大学院：固体物理1

内容

1. 結晶の周期性と電子の振舞い
2. 多電子波動関数とハートレー・フォック近似
3. 温度グリーン関数
4. 電子ガス
5. フェルミ液体
6. 密度汎関数理論
7. 電子相関
8. 金属・絶縁体転移

6．密度汎関数理論

エネルギー汎関数

$$Q[n_\uparrow, n_\downarrow] = \underset{\Psi\in\{n_\uparrow n_\downarrow\}}{\mathrm{Min}} \langle \Psi_{n_\uparrow n_\downarrow} | \hat{T} + \hat{V}_{e-e} | \Psi_{n_\uparrow n_\downarrow} \rangle$$

$Q[n_\uparrow, n_\downarrow]$:電子密度のユニバーサルな汎関数

$$E_{DTF}[n_\uparrow, n_\downarrow] \equiv Q[n_\uparrow, n_\downarrow] + \int d\boldsymbol{r} w_{ext}(\boldsymbol{r}) n(\boldsymbol{r}) \geq E_{g.s.}$$

$$n(\boldsymbol{r}) = n_\uparrow(\boldsymbol{r}) + n_\downarrow(\boldsymbol{r})$$

$$\begin{aligned} E_{DTF}[n_\uparrow, n_\downarrow] &= T[n_\uparrow, n_\downarrow] + E^{e-e}[n_\uparrow, n_\downarrow] + \int d\boldsymbol{r} w_{ext}(\boldsymbol{r}) n(\boldsymbol{r}) \ . \\ &= T_0[n_\uparrow, n_\downarrow] + U[n] + E_{xc}[n_\uparrow, n_\downarrow] + \int d\boldsymbol{r} w_{ext}(\boldsymbol{r}) n(\boldsymbol{r}) \end{aligned}$$

$T_0[n_\uparrow, n_\downarrow]$:同じ電子密度を持った相互作用のない系の運動エネルギー

$$U[n] = \frac{1}{2} \int d\boldsymbol{r} d\boldsymbol{r}' \frac{n(\boldsymbol{r}) n(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|}$$

Kohn-Sham 方程式

$$n_\sigma(\boldsymbol{r}) = \sum_\alpha f_{\alpha\sigma} |\psi_{\alpha\sigma}(\boldsymbol{r})|^2$$

$$f_{\alpha\sigma} = 0,\ 1$$

$$T_0[\{f_{\alpha\sigma}, \psi_{\alpha\sigma}\}] = \sum_{\alpha\sigma} f_{\alpha\sigma} \langle \psi_{\alpha\sigma} | -\frac{1}{2}\Delta | \psi_{\alpha\sigma} \rangle$$

$$\left[-\frac{1}{2}\Delta + v^\sigma_{eff}(\boldsymbol{r})\right]\psi_{\alpha\sigma}(\boldsymbol{r}) = \varepsilon_{\alpha\sigma}\psi_{\alpha\sigma}(\boldsymbol{r})\ .$$

$$v^\sigma_{eff}(\boldsymbol{r}) = w_{ext}(\boldsymbol{r}) + \int d\boldsymbol{r}' \frac{n(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} + \frac{\delta E_{xc}[n_\uparrow, n_\downarrow]}{\delta n_\sigma(\boldsymbol{r})} = w_{ext}(\boldsymbol{r}) + v_H(\boldsymbol{r}) + \mu^\sigma_{xc}(\boldsymbol{r})$$

$$\frac{\partial}{\partial f_{\alpha\sigma}} E_{DFT} = \varepsilon_{\alpha\sigma}$$

「ヤナック (Janak) の定理」

$$E_{DFT} = \sum_{\alpha\sigma} f_{\alpha\sigma}\varepsilon_{\alpha\sigma} - \frac{1}{2}\int d\boldsymbol{r} \int d\boldsymbol{r}' \frac{n(\boldsymbol{r})n(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} + E_{xc}[n_\uparrow, n_\downarrow] - \sum_\sigma \int d\boldsymbol{r} n_\sigma(\boldsymbol{r})\mu^\sigma_{xc}(\boldsymbol{r})$$

