The kohn-Sham method: Elaboration
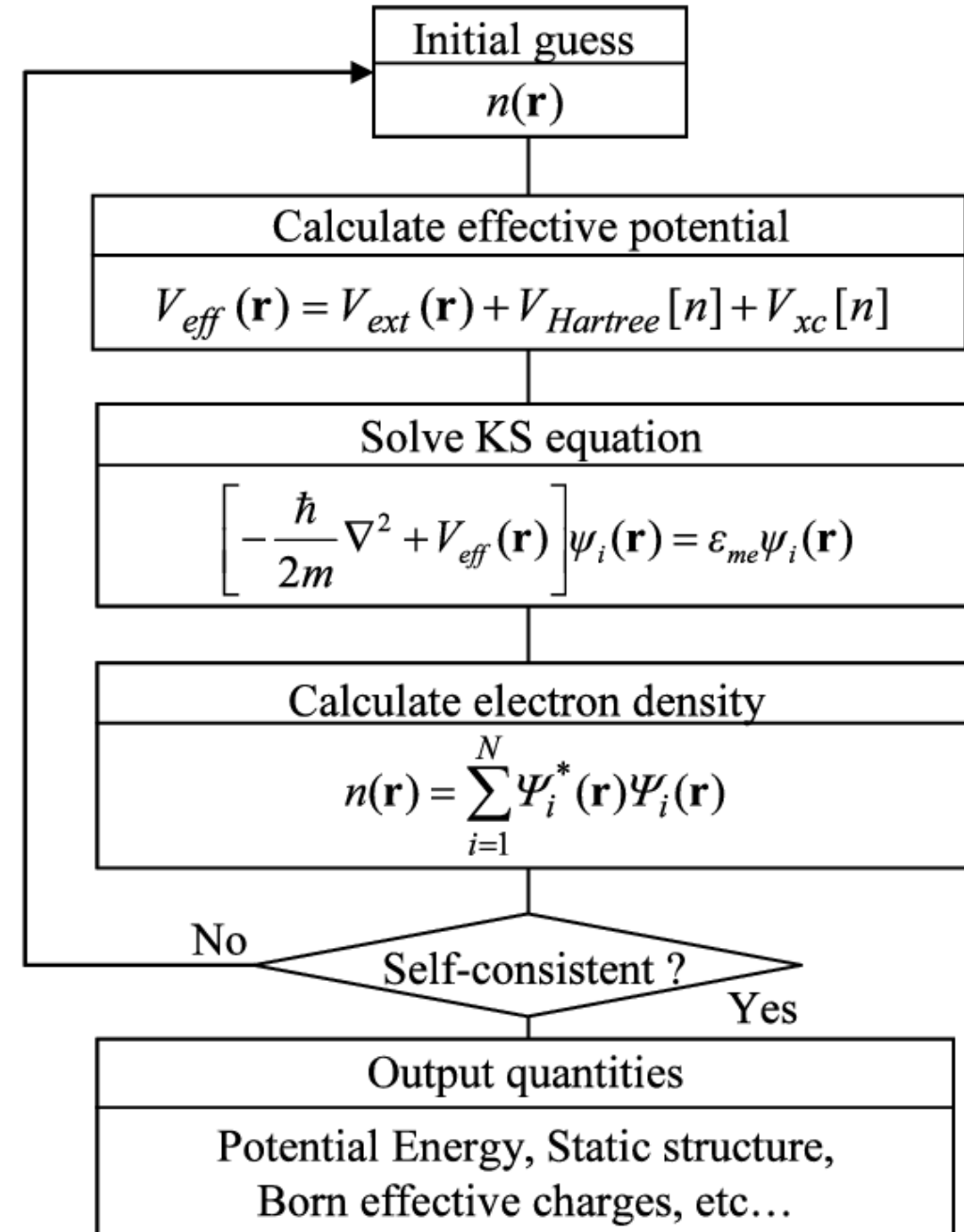
Density-Functional Theory of Atoms and Molecules
– Robert G. Parr and Weitao Yang

Chapter 8

Kohn-Sham method

$$v_{\text{eff}}(\mathbf{r}) = v(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{xc}(\mathbf{r})$$

Initial guess

$n(\mathbf{r})$

Calculate effective potential

$V_{eff}(\mathbf{r}) = V_{ext}(\mathbf{r}) + V_{Hartree}[n] + V_{xc}[n]$

Solve KS equation

$\left[-\frac{\hbar}{2m}\nabla^2 + V_{eff}(\mathbf{r}) \right]\psi_i(\mathbf{r}) = \varepsilon_{me}\psi_i(\mathbf{r})$

