

Optimized Effective Potential Method in DFT Part II

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Outline

- Introduction to the **DFT** 😊
- Approximations in DFT
- Success and Failures of the Approximations
- **OEP** method
- Application of OEP to **Metal clusters**
- Conclusions

Homogeneous Electron Gas System

Composed of N extended electrons in a uniform positive charge background.

$$\frac{E_{xc}}{N} = \varepsilon_{xc}(r_s) = -\frac{3k_F}{4\pi} + \varepsilon_c(r_s)$$

$$\varepsilon_c(r_s) = \frac{3}{2\alpha^2 r_s^2} \int_{u=0}^{\infty} du u \int_{r'_s=0}^{r_s} dr'_s [h(u; r'_s) - 1],$$

$$u \equiv k_F r, \quad r \equiv |r_1 - r_2|, \quad \alpha \equiv \left(\frac{9\pi}{4}\right)^{1/3}$$

$$k_F = (3\pi^2 n)^{1/3}, \quad n = \frac{3}{4\pi r_s^3}.$$

Homogeneous Electron Gas System

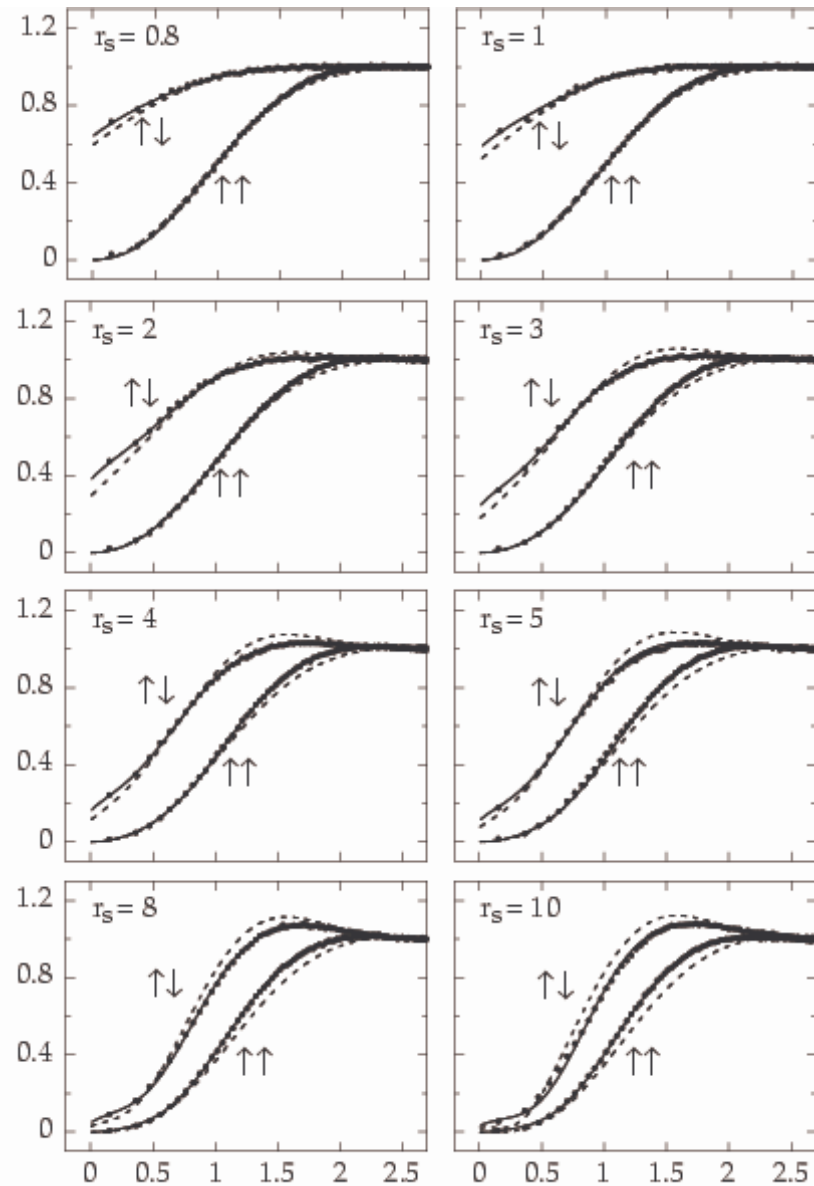
How to determine $\varepsilon_c(r_s)$ for EG system?

1. RPA : Good at high density ($r_s \rightarrow 0$)
2. Wigner : Exact at $r_s \rightarrow 0$ and $r_s \rightarrow \infty$
3. *GW* : Holme and von Barth 1998
4. QMC : Ceperley - Alder 1980
5. QMC : Ortiz - Harris - Ballone 1999

Exchange-correlation hole in homogeneous electron gas

- Exchange dominates at high density (small r_s)
- Correlation dominates at low density (large r_s)

Gori-Giorgi, Sacchetti and Bachelet, PRB 61, 7353 (2000).



Local-Density Approximation(LDA)

Assume $E_{xc}[\rho]$ is sum of contributions from each point \vec{r} , *independent of other* points.

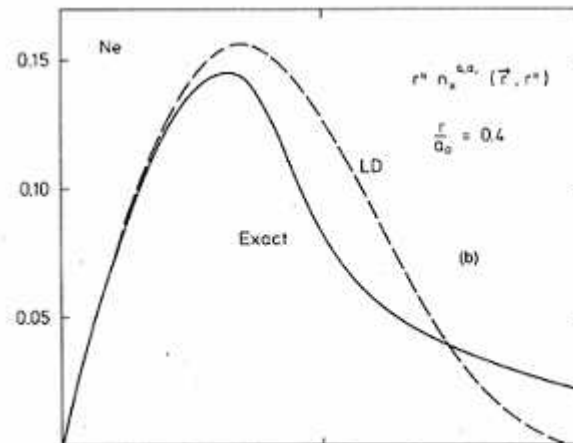
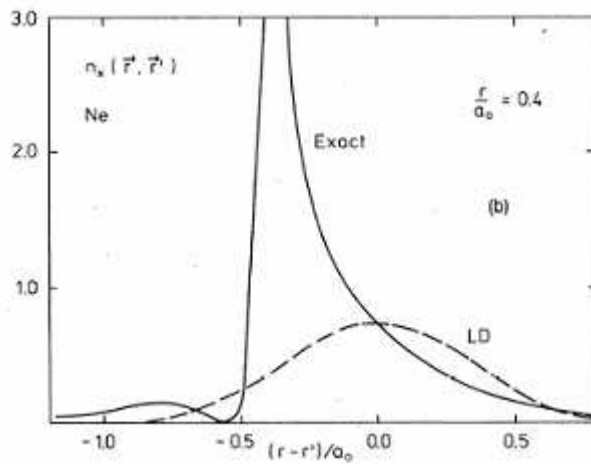
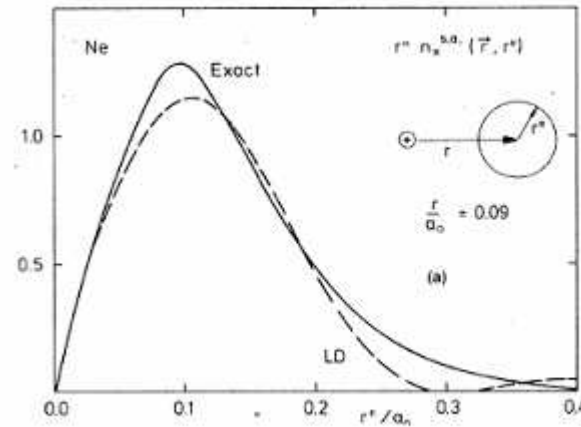
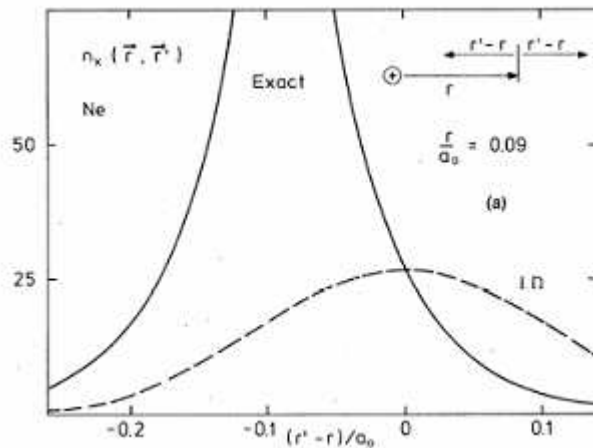
$$E_{xc}^{\text{LDA}}[\rho] = \int dr \rho(r) \varepsilon_{xc}^{\text{EG}}(\rho(r))$$

Since $\varepsilon_{xc}(\rho)$ SHOULD BE UNIVERSAL,
must be the same as for homogeneous EG of
density ρ .

