

Lecture on First-principles Computations (17): The Generalized Kohn-Sham Scheme and Optimized Effective Potential Method

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Hefei, 2018.11.14

Recall: Kohn-Sham DFT

The Kohn-Sham energy functional

$$E_{\text{KS}}[\{\psi_l\}] = - \sum_{l=1}^{\text{occ.}} \langle \psi_l | \frac{\nabla^2}{2m} | \psi_l \rangle + E_{\text{ext}}[n] + E_H[n] + E_{xc}[n]$$

$$\left(-\frac{1}{2m} \nabla^2 + V_{\text{eff}}(\mathbf{r}) \right) \psi_l(\mathbf{r}) = \epsilon_l \psi_l(\mathbf{r})$$

$$V_{\text{eff}}(\mathbf{r}) = V_{\text{ext}}(\mathbf{r}) + V_H(\mathbf{r}) + \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})}$$

How to evaluate the functional derivative $\frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})}$?

The XC potential within LDA and GGAs

- Local spin density approximation (LSDA)

$$E_{xc}^{\text{LSDA}}[n] = \int d^3 r n(\mathbf{r}) \epsilon_{xc}^{\text{HEG}}(n_{\uparrow}(\mathbf{r}), n_{\downarrow}(\mathbf{r})),$$

$$\delta E_{xc}^{\text{LSDA}}[n] = \sum_{\sigma} \int d^3 r \left[\epsilon_{xc}^{\text{HEG}}(n_{\uparrow}(\mathbf{r}), n_{\downarrow}(\mathbf{r})) + n(\mathbf{r}) \frac{\partial \epsilon_{xc}^{\text{HEG}}(n_{\uparrow}(\mathbf{r}), n_{\downarrow}(\mathbf{r}))}{\partial n_{\sigma}(\mathbf{r})} \right] \delta n_{\sigma}(\mathbf{r})$$

$$V_{xc,\sigma}^{\text{LSDA}}(\mathbf{r}) = \epsilon_{xc}^{\text{HEG}}(n_{\uparrow}(\mathbf{r}), n_{\downarrow}(\mathbf{r})) + n(\mathbf{r}) \frac{\partial \epsilon_{xc}^{\text{HEG}}(n_{\uparrow}(\mathbf{r}), n_{\downarrow}(\mathbf{r}))}{\partial n_{\sigma}(\mathbf{r})}$$

- Generalized gradient approximation (GGA)

$$E_{xc}^{\text{GGA}}[n] = \int d^3 r n(\mathbf{r}) \epsilon_{xc}^{\text{GGA}}(n(\mathbf{r}), \nabla n(\mathbf{r}))$$

$$\delta E_{xc}^{\text{GGA}}[n] = \int d^3 r \left[\epsilon_{xc}^{\text{GGA}} + n(\mathbf{r}) \frac{\partial \epsilon_{xc}^{\text{GGA}}}{\partial n(\mathbf{r})} - \nabla \left(n(\mathbf{r}) \frac{\partial \epsilon_{xc}^{\text{GGA}}}{\partial \nabla n(\mathbf{r})} \right) \right] \delta n(\mathbf{r})$$

$$V_{xc}^{\text{GGA}}(\mathbf{r}) = \epsilon_{xc} + n \frac{\partial \epsilon_{xc}}{\partial n(\mathbf{r})} - \nabla \left(n(\mathbf{r}) \frac{\partial \epsilon_{xc}}{\partial \nabla n(\mathbf{r})} \right)$$

How about hybrid density functionals?

- Hybrid density functionals

$$E_{xc}^{\text{hyd}} = E_{xc}^{\text{GGA}} + a_0 (E_x^{\text{exact}} - E_x^{\text{GGA}})$$



$$V_{xc}^{\text{hyd}}(\mathbf{r}) = \frac{\delta E_{xc}^{\text{hyd}}}{\delta n(\mathbf{r})} = V_{xc}^{\text{GGA}} + a_0 \left(\frac{\delta E_x^{\text{exact}}}{\delta n(\mathbf{r})} - V_x^{\text{GGA}} \right)$$

$$E_x^{\text{exact}} = -\frac{1}{2} \sum_{lm}^{\text{occ}} \int d^3 r_1 d^3 r_2 \frac{\psi_l^*(\mathbf{r}_1) \psi_m(\mathbf{r}_1) \psi_m^*(\mathbf{r}_2) \psi_l(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

E_x^{exact} is not an explicit functional of the density $n(\mathbf{r})$!