Calculate electron density

$n(\mathbf{r}) = \sum_{i=1}^{N} \Psi_i^*(\mathbf{r})\Psi_i(\mathbf{r})$

No   Self-consistent ?   Yes

Output quantities

Potential Energy, Static structure,
Born effective charges, etc…

Article to read

Perspective: Fifty years of density-functional theory in chemical physics

Axel D. Becke

Local density approximation

$$E_{xc}^{\text{LDA}}[\rho] = \int \rho(\mathbf{r})\varepsilon_{xc}(\rho)\, d\mathbf{r}$$

$$v_{xc}^{\text{LDA}}(\mathbf{r}) = \frac{\delta E_{xc}^{\text{LDA}}}{\delta\rho(\mathbf{r})} = \varepsilon_{xc}(\rho(\mathbf{r})) + \rho(\mathbf{r})\frac{\delta\varepsilon_{xc}(\rho)}{\delta\rho}$$

$$\left[-\frac{1}{2}\nabla^2 + v(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\, d\mathbf{r}' + v_{xc}^{\text{LDA}}(\mathbf{r}) \right]\psi_i = \varepsilon_i\psi_i.$$

Local density approximation

$$\varepsilon_{xc}(\rho) = \varepsilon_x(\rho) + \varepsilon_c(\rho)$$

$$\varepsilon_x(\rho) = -C_x \rho(\mathbf{r})^{1/3}, \qquad C_x = \frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3}$$

$$\varepsilon_c(r_s) = \frac{A}{2}\left\{\ln\frac{x}{X(x)} + \frac{2b}{Q}\tan^{-1}\frac{Q}{2x+b}\right.$$
$$\left. - \frac{bx_0}{X(x_0)}\left[\ln\frac{(x-x_0)^2}{X(x)} + \frac{2(b+2x_0)}{Q}\tan^{-1}\frac{Q}{2x+b}\right]\right\} \quad (E.27)$$

where $x = r_s^{1/2}$, $X(x) = x^2 + bx + c$, and $Q = (4c - b^2)^{1/2}$. For $\varepsilon_c^0(r_s)$, $A = 0.0621814$, $x_0 = -0.409286$, $b = 13.0720$, and $c = 42.7198$; for $\varepsilon_c^1(r_s)$, $A = \frac{1}{2}(0.0621814)$, $x_0 = -0.743294$, $b = 20.1231$, and $c = 101.578$. These formulas are generally accepted as the most accurate available for the uniform-gas correlation energy per particle.

Spin-density functional theory

In the presence of a magnetic field $\mathbf{B(r)}$ that acts only on the spins of the electrons, the Hamiltonian of the system becomes

$$\hat{H} = -\frac{1}{2}\sum_i^N \nabla_i^2 + \sum_{i<j}^N \frac{1}{r_{ij}} + \sum_i^N v(\mathbf{r}_i) + 2\beta_e \sum_i^N \mathbf{B(r)} \cdot \mathbf{s}_i \qquad (8.1.1)$$

where $\beta_e = e\hbar/2mc$ is the Bohr magneton and $\mathbf{s}_i$ is the electron spin angular momentum vector for the ith electron (Levine 1983, p. 285).

Spin-density functional theory

$$\hat{V} = \sum_{i}^{N} v(\mathbf{r}_i) + 2\beta_e \sum_{i}^{N} \mathbf{B}(\mathbf{r}_i) \cdot \mathbf{s}_i$$

$$= \int v(\mathbf{r})\hat{\rho}(\mathbf{r})\, d\mathbf{r} - \int \mathbf{B}(\mathbf{r}) \cdot \hat{\mathbf{m}}(\mathbf{r})\, d\mathbf{r}$$

$$\langle \Psi | \hat{V} | \Psi \rangle = \int v(\mathbf{r})\rho(\mathbf{r})\, d\mathbf{r} - \int \mathbf{B}(\mathbf{r}) \cdot \mathbf{m}(\mathbf{r})\, d\mathbf{r}$$

$$\langle \Psi | \hat{V} | \Psi \rangle = \int v(\mathbf{r})\rho(\mathbf{r})\, d\mathbf{r} - \int b(\mathbf{r})m(\mathbf{r})\, d\mathbf{r}$$

$$\hat{\mathbf{m}}(\mathbf{r}) = -2\beta_e \sum_{i}^{N} \mathbf{s}_i\, \delta(\mathbf{r} - \mathbf{r}_i)$$

$$\hat{\rho}(\mathbf{r}) = \sum_{i}^{N} \delta(\mathbf{r} - \mathbf{r}_i)$$

$$\rho(\mathbf{r}) = \langle \Psi | \hat{\rho}(\mathbf{r}) | \Psi \rangle$$

$$\mathbf{m}(\mathbf{r}) = \langle \Psi | \hat{\mathbf{m}}(\mathbf{r}) | \Psi \rangle$$