Exchange hole for Ne atom

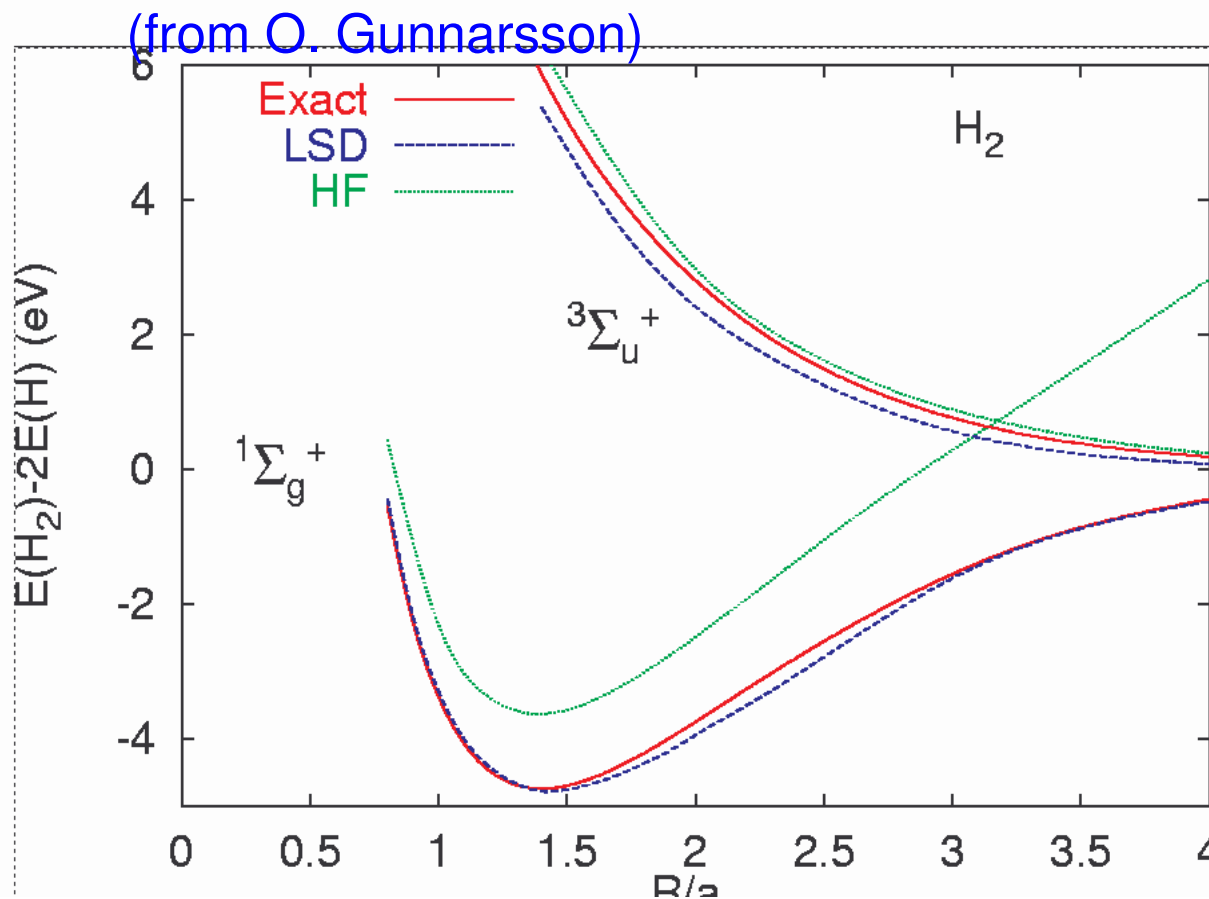
- Spherical average close to LDA!

Gunnarsson, et al,
PRB 20, 3136 (79).



Examples of Results

- Hydrogen molecules - using the LSDA



Examples of Results

- Phase transformations of Si, Ge

- from Yin and Cohen (1982)
- (1995)

Needs and Mujica

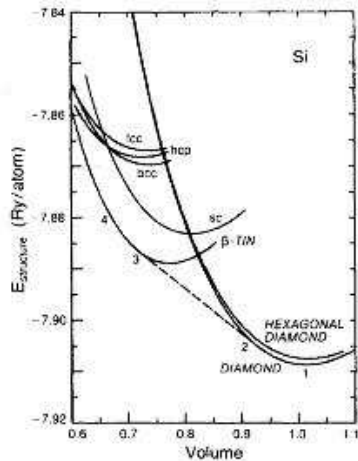


FIG. 5. Total-energy curves of the seven phases of Si as a function of the atomic volume normalized to Ω_{expt} (Ref. 31). Dashed line is the common tangent of the energy curves for the diamond phase and the β -tin phase ($c/a=0.552$).

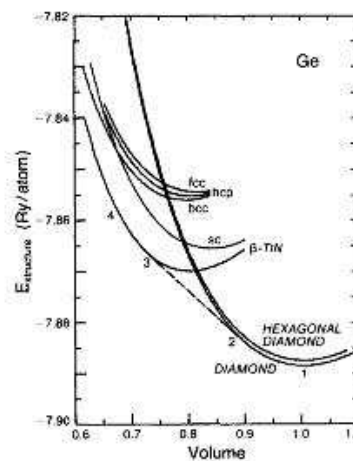


FIG. 6. Total-energy curves of the seven phases of Ge as a function of the atomic volume normalized to Ω_{expt} (Ref. 31). Dashed line is the common tangent of the energy curves for the diamond phase and the β -tin phase ($c/a=0.551$).

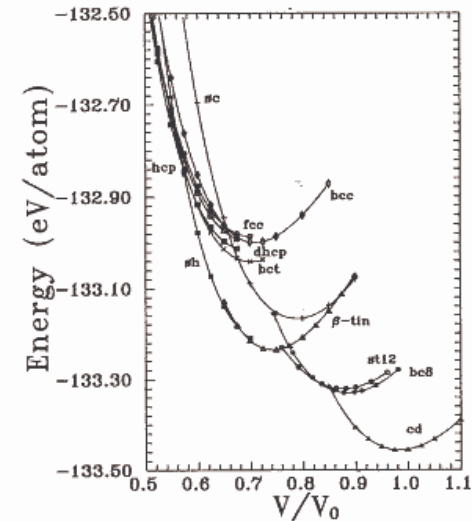
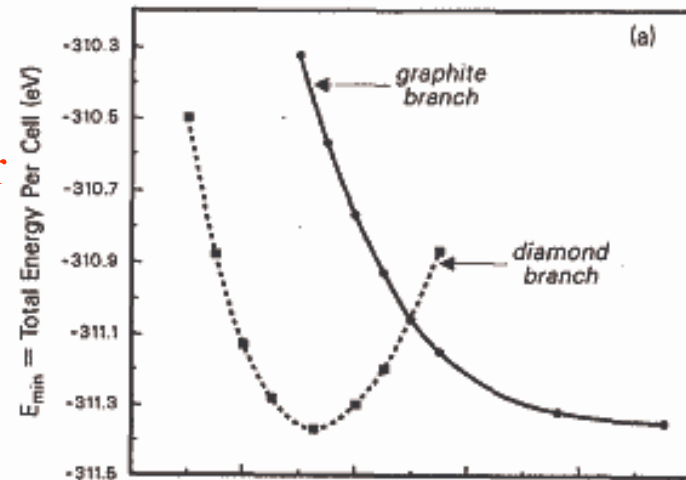
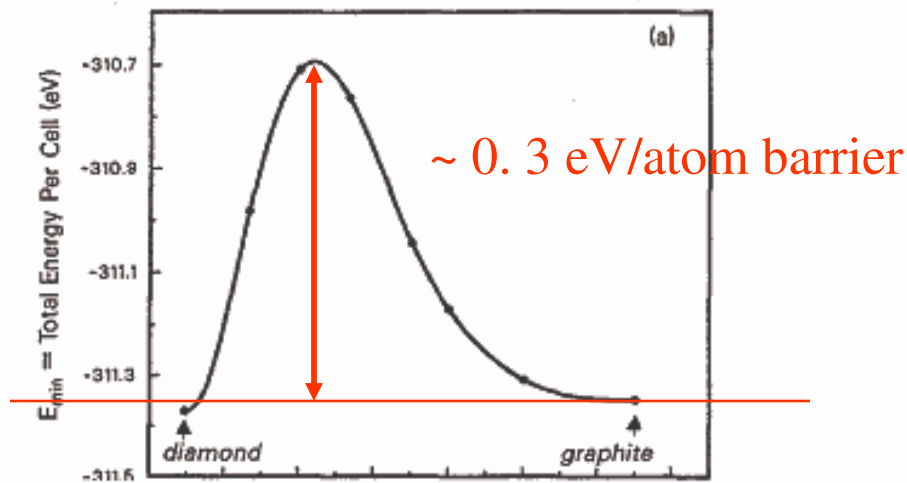


FIG. 1. The energy E in eV per atom vs the volume V for the 11 phases under consideration. The volume is given in terms of the reduced volume V/V_0^{exp} , where $V_0^{\text{exp}}=20.024 \text{ \AA}^3$ per atom is the experimental equilibrium volume of cd-Si. The different symbols indicate our theoretical values, and the lines are fits to these data.

Graphite vs Diamond

- A very severe test
- Fahy, Louie, Cohen calculated energy along a path connecting the phases
- Most important - energy of graphite and diamond essentially the same!



[Phys. Rev. Lett. **88**, 135701](#)

27 March 2002

(print issue of 1 April 2002)

[Title and Authors](#)

Osmium is Stiffer than Diamond

Move over diamond: the element osmium can withstand compression better than any known material, according to the 1 April print issue of *PRL*. A research team squeezed a tiny sample of the metal to extremely high pressure and found that it shrunk even less than diamond, the former record holder. The finding may allow researchers to develop new superhard materials.

Diamond is the hardest material, resisting scratches, dents, and chipping better than any other, so industrial strength machine tools often have diamond tips. But theoretically predicting new superhard materials is, well, hard. Instead, theorists prefer to model a material's bulk modulus--its resistance to compression--which is easier to calculate than hardness. The stiffest materials also tend to be the hardest ones.



