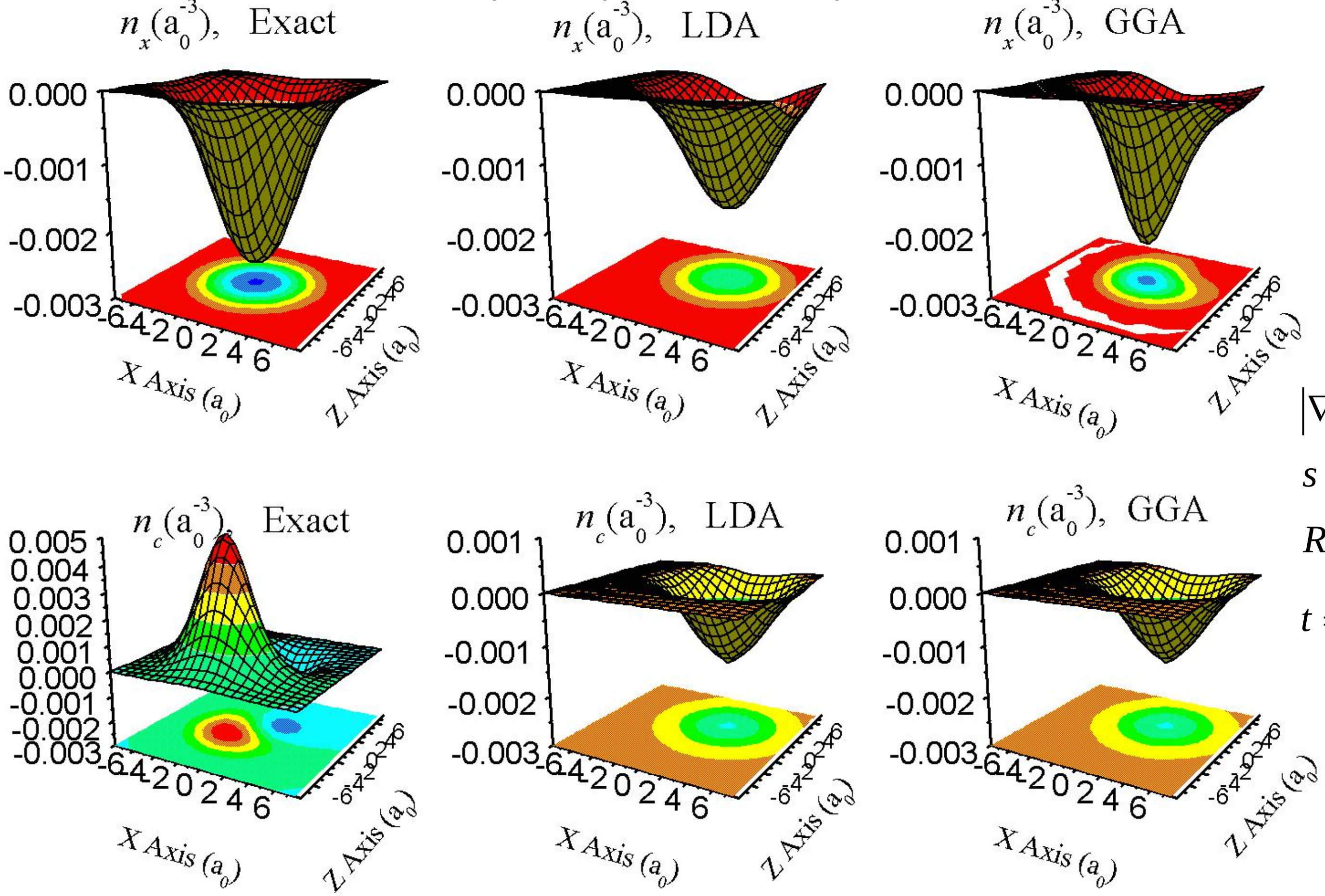
$$n_c^{\lambda=1}\left(\vec{r},\vec{r}'\right) = n\left(\vec{r}'\right)\left(1 + r_s\frac{\partial}{\partial r_s}\right)\frac{n_c\left(\vec{r},\vec{r}'\right)}{n\left(\vec{r}'\right)} \qquad \text{where} \qquad r_s = \left(\frac{3}{4\pi n(\vec{r}')}\right)^{1/3}$$

System and Angular Averaged Hole Densities

$$n_{x,c}\left(u\right) = \frac{1}{2}\int d\vec{r}'\left[n\left(\vec{r}'\right)\frac{1}{4\pi}\int d\Omega_u n_{x,c}\left(\vec{r}' + \vec{u},\vec{r}'\right)\right]$$