We shall discuss only the simple case of z-direction $b(\mathbf{r})$

Spin-density functional theory

$$m(\mathbf{r}) = -2\beta_e \langle \Psi | \sum_i^N s_z(i)\, \delta(\mathbf{r} - \mathbf{r}_i) | \Psi \rangle$$

$$= -2\beta_e \int s_z\, \delta(\mathbf{r} - \mathbf{r}')\gamma_1(\mathbf{x}', \mathbf{x}')\, d\mathbf{x}'$$

$$= -2\beta_e \sum_{s=\alpha,\beta} s_z \gamma_1(\mathbf{r}s, \mathbf{r}s)$$

$$= -2\beta_e[\tfrac{1}{2}\gamma_1(\mathbf{r}\alpha, \mathbf{r}\alpha) + (-\tfrac{1}{2})\gamma_1(\mathbf{r}\beta, \mathbf{r}\beta)]$$

$$= \beta_e[\rho^\beta(\mathbf{r}) - \rho^\alpha(\mathbf{r})]$$

Spin-density functional theory

$$E_0 = \underset{\Psi}{\text{Min}} \langle \Psi | \; \hat{T} + \hat{V}_{ee} + \sum_i^N v(\mathbf{r}_i) + 2\beta_e \sum_i^N b(\mathbf{r}_i) \cdot \mathbf{s}_z(i) \; | \Psi \rangle$$

$$= \underset{\rho^\alpha, \rho^\beta}{\text{Min}} \left\{ \underset{\Psi \to \rho^\alpha, \rho^\beta}{\text{Min}} \langle \Psi | \; \hat{T} + \hat{V}_{ee} \; | \Psi \rangle + \int [v(\mathbf{r})\rho(\mathbf{r}) - b(\mathbf{r})m(\mathbf{r})] \, d\mathbf{r} \right\}$$

$$= \underset{\rho^\alpha, \rho^\beta}{\text{Min}} \left\{ F[\rho^\alpha, \rho^\beta] + \int d\mathbf{r}[(v(\mathbf{r}) + \beta_e b(\mathbf{r}))\rho^\alpha(\mathbf{r}) + (v(\mathbf{r}) - \beta_e b(\mathbf{r}))\rho^\beta(\mathbf{r})] \right\}$$

where

$$F[\rho^\alpha, \rho^\beta] = \underset{\Psi \to \rho^\alpha, \rho^\beta}{\text{Min}} \langle \Psi | \; \hat{T} + \hat{V}_{ee} \; | \Psi \rangle$$

Spin-density functional theory

The Kohn–Sham method can now be introduced to rigorously handle the kinetic-energy contribution to $F[\rho^\alpha, \rho^\beta]$. In the manner of (7.1.13), define

$$F[\rho^\alpha, \rho^\beta] = T_s[\rho^\alpha, \rho^\beta] + J[\rho^\alpha + \rho^\beta] + E_{xc}[\rho^\alpha, \rho^\beta] \qquad (8.1.12)$$

where $T_s[\rho^\alpha, \rho^\beta]$ is the Kohn–Sham kinetic-energy functional corresponding to a system of noninteracting electrons with densities ρ^α and ρ^β, and $E_{xc}[\rho^\alpha, \rho^\beta]$ is the exchange-correlation-energy functional.

$$T_s[\rho^\alpha, \rho^\beta] = \text{Min}\left[\sum_{i\sigma} n_{i\sigma} \int d\mathbf{r}\, \phi_{i\sigma}^*(\mathbf{r})\left(-\tfrac{1}{2}\nabla^2\right)\phi_{i\sigma}(\mathbf{r})\right]$$

$$\sum_i n_{i\alpha}\,|\phi_{i\alpha}(\mathbf{r})|^2 = \rho^\alpha(\mathbf{r}), \qquad \sum_i n_{i\beta}\,|\phi_{i\beta}(\mathbf{r})|^2 = \rho^\beta(\mathbf{r})$$

Spin-density functional theory

$$T_s[\rho^\alpha, \rho^\beta] = \sum_{i\sigma} n_{i\sigma} \int d\mathbf{r}\phi_{i\sigma}^*(\mathbf{r})(-\tfrac{1}{2}\nabla^2)\phi_{i\sigma}(\mathbf{r})$$

$$E[\rho^\alpha, \rho^\beta] = \sum_{i\sigma} n_{i\sigma} \int d\mathbf{r}\phi_{i\sigma}^*(\mathbf{r})(-\tfrac{1}{2}\nabla^2)\phi_{i\sigma}(\mathbf{r}) + J[\rho^\alpha + \rho^\beta] + E_{xc}[\rho^\alpha, \rho^\beta]$$

$$+ \int d\mathbf{r}[(v(\mathbf{r}) + \beta_e b(\mathbf{r}))\rho^\alpha(\mathbf{r}) + (v(\mathbf{r}) - \beta_e b(\mathbf{r})\rho^\beta(\mathbf{r}))] \quad (8.1.16)$$