D. Mao/Carnegie Institution of Washington

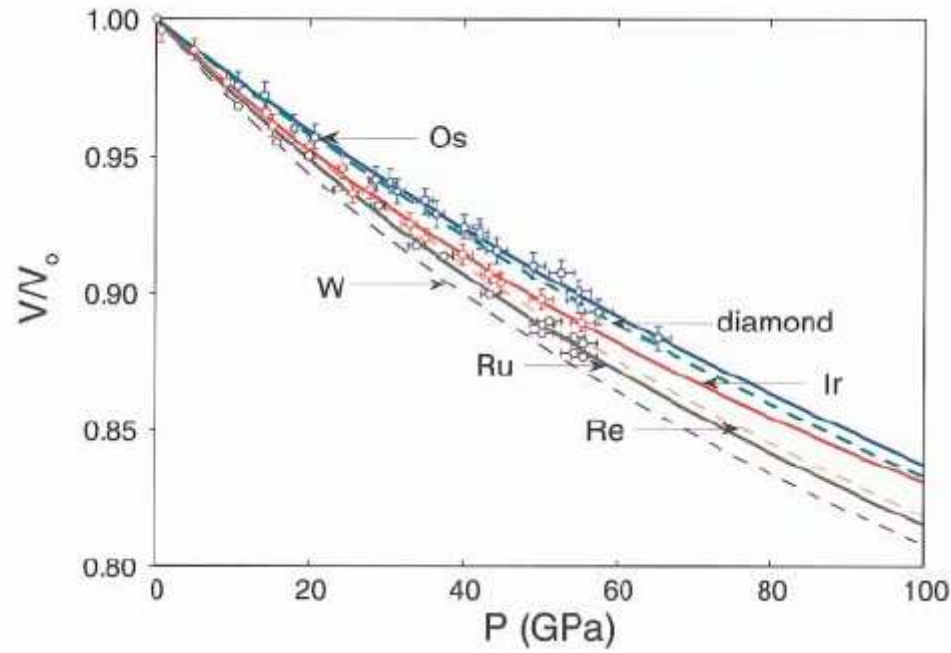
Test under pressure. Osmium holds up better than any other known material when squeezed at extremely high pressures in a diamond anvil (above).

Less compressible than Diamond

- Bulk Modulus B (Gpa)

	Exp	Th (LDA)
C	444	467
Os	462	444

Cynn, et al,
PRL March 14 (2002)



GGA-Generalized Gradient Approximation

Next approximation :

$\epsilon_{xc}(\rho)$ is a function of the density and the *gradient of the density* at each point \vec{r} .

⊕ Widely used especially in chemistry :

GGA's lower energy of systems with larger gradients - improve the estimates of dissociation energies.

GGA-Generalized Gradient Approximation

$$E_{xc}^{\text{GGA}}[\rho] \equiv \int dr \rho(r) \epsilon_x^{\text{hom}}(\rho) F_{xc}(\rho, |\nabla\rho|, \dots).$$

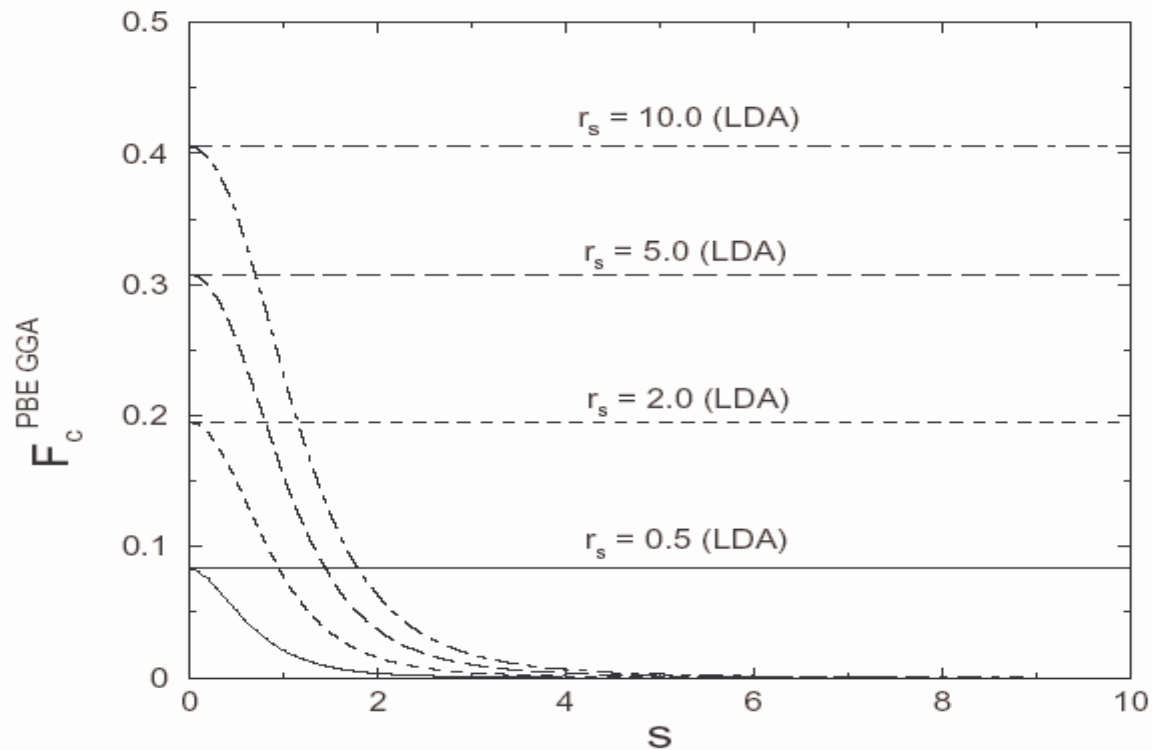
It is expressed in terms of *reduced gradients* :

$$s \equiv \frac{|\nabla\rho|}{2k_F\rho}, \quad k_F = (3\pi^2\rho)^{1/3}.$$

* Different *cut offs* at large gradients \Rightarrow Different GGAs :
Perdew, Burke, Int. J. Quant. Chem. 57, 309 (1996).

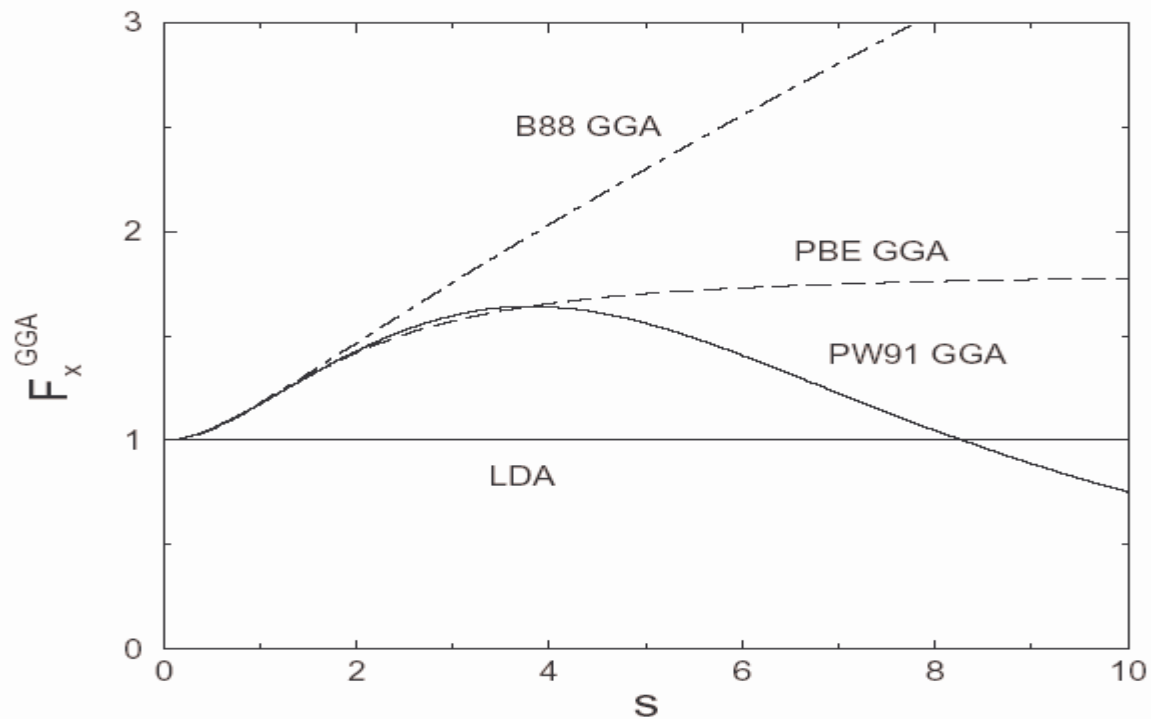
GGA-Correlation factor F_c

Figure 2: Correlation enhancement factor F_x as a function of the dimensionless density gradient s for The PBE functional. Other functionals are similar. (From paper by H. Kim, similar to Figure 1, of Perdew, et al., but for a larger range of s).



