10th ABINIT International Developer Workshop
May 31 - June 4, 2021

Are plane-waves basis packages able to predict the correct long range behavior of the local kinetic energy per particle?

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Summary

1. Background and Motivation.
2. Two theorems involving $n(\boldsymbol{r})$ and $G(\boldsymbol{r})$ in finite systems.
3. Computing the asymptotic behavior of $G(\boldsymbol{r})$ in `ABINIT` for atoms and molecules.
4. Conclusions and perspectives.

Background and Motivation

nature materials

ARTICLES

https://doi.org/10.1038/s41563-017-0012-2

X-ray electron density investigation of chemical bonding in van der Waals materials

Hidetaka Kasai[1,2], Kasper Tolborg[2], Mattia Sist[2], Jiawei Zhang[2], Venkatesha R. Hathwar[1], Mette Ø. Filsø[2], Simone Cenedese[2], Kunihisa Sugimoto[3], Jacob Overgaard[2], Eiji Nishibori[1] and Bo B. Iversen[2*]

Nature Materials 17:249 (2018)

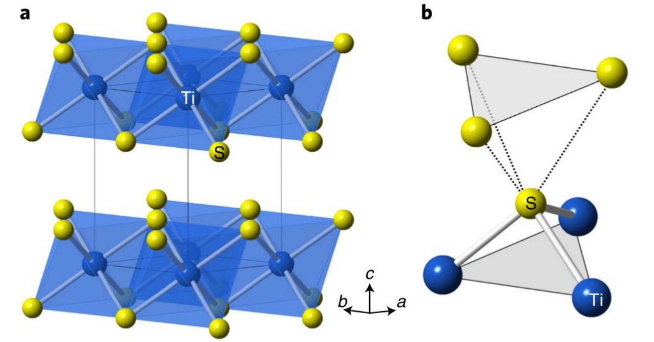
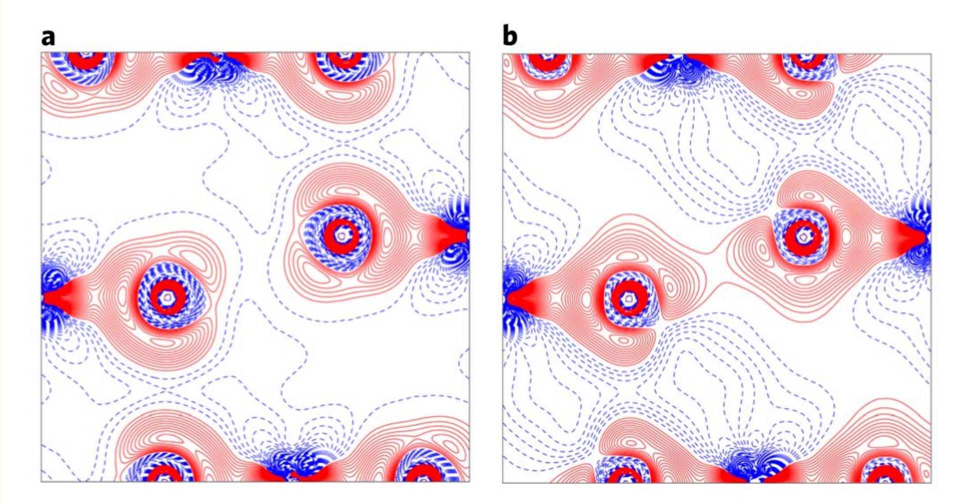


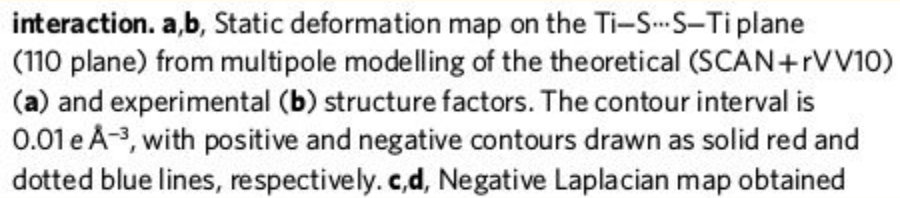
Fig. 1 | Structure of 1*T*-TiS$_2$. a, Ti atom is at the edge of a unit cell (Space group: $P\overline{3}m1$, $a = 3.3976(3)$ and $c = 5.6654(3)$ Å) forming a TiS$_6$ octahedron. **b**, S atom and its adjacent atoms in the direction of the *c*-axis.

Background and Motivation

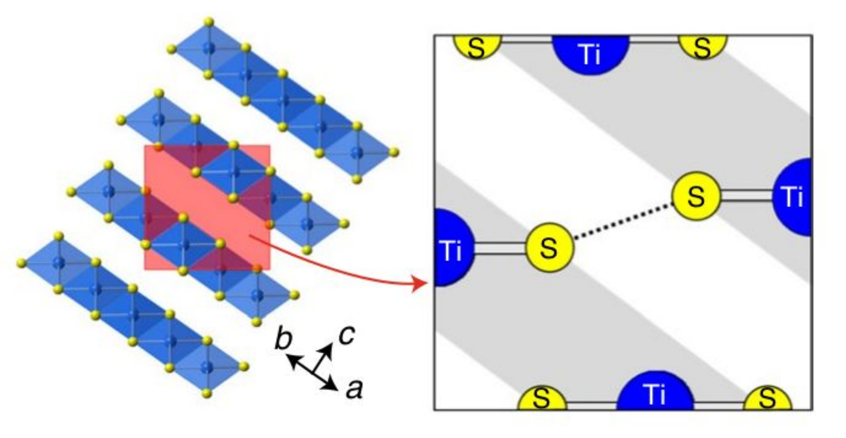
Experiment

Theory(SCAN+rVV10)





interaction. a,**b**, Static deformation map on the Ti–S···S–Ti plane (110 plane) from multipole modelling of the theoretical (SCAN+rVV10) (**a**) and experimental (**b**) structure factors. The contour interval is 0.01 e Å^{-3}, with positive and negative contours drawn as solid red and dotted blue lines, respectively. **c**,**d**, Negative Laplacian map obtained



Even though both equilibrium interlayer distance and binding energy follow the experimental trend, there are important differences in the ground state electronic density.