The variational search for the minimum of $E[\rho^\alpha, \rho^\beta]$ can then be carried out through orbitals, subject to normalization constraints:

$$\int \phi_{i\sigma}(\mathbf{r})\phi_{i\sigma}(\mathbf{r})\, d\mathbf{r} = 1 \quad (8.1.17)$$

Spin-density functional theory

The resulting Kohn–Sham equations are

$$\hat{h}_{\text{eff}}^{\alpha}\phi_{i\alpha}(\mathbf{r}) = \left[-\tfrac{1}{2}\nabla^2 + v_{\text{eff}}^{\alpha}(\mathbf{r})\right]\phi_{i\alpha}(\mathbf{r})$$

$$= \frac{\varepsilon_{i\alpha}'}{n_{i\alpha}}\phi_{i\alpha}(\mathbf{r}) = \varepsilon_{i\alpha}\phi_{i\alpha}(\mathbf{r}), \qquad i = 1, 2, \ldots, N^{\alpha}$$

$$\hat{h}_{\text{eff}}^{\beta}\phi_{j\beta}(\mathbf{r}) = \left[-\tfrac{1}{2}\nabla^2 + v_{\text{eff}}^{\beta}(\mathbf{r})\right]\phi_{j\beta}(\mathbf{r})$$

$$= \frac{\varepsilon_{j\beta}'}{n_{j\beta}}\phi_{j\beta}(\mathbf{r}) = \varepsilon_{j\beta}\phi_{j\beta}(\mathbf{r}), \qquad j = 1, 2, \ldots, N^{\beta}$$

$$N^{\alpha} = \int d\mathbf{r}\, \rho^{\alpha}(\mathbf{r}), \qquad N^{\beta} = \int d\mathbf{r}\, \rho^{\beta}(\mathbf{r}) \qquad\qquad N = N^{\alpha} + N^{\beta}$$

Spin-density functional theory

where the spin-dependent effective potentials are

$$v_{eff}^{\alpha} = v(\mathbf{r}) + \beta_e b(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{r}' + \frac{\delta E_{xc}[\rho^{\alpha}, \rho^{\beta}]}{\delta \rho^{\alpha}(\mathbf{r})}$$

$$v_{eff}^{\beta} = v(\mathbf{r}) - \beta_e b(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{r}' + \frac{\delta E_{xc}[\rho^{\alpha}, \rho^{\beta}]}{\delta \rho^{\beta}(\mathbf{r})}$$

$$N^{\alpha} = \int d\mathbf{r} \, \rho^{\alpha}(\mathbf{r}), \qquad N^{\beta} = \int d\mathbf{r} \, \rho^{\beta}(\mathbf{r})$$

$$N = N^{\alpha} + N^{\beta}$$

Spin-density functional theory

$$T_s[\rho^\alpha, \rho^\beta] = \sum_{i\sigma} n_{i\sigma} \int d\mathbf{r} \phi_{i\sigma}^*(\mathbf{r})(-\tfrac{1}{2}\nabla^2)\phi_{i\sigma}(\mathbf{r})$$

$$T_s[\rho^\alpha, \rho^\beta] = T_s[\rho^\alpha, 0] + T_s[0, \rho^\beta]$$

$$T_s[\rho^\alpha, 0] = \sum_{i\alpha} n_{i\alpha} \int d\mathbf{r}\, \phi_{i\alpha}^*(\mathbf{r})(-\tfrac{1}{2}\nabla^2)\phi_{i\alpha}(\mathbf{r})$$

$$\rho^\alpha(\mathbf{r}) = \rho^\beta(\mathbf{r}) = \tfrac{1}{2}\rho(\mathbf{r})$$

Spin-density functional theory

$$T_s[\tfrac{1}{2}\rho, \tfrac{1}{2}\rho] = T_s[\tfrac{1}{2}\rho, 0] + T_s[0, \tfrac{1}{2}\rho]$$
$$= 2T_s[\tfrac{1}{2}\rho, 0]$$

$$\rho^{\alpha}(\mathbf{r}) = \rho^{\beta}(\mathbf{r}) = \tfrac{1}{2}\rho(\mathbf{r})$$

$$T_s[\rho^{\alpha}, \rho^{\beta}] = T_s[\rho^{\alpha}, 0] + T_s[0, \rho^{\beta}]$$

$$T_s[\tfrac{1}{2}\rho, 0] = T_s[0, \tfrac{1}{2}\rho]$$

$$T_s^0[\rho] = T_s[\tfrac{1}{2}\rho, \tfrac{1}{2}\rho]$$

$$T_s[\rho^{\alpha}, \rho^{\beta}] = \tfrac{1}{2}T_s^0[2\rho^{\alpha}] + \tfrac{1}{2}T_s^0[2\rho^{\beta}]$$