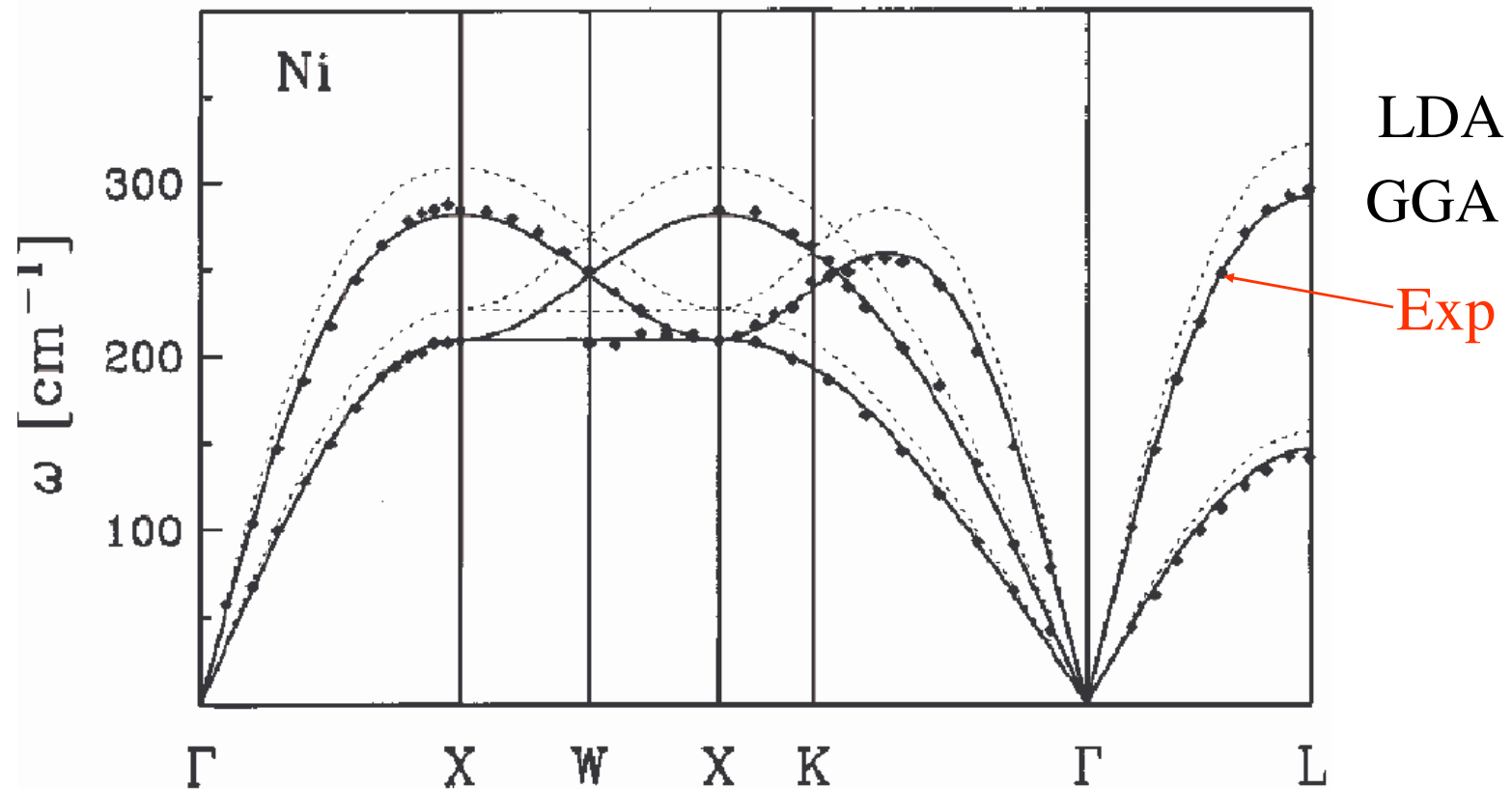
GGA-Exchange factor F_c

Figure 1: Exchange enhancement factor F_x as a function of the dimensionless density gradient s for various GGAs. (From paper by H. Kim, similar to Figure 1, of Perdew, et al., but for a larger range of s).



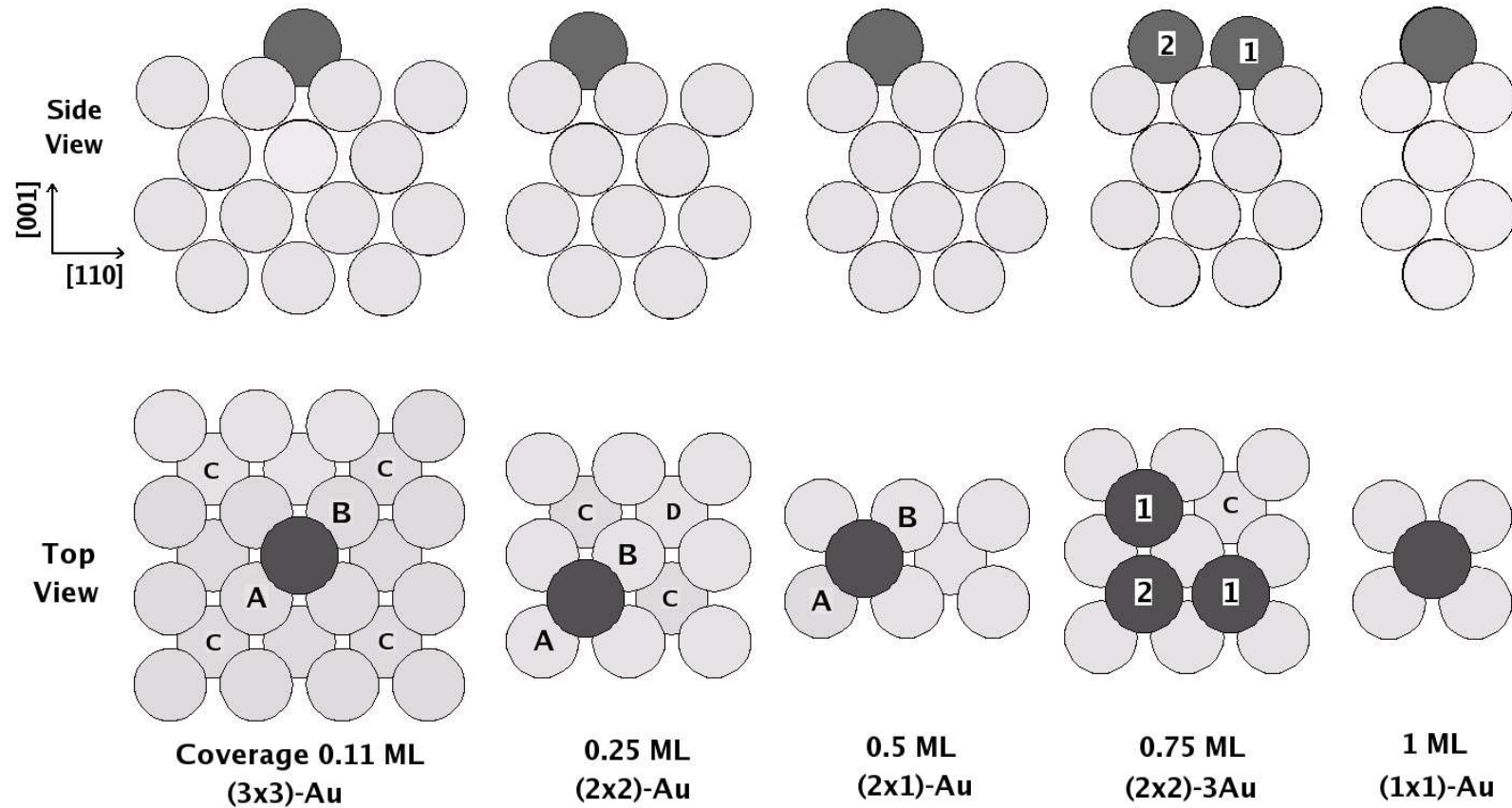
Phonons - LDA and GGA

- Calculated by response function method



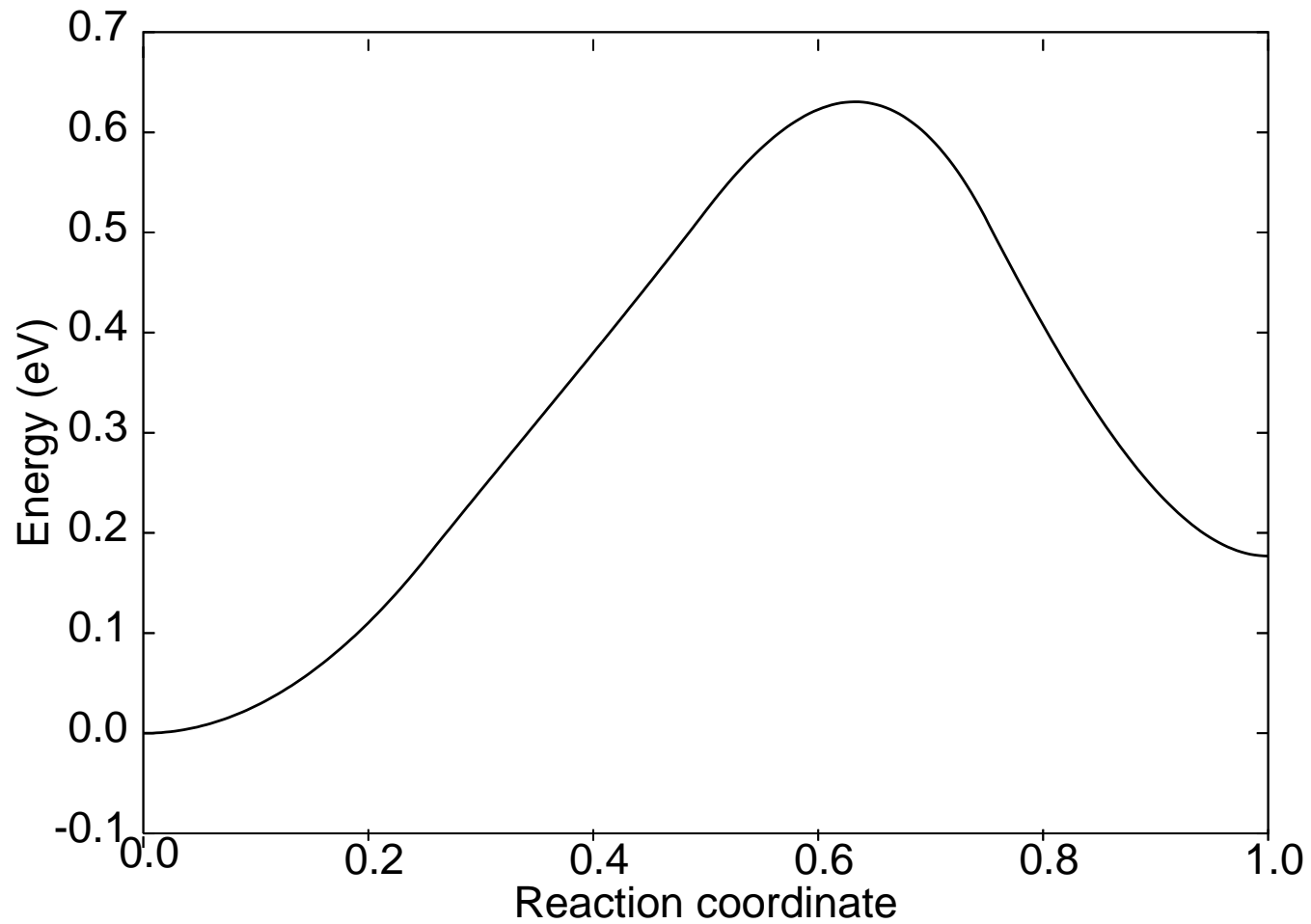
Baroni, et al, RMP 73, 515 (2000).