So, how to evaluate $\frac{\delta E_x^{\text{exact}}}{\delta n(\mathbf{r})}$?

Practical approach to hybrid functionals

$$E_x^{exact} = -\frac{1}{2} \sum_{lm}^{occ} \int d^3 r_1 d^3 r_2 \frac{\psi_l^*(\mathbf{r}_1) \psi_m(\mathbf{r}_1) \psi_m^*(\mathbf{r}_2) \psi_l(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

$$\frac{\delta E_x^{exact}}{\delta \psi_n^*(\mathbf{r})} = - \sum_l^{occ} \int d^3 r_1 \frac{\psi_l^*(\mathbf{r}_1) \psi_l(\mathbf{r})}{|\mathbf{r} - \mathbf{r}_1|} \psi_n(\mathbf{r}_1)$$

Make the replacement :

$$\frac{\delta E_x^{exact}}{\delta n(\mathbf{r})} \psi_n(\mathbf{r}) \quad \longrightarrow \quad - \sum_l \int d^3 r_1 \frac{\psi_l^*(\mathbf{r}_1) \psi_l(\mathbf{r})}{|\mathbf{r} - \mathbf{r}_1|} \psi_n(\mathbf{r}_1)$$

$$V_x(\mathbf{r}) \psi_n(\mathbf{r}) \quad \longrightarrow \quad \int d^3 r_1 V_x^{HF}(\mathbf{r}, \mathbf{r}_1) \psi_n(\mathbf{r}_1)$$

Local exchange \Rightarrow Hartree-Fock non-local exchange

Effective single-particle equation

Hybrid density functional:

$$E[\{\psi_l\}] = - \sum_l \langle \psi_l | \frac{\nabla^2}{2m} | \psi_l \rangle + E_{ext}[n] + E_H[n] + E_{xc}^{hyd}[\{\psi_l\}]$$

Euler-Lagrange procedure

$$\frac{\delta \{E[\{\psi_l\}] - \sum_{l,m} \epsilon_{lm} [\langle \psi_l | \psi_m \rangle - \delta_{lm}]\}}{\delta \psi_n^*(\mathbf{r})} = 0 \quad \rightarrow$$

$$\left(-\frac{\nabla^2}{2m} + V_{ext}(\mathbf{r}) + V_H(\mathbf{r}) + V_{xc}^{GGA}(\mathbf{r}) - a_0 V_x^{GGA}(\mathbf{r}) \right) \psi_n(\mathbf{r}) \\ + a_0 \int d^3 r_1 V_x^{HF}(\mathbf{r}, \mathbf{r}_1) \psi_n(\mathbf{r}_1) = \sum_m \epsilon_{nm} \psi_m(\mathbf{r})$$

$$V_x^{HF}(\mathbf{r}, \mathbf{r}_1) = - \sum_m \frac{\psi_m^*(\mathbf{r}_1) \psi_m(\mathbf{r})}{|\mathbf{r} - \mathbf{r}_1|}$$

Remarks on hybrid functional calculations

- In hybrid functional calculations, the effective single-particle equation is similar to the Hartree-Fock equation, where **the effective potential is *non-local***. This is different from the Kohn-Sham (KS) equation, in which the effective potential is local.
- The hybrid functional method is not a KS theory in the strict sense. Instead, it can be understood in the so-called **generalized KS framework**. The band gap obtained from hybrid functional calculations are typically larger than the KS gap, and in better agreement with experiment.

Generalized Kohn-Sham (GKS) scheme

Seidl et. al., *Phys. Rev. B* **53**, 3764 (1996)

The Kohn-Sham scheme:

$$E_{KS} = T_s[\{\psi_l(\mathbf{r})\}] + E_{ext}[n] + E_H[n] + E_{xc}[n]$$

The Kohn-Sham equation:

$$\frac{\delta E_{KS}}{\delta \psi_n^*(\mathbf{r})} = \frac{\delta T_s}{\delta \psi_n^*(\mathbf{r})} + \frac{\delta(E_{ext}[n] + E_H[n] + E_{xc}[n])}{\delta n(\mathbf{r})} \frac{\delta n(\mathbf{r})}{\delta \psi_n^*(\mathbf{r})} = \epsilon_n \psi_n(\mathbf{r})$$