Exact and Approx. X and C Hole Densities for HA; **B = 0**

$$n(2a_0, 0, 2a_0) = 0.00374 a_0^{-3}$$



$$|\nabla n| = 0.00134 a_0^{-4}$$

$$s = 0.317$$

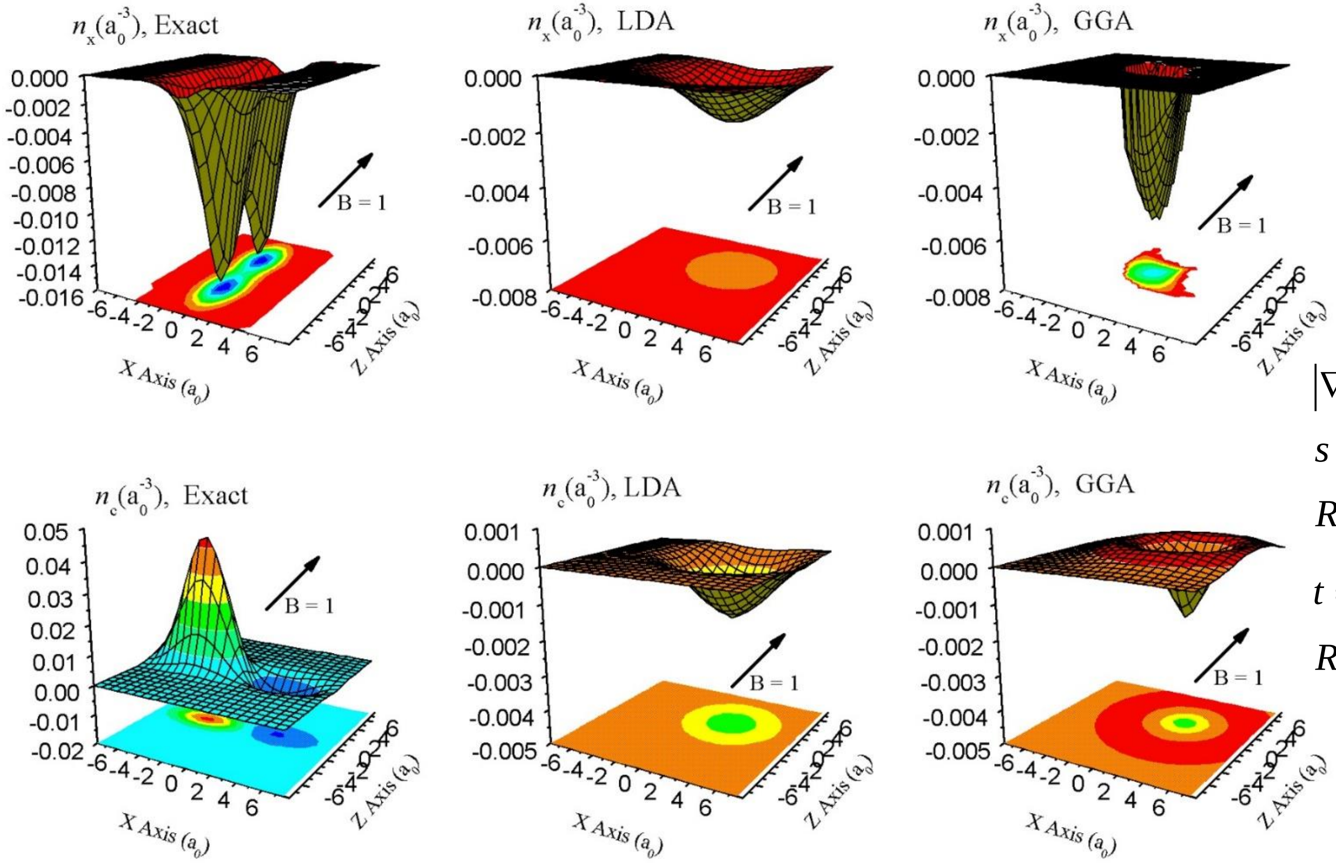
$$R_x^{cutoff} = 37.8 a_0$$

$$t = 0.194 a_0^{-1/2}$$

Exact and approximate X and C hole densities (n_x , n_c) for singlet state HA (ω = 1/10, m = 0) at* B *= 0. The electron is at (x',y',z') = (2,0,2)a_0.

Exact and Approx. X and C Hole Densities for HA; **B = 1 au.**

$$n(2a_0, 0, 2a_0) = 0.00399a_0^{-3}$$



$$|\nabla n| = 0.00795a_0^{-4}$$

$$s = 2.034$$

$$R_x^{cutoff} = 4.68a_0$$

$$t = 1.26a_0^{-1/2}$$

$$R_c^{cutoff} = 3.58a_0$$

Exact and approximate X and C hole densities (n_x , n_c) for singlet state HA (ω = 1/10, m = 0) at* B *= 1 au. The electron is at (x',y',z') = (2,0,2)a_0.

Some findings -

- *Both LDA and GGA tend to overestimate* E_x *with increasing* B *because they over-localize the X holes; the GGA overestimation is more severe;*
- *Correlation becomes more important with increasing* B;
- *__But__ the* E_c *from LDA or GGA is almost* B*-independent -* B *field effects on C holes are smoothed out in either approximation*;
- *All the approximations give too shallow a* v_{xc}*, even though they have qualitatively right shape;*
- A_{xc} *from the VRG approximation has no resemblance to the exact one*;
- *Vorticity is a rather difficult variable computationally*;
- *The cutoff scheme in GGA to ensure hole density normalization gives too small a cutoff radius for the exchange hole*.