Au/Al(100)



Zare, Payami, Int. J. Mod. Phys. C (2008)

Au/Al(100)



Zare, Payami, Int. J. Mod. Phys. C (2008)

Typical errors for atoms, molecules and solids from KS scf-calculations

Property	LSD	GGA
E_x	5% (not negative enough)	0.5%
E_c	100% (too negative)	5%
Bond length	1% (too short)	1% (too long)
Structure	overly favors close packing	more correct
Energy barrier	100% (too low)	30% (too low)

Mean absolute error of the atomization energies for 20 molecules

Approximation	Mean absolute error (eV)
UHF	3.1 (underbinding)
LSD	1.3 (overbinding)
GGA	0.3 (mostly overbinding)
Desired “chemical accuracy”	0.05

J. P. Perdew, K. Burke, and M. Ernzerhof, PRL **77**, 3865 (1996);
Ibid. **78**, 1396 (1997) (E)

The “Band Gap Problem”

- Kohn-Sham eigenvalues have no meaning, except for $\epsilon_N = -I$ (for finite system).
- Energy to add or subtract an electron in the non-interacting system - *not* an excitation energy of the interacting system
- Naïve use of the eigenvalues as excitation energies is the famous “band gap problem”
- **Origin:** Derivative discontinuity in E_{xc} .

Failures of LDA and GGA

- Simple functionals for example LDA, GGAs, etc. **do not** have this **DISCONTINUITY**,
 1. LDA does not incorporate gradient corrections to the xc-hole near the electron,
 2. LDA does not satisfy the high-density correlation scaling requirement,

$$\lim_{\gamma \rightarrow \infty} E_c[\rho_\gamma] = \text{const.}$$

Failures of LDA and GGA

3. LDA is not exact in $N=1$ limit.
4. Although the **self-interaction error** is small for xc energy, it is more substantial for the xc potential and orbital eigenvalues,
5. LDA does not guarantee satisfaction of

$$\bar{\rho}_{xc}(r, r') \geq -\rho(r')$$

Failures of LDA and GGA

- GGA preserves all the good features of LDA, while eliminating bad features 1 and 2.
- GGA does not eliminate the bad features 3-5 of LDA.

Improvements over LDA and GGA

- **SIC** to LDA eliminates most of the bad features 3 and 4, but not in an entirely satisfactory way.
- Elimination of **bad** features will probably require the construction of **xc functional** from Kohn-Sham **orbitals**.

Motivations for Orbital-Dependent xc-Functionals

- **Heavy Elements:** GGA loses accuracy with increasing nuclear charge (higher l 's). GGA has some difficulties with the d and f orbitals, similarly to the LDA.

R. N. Schmid *et al.*, *Adv. Quant. Chem.* **33**, 209 (1998)

S. Varga *et al.*, *J. Phys. Chem. A* **104**, 6495 (2000)

W. Liu and C. van Wüllen, *J. Chem. Phys.* **113**, 2506 (2000)

...Motivations for Orbital-Dependent xc-Functionals

- Failure of **GGA** and **LDA** for **negative ions**, because of (semi-)local density-dependence of exchange potential.
- Failure of **GGA** and **LDA** in reproducing **van der Waals forces**.
- **Strongly Correlated Systems**: **3d** transition metal monoxides MnO, FeO, CoO, NiO (Mott insulators). **GGA** and **LDA** predict metallic behaviors for FeO and CoO, and by far underestimate band gap in MnO and NiO.

...Motivations for Orbital-Dependent xc-Functionals

- One variant of **GGA** which reproduce exact atomic **exchange** potential and correctly predicts FeO and CoO to be antiferr. insul. (although with gaps much too small).
- SIC-**LDA** leads to correct ground-states.

P. Dufek, P. Blaha, and K. Schwarz, PRB **50**, 7279 (1994)

E. Engel and S. H. Vosko, PRB **47**, 13164 (1993)

A. Svane and O. Gunnarsson, PRL **65**, 1148 (1990).

Conclusions from these observations:

The inappropriate handling of the **self-interaction** is responsible for the failure of the **LDA** and the standard **GGA**s.

Optimized Effective Potential method

Orbital-dependent exchange functional:

$$E_x[\{\varphi_{i\sigma}\}] = -\frac{e^2}{2} \sum_{\sigma=\uparrow,\downarrow} \sum_{i,j=1}^{N_\sigma} \int d^3r d^3r' \frac{\varphi_{i\sigma}^*(\vec{r}) \varphi_{j\sigma}^*(\vec{r}') \varphi_{j\sigma}(\vec{r}) \varphi_{i\sigma}(\vec{r}')}{|\vec{r} - \vec{r}'|}$$

$\varphi_{i\sigma}(\vec{r})$: Kohn-Sham orbitals

Derivation of local KS exchange potential

$$v_x(\vec{r}) = \frac{\delta E_x[\varphi_k]}{\delta n(\vec{r})} = \int d^3 r' \frac{\delta v_{eff}(\vec{r}')}{\delta n(\vec{r})} \sum_k \left\{ \int d^3 r'' \left[\frac{\delta \varphi_k^*(\vec{r}'')}{\delta v_{eff}(\vec{r}')} \frac{\delta E_x}{\delta \varphi_k^*(\vec{r}'')} + c.c. \right] \right\}$$

Integral Equation for the exchange potential:

$$\int d^3 r' \chi_s(\vec{r}, \vec{r}') v_x(\vec{r}') = \Lambda_x(\vec{r})$$

$$\delta n(\vec{r}) / \delta v_{eff}(\vec{r}') = \chi_s(\vec{r}, \vec{r}')$$

$$\Lambda_x(\vec{r}) = - \sum_k \int d^3 r' \left[\varphi_k^*(\vec{r}) \sum_{l \neq k} \frac{\varphi_l(\vec{r}) \varphi_l^*(\vec{r}')}{\epsilon_l - \epsilon_k} \frac{\delta E_x}{\delta \varphi_k^*(\vec{r}')} + c.c. \right]$$

Very Complicated Equation to handle for 3D systems...!

OEP Made Simple

S. Kümmel and J. P. Perdew, PRL **90**, 43004 (2003)

OEP integral equation is equivalent to:

$$\sum_{i=1}^{N_{\sigma}} \psi_{i\sigma}^*(\vec{r}) \varphi_{i\sigma}(\vec{r}) + c.c. = 0$$

$\psi_{i\sigma}(\vec{r})$: Orbital Shifts

Equations for orbital shifts

$$(\hat{h}_{KS\sigma} - \varepsilon_{i\sigma}) \psi_{i\sigma}^*(\vec{r}) = -[v_{xc\sigma}(\vec{r}) - u_{xc\sigma}(\vec{r}) - (\bar{v}_{xc\sigma} - \bar{u}_{xc\sigma})] \varphi_{i\sigma}^*(\vec{r})$$

$$\hat{h}_{KS\sigma} = -\frac{\hbar^2}{2m} \Delta + v_{eff\sigma}(\vec{r})$$

$$v_{eff\sigma}(\vec{r}) = v(\vec{r}) + v_H(\vec{r}) + v_{xc\sigma}(\vec{r})$$

$$v_H(\vec{r}) = e^2 \int d^3 r' \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|}$$

$$(\hat{h}_{KS\sigma} - \varepsilon_{i\sigma}) \varphi_{i\sigma}(\vec{r}) = 0$$

Equations for orbital shifts

$$u_{xci\sigma}(\vec{r}) = -\frac{e^2}{\varphi_{i\sigma}^*(\vec{r})} \sum_{j=1}^{N_\sigma} \varphi_{j\sigma}^*(\vec{r}) \int d^3 r' \frac{\varphi_{i\sigma}^*(\vec{r}') \varphi_{j\sigma}(\vec{r}')}{|\vec{r} - \vec{r}'|}$$

$$\bar{v}_{xci\sigma} = \int d^3 r \varphi_{i\sigma}^*(\vec{r}) v_{xc\sigma}(\vec{r}) \varphi_{i\sigma}(\vec{r})$$

$$\bar{u}_{xci\sigma} = \int d^3 r \varphi_{i\sigma}^*(\vec{r}) u_{xci\sigma}(\vec{r}) \varphi_{i\sigma}(\vec{r})$$

Measure for self-consistency

At self-consistent stage:

$$S_{\sigma}(\vec{r}) = \sum_{i=1}^{N_{\sigma}} \psi_{i\sigma}^*(\vec{r}) \phi_{i\sigma}(\vec{r}) + c.c. = 0$$

At each **cycle** we take:

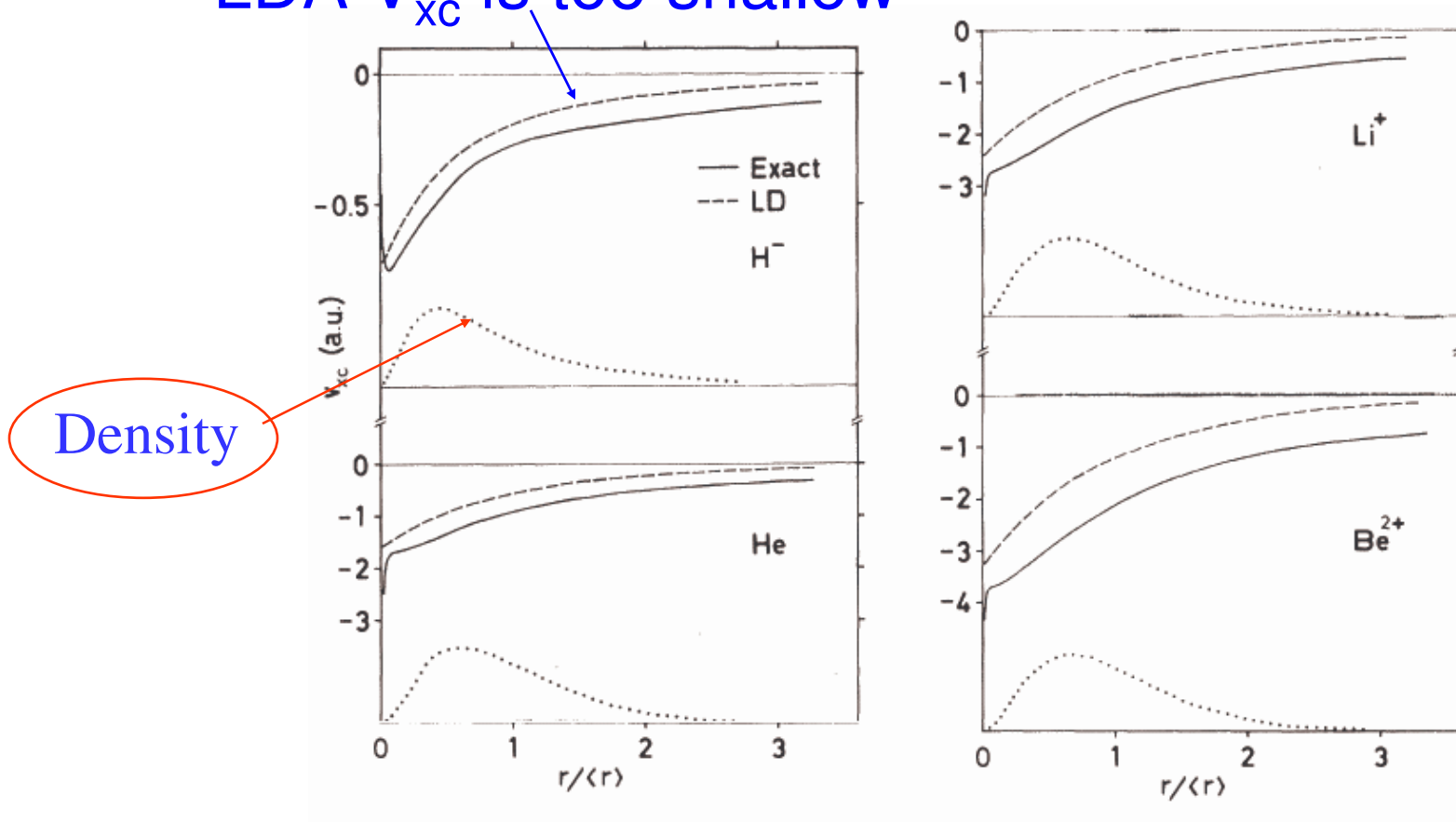
$$v_{xc\sigma}^{new}(\vec{r}) = v_{xc\sigma}^{old}(\vec{r}) + c S_{\sigma}(\vec{r})$$

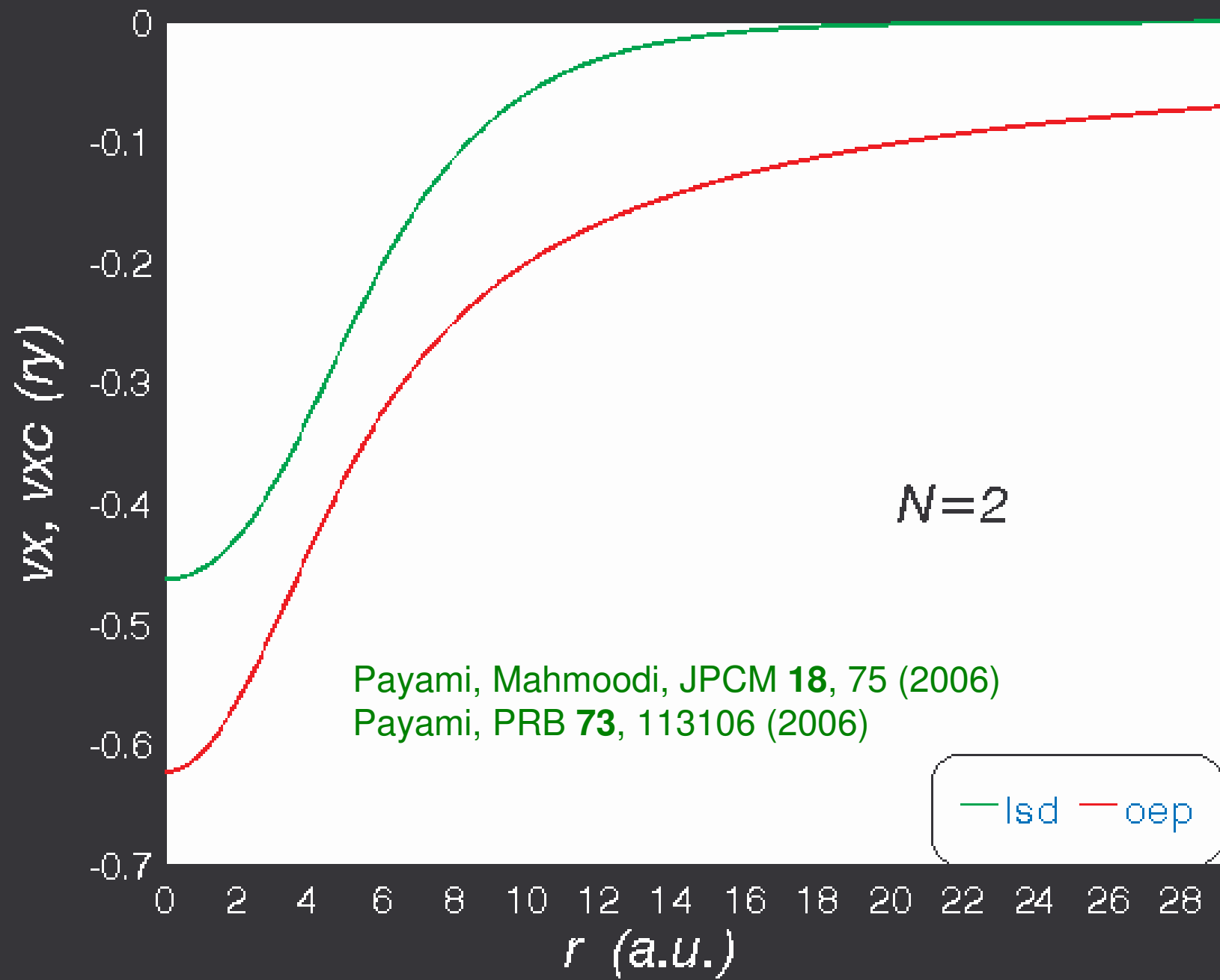
and solve the inhomogeneous KS equations until S diminishes. Then **iterate** by solving KS equations using the new xc-potential.