Generalized Kohn-Sham scheme:

$$E_{GKS} = S[\Phi] + E_{ext}[n] + R^S[n], \quad \Phi = \det\{\psi_l(\mathbf{r})\}$$

Generalized Kohn-Sham (GKS) scheme

Generalized Kohn-Sham scheme:

$$E_{\text{GKS}} = S[\Phi] + E_{\text{ext}}[n] + R^S[n], \quad \Phi = \det\{\psi_l(\mathbf{r})\}$$

$$S[\Phi] = \langle \Phi | \hat{T} | \Phi \rangle$$

➡ The Kohn-Sham scheme

$$S[\Phi] = \langle \Phi | \hat{T} + \hat{V}_{ee} | \Phi \rangle = \langle \Phi | \hat{T} | \Phi \rangle + E_H[\{\psi_n\}] + E_x^{\text{exact}}[\{\psi_n\}]$$

➡ The Hartree-Fock Kohn-Sham scheme

$$S[\Phi] = \langle \Phi | \hat{T} + a_0 \hat{V}_{ee} | \Phi \rangle = \langle \Phi | \hat{T} | \Phi \rangle + a_0 E_H[\{\psi_n\}] + a_0 E_x^{\text{exact}}[\{\psi_n\}]$$

➡ The hybrid functional scheme

Effective single-particle equation within the GKS scheme

$$E_{\text{GKS}} = S[\Phi] + E_{\text{ext}}[n] + R^S[n], \quad \Phi = \det\{\psi_l(\mathbf{r})\}$$

$$S[\Phi] = \langle \Phi | \hat{T} + a_0 \hat{V}_{ee} | \Phi \rangle = \langle \Phi | \hat{T} | \Phi \rangle + a_0 E_H[\{\psi_n\}] + a_0 E_x^{\text{exact}}[\{\psi_n\}]$$

$$\frac{\delta E_{\text{GKS}}}{\delta \psi_n^*(\mathbf{r})} = \frac{\delta T_s}{\delta \psi_n^*(\mathbf{r})} + \frac{\delta(E_{\text{ext}}[n] + a_0 E_H[n] + R^S[n])}{\delta n(\mathbf{r})} \frac{\delta n(\mathbf{r})}{\delta \psi_n^*(\mathbf{r})} + a_0 \int d^3 r_1 V_x(\mathbf{r}, \mathbf{r}_1) \psi_n(\mathbf{r}_1) = \epsilon_n \psi_n(\mathbf{r})$$

The GKS scheme is still DFT. The KS scheme is only one of the infinitely many ways to implement DFT.

Can we implement orbital-dependent DFT functionals within the strict Kohn-Sham scheme ?

YES!

The Optimized Effective Potential (OEP) method!

Local potential corresponding to Hartree-Fock


*J. D. Talman and W. F. Shadwick, PRA **14**, 36 (1976)*

Consider the exchange-only case:

$$E[\{\psi_l\}] = - \sum_l \langle \psi_l | \frac{\nabla^2}{2m} | \psi_l \rangle + E_{ext}[n(\mathbf{r})] + E_H[n(\mathbf{r})] + E_x^{exact}[\{\psi_l\}]$$

Minimizing $E[\{\psi_l\}]$ under the constraint that $\psi_l(\mathbf{r})$ is an **eigenfunction of a local potential**,

$$\left(-\frac{\nabla^2}{2m} + V_s(\mathbf{r}) \right) \psi_l(\mathbf{r}) = \epsilon_l \psi_l(\mathbf{r}) \quad (\psi_l = \psi_l[V_s])$$

 $\frac{\delta E[\{\psi_l\}]}{\delta V_s(\mathbf{r})} = \sum_n \int d^3 r_1 \frac{\delta E[\{\psi_l\}]}{\delta \psi_n(\mathbf{r}_1)} \frac{\delta \psi_n(\mathbf{r}_1)}{\delta V_s(\mathbf{r})} = 0$

(Consider real orbitals for simplicity)