Background and motivation

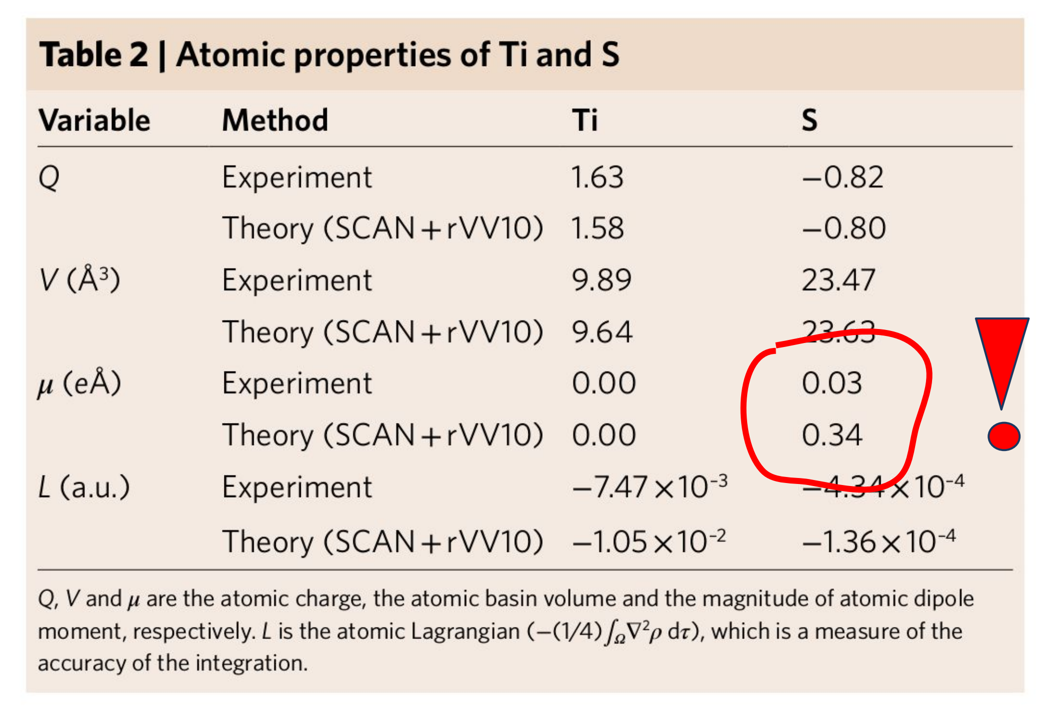


Table 2 | Atomic properties of Ti and S

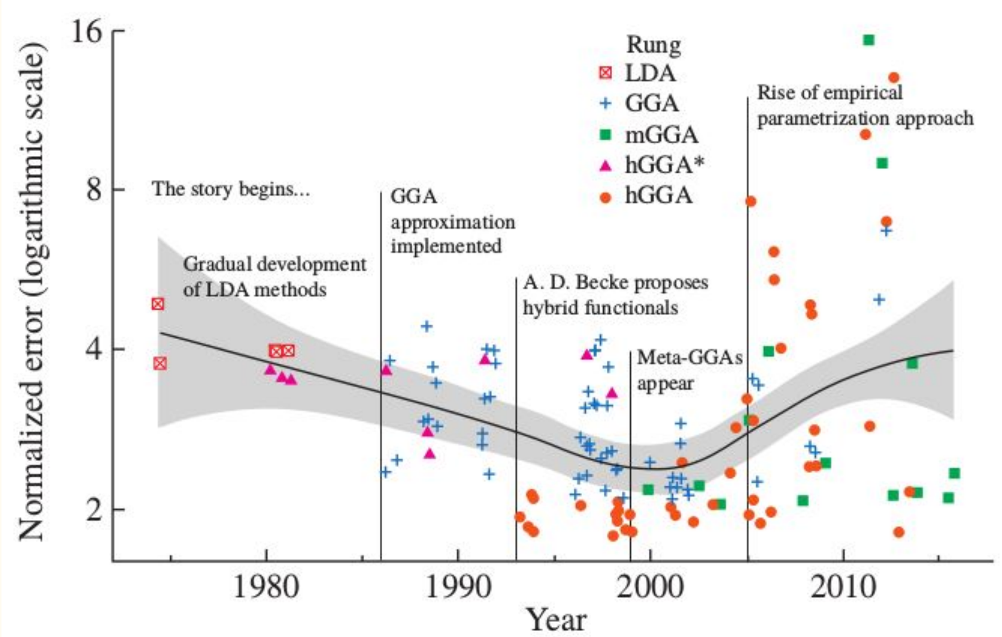
Variable	Method	Ti	S
Q	Experiment	1.63	−0.82
	Theory (SCAN+rVV10)	1.58	−0.80
V (Å^3)	Experiment	9.89	23.47
	Theory (SCAN+rVV10)	9.64	23.63
μ (eÅ)	Experiment	0.00	0.03
	Theory (SCAN+rVV10)	0.00	0.34
L (a.u.)	Experiment	-7.47×10^{-3}	-4.34×10^{-4}
	Theory (SCAN+rVV10)	-1.05×10^{-2}	-1.36×10^{-4}

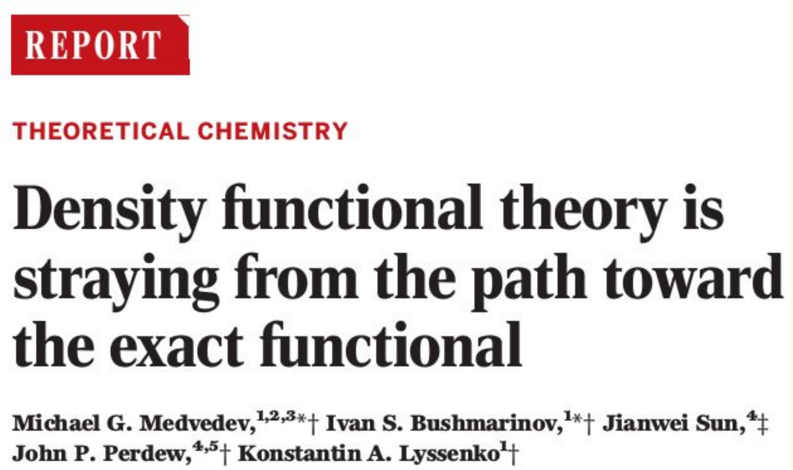
Q, V and μ are the atomic charge, the atomic basin volume and the magnitude of atomic dipole moment, respectively. L is the atomic Lagrangian ($-(1/4)\int_{\Omega}\nabla^2\rho\,d\tau$), which is a measure of the accuracy of the integration.

Nature Materials 17:249 (2018)

Houston, we have a problem!

Medvedev, *et. al. Science* **355,** 49-52(2017)





REPORT

THEORETICAL CHEMISTRY

Density functional theory is straying from the path toward the exact functional

Michael G. Medvedev,[1,2,3*]† Ivan S. Bushmarinov,[1*]† Jianwei Sun,[4]‡
John P. Perdew,[4,5]† Konstantin A. Lyssenko[1]†

Mendeleev Commun., 2018, 28, 225–235

"The reproduction of the exact energy is not a characteristic of the exact functional unless the input electronic density is exact as well."

Houston, we have a problem!

Medvedev, *et. al.* *Science* **355,** 49-52(2017)

REPORT

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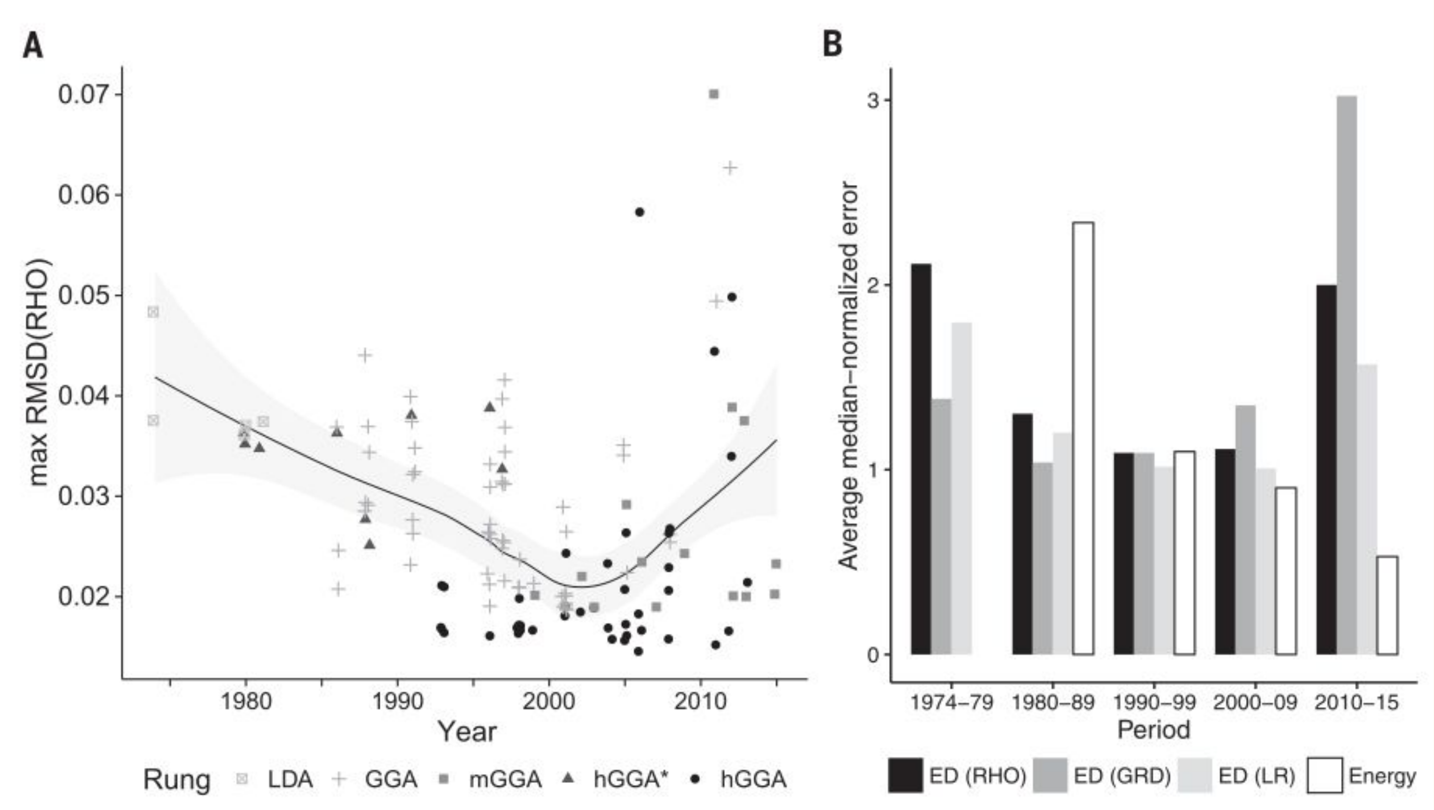