Atoms in High B-field: Back to Naïve B-DFT

$$\mathbf{A}(\mathbf{r}) = \frac{1}{2}\mathbf{B}\times\mathbf{r}$$

$$\left[-\frac{1}{2}\nabla^2 - \frac{Z}{r} + \frac{B^2}{8}\left(x^2+y^2\right) + \frac{B}{2}\left(m_i + 2m_{s,i}\right) + v_H(\mathbf{r}) + v_{xc}(\mathbf{r}) + \frac{1}{i}\mathbf{A}_{xc}(\mathbf{r})\cdot\nabla\right]\phi_i(\mathbf{r}) = \varepsilon_i\phi_i(\mathbf{r})$$

$$E_{tot} = T_s + J + E_{xc}[n,\mathbf{j}_p] + \int d\mathbf{r}\,n(\mathbf{r})\left\{-\frac{Z}{r} + \frac{B^2}{8}\left(x^2+y^2\right)\right\} + \frac{B}{2}\sum_i\left(m_i + 2m_{s,i}\right)$$

If we drop the $\mathbf{A}_{xc}$ we can avoid the awkward fact that there are no good current-DFT XC approximations for real systems.

These are highly confined systems, so must have

- ***Highly anisotropic basis set***
- ***A Self-Interaction-Corrected E_{xc}***

Hyper-GGA XC functional

$$E_{xc} = E_x^{XX} + E_c^{tpss}$$

$$E_x^{XX}\left[\{\phi_i(\mathbf{r})\}\right] = -\frac{1}{2}\sum_{i,j}\left[\int \frac{\phi_i^*(\mathbf{r})\phi_j^*(\mathbf{r}')\phi_j(\mathbf{r})\phi_i(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}'\right]$$

TPSS E_C is [integer] self-interaction free.

Therefore the combination is self-interaction free.

Important property for confined systems.

Bad news – 4th rung functional (both KE density and orbitals themselves)

Good news – It works up to very high B fields.

Similar results for molecules found a few months later by Helgaker et al.

"Comparative Studies of Density Functional Approximations for Light Atoms in Strong Magnetic Fields', W. Zhu, L. Zhang, and S.B. Trickey, Phys. Rev. A **90**, 022504 (2014)

Naïve-B Hyper-GGA XC Calculations

- **B *fields: 0 – 2000 au***
- ***Approximations: Hartree-Fock, LDA(VWN), GGA(PBE), meta-GGA (TPSS), hyper-GGA (EXX+E_c^{tpss})***
- ***Atoms and Ions treated:***

He ($1s^2$,$1s2s$, $1s2p_0$, $1s2p_{-1}$, $1s3d_{-1}$, $1s3d_{-2}$, $1s4f_{-2}$, $1s4f_{-3}$, $1s5g_{-3}$)

Li^+ ($1s^2$, $1s2p_{-1}$);

Li ($1s^22s$, $1s^22p_{-1}$, $1s2s2p_{-1}$, $1s2p_02p_{-1}$, $1s2p_{-1}3d_{-2}$);

Be^+ ($1s^22s$, $1s^22p_{-1}$, $1s2p_{-1}3d_{-2}$);

Be, B^+ ($1s^22s^2$, $1s^22s2p_{-1}$, $1s^22p_{-1}3d_{-2}$, $1s2p_{-1}3d_{-2}4f_{-3}$);

B ($1s^22s^22p_{-1}$, $1s^22s2p_02p_{-1}$, $1s^22s2p_{-1}3d_{-2}$, $1s^22p_02p_{-1}3d_{-2}$,
$1s^22p_{-1}3d_{-2}4f_{-3}$, $1s2p_{-1}3d_{-2}4f_{-3}5g_{-4}$);

C ($1s^22s^22p_02p_{-1}$, $1s^22s2p_02p_{-1}2p_{+1}$, $1s^22s2p_02p_{-1}3d_{-2}$, $1s^22p_02p_{-1}3d_{-2}4f_{-3}$,
$1s^22p_{-1}3d_{-2}4f_{-3}5g_{-4}$, $1s2p_02p_{-1}3d_{-2}4f_{-3}5g_{-4}$, $1s2p_{-1}3d_{-2}4f_{-3}5g_{-4}6h_{-5}$)