The optimized effective potential method (I)

$$\frac{\delta E[\{\psi_l\}]}{\delta V_s(\mathbf{r})} = \sum_n \int d^3 r_1 \frac{\delta E[\{\psi_l\}]}{\delta \psi_n(\mathbf{r}_1)} \frac{\delta \psi_n(\mathbf{r}_1)}{\delta V_s(\mathbf{r})} = 0 \quad (1)$$

$$\frac{\delta E[\{\psi_l\}]}{\delta \psi_n(\mathbf{r}_1)} = \left(-\frac{\nabla^2}{2m} + V_{ext}(\mathbf{r}_1) + V_H(\mathbf{r}_1) \right) \psi_n(\mathbf{r}_1) + \int d^3 r_2 V_x^{HF}(\mathbf{r}_1, \mathbf{r}_2) \psi_n(\mathbf{r}_2) \quad (2)$$

$$\frac{\delta \psi_n(\mathbf{r}_1)}{\delta V_s(\mathbf{r})} = - \sum_{n \neq m} \frac{\psi_m(\mathbf{r}_1) \psi_m(\mathbf{r}) \psi_n(\mathbf{r})}{\epsilon_n - \epsilon_m} = -G_n(\mathbf{r}_1, \mathbf{r}) \psi_n(\mathbf{r}) \quad (3)$$

Inserting (3), (2) into (1) \longrightarrow

$$\begin{aligned} & - \sum_n \int d^3 r_1 \left(-\frac{\nabla^2}{2m} + V_{ext}(\mathbf{r}_1) + V_H(\mathbf{r}_1) \right) \psi_n(\mathbf{r}_1) G_n(\mathbf{r}_1, \mathbf{r}) \psi_n(\mathbf{r}) \\ & = \sum_n \int d^3 r_1 d^3 r_2 v_x^{HF}(\mathbf{r}_1, \mathbf{r}_2) \psi_n(\mathbf{r}_2) G_n(\mathbf{r}_1, \mathbf{r}) \psi_n(\mathbf{r}) \end{aligned}$$

The optimized effective potential method (II)

$$\begin{aligned}
 & - \sum_n \int d^3 r_1 \left(-\frac{\nabla^2}{2m} + V_{\text{ext}}(\mathbf{r}_1) + V_H(\mathbf{r}_1) \right) \psi_n(\mathbf{r}_1) G_n(\mathbf{r}_1, \mathbf{r}) \psi_n(\mathbf{r}) \\
 & = \sum_n \int d^3 r_1 d^3 r_2 v_x^{\text{HF}}(\mathbf{r}_1, \mathbf{r}_2) \psi_n(\mathbf{r}_2) G_n(\mathbf{r}_1, \mathbf{r}) \psi_n(\mathbf{r})
 \end{aligned}$$

$$\left(-\frac{\nabla^2}{2m} - V_S(\mathbf{r}_1) \right) \psi_n(\mathbf{r}_1) = \epsilon_n \psi_n(\mathbf{r}_1)$$

$$V_S(\mathbf{r}_1) = V_{\text{OEP}}(\mathbf{r}_1) = V_{\text{ext}}(\mathbf{r}_1) + V_H(\mathbf{r}_1) + v_x^{\text{OEP}}(\mathbf{r}_1)$$

$$\left(-\frac{\nabla^2}{2m} + V_{\text{ext}}(\mathbf{r}_1) + V_H(\mathbf{r}_1) \right) \psi_n(\mathbf{r}_1) = \left(\epsilon_n - v_x^{\text{OEP}}(\mathbf{r}_1) \right) \psi_n(\mathbf{r}_1)$$

$$\begin{aligned}
 & \sum_n \int d^3 r_1 (v_x^{\text{OEP}}(\mathbf{r}_1) - \epsilon_n) \psi_n(\mathbf{r}_1) G_n(\mathbf{r}_1, \mathbf{r}) \psi_n(\mathbf{r}) \\
 & = \sum_n \int d^3 r_1 d^3 r_2 v_x^{\text{HF}}(\mathbf{r}_1, \mathbf{r}_2) \psi_n(\mathbf{r}_2) G_n(\mathbf{r}_1, \mathbf{r}) \psi_n(\mathbf{r})
 \end{aligned}$$