Measuring the accuracy of the electronic density

Two main groups of methods:

- Metrics based on integrals of the density:

  Density moments, Total kinetic energy.

  Problems can arise due to possible cancellation of errors!

- Metrics based on point to point measurements. (Local values)

Measuring the accuracy of the electronic density

Some metrics based on point to point comparisons:

$$\mathrm{RMSD} = \sqrt{\frac{1}{N}\sum_{i}^{N}\{\pi r_i^{\,2}[P_{\mathrm{approx}}(r_i) - P_{\mathrm{ref}}(r_i)]\}^2}\,,$$

Root mean-square deviation

$$\mathrm{ISD} = \iiint [P_{\mathrm{approx}}(r) - P_{\mathrm{ref}}(r)]^2\,\mathrm{d}^3 r\,,$$

Integral squared deviation.

$$\mathrm{IAD} = \iiint \left| P_{\mathrm{approx}}(r) - P_{\mathrm{ref}}(r) \right| \mathrm{d}^3 r\,.$$

Integral absolute deviation.

P can be any local descriptor such as the density, norm of the gradient, the laplacian, etc...

Mendeleev Commun., 2018, 28, 225–235

2. Two theorems for *n(**r**)* and *G(**r**)* in finite systems.

Kinetic energy density:

$$\tau_{ks} = \frac{1}{2}\sum_{i}^{occup} f_i |\nabla\phi_i|^2$$

Kinetic energy per particle:

$$G(\mathbf{r}) = \frac{\tau_{ks}(\mathbf{r})}{n(\mathbf{r})}$$

2. Two theorems for the single particle density in finite systems.

From Kato's theorem (Kato cusp condition): $Z_k = -\frac{a_0}{2n(\mathbf{r})}\frac{\mathrm{d}n(\mathbf{r})}{\mathrm{d}r}\Big|_{r\to R_k}$

$$\lim_{r\to R_k} G(\mathbf{r}) = \frac{Z_k^2}{2}$$

Communications on Pure and Applied Mathematics. **10** (2): 151–177 (1957)

2. Two theorems for the single particle density in finite systems.

From Hoffmann-Ostenhof theorems for the asymptotic behavior of the multi-electronic wave function of finite coulombic systems:

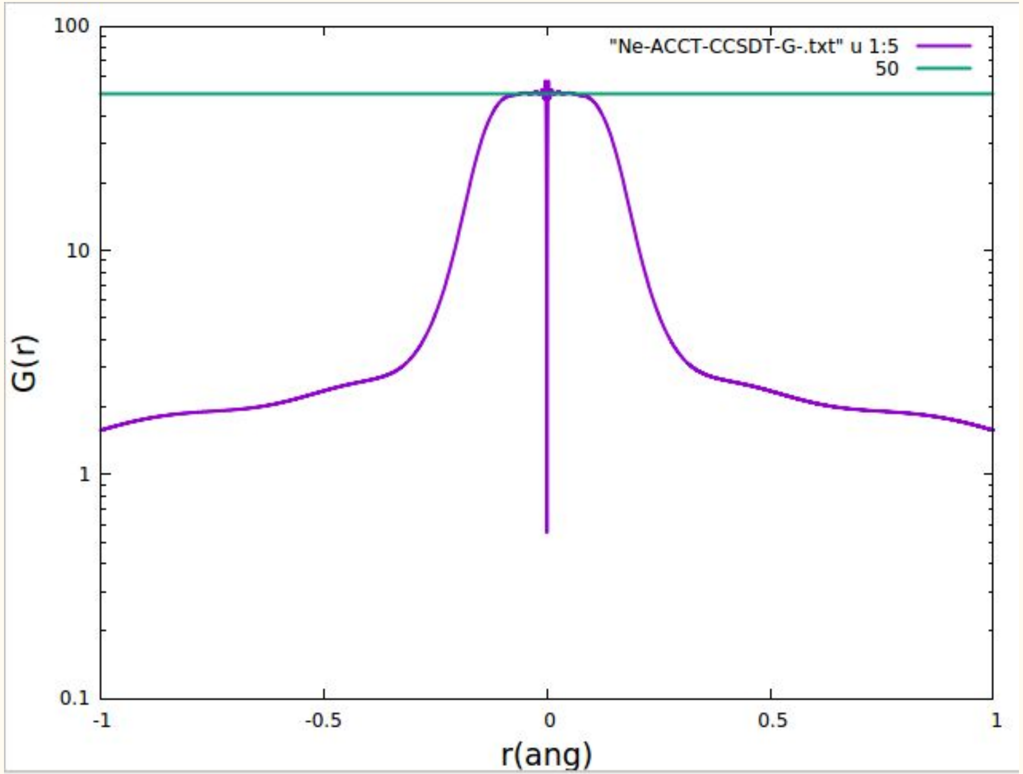
$$\lim_{r\to\infty} G(\mathbf{r}) = I$$

J. Phys.B: Atom. Molec. Phys., ***11****:17 (1978), Chem. Phys. Lett.* ***258****:30 (1996)*

3. Computing the asymptotic behavior of *G(**r**)* in `ABINIT` for atoms and molecules.

First some reference calculations: Ne atom CCSDT (ACCT) in GAMESS

$$Z_{\mathrm{Ne}} = 10$$



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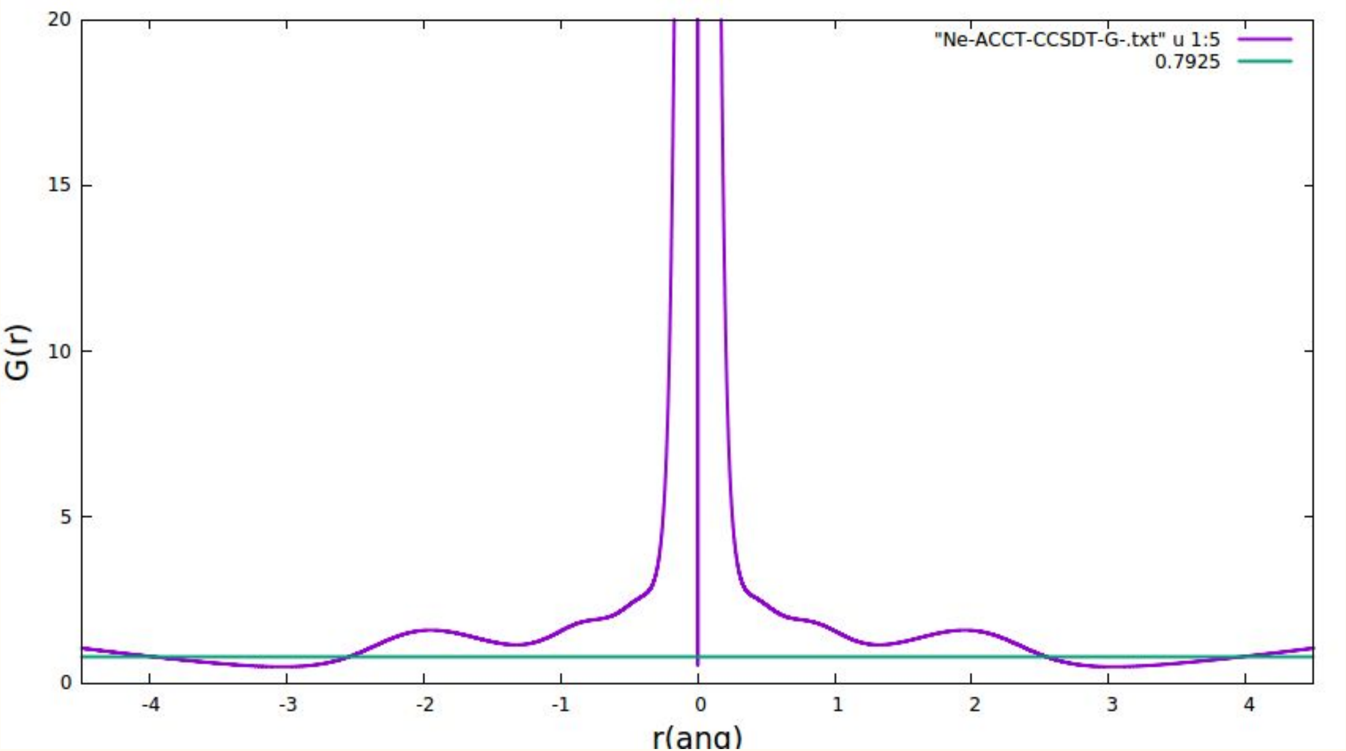
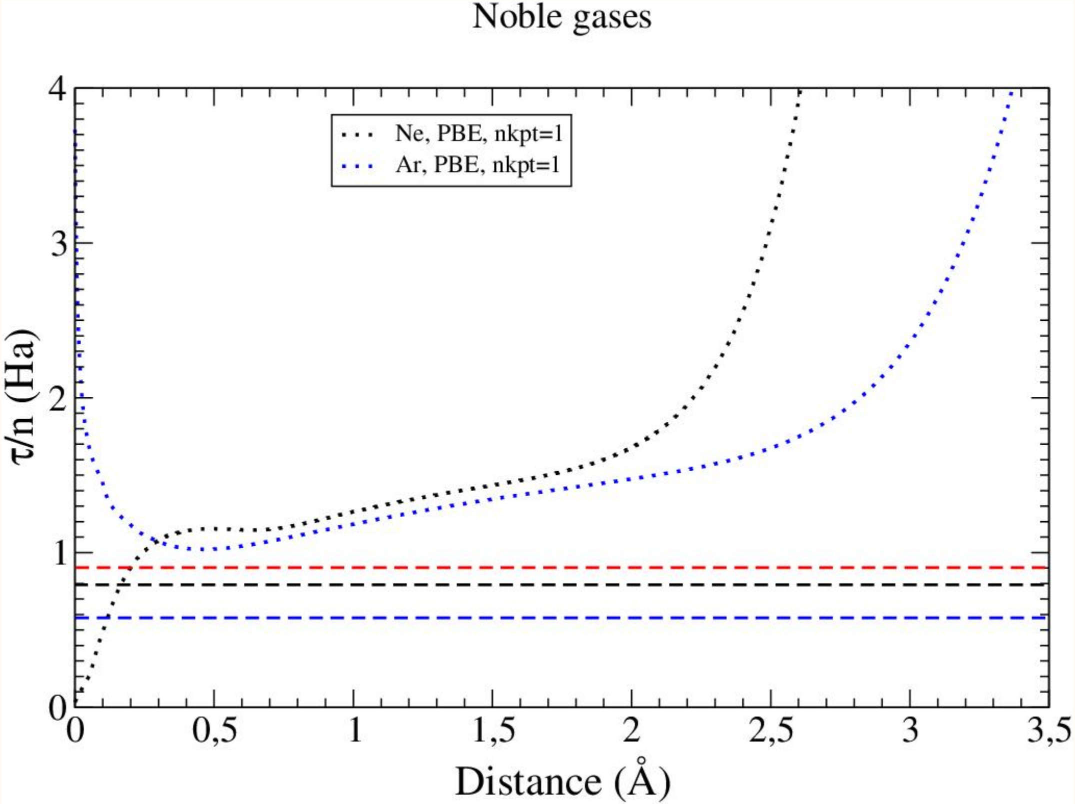
First some reference calculations: Ne atom CCSDT (ACCT) in GAMESS

I=0.7925 Ha



3. Computing the asymptotic behavior of *G(**r**)* in `ABINIT` for atoms and molecules.

ecut=80 Ha
acell=3*15 A



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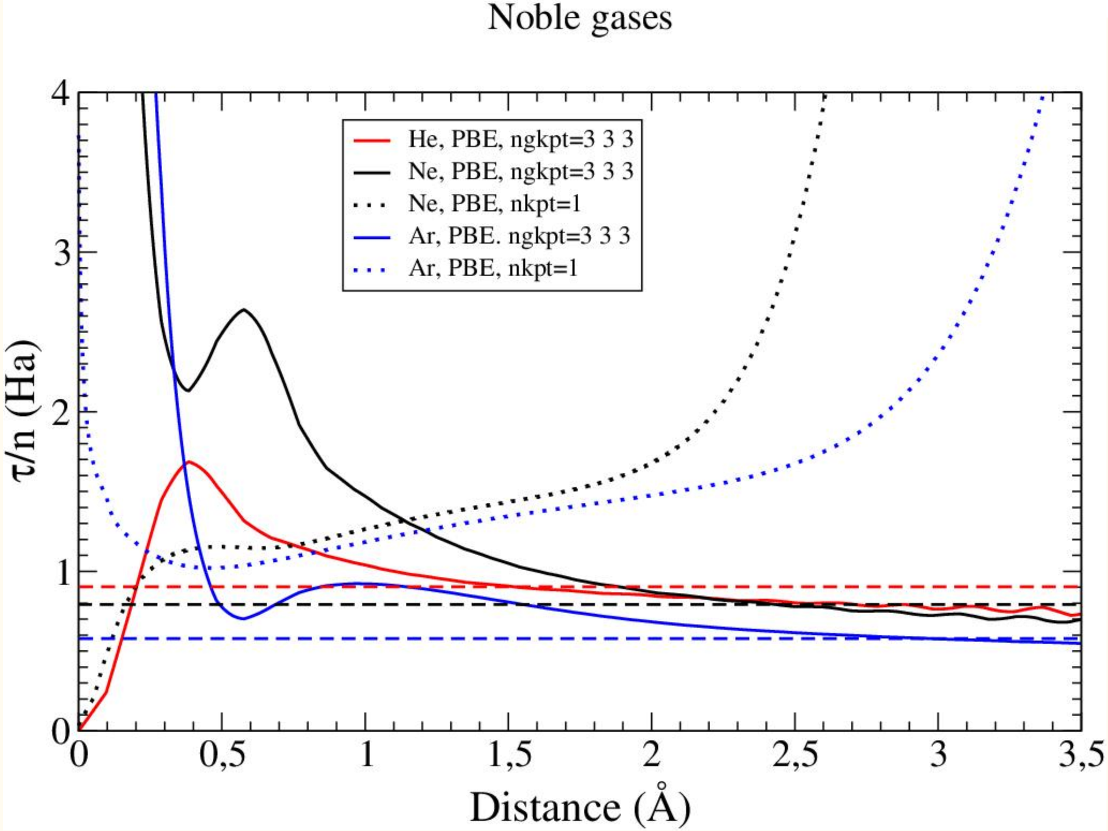