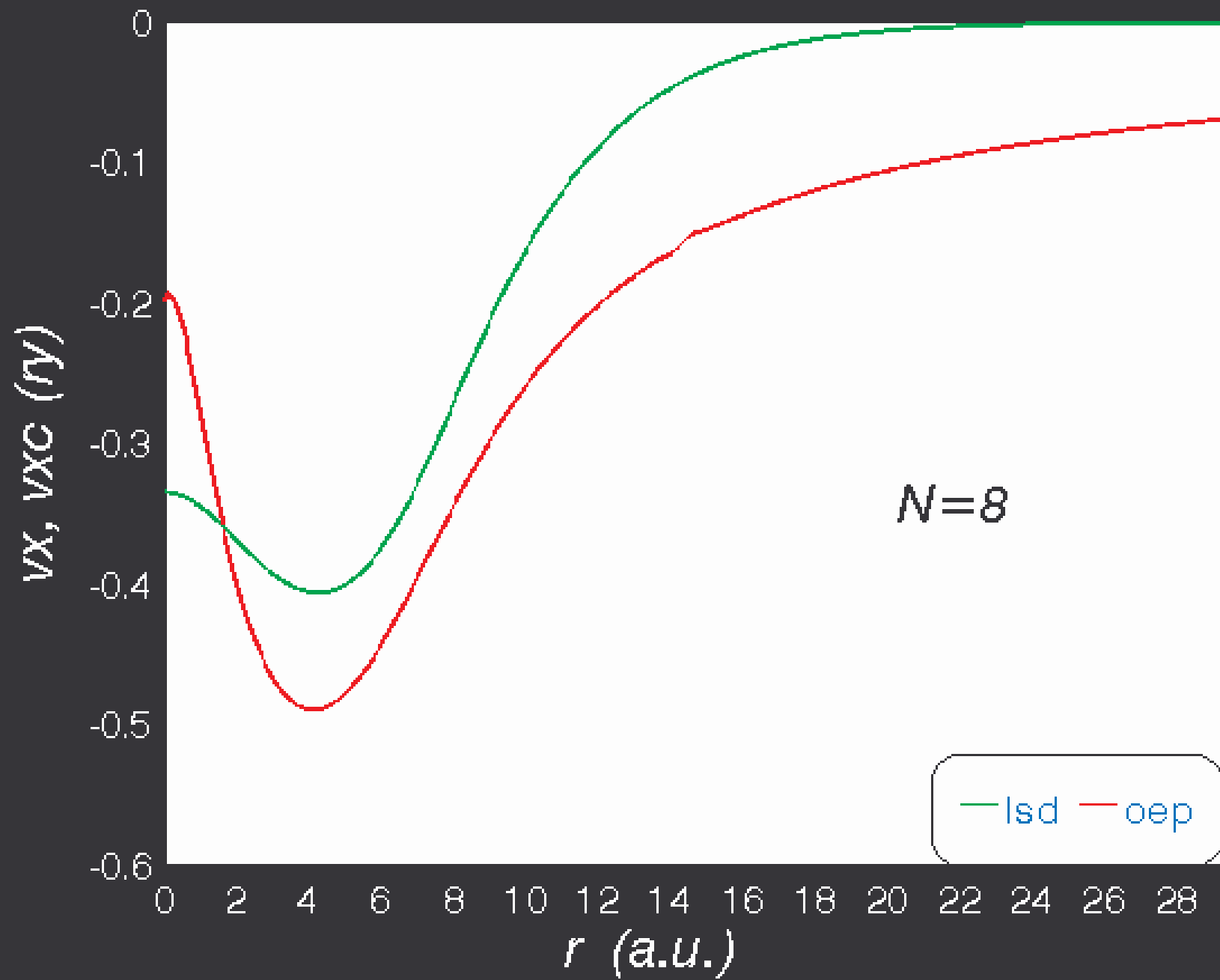
Exchange potential in atoms

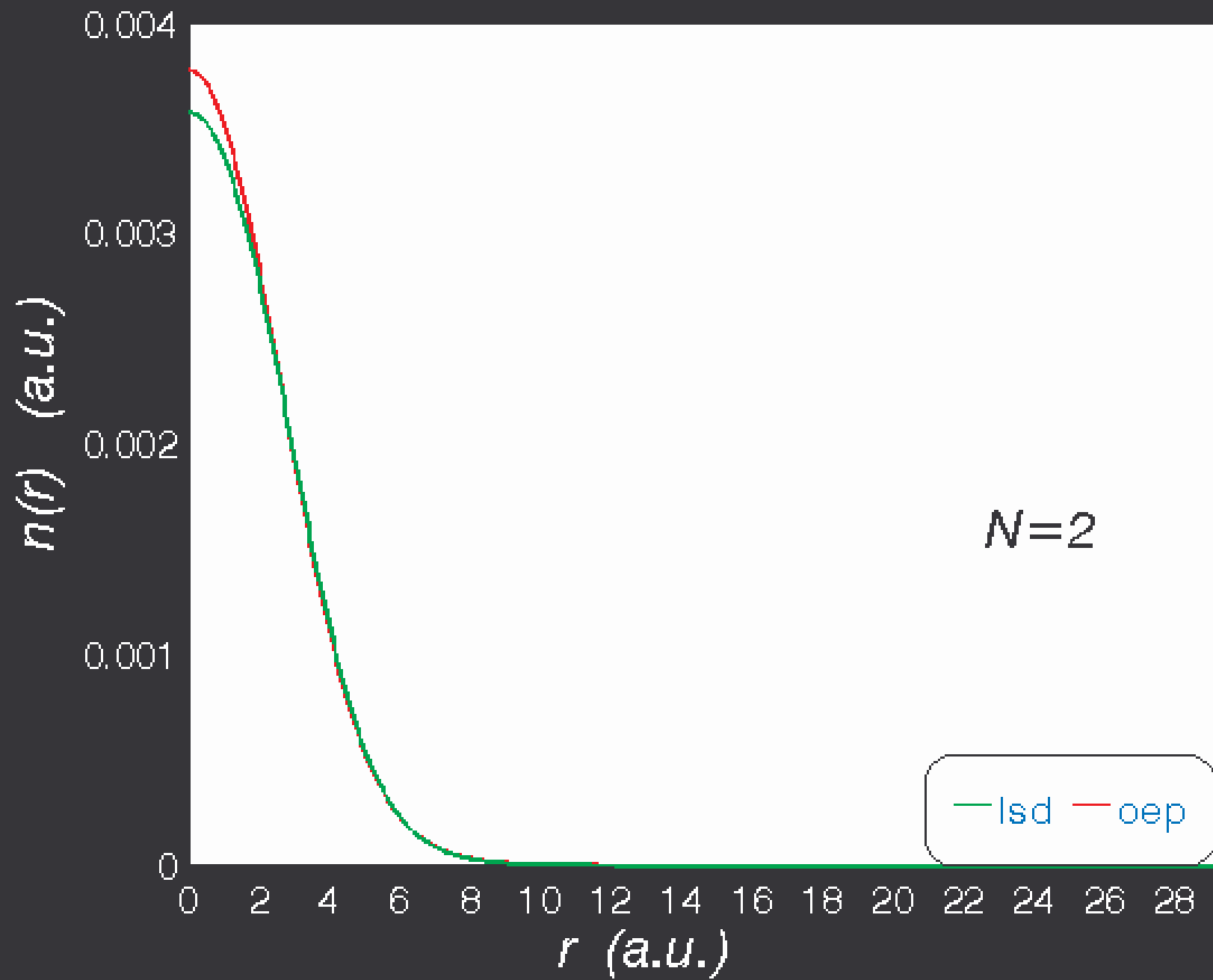
- 2-electron systems
- LDA V_{xc} is too shallow

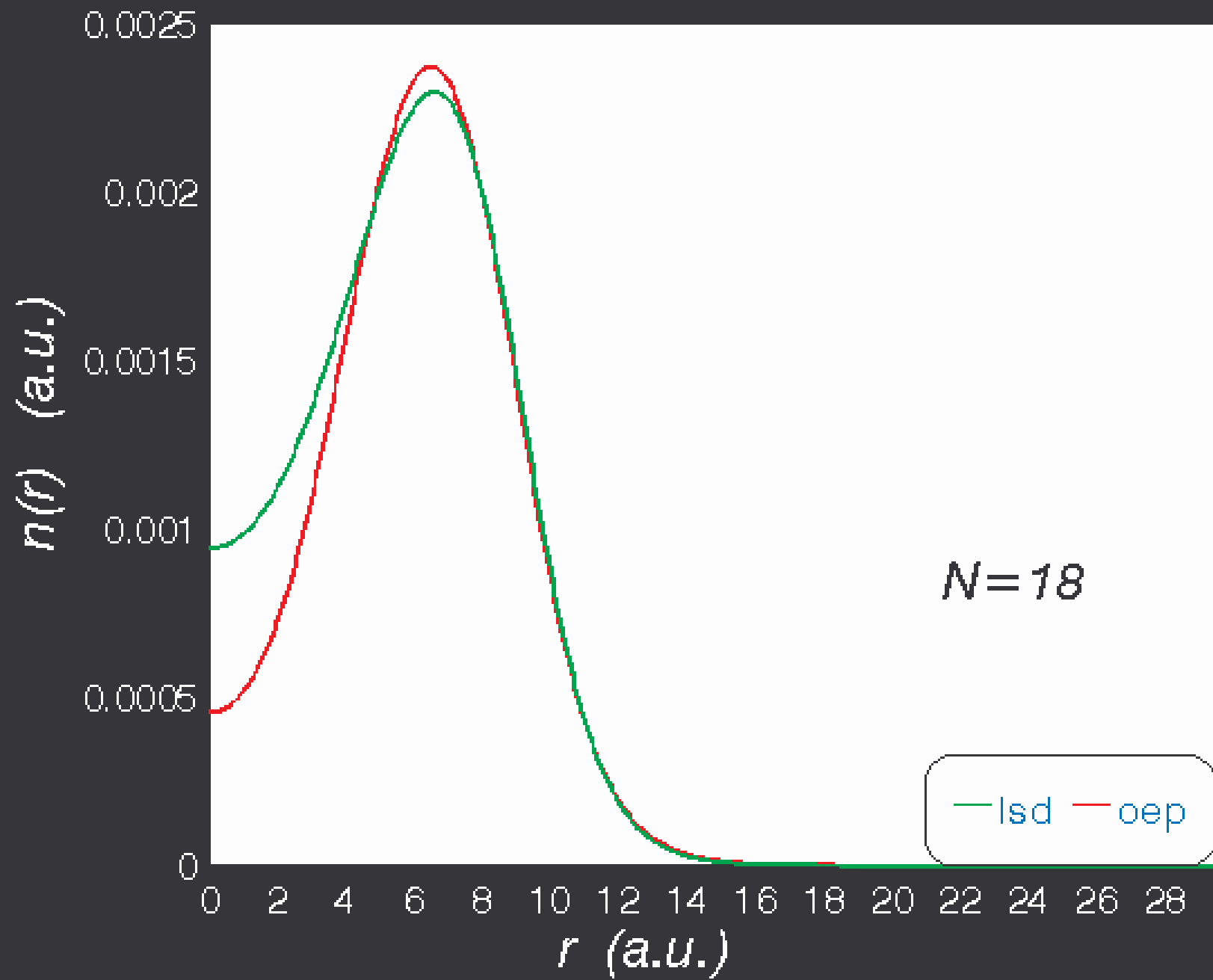
Almbladh and Pedroza, PR A 29, 2322 (84).