The optimized effective potential method (II)

$$\begin{aligned}
 & - \sum_n \int d^3 r_1 \left(-\frac{\nabla^2}{2m} + V_{\text{ext}}(\mathbf{r}_1) + V_H(\mathbf{r}_1) \right) \psi_n(\mathbf{r}_1) G_n(\mathbf{r}_1, \mathbf{r}) \psi_n(\mathbf{r}) \\
 & = \sum_n \int d^3 r_1 d^3 r_2 v_x^{\text{HF}}(\mathbf{r}_1, \mathbf{r}_2) \psi_n(\mathbf{r}_2) G_n(\mathbf{r}_1, \mathbf{r}) \psi_n(\mathbf{r})
 \end{aligned}$$

$$\left(-\frac{\nabla^2}{2m} - V_s(\mathbf{r}_1) \right) \psi_n(\mathbf{r}_1) = \epsilon_n \psi_n(\mathbf{r}_1)$$

$$V_s(\mathbf{r}_1) = V_{\text{OEP}}(\mathbf{r}_1) = V_{\text{ext}}(\mathbf{r}_1) + V_H(\mathbf{r}_1) + V_x^{\text{OEP}}(\mathbf{r}_1)$$

$$\left(-\frac{\nabla^2}{2m} + V_{\text{ext}}(\mathbf{r}_1) + V_H(\mathbf{r}_1) \right) \psi_n(\mathbf{r}_1) = \left(\epsilon_n - v_x^{\text{OEP}}(\mathbf{r}_1) \right) \psi_n(\mathbf{r}_1)$$

$$\begin{aligned}
 & \sum_n \int d^3 r_1 (V_x^{\text{OEP}}(\mathbf{r}_1) - \cancel{\epsilon_n}) \psi_n(\mathbf{r}_1) G_n(\mathbf{r}_1, \mathbf{r}) \psi_n(\mathbf{r}) \\
 & = \sum_n \int d^3 r_1 d^3 r_2 v_x^{\text{HF}}(\mathbf{r}_1, \mathbf{r}_2) \psi_n(\mathbf{r}_2) G_n(\mathbf{r}_1, \mathbf{r}) \psi_n(\mathbf{r})
 \end{aligned}$$



The optimized effective potential method (II)

$$V_S(\mathbf{r}) = V_{OEP}(\mathbf{r}) = V_{ext}(\mathbf{r}) + V_H(\mathbf{r}) + V_x^{OEP}(\mathbf{r})$$

$V_x^{OEP}(\mathbf{r})$ is determined by

$$\int d^3 \mathbf{r}_1 \chi_s(\mathbf{r}_1, \mathbf{r}) V_x^{OEP}(\mathbf{r}_1) = t(\mathbf{r})$$

$$\chi_s(\mathbf{r}_1, \mathbf{r}) = \sum_n \psi_n(\mathbf{r}_1) G_n(\mathbf{r}_1, \mathbf{r}) \psi_n(\mathbf{r}) = \sum_n^{occ} \sum_m^{unocc} \frac{\psi_n(\mathbf{r}_1) \psi_m(\mathbf{r}_1) \psi_m(\mathbf{r}) \psi_n(\mathbf{r})}{\epsilon_n - \epsilon_m}$$

(The KS response function)

$$t(\mathbf{r}) = \sum_n \int d^3 r_1 d^3 r_2 \psi_n(\mathbf{r}) G_n(\mathbf{r}, \mathbf{r}_1) V_x^{HF}(\mathbf{r}_1, \mathbf{r}_2) \psi_n(\mathbf{r}_2)$$

Exact-exchange OEP potential

$$V_x^{OEP}(\mathbf{r}) = \frac{\delta E_x^{exact}}{\delta n(\mathbf{r})}$$

The OEP exact-exchange concept can be easily extended to more complex orbital-dependent functionals (including the correlation effect), but solving the OEP equations is exceedingly difficult (and sometimes numerically unstable) !