Spin-density functionals and the local spin-density approximations

With the spin-polarized Kohn–Sham equations of §8.1, the kinetic energy is handled exactly and only the exchange-correlation energy remains to be determined. The exchange-correlation contribution can be separated into exchange and correlation pieces:

$$E_{xc}[\rho^\alpha, \rho^\beta] = E_x[\rho^\alpha, \rho^\beta] + E_c[\rho^\alpha, \rho^\beta] \tag{8.2.11}$$

where the exchange part is defined from (2.5.24) as

$$E_x[\rho^\alpha, \rho^\beta] = -\frac{1}{2} \int\int \frac{1}{r_{12}} \left[|\rho_1^{\alpha\alpha}(\mathbf{r}_1, \mathbf{r}_2)|^2 + |\rho_1^{\beta\beta}(\mathbf{r}_1, \mathbf{r}_2)|^2\right] d\mathbf{r}_1 \, d\mathbf{r}_2$$

Spin-density functionals and the local spin-density approximations

$$E_x[\rho^\alpha, \rho^\beta] = -\frac{1}{2} \iint \frac{1}{r_{12}} [|\rho_1^{\alpha\alpha}(\mathbf{r}_1, \mathbf{r}_2)|^2 + |\rho_1^{\beta\beta}(\mathbf{r}_1, \mathbf{r}_2)|^2] \, d\mathbf{r}_1 \, d\mathbf{r}_2$$

$$\rho_1^{\alpha\alpha}(\mathbf{r}_1, \mathbf{r}_2) = \sum_i n_{i\alpha} \phi_{i\alpha}(\mathbf{r}_1) \phi_{i\alpha}^*(\mathbf{r}_2)$$

$$\rho_1^{\beta\beta}(\mathbf{r}_1, \mathbf{r}_2) = \sum_i n_{i\beta} \phi_{i\beta}(\mathbf{r}_1) \phi_{i\beta}^*(\mathbf{r}_2)$$

Spin-density functionals and the local spin-density approximations

$$E_x[\rho^\alpha, \rho^\beta] = \tfrac{1}{2}E_x[\rho^\alpha, \rho^\alpha] + \tfrac{1}{2}E_x[\rho^\beta, \rho^\beta]$$

$$= \tfrac{1}{2}E_x^0[2\rho^\alpha] + \tfrac{1}{2}E_x^0[2\rho^\beta]$$

$$E_x^0[\rho] = E_x[\tfrac{1}{2}\rho, \tfrac{1}{2}\rho]$$

$$E_x^{\text{LSD}}[\rho^\alpha, \rho^\beta] = 2^{1/3}C_x \int [(\rho^\alpha)^{4/3} + (\rho^\beta)^{4/3}]\, d\mathbf{r}$$

Local spin-density approximation (LSD)

Define the spin polarization parameter ζ by

$$\zeta = \frac{\rho^{\alpha} - \rho^{\beta}}{\rho} = \frac{\rho^{\alpha} - \rho^{\beta}}{\rho^{\alpha} + \rho^{\beta}}$$

Then $\rho^{\alpha} = \frac{1}{2}(1 + \zeta)\rho$, $\rho^{\beta} = \frac{1}{2}(1 - \zeta)\rho$, and the LSD exchange energy becomes

$$E_x^{\text{LSD}}[\rho^{\alpha}, \rho^{\beta}] = \frac{1}{2}C_x \int \rho^{4/3}[(1 + \zeta)^{4/3} + (1 - \zeta)^{4/3}]\, d\mathbf{r}$$

$$= \int \rho \varepsilon_x(\rho, \zeta)\, d\mathbf{r} \qquad (8.2.18)$$

where

$$\varepsilon_x(\rho, \zeta) = \varepsilon_x^0(\rho) + [\varepsilon_x^1(\rho) - \varepsilon_x^0(\rho)]f(\zeta) \qquad (8.2.19)$$

with the exchange density for the spin-compensated ("paramagnetic") homogeneous electron gas given by

$$\varepsilon_x^0(\rho) = \varepsilon_x(\rho, 0) = C_x \rho^{1/3} \qquad (8.2.20)$$

for spin-completely-polarized ("ferromagnetic") homogeneous electron gas

$$\varepsilon_x^1(\rho) = \varepsilon_x(\rho, 1) = 2^{1/3} C_x \rho^{1/3} \qquad (8.2.21)$$

and

$$f(\zeta) = \tfrac{1}{2}(2^{1/3} - 1)^{-1}[(1 + \zeta)^{4/3} + (1 - \zeta)^{4/3} - 2] \qquad (8.2.22)$$

The LSD exchange energy density was originally cast in the form (8.2.19) by von Barth and Hedin (1972); the quantity $f(\zeta)$ serves as a weight factor between the two extreme cases $\zeta = 0$ and $\zeta = 1$.