Success - Small sample of results

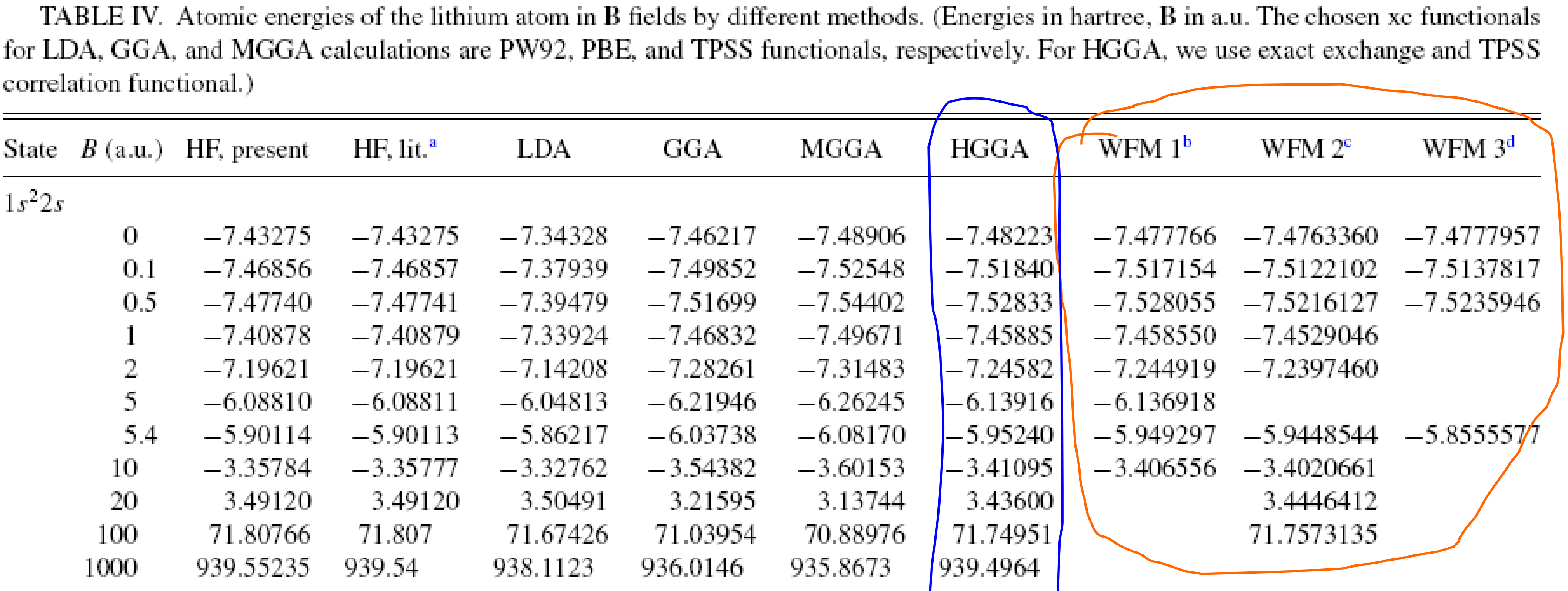


TABLE IV. Atomic energies of the lithium atom in **B** fields by different methods. (Energies in hartree, **B** in a.u. The chosen xc functionals for LDA, GGA, and MGGA calculations are PW92, PBE, and TPSS functionals, respectively. For HGGA, we use exact exchange and TPSS correlation functional.)

State	B (a.u.)	HF, present	HF, lit.[a]	LDA	GGA	MGGA	HGGA	WFM 1[b]	WFM 2[c]	WFM 3[d]
$1s^2 2s$										
	0	−7.43275	−7.43275	−7.34328	−7.46217	−7.48906	−7.48223	−7.477766	−7.4763360	−7.4777957
	0.1	−7.46856	−7.46857	−7.37939	−7.49852	−7.52548	−7.51840	−7.517154	−7.5122102	−7.5137817
	0.5	−7.47740	−7.47741	−7.39479	−7.51699	−7.54402	−7.52833	−7.528055	−7.5216127	−7.5235946
	1	−7.40878	−7.40879	−7.33924	−7.46832	−7.49671	−7.45885	−7.458550	−7.4529046	
	2	−7.19621	−7.19621	−7.14208	−7.28261	−7.31483	−7.24582	−7.244919	−7.2397460	
	5	−6.08810	−6.08811	−6.04813	−6.21946	−6.26245	−6.13916	−6.136918		
	5.4	−5.90114	−5.90113	−5.86217	−6.03738	−6.08170	−5.95240	−5.949297	−5.9448544	−5.8555577
	10	−3.35784	−3.35777	−3.32762	−3.54382	−3.60153	−3.41095	−3.406556	−3.4020661	
	20	3.49120	3.49120	3.50491	3.21595	3.13744	3.43600		3.4446412	
	100	71.80766	71.807	71.67426	71.03954	70.88976	71.74951		71.7573135	
	1000	939.55235	939.54	938.1123	936.0146	935.8673	939.4964			

HGGA

High-precision wavefunction results

"Comparative Studies of Density Functional Approximations for Light Atoms in Strong Magnetic Fields", W. Zhu, L. Zhang, and S.B. Trickey, Phys. Rev. A **90**, 022504 (2014)

Doing Even Better

- ***DFT+B (naïve B DFT) approaches can give nearly quantitatively correct results for atoms in a wide range of B fields***
- ***The error in DFT + B is mainly from electron exchange. Using exact exchange, E_{xx}, can significantly reduce that error***
- ***E_{xx} + TPSS E_c is an effective combination for light atoms in B field Since the XC hole of an atom is relatively local, one may use E_{xx} + TPSS E_c. However, the combination maybe not applicable to large molecular or larger extended systems. See, however, J.W. Furness, J. Verbeke, E.I. Tellgren, S. Stopkowicz, U. Ekström, T. Helgaker, and A.M. Teale, J. Chem. Theory Comput. 11, 4169 (2015)***
- ***Although self-interaction free, TPSS E_c is not fully compatible with E_{xx}, since semi-local functionals still rely on error cancellation between the long-range parts of the X and C holes***
- ***What about RPA correlation as compatible with E_{xx} ?***

Ground state degeneracy and "current carrying" states

Spurious non-degeneracy:

Consider Boron $1s^2 2s^2 2p^1$

GGA (PBE): $E[1s^2 2s^2 2p^1_0]$ $(\mathbf{j}_p = 0)$ $<$ $E[1s^2 2s^2 2p^1_{\pm 1}]$ $(\mathbf{j}_p \neq 0)$

Can the degeneracy be restored by using expressions that actually depend on the paramagnetic current density?

Must have a correlation expression that recognizes difference between real and complex orbitals.