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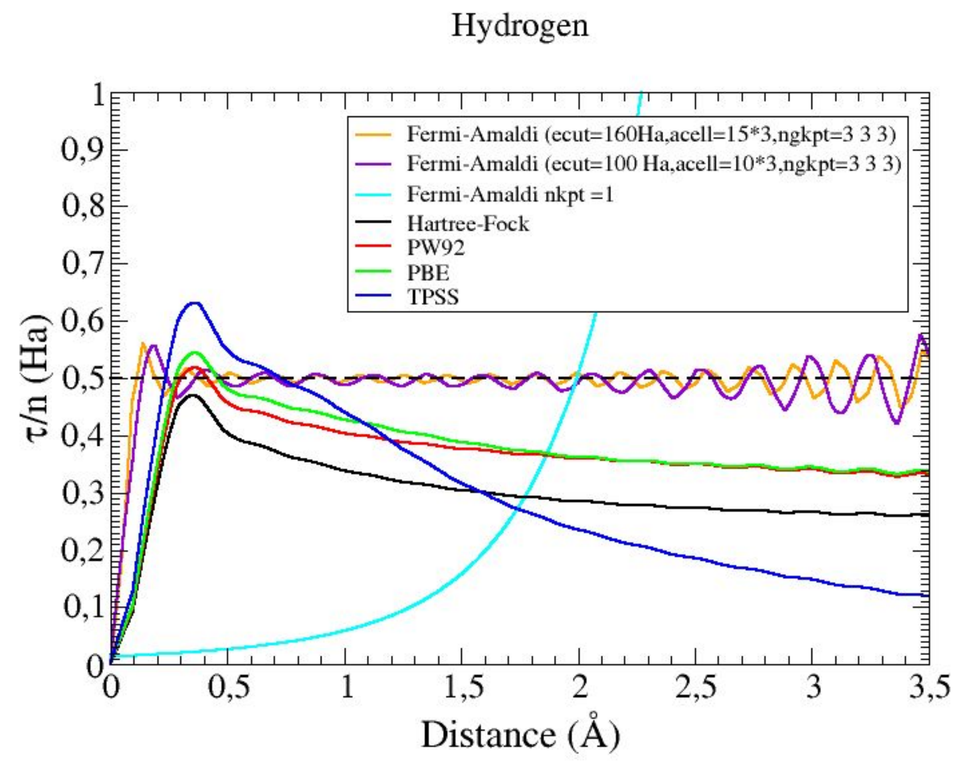

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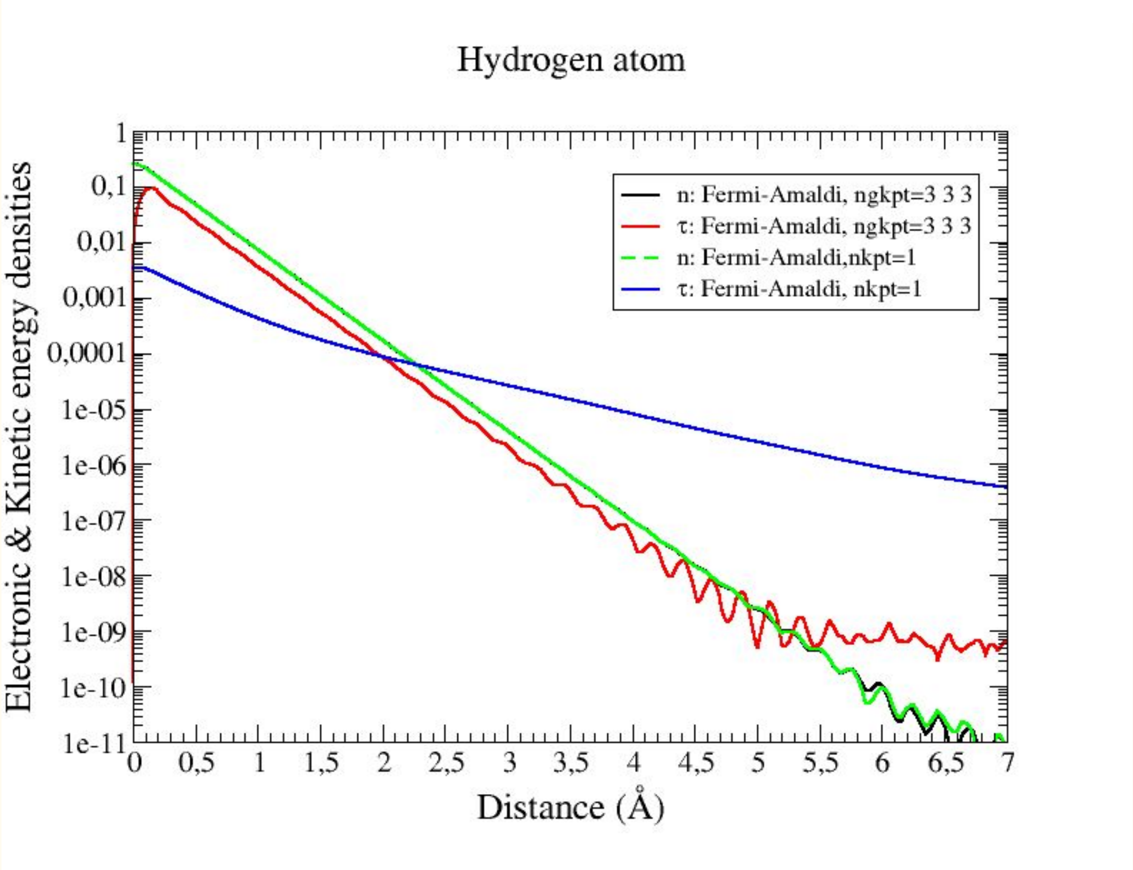