Table 8.1 Ionization Potentials in electron volts of Some Light Atoms Calculated in the LSD, LDA, and HF Approximations

Atom	LSD	LDA	HF	Exptl.
H	13.4	12.0	—	13.6
He	24.5	26.4	—	24.6
Li	5.7	5.4	5.3	5.4
Be	9.1	—	8.0	9.3
B	8.8	—	7.9	8.3
C	12.1	—	10.8	11.3
N	15.3	—	14.0	14.5
O	14.2	16.5	11.9	13.6
F	18.4	—	16.2	17.4
Ne	22.6	22.5	19.8	21.6
Na	5.6	5.3	4.9	5.1
Ar	16.2	16.1	14.8	15.8
K	4.7	4.5	4.0	4.3

Note: LSD = local spin-density method; LDA = local-density approximation; HF = Hartree–Fock.

Table 8.2 LSD Spectroscopic Constants for Diatomic Molecules[a]

	r_e (bohrs)		D_e (eV)		ω_e (cm^{-1})	
	Expt.	LSD	Expt.	LSD	Expt.	LSD
H_2	1.40	1.45	4.8	4.9	4400	4190
Li_2	5.05	5.12	1.1	1.0	350	330
B_2	3.00	3.03	3.0	3.9	1050	1030
C_2	2.35	2.35	6.3	7.3	1860	1880
N_2	2.07	2.07	9.9	11.6	2360	2380
O_2	2.28	2.27	5.2	7.6	1580	1620
F_2	2.68	2.61	1.7	3.4	890	1060
Na_2	5.82	5.67	0.8	0.9	160	160
Al_2	4.66	4.64	1.8	2.0	350	350
Si_2	4.24	4.29	3.1	4.0	510	490
P_2	3.58	3.57	5.1	6.2	780	780
S_2	3.57	3.57	4.4	5.9	730	720
Cl_2	3.76	3.74	2.5	3.6	560	570

More to read

- Self-interaction correction

- The exchange-correlation-energy functional via the exchange-correlation hole

- The exchange-correlation-energy functional via wave-vector analysis

TOPICAL REVIEW

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Thirty years of density functional theory in computational chemistry: an overview and extensive assessment of 200 density functionals

Narbe Mardirossian[a] and Martin Head-Gordon[a,b]

[a]Kenneth S. Pitzer Center for Theoretical Chemistry, Department of Chemistry, University of California, Berkeley, CA, USA; [b]Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA, USA

Generalized gradient approximation (GGA)

$$E_x^{GGA}[\rho] = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3} \int d\mathbf{r}\ \rho^{4/3} F(s)$$

$$s = \frac{|\nabla\rho(r)|}{(2k_F\rho)}$$

$$k_F = (3\pi^2\rho)^{1/3}$$

$$F(s) = (1 + 1.296s^2 + 14s^4 + 0.2s^6)^{1/15}$$

Table 8.5 Exchange Energies E_x of Neutral Atoms Calculated from Nonrelativistic Hartree–Fock Densities[a,b]