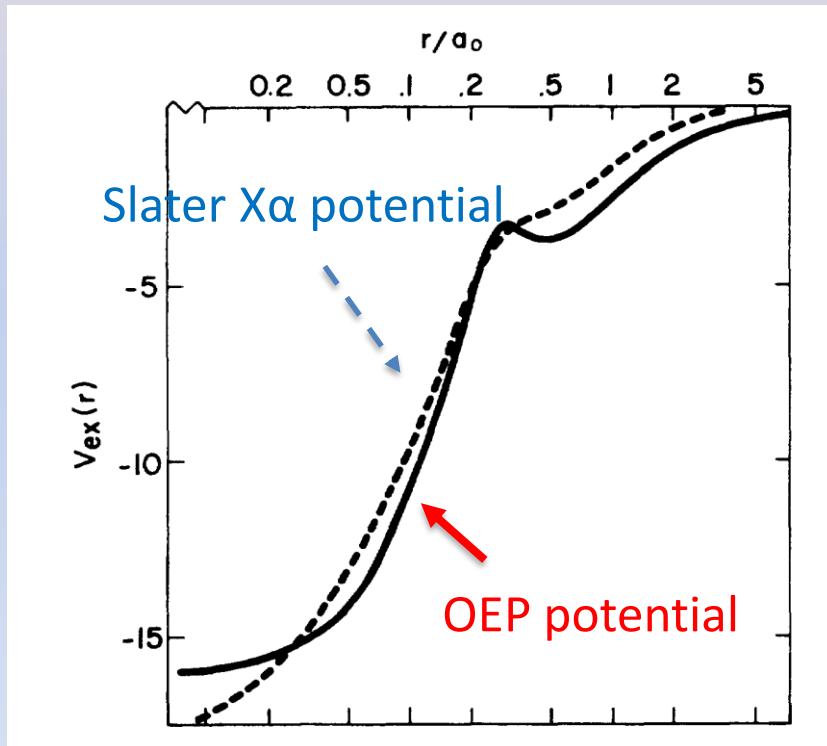
Some results: the Ar atom

TABLE I. Total energy and eigenvalues (absolute values) in hartrees for the Ar atom. First line, LDA, using the parametrization of [Perdew and Wang \(1992\)](#); second line, OEP values from the exchange-only functional; third line, exchange-only KLI approximation (both from [Kümmel and Perdew, 2003a](#)); fourth line, Hartree-Fock values (from [Heinemann *et al.*, 1990](#); [Li *et al.*, 1993](#)).

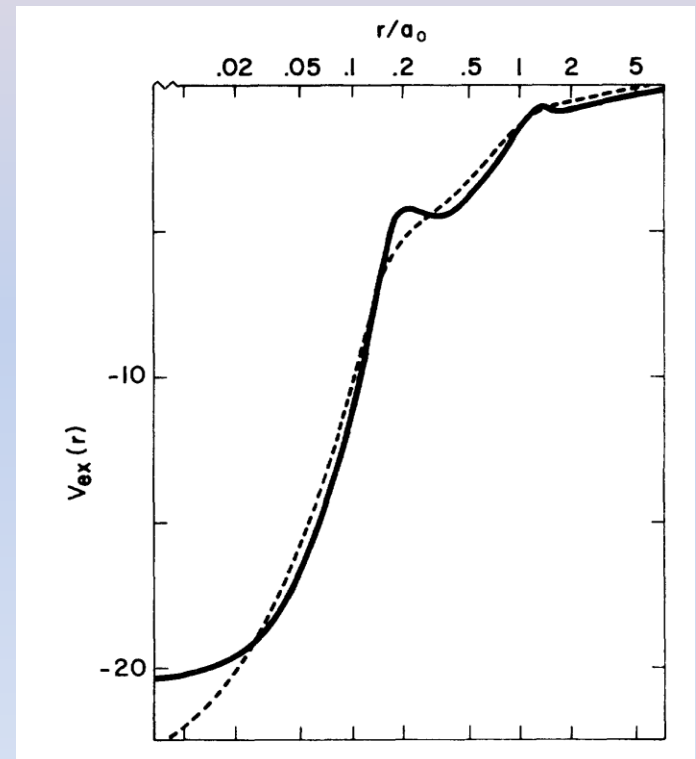
v_{xc}	E	ε_1	ε_2	ε_3	ε_4	ε_5
xc-LDA	525.9398	113.8001	10.7940	8.4433	0.8832	0.3822
x-OEP	526.8122	114.4522	11.1532	8.7338	1.0993	0.5908
x-KLI	526.8105	114.4279	11.1820	8.7911	1.0942	0.5893
HF	526.8175	118.6104	12.3222	9.5715	1.2774	0.5910