局所(スピン)密度近似

$$E_{xc} = \int d\boldsymbol{r} n(\boldsymbol{r}) \epsilon_{xc}(n_\uparrow(\boldsymbol{r}), n_\downarrow(\boldsymbol{r}))$$

$$E_{xc} = \sum_\sigma \int d\boldsymbol{r} n_\sigma(\boldsymbol{r}) \epsilon^\sigma_{xc}(n_\uparrow(\boldsymbol{r}), n_\downarrow(\boldsymbol{r}))$$

$$\mu^\sigma_{xc}(\boldsymbol{r}) \equiv \frac{d}{dn_\sigma}\{n\epsilon_{xc}(n_\uparrow, n_\downarrow)\}\Big|_{n_\sigma = n_\sigma(\boldsymbol{r}),\ n_{-\sigma}=n_{-\sigma}(\boldsymbol{r})}$$

$$\mu^\sigma_{xc}(\boldsymbol{r}) \equiv \frac{d}{dn_\sigma}\{\sum_{\sigma'} n_{\sigma'}\epsilon^{\sigma'}_{xc}(n_\uparrow, n_\downarrow)\}\Big|_{n_\sigma = n_\sigma(\boldsymbol{r}),\ n_{-\sigma}=n_{-\sigma}(\boldsymbol{r})}$$

$$\epsilon_x[n(\boldsymbol{r})] = -\frac{3}{4\pi}[3\pi^2 n(\boldsymbol{r})]^{1/3}$$

$$\mu_x(n(\boldsymbol{r})) = \frac{d}{dn} n\epsilon_x[n] = -\frac{1}{\pi}[3\pi^2 n(\boldsymbol{r})]^{1/3} = -\left[\frac{3}{\pi} n(\boldsymbol{r})\right]^{1/3}$$

交換相関エネルギーのパラメータ化

$$\mu = \frac{\partial}{\partial n}(n\epsilon) = \epsilon - \frac{r_s}{3}\frac{\partial \epsilon}{\partial r_s}$$

$$\mu_x = \epsilon_x - \frac{r_s}{3}\frac{\partial \epsilon_x}{\partial r_s}\ , \quad \mu_c = \epsilon_c - \frac{r_s}{3}\frac{\partial \epsilon_c}{\partial r_s}$$

$$\epsilon_x = * - \frac{3}{8}\left(\frac{6}{\pi}\right)^{2/3}\frac{1}{r_s}\{x^{4/3} + (1-x)^{4/3}\}, \quad \mu_x = \frac{4}{3}\epsilon_x\ ,$$

$$\epsilon_x = \epsilon_x^P + \gamma^{-1}\mu_x^P \cdot f(x) \ = \epsilon_x^P + (\epsilon_x^F - \epsilon_x^P)\cdot f(x)\ ,$$

$$f(x) = \frac{1}{1-2^{-1/3}}\{x^{4/3} + (1-x)^{4/3} - 2^{-1/3}\}$$

$$\gamma = \frac{4}{3}\cdot\frac{2^{-1/3}}{1-2^{-1/3}} \simeq 5.1297628\cdots\ ,$$

$$\mu_x = \mu_x^P + (\mu_x^F - \mu_x^P)\cdot f(x)$$

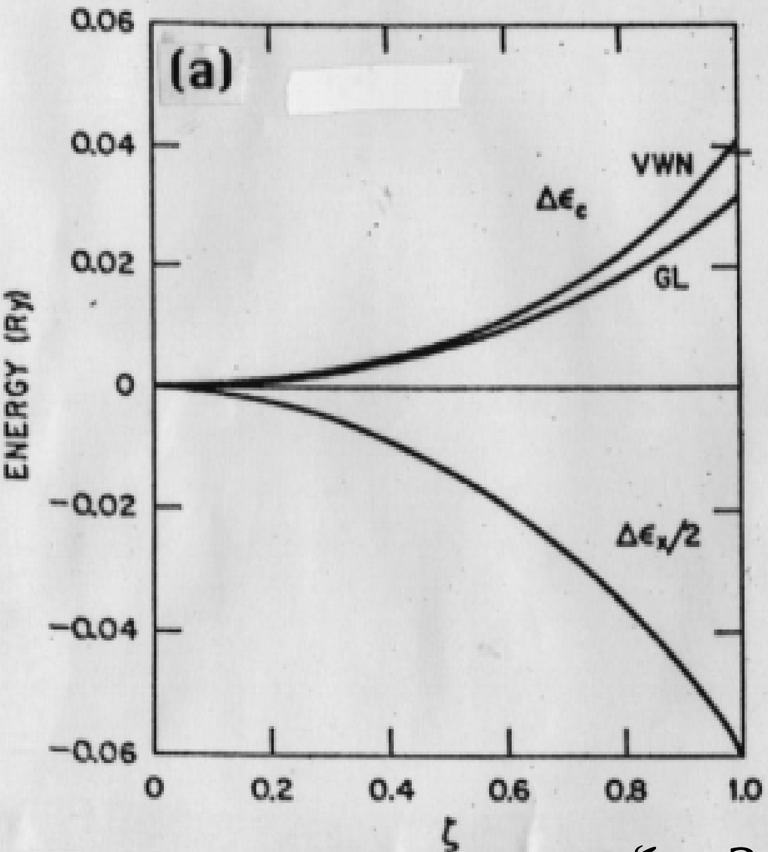
$$\mu_x^P = \frac{4}{3}\epsilon_x^P\ , \quad \mu_x^F = \frac{4}{3}\epsilon_x^F$$