RPA and RPA-like Correlation

RPA-like: $E_{xc}\left[\left\{\phi_q(\mathbf{r})\right\}\right]$ directRPA = dRPA

$$E_{XC} = \int_0^1 W_\lambda[n]\,d\lambda$$

$$W_\lambda[n] = \left\langle \psi_\lambda[n]\,|\,\hat{W}\,|\,\psi_\lambda[n]\right\rangle - \frac{1}{2}\iint d\mathbf{r}\,d\mathbf{r}'\frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

$\hat{W}$ = electron-electron repulsion

$$W_\lambda = W_0 - \int_0^\infty \frac{d\omega}{2\pi}\,\mathrm{Im}\left\{\iint dx\,dx'\frac{\chi_\lambda(\omega,x,x')-\chi_0(\omega,x,x')}{|\mathbf{r}-\mathbf{r}'|}\right\}$$

$x := (\mathbf{r},\sigma)$

χ_λ **= freq. dependent density response function with scaled interaction and fixed density**

$$\chi_\lambda^{\mathrm{RPA}}(\omega,x,x') = \chi_0(\omega,x,x') + \iint \chi_0(\omega,x,x_1)\left(\frac{\lambda}{|r_1-r_1'|}\right)\chi_\lambda^{\mathrm{RPA}}(\omega,x_1',x')\,dx_1\,dx_1'$$

$$\chi_0(i\omega,x,x') = 2\sum_i\sum_a\frac{\phi_i^*(x)\phi_a^*(x')\phi_a(x)\phi_i(x')}{i\omega+\epsilon_i-\epsilon_a}$$

--- KS density response function

F. Furche, Phys. Rev. B **64**, 195120 (2001).

RPA Correlation in a real-valued orbital basis set

$$E_C^{RPA} = \frac{1}{2}\int_0^1 d\lambda \sum_{ia,jb} \langle ib|aj\rangle \left(\mathbf{P}_{c,\lambda}\right)_{ia,jb}$$

$$\mathbf{P}_{c,\lambda} = \sum_n \left(\mathbf{X}_{n,\lambda} + \mathbf{Y}_{n,\lambda}\right)\left(\mathbf{X}_{n,\lambda} + \mathbf{Y}_{n,\lambda}\right)^{\mathrm{T}} - \mathbf{1}$$

$$\mathbf{M}_\lambda \mathbf{Z}_{n,\lambda} = \omega_{n,\lambda}^2 \mathbf{Z}_{n,\lambda} \qquad \mathbf{M}_\lambda = \left(\mathbf{A}_\lambda - \mathbf{B}_\lambda\right)^{1/2}\left(\mathbf{A}_\lambda + \mathbf{B}_\lambda\right)\left(\mathbf{A}_\lambda - \mathbf{B}_\lambda\right)^{1/2}$$

$$\mathbf{Z}_{n,\lambda} = \sqrt{\omega_{n,\lambda}}\left(\mathbf{A}_\lambda - \mathbf{B}_\lambda\right)\left(\mathbf{X}_{n,\lambda} + \mathbf{Y}_{n,\lambda}\right)$$

$$\left(\mathbf{A}_\lambda\right)_{ia,jb} = \left(\varepsilon_a - \varepsilon_i\right)\delta_{ij}\delta_{ab} + \lambda\left[\langle ib|aj\rangle - x\langle ib|ja\rangle\right]$$

$$\left(\mathbf{B}_\lambda\right)_{ia,jb} = \lambda\left[\langle ab|ij\rangle - x\langle ab|ji\rangle\right]$$

$x = 0$ (d-RPA)

$x = 1$ (RPA with exchange)

$$\langle pq|rs\rangle = \iint \frac{\phi_p(\vec{r})\phi_q(\vec{r}\,')\phi_r(\vec{r})\phi_s(\vec{r}\,')}{|\vec{r} - \vec{r}\,'|}\, d\vec{r}\, d\vec{r}\,'$$

F. Furche, Phys. Rev. B **64**, 195120 (2001).

RPA Correlation in a complex-valued orbital basis set

Extension of RPA to complex orbitals is straightforward, but a little bit tedious ...

$$E_C = \frac{1}{4}\int_0^1 d\lambda \sum_{ia,jb} \left\{ \langle ib|aj\rangle \left[\left(\mathbf{P}_{+,\lambda}\right)_{ia,jb} + \left(\mathbf{P}_{-,\lambda}\right)_{ia,jb} \right] + \langle ij|ab\rangle \left[\left(\mathbf{P}_{+,\lambda}\right)_{ia,jb} - \left(\mathbf{P}_{-,\lambda}\right)_{ia,jb} \right] \right\}$$

$$\mathbf{P}_{\pm,\lambda} = \sum_n \left(\mathbf{X}_{n,\lambda} \pm \mathbf{Y}_{n,\lambda}\right)\left(\mathbf{X}_{n,\lambda} \pm \mathbf{Y}_{n,\lambda}\right)^{\mathrm{T}} - \mathbf{1}$$

$$\mathbf{M}_{\pm,\lambda}\mathbf{Z}_{\pm,n,\lambda} = \omega_{n,\lambda}^2 \mathbf{Z}_{\pm,n,\lambda} \qquad \mathbf{M}_{\pm,\lambda} = \left(\mathbf{A}_\lambda \mp \mathbf{B}_\lambda\right)^{1/2}\left(\mathbf{A}_\lambda \pm \mathbf{B}_\lambda\right)\left(\mathbf{A}_\lambda \mp \mathbf{B}_\lambda\right)^{1/2}$$