The exact-exchange OEP potential

J. D. Talman and W. F. Shadwick, Phys. Rev. A, 14, 36 (1976)



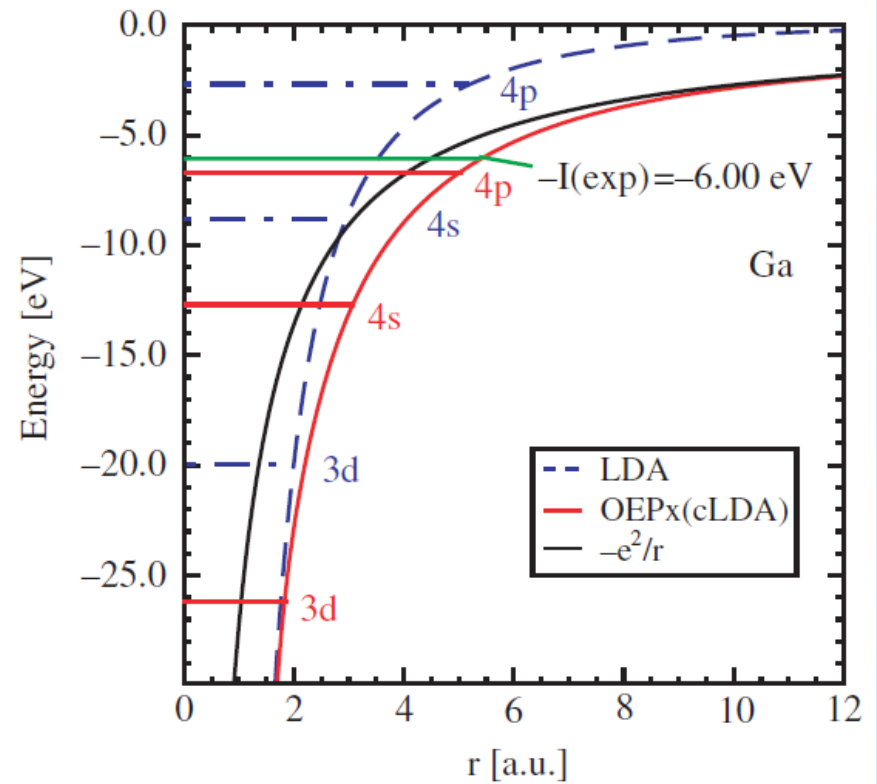
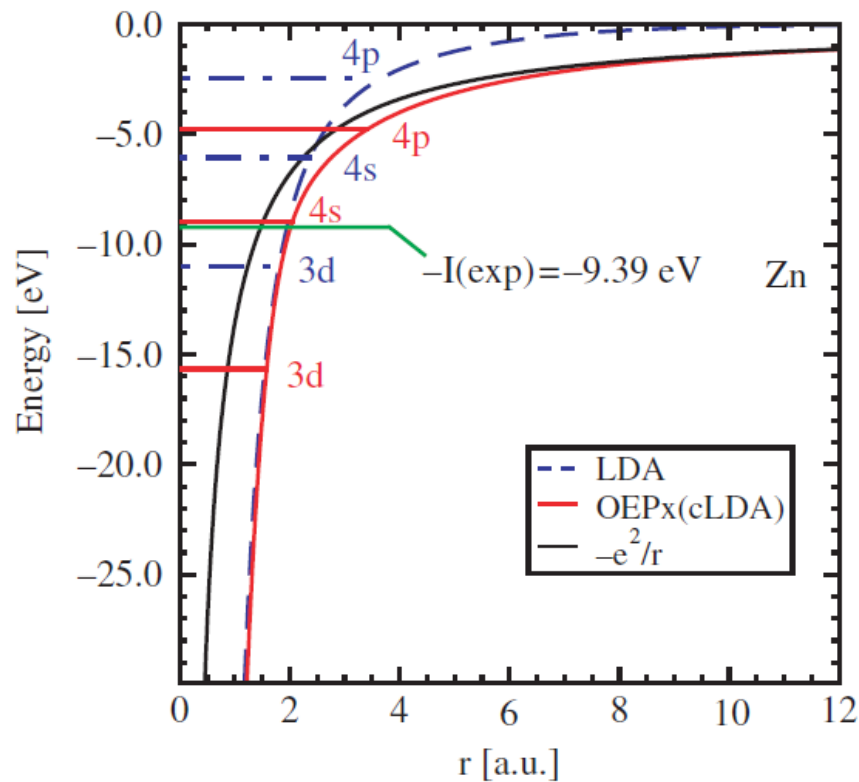
Ne atom



Al atom

Atomic energy levels

P. Rinke et al. New J. Phys. 7, 126 (2005)



Band gaps

P. Rinke et al. New J. Phys. 7, 126 (2005)