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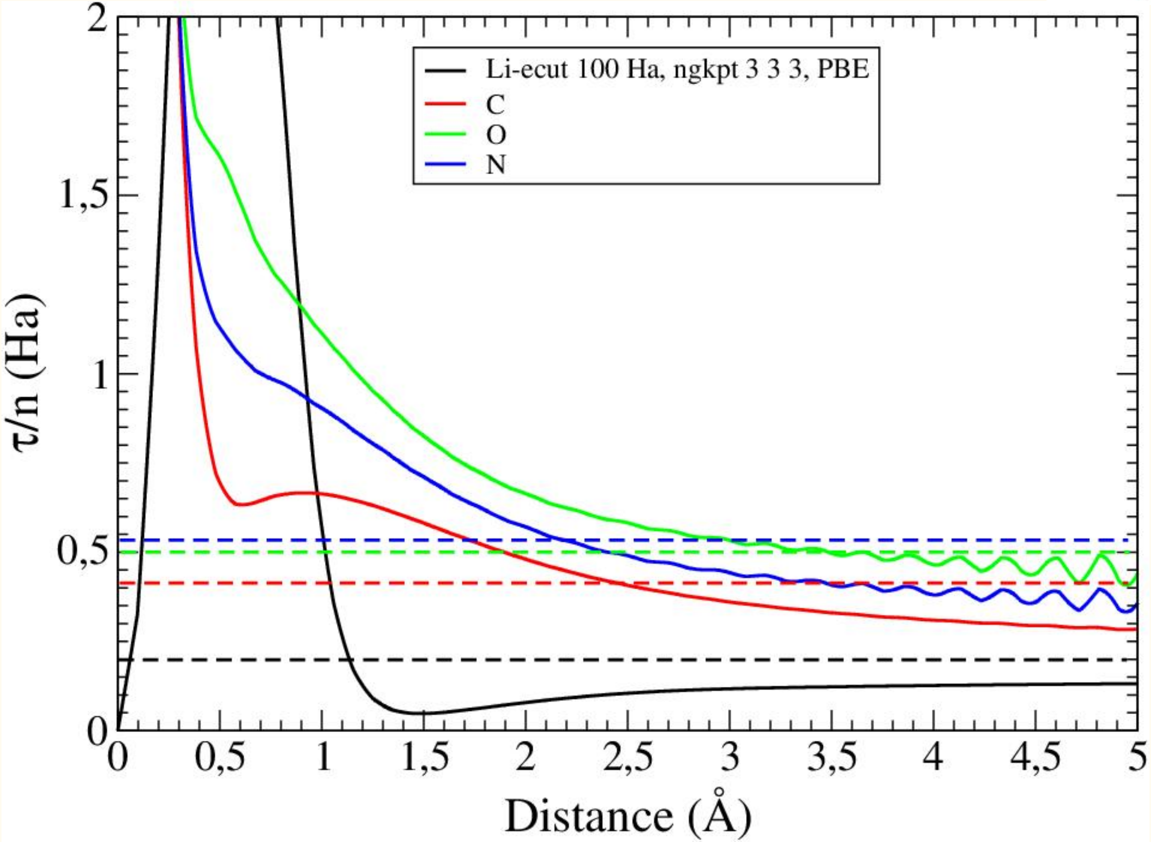
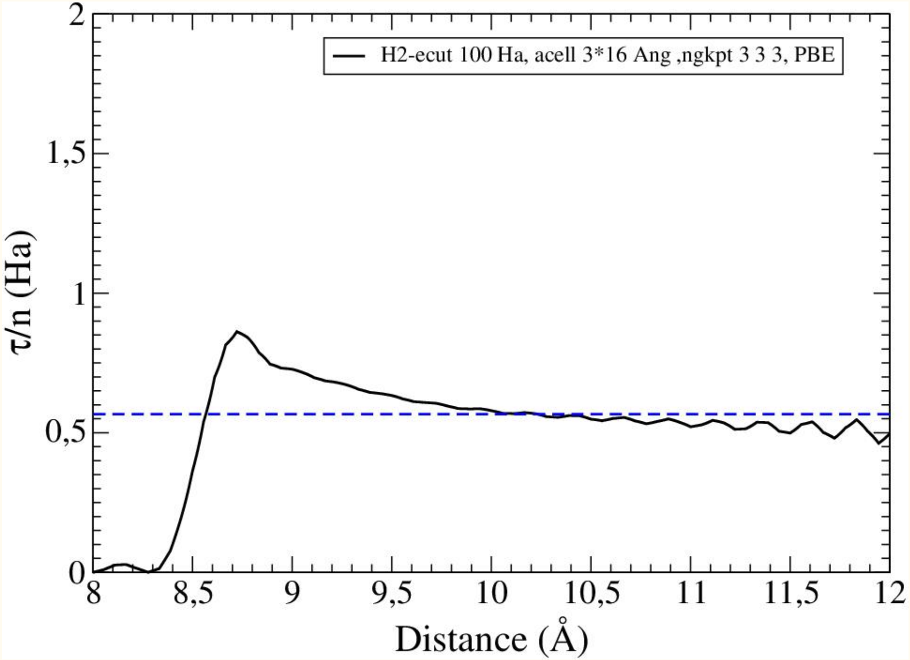
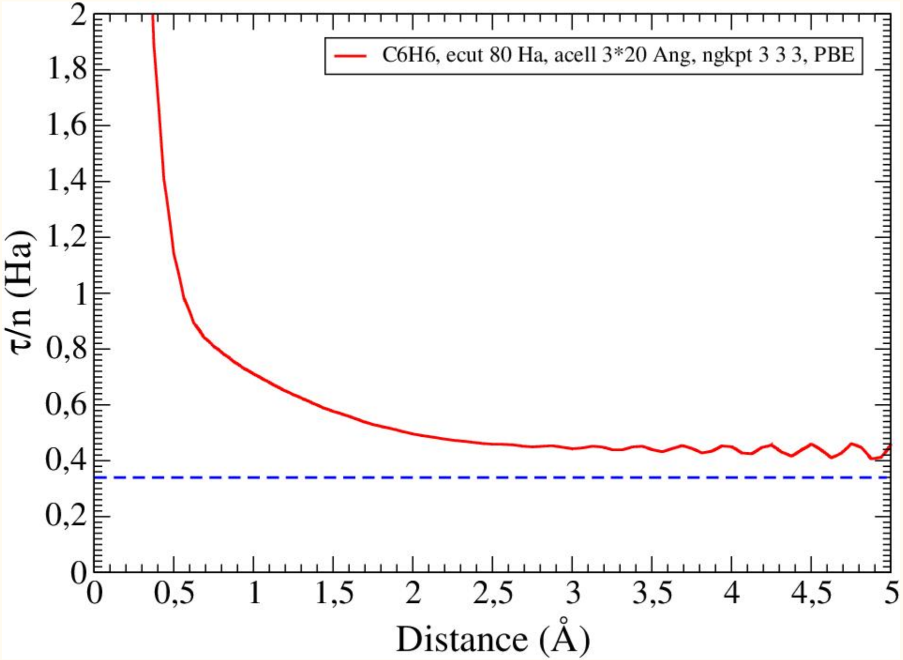


3. Computing the asymptotic behavior of $G(\mathbf{r})$ in `ABINIT` for atoms and molecules.





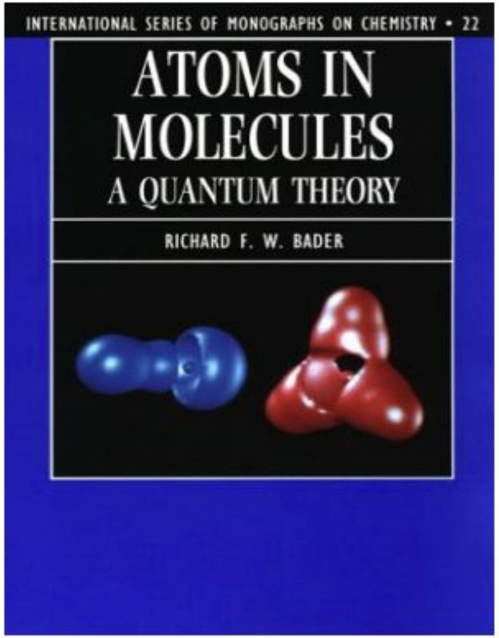
4. Conclusions and perspectives.

- It is possible to obtain a reasonable behavior of G(**r**) within the ncpp + plane-waves framework for finite systems if a fine enough k sampling is used.
- Since τ in real space is an input for meta-GGA functionals it is important to add k points convergence studies when dealing with finite systems (i.e. adsorption of molecules on surfaces).
- G(r) can play an important role in the benchmarking of vdW self-consistent functionals from the density point of view.
- What could be the effect of the Coulomb truncation methods (from the last talk) on the asymptotic behavior of G?
- What is the meaning of the limit of G in extended systems (2D materials, surfaces)??

Thank you for your attention!