$$\mathbf{Z}_{\pm,n,\lambda} = \sqrt{\omega_{n,\lambda}}\left(\mathbf{A}_\lambda \mp \mathbf{B}_\lambda\right)\left(\mathbf{X}_{n,\lambda} \pm \mathbf{Y}_{n,\lambda}\right)$$

$$\left(\mathbf{A}_\lambda\right)_{ia,jb} = \left(\varepsilon_a - \varepsilon_i\right)\delta_{ij}\delta_{ab} + \lambda\left[\langle ib|aj\rangle - \xi\langle ib|ja\rangle\right]$$

$$\left(\mathbf{B}_\lambda\right)_{ia,jb} = \lambda\left[\langle ab|ij\rangle - \xi\langle ab|ji\rangle\right]$$

$\xi = 0$ (d-RPA)

$\xi = 1$ (RPA with exchange)

$$\langle pq|rs\rangle = \iint \frac{\phi_p^*(\vec{r})\phi_q^*(\vec{r}')\phi_r(\vec{r})\phi_s(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}\, d\vec{r}'$$

W. Zhu, L. Zhang, and S.B. Trickey, J. Chem. Phys. (submitted)

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RPA Correlation +Second-order Screened Exchange (SOSEX)

$$E_C^{RPA+SOSEX} = \frac{1}{2}\int_0^1 d\lambda \sum_{ia,jb} \left\{ \langle ib \| aj \rangle \sum_n \left[Y_n^* Y_n + X_n^* X_n - I \right] + \langle ij \| ab \rangle \sum_n \left[X_n^* Y_n + Y_n^* X_n \right] \right\}$$

where $\langle ib \| aj \rangle = \langle ib | aj \rangle - \langle ia^* | b^* j \rangle$

and $\langle ij \| ab \rangle = \langle ij | ab \rangle - \langle ij | ba \rangle$

Complete basis set extrapolation

Post SCF evaluation of RPA expressions:

PBE orbitals
TPSS orbitals
HGGA orbitals (Exx + TPSS Ec)
HF orbitals
"Hybrid 1" = Exx HF orbs + Ec (PBE-orb, RPA+SOSEX)
"Hybrid 2" = 1/2 Exx (HF orbs) + 1/2 Exx (PBE orbs)
+ Ec (PBE-orb, RPA+SOSEX)