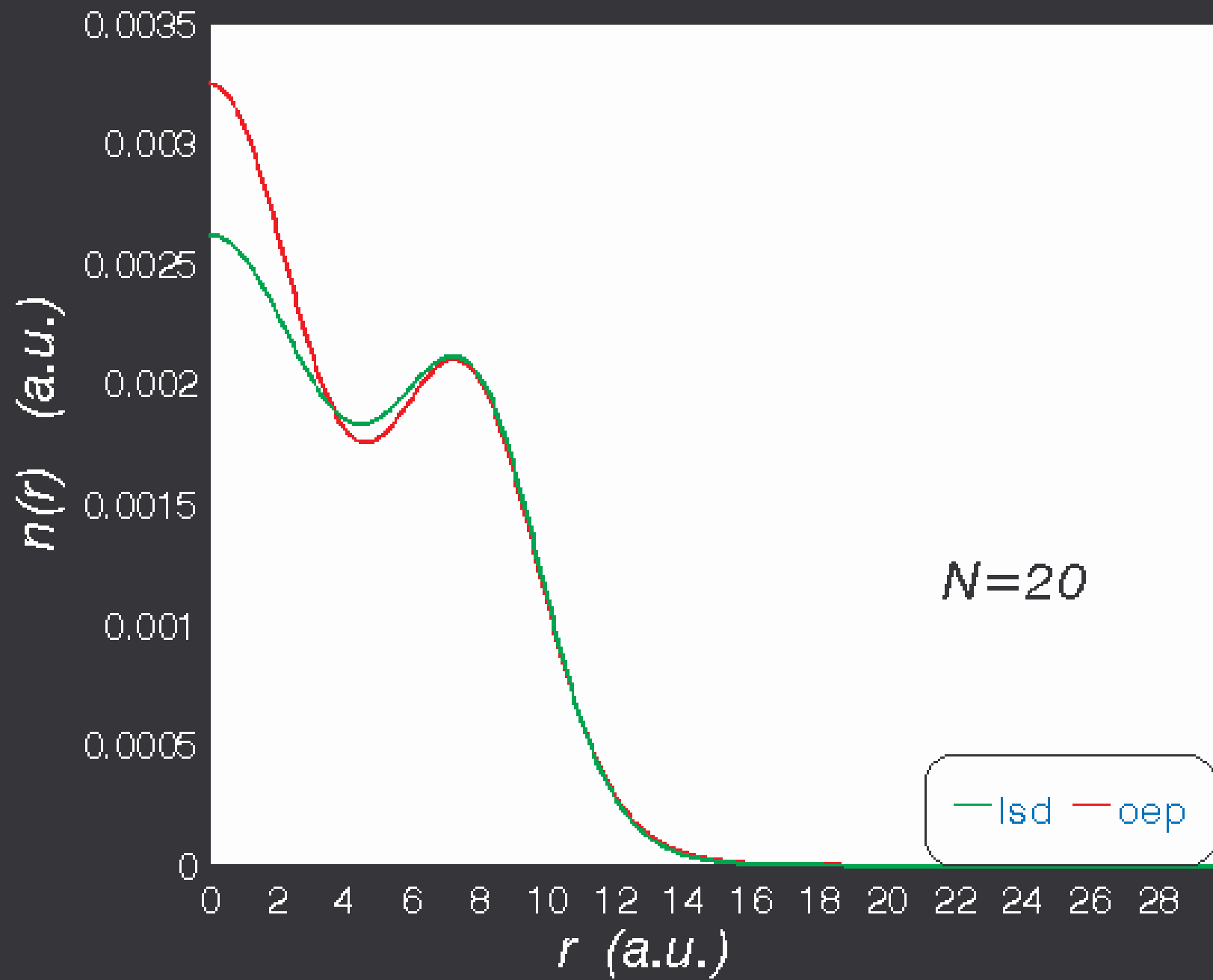


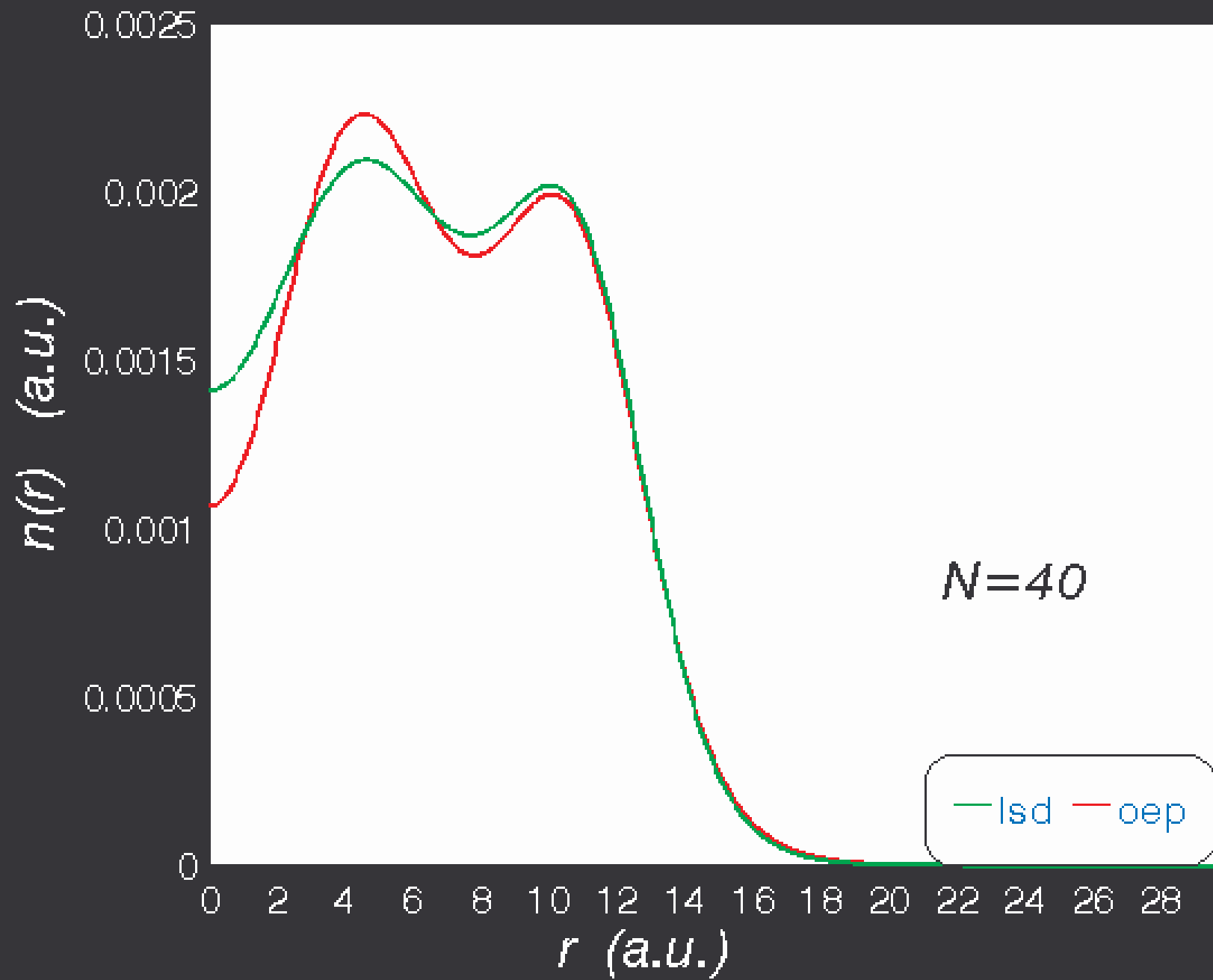












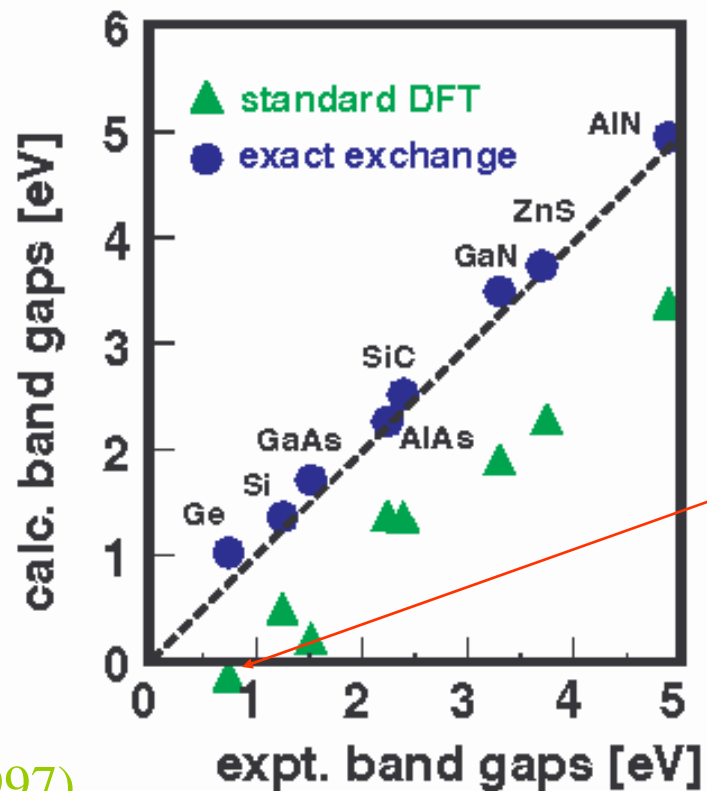
The “Band Gap Problem”

- Excitations are NOT well-predicted by the “standard” LDA, GGA forms of DFT

The “Band Gap Problem”:

Orbital dependent DFT is more complicated but gives improvements - treat exchange better, e.g, “Exact Exchange”

M. Staedele et al, PRL 79, 2089 (1997)



Ge is a metal in LDA!

Status of “Band Gap Problem”

- It should be possible to calculate all excitation energies from the Kohn-Sham approach
- But not clear how close Kohn-Sham eigenvalues should be to true excitation energies
- Not clear how much of the “band gap problem” is due to approximate functionals
- Size of derivative discontinuity?

Conclusion

- DFT is a general approach to interacting many-body problems
 - Kohn-Sham approach is a practical tool
- Ground state properties are predicted with remarkable success by LDA and GGAs.
 - Structures, phonons ($\sim 5\%$),
- Excitations are NOT well-predicted by the LDA, GGA approximations
 - The “Band Gap Problem”:
 - Orbital dependant functionals increase the gaps – better agreement with experiment
 - “Derivative discontinuity” enters naturally in orbital functionals