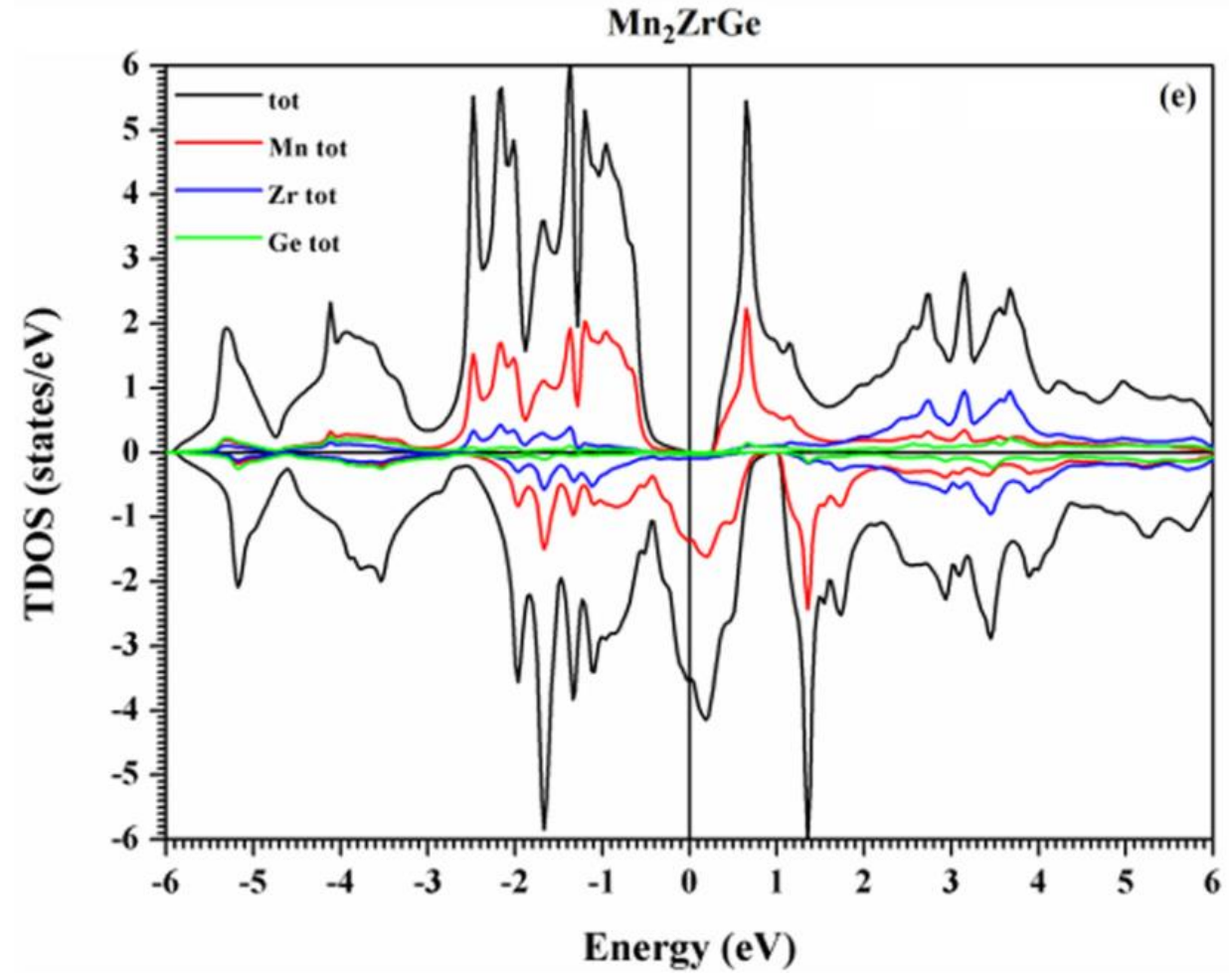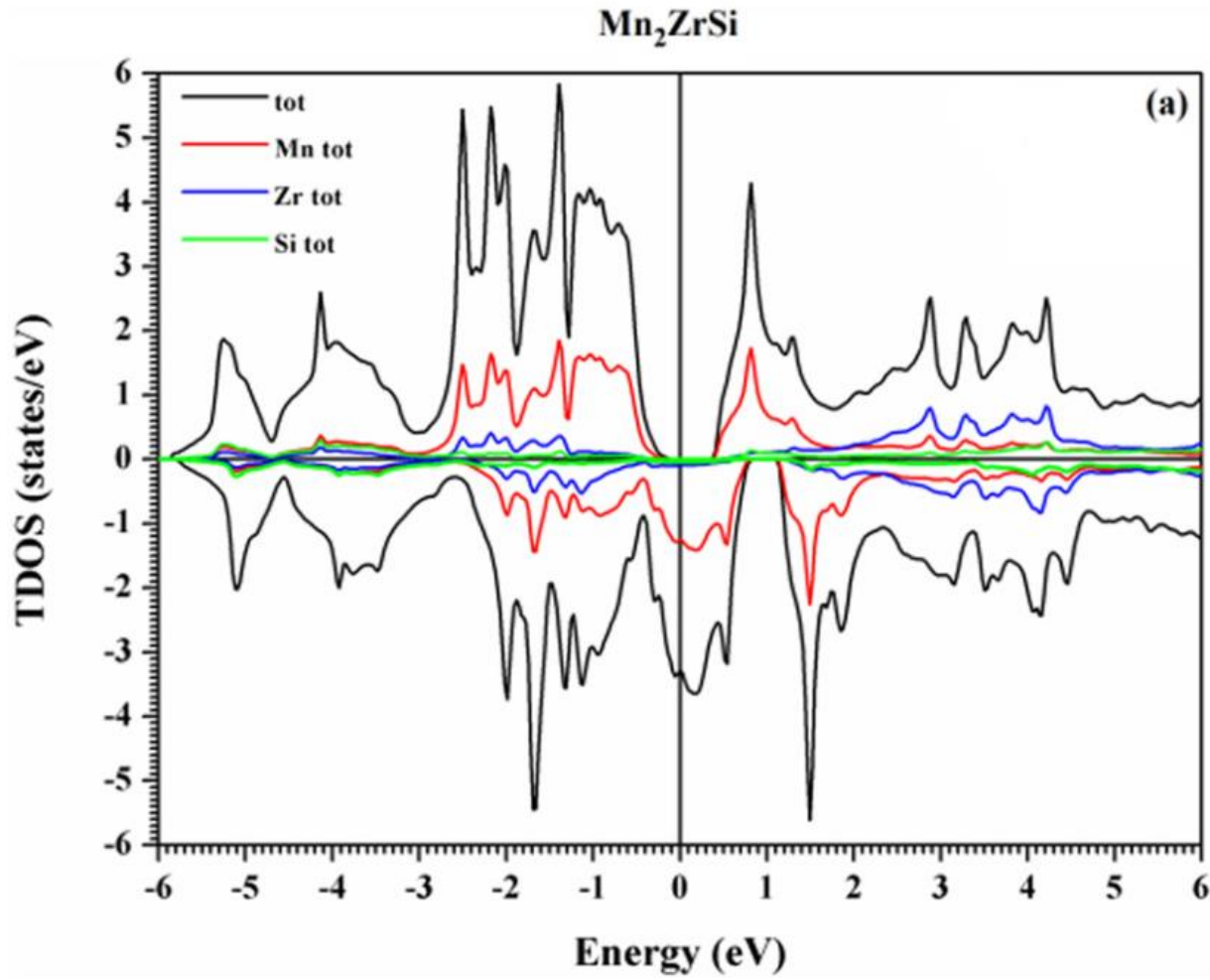| Atom	LSD	IM	GGA	Exact
H	−0.268	−0.308	−0.311	−0.3125
He	−0.884	−1.015	−1.033	−1.026
Li	−1.538	−1.747	−1.789	−1.781
Be	−2.31	−2.60	−2.68	−2.67
Ne	−11.03	−11.82	−12.22	−12.11
Ar	−27.86	−29.39	−30.29	−30.18
Zn	−65.63	−68.25	−69.93	−69.7
Kr	−88.6	−91.8	−93.8	−93.9
Xe	−170.6	−175.6	−178.6	−179.1