W. Zhu, L. Zhang, and S.B. Trickey, J. Chem. Phys. (submitted)

Results – Atomic total energies

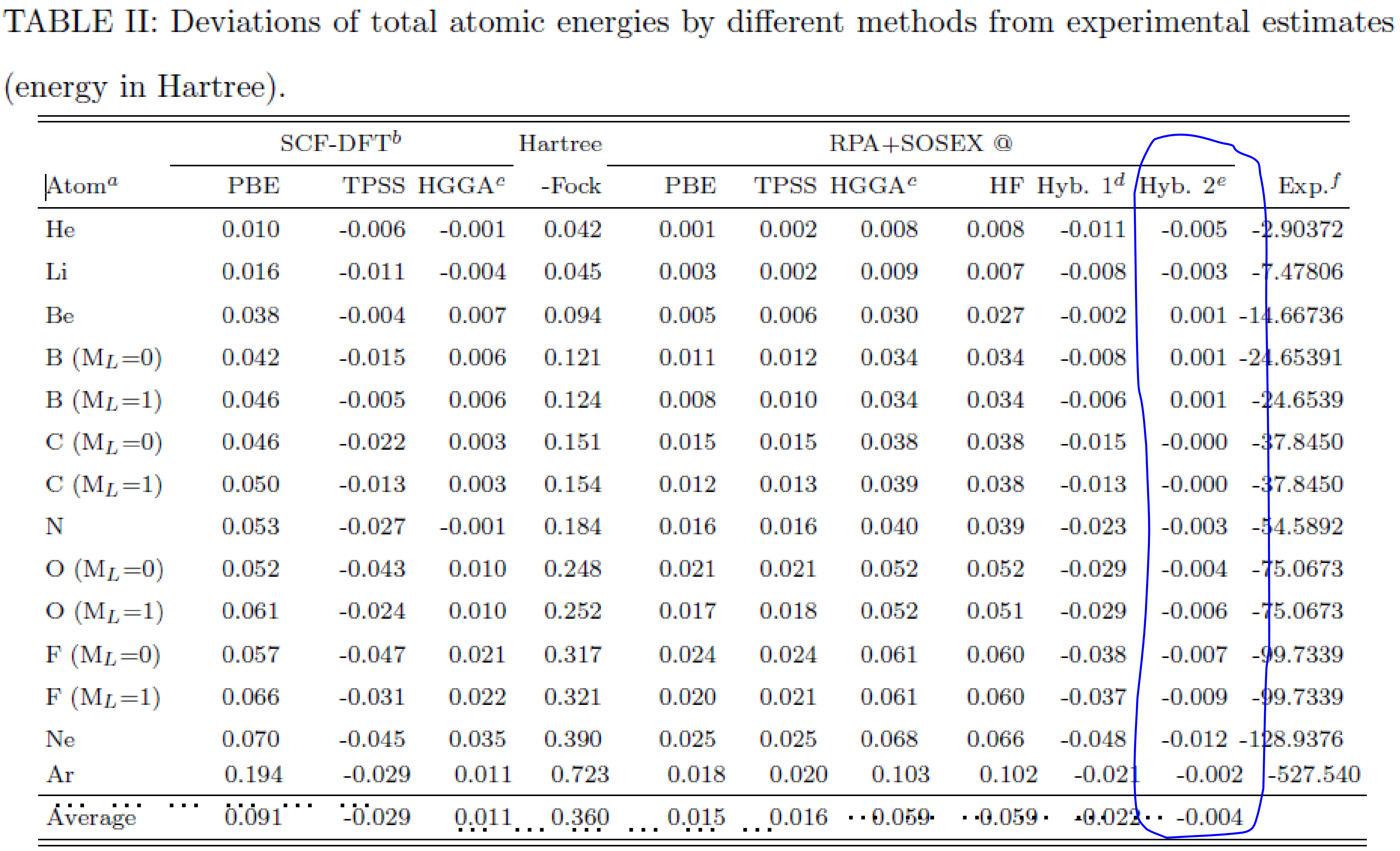

TABLE II: Deviations of total atomic energies by different methods from experimental estimates (energy in Hartree).

	SCF-DFT[b]			Hartree	RPA+SOSEX @						
Atom[a]	PBE	TPSS	HGGA[c]	-Fock	PBE	TPSS	HGGA[c]	HF	Hyb. 1[d]	Hyb. 2[e]	Exp.[f]
He	0.010	-0.006	-0.001	0.042	0.001	0.002	0.008	0.008	-0.011	-0.005	-2.90372
Li	0.016	-0.011	-0.004	0.045	0.003	0.002	0.009	0.007	-0.008	-0.003	-7.47806
Be	0.038	-0.004	0.007	0.094	0.005	0.006	0.030	0.027	-0.002	0.001	-14.66736
B ($M_L=0$)	0.042	-0.015	0.006	0.121	0.011	0.012	0.034	0.034	-0.008	0.001	-24.65391
B ($M_L=1$)	0.046	-0.005	0.006	0.124	0.008	0.010	0.034	0.034	-0.006	0.001	-24.6539
C ($M_L=0$)	0.046	-0.022	0.003	0.151	0.015	0.015	0.038	0.038	-0.015	-0.000	-37.8450
C ($M_L=1$)	0.050	-0.013	0.003	0.154	0.012	0.013	0.039	0.038	-0.013	-0.000	-37.8450
N	0.053	-0.027	-0.001	0.184	0.016	0.016	0.040	0.039	-0.023	-0.003	-54.5892
O ($M_L=0$)	0.052	-0.043	0.010	0.248	0.021	0.021	0.052	0.052	-0.029	-0.004	-75.0673
O ($M_L=1$)	0.061	-0.024	0.010	0.252	0.017	0.018	0.052	0.051	-0.029	-0.006	-75.0673
F ($M_L=0$)	0.057	-0.047	0.021	0.317	0.024	0.024	0.061	0.060	-0.038	-0.007	-99.7339
F ($M_L=1$)	0.066	-0.031	0.022	0.321	0.020	0.021	0.061	0.060	-0.037	-0.009	-99.7339
Ne	0.070	-0.045	0.035	0.390	0.025	0.025	0.068	0.066	-0.048	-0.012	-128.9376
Ar	0.194	-0.029	0.011	0.723	0.018	0.020	0.103	0.102	-0.021	-0.002	-527.540
Average	0.091	-0.029	0.011	0.360	0.015	0.016	0.059	0.059	-0.022	-0.004	