Appendix

QTAIM Basics (Bader and Co)



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ATOMS IN MOLECULES

A QUANTUM THEORY

RICHARD F. W. BADER

QTAIM Basics (Bader and Co)

$$\nabla\rho = \mathbf{i}\frac{d\rho}{dx} + \mathbf{j}\frac{d\rho}{dy} + \mathbf{k}\frac{d\rho}{dz} \rightarrow \begin{cases} = \vec{\mathbf{0}} & \text{(At critical points and at } \infty\text{)} \\ \text{Generally} \neq \vec{\mathbf{0}} & \text{(At all other points)} \end{cases}$$

$$\mathbf{A}(\mathbf{r}_c) = \left.\begin{pmatrix} \dfrac{\partial^2\rho}{\partial x^2} & \dfrac{\partial^2\rho}{\partial x\partial y} & \dfrac{\partial^2\rho}{\partial x\partial z} \\ \dfrac{\partial^2\rho}{\partial y\partial x} & \dfrac{\partial^2\rho}{\partial y^2} & \dfrac{\partial^2\rho}{\partial y\partial z} \\ \dfrac{\partial^2\rho}{\partial z\partial x} & \dfrac{\partial^2\rho}{\partial z\partial y} & \dfrac{\partial^2\rho}{\partial z^2} \end{pmatrix}\right|_{\mathbf{r}=\mathbf{r}_c}.$$

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ISBN: 978-3-527-30748-7

QTAIM Basics (Bader and Co)

$$\mathbf{\Lambda} = \begin{pmatrix} \dfrac{\partial^2 \rho}{\partial x'^2} & 0 & 0 \\ 0 & \dfrac{\partial^2 \rho}{\partial y'^2} & 0 \\ 0 & 0 & \dfrac{\partial^2 \rho}{\partial z'^2} \end{pmatrix}_{\mathbf{r}'=\mathbf{r}_c} = \begin{pmatrix} \lambda_1 & 0 & 0 \\ 0 & \lambda_2 & 0 \\ 0 & 0 & \lambda_3 \end{pmatrix},$$

$$\nabla^2 \rho(\mathbf{r}) = \nabla \cdot \nabla \rho(\mathbf{r}) = \underbrace{\frac{\partial^2 \rho(\mathbf{r})}{\partial x^2}}_{\lambda 1} + \underbrace{\frac{\partial^2 \rho(\mathbf{r})}{\partial y^2}}_{\lambda 2} + \underbrace{\frac{\partial^2 \rho(\mathbf{r})}{\partial z^2}}_{\lambda 3}$$

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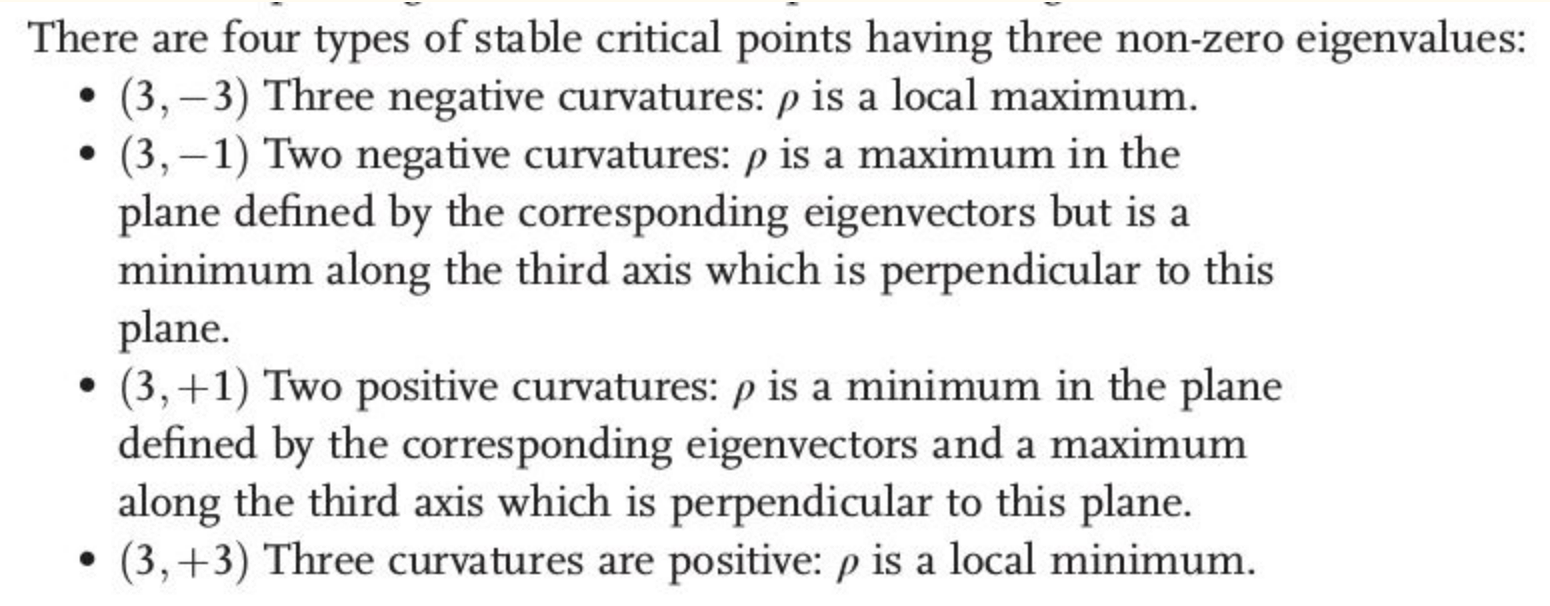
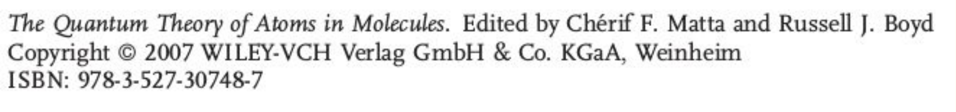


There are four types of stable critical points having three non-zero eigenvalues:

- $(3, -3)$ Three negative curvatures: ρ is a local maximum.
- $(3, -1)$ Two negative curvatures: ρ is a maximum in the plane defined by the corresponding eigenvectors but is a minimum along the third axis which is perpendicular to this plane.
- $(3, +1)$ Two positive curvatures: ρ is a minimum in the plane defined by the corresponding eigenvectors and a maximum along the third axis which is perpendicular to this plane.
- $(3, +3)$ Three curvatures are positive: ρ is a local minimum.



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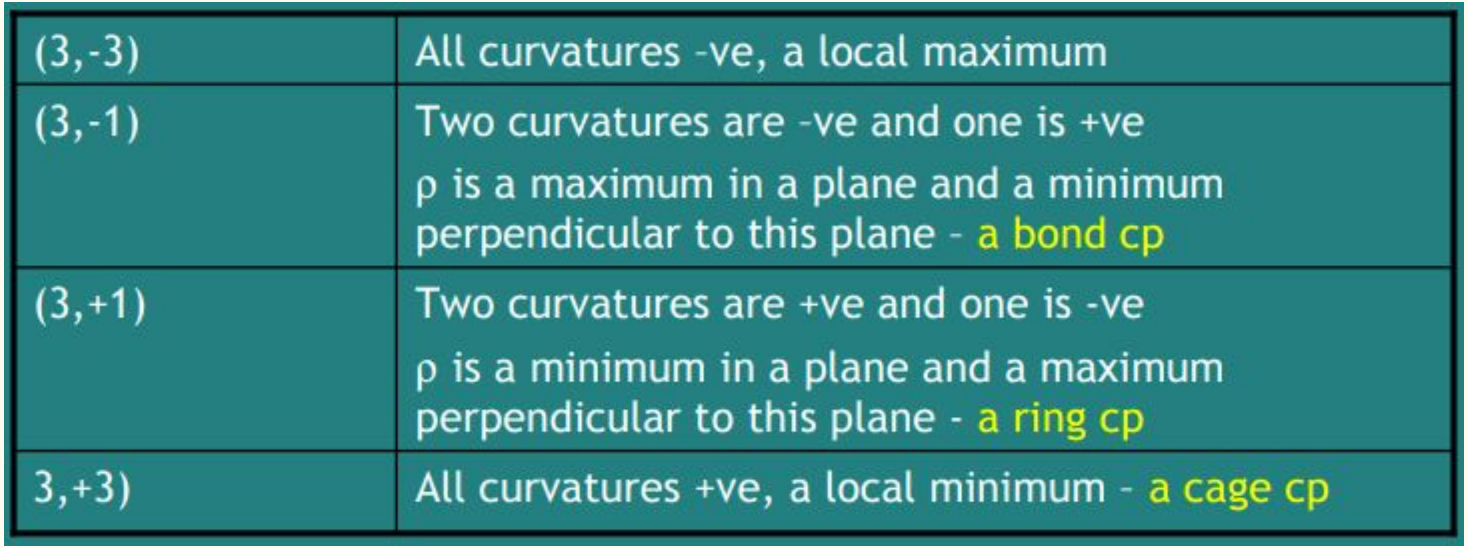
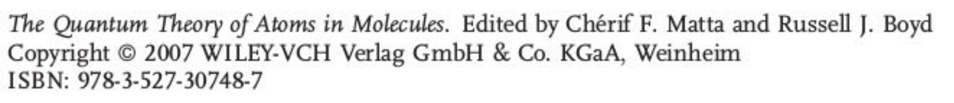