$$\epsilon_x^P = -\frac{3}{8}(\frac{6}{\pi})^{2/3}2^{-1/3}\frac{1}{r_s},$$

$$\epsilon_x^F = -\frac{3}{8}(\frac{6}{\pi})^{2/3}\frac{1}{r_s}$$

$$\epsilon_c = \epsilon_c^P + \gamma^{-1}\nu_c \cdot f(x)\ , \quad \nu_c = \gamma(\epsilon_c^F - \epsilon_c^P)$$

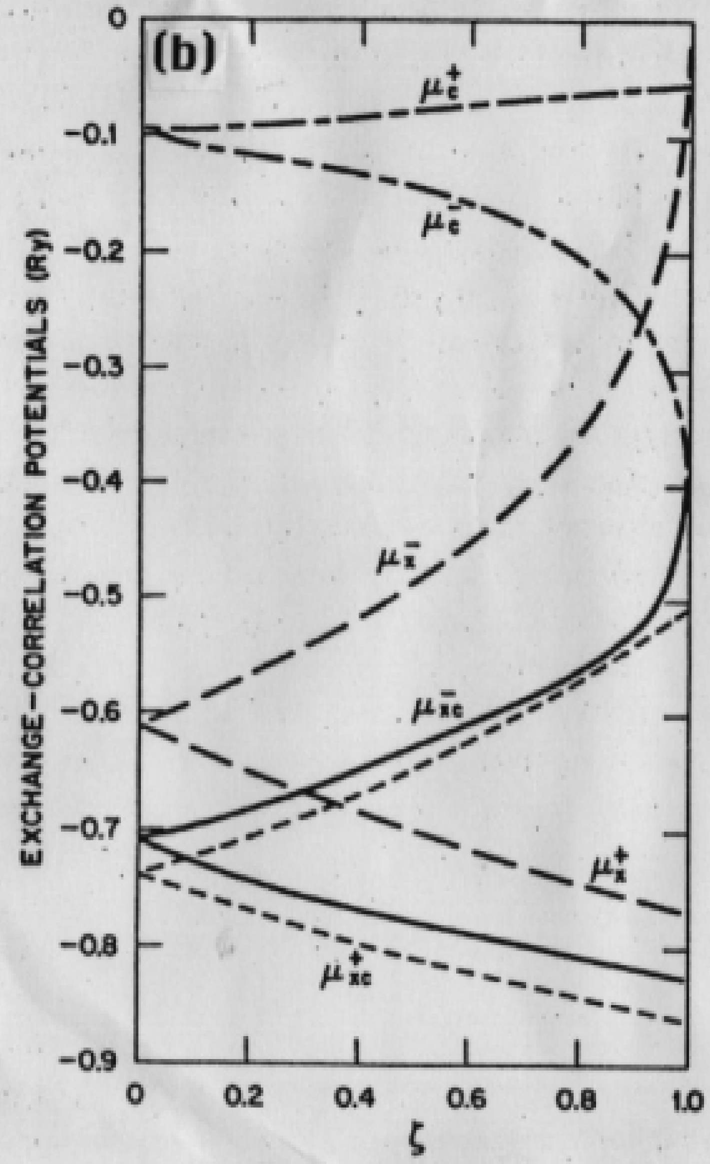
$$\mu_c = \mu_c^P + (\mu_c^F - \mu_c^P)\cdot f(x)$$



$$\zeta = 2x - 1$$

交換エネルギー $\varepsilon_x(r_s) = -\varepsilon_x^0 / r_s + \Delta\varepsilon_x(r_s, \zeta)$