[a] From Perdew and Yue (1986).

[b] LSD is the local spin density formula of (8.2.16), IM is the Langreth–Mehl formula of (8.6.21), GGA is the Perdew–Yue formula (8.7.1).
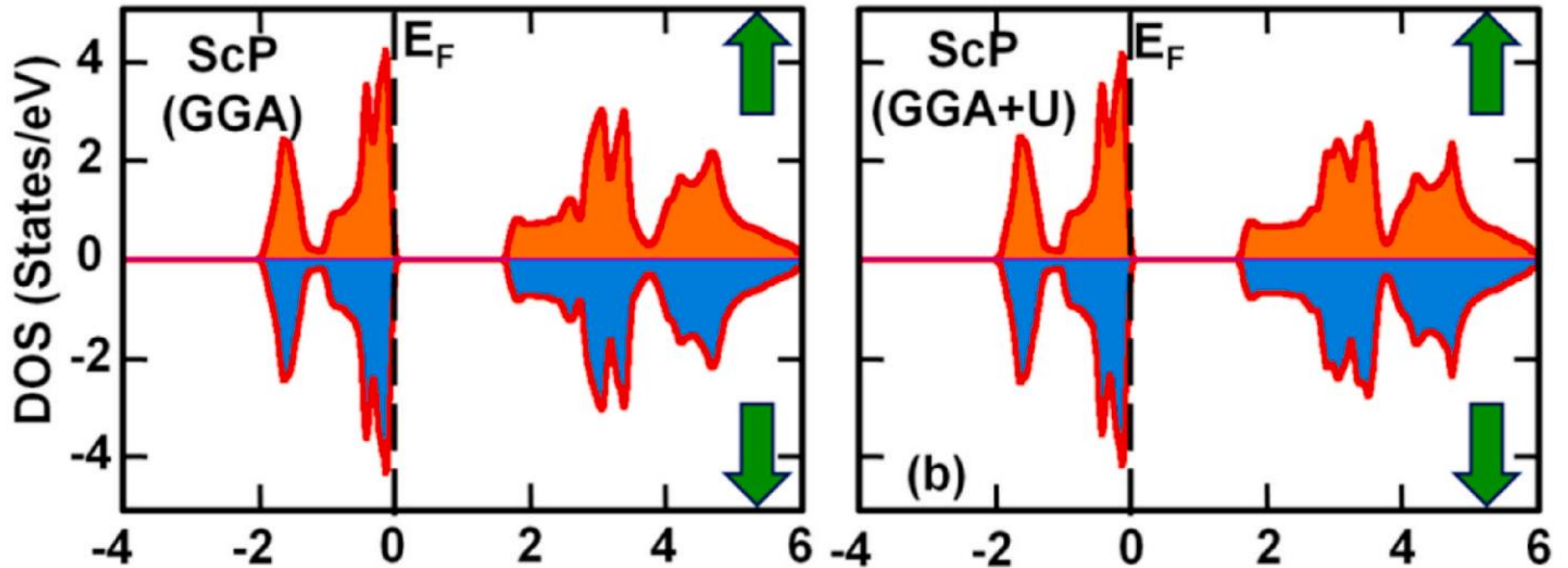
Next topic

Plasmons, Polaritons, Polarons and Phonons: Dielectric function of the electron gas, Dispersion relation for electromagnetic waves, Plasma oscillations, Plasmons, Electrostatic screening, Screening & phonons in metals, Polaritons and L.S.T relation, Electron-electron interaction, polaron and electron phonon interaction.

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