Results – Spurious Non-degeneracy

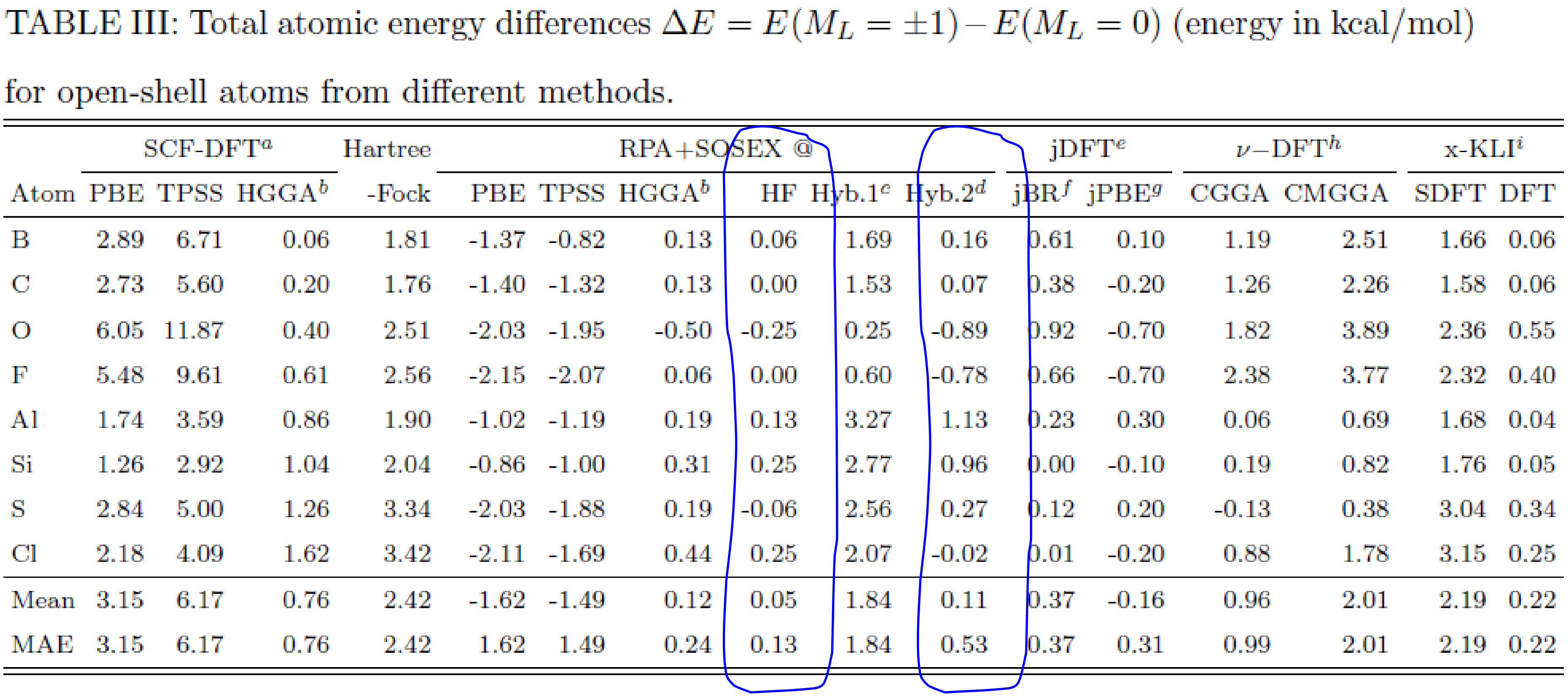

TABLE III: Total atomic energy differences $\Delta E = E(M_L = \pm 1) - E(M_L = 0)$ (energy in kcal/mol) for open-shell atoms from different methods.

	SCF-DFT^a			Hartree	RPA+SOSEX @						jDFT^e		ν−DFT^h		x-KLI^i	
Atom	PBE	TPSS	HGGA^b	-Fock	PBE	TPSS	HGGA^b	HF	Hyb.1^c	Hyb.2^d	jBR^f	jPBE^g	CGGA	CMGGA	SDFT	DFT
B	2.89	6.71	0.06	1.81	-1.37	-0.82	0.13	0.06	1.69	0.16	0.61	0.10	1.19	2.51	1.66	0.06
C	2.73	5.60	0.20	1.76	-1.40	-1.32	0.13	0.00	1.53	0.07	0.38	-0.20	1.26	2.26	1.58	0.06
O	6.05	11.87	0.40	2.51	-2.03	-1.95	-0.50	-0.25	0.25	-0.89	0.92	-0.70	1.82	3.89	2.36	0.55
F	5.48	9.61	0.61	2.56	-2.15	-2.07	0.06	0.00	0.60	-0.78	0.66	-0.70	2.38	3.77	2.32	0.40
Al	1.74	3.59	0.86	1.90	-1.02	-1.19	0.19	0.13	3.27	1.13	0.23	0.30	0.06	0.69	1.68	0.04
Si	1.26	2.92	1.04	2.04	-0.86	-1.00	0.31	0.25	2.77	0.96	0.00	-0.10	0.19	0.82	1.76	0.05
S	2.84	5.00	1.26	3.34	-2.03	-1.88	0.19	-0.06	2.56	0.27	0.12	0.20	-0.13	0.38	3.04	0.34
Cl	2.18	4.09	1.62	3.42	-2.11	-1.69	0.44	0.25	2.07	-0.02	0.01	-0.20	0.88	1.78	3.15	0.25
Mean	3.15	6.17	0.76	2.42	-1.62	-1.49	0.12	0.05	1.84	0.11	0.37	-0.16	0.96	2.01	2.19	0.22
MAE	3.15	6.17	0.76	2.42	1.62	1.49	0.24	0.13	1.84	0.53	0.37	0.31	0.99	2.01	2.19	0.22

W. Zhu, L. Zhang, and S.B. Trickey, J. Chem. Phys. (submitted)

Concluding Observations

- CBS extrapolation is necessary; (Ec compared with reference)
- RPA over-estimates correlation energy (well known); RPA+SOSEX is better than d-RPA
- PBE-orbital-based RPA+SOSEX and TPSS-orbital based RPA+SOSEX are very close, but not materially better than Exx + TPSS-Ec
- HF-orbital based RPA+SOSEX and Exx+ TPSS-Ec orbital-based RPA+SOSEX behave essentially the same, and are not as good as results from semi-local functional orbitals
- Good degeneracy is found whenever Exx is used
- Best balance of Etot and degeneracy restoration is from 1/2 Ex from HF orbitals + 1/2 Exx from PBE orbitals + Ec from PBE-orbital-based RPA+SOSEX

Future Work

- **In general, an explicitly orbital-dependent functional includes the paramagnetic current density automatically, provided complex orbitals are used. Beyond RPA, are there other orbital-dependent functionals to check?**

- **Atoms in B > 0 need correlation-consistent basis sets. How can they be constructed?**

- **Molecules (especially with rings, e.g. benzene) in B are more interesting. They raise issues of gauge-independent basis and multi-center electron integrals for the use of highly anisotropic gaussians.**