(3,-3)	All curvatures -ve, a local maximum
(3,-1)	Two curvatures are -ve and one is +ve ρ is a maximum in a plane and a minimum perpendicular to this plane - a bond cp
(3,+1)	Two curvatures are +ve and one is -ve ρ is a minimum in a plane and a maximum perpendicular to this plane - a ring cp
3,+3)	All curvatures +ve, a local minimum - a cage cp



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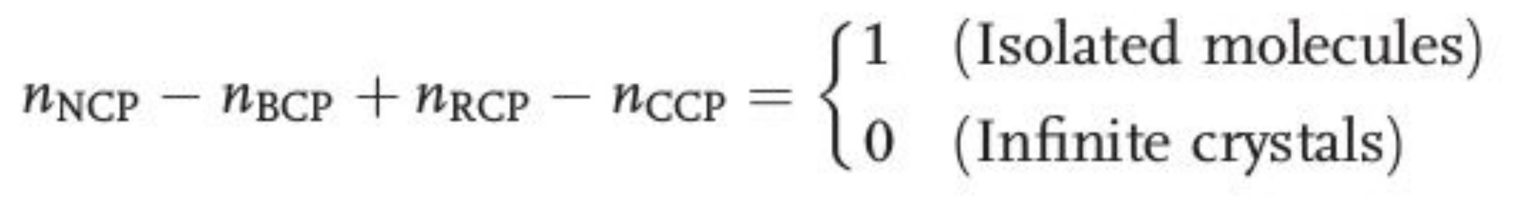
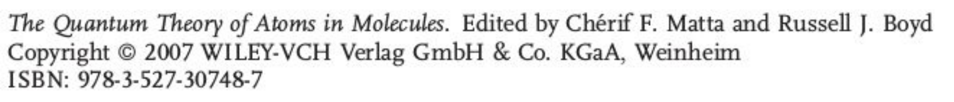
QTAIM Basics (Bader and Co)

Poincaré-Hopf relationships:



$$n_{\text{NCP}} - n_{\text{BCP}} + n_{\text{RCP}} - n_{\text{CCP}} = \begin{cases} 1 & \text{(Isolated molecules)} \\ 0 & \text{(Infinite crystals)} \end{cases}$$



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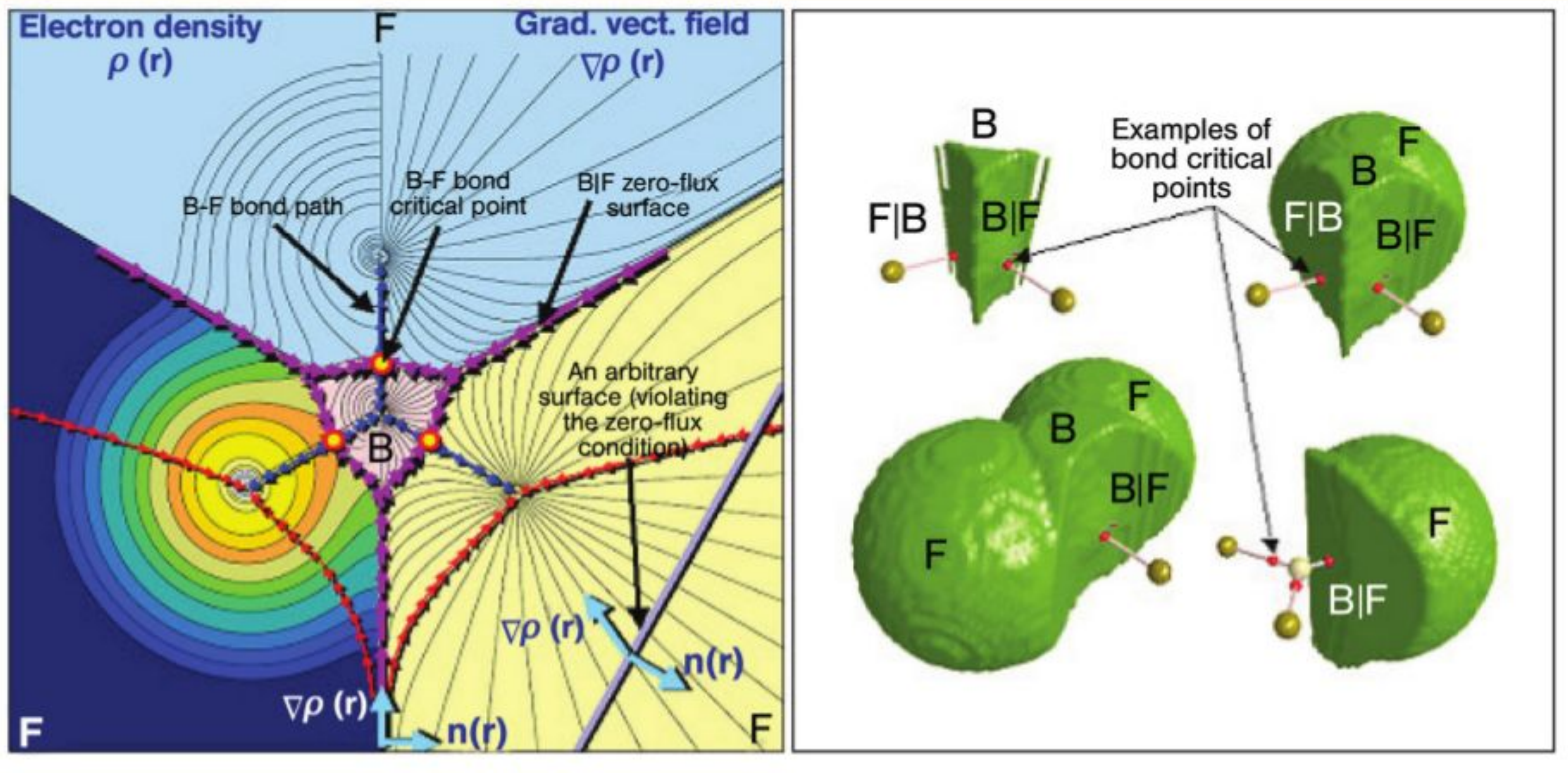

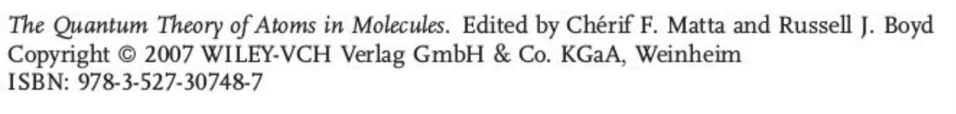
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