相関エネルギー $\varepsilon_c(r_s) = \varepsilon_c^P + \Delta\varepsilon_c(r_s, \zeta)$



交換相関ポテンシャル

局所近似による交換相関ホール

$$
\begin{aligned}
E_{xc} &= \frac{1}{2}\int d\boldsymbol{r}d\boldsymbol{r}'\frac{n(\boldsymbol{r})n(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}\{\tilde{g}(\boldsymbol{r},\boldsymbol{r}')-1\} \\
\tilde{g}(\boldsymbol{r},\boldsymbol{r}') &= \int_0^{e^2} g_\lambda(\boldsymbol{r},\boldsymbol{r}')d\lambda, \\
n(\boldsymbol{r})n(\boldsymbol{r}')\{g_\lambda(\boldsymbol{r},\boldsymbol{r}')-1\} &= \langle[\hat{n}(\boldsymbol{r})-n(\boldsymbol{r})][\hat{n}(\boldsymbol{r}')-n(\boldsymbol{r}')]\rangle_\lambda - \delta(\boldsymbol{r}-\boldsymbol{r}')n(\boldsymbol{r}) \\
n_{xc}(\boldsymbol{r}_1,\boldsymbol{r}_2) &= n(\boldsymbol{r}_2)\{\tilde{g}(\boldsymbol{r}_1,\boldsymbol{r}_2)-1\}
\end{aligned}
$$

$$\int d\boldsymbol{r}_2 n_{xc}(\boldsymbol{r}_1,\boldsymbol{r}_2) = -1$$

$$n_x(\boldsymbol{r}_1,\boldsymbol{r}_2) = -\frac{\sum_\sigma|\sum_\alpha f_{\alpha\sigma}\psi^*_{\alpha\sigma}(\boldsymbol{r}_1)\psi_{\alpha\sigma}(\boldsymbol{r}_2)|^2}{n(\boldsymbol{r}_1)}$$

$$n_x(\boldsymbol{r}_1,\boldsymbol{r}_2) \le 0\ ,$$

$$n_x(\boldsymbol{r},\boldsymbol{r}) = -\frac{1}{2}n(\boldsymbol{r})\ ,$$

$$\int d\boldsymbol{r}_2 n_x(\boldsymbol{r}_1,\boldsymbol{r}_2) = -1$$

ホールの総和則は交換ホールが担う

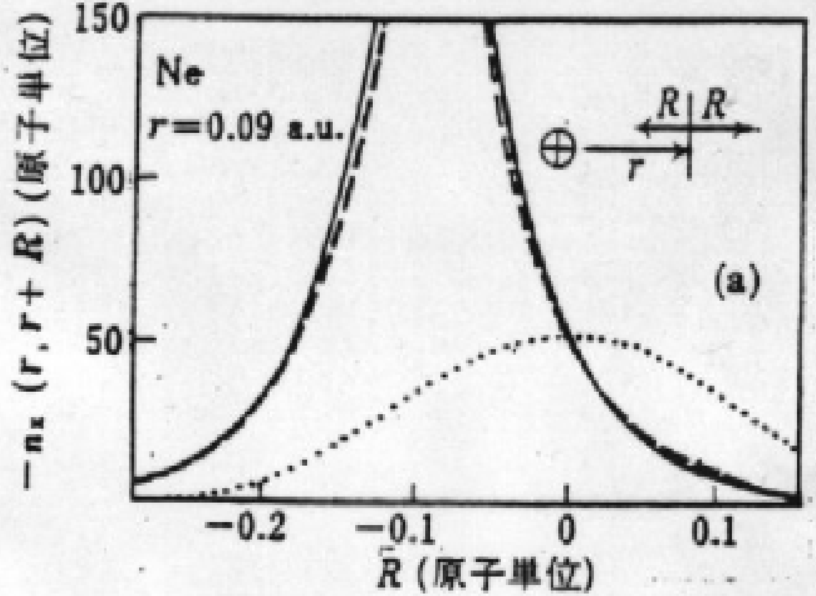
局所近似による交換相関エネルギー

$$n_{xc}(\boldsymbol{r}_1, \boldsymbol{r}_2) = \sum_{\ell=0}^{\infty} \sum_{m} n_{\ell m}(\boldsymbol{r}_1, |\boldsymbol{r}_2 - \boldsymbol{r}_1|) Y_{\ell m}(\widehat{\boldsymbol{r}_2 - \boldsymbol{r}_1}).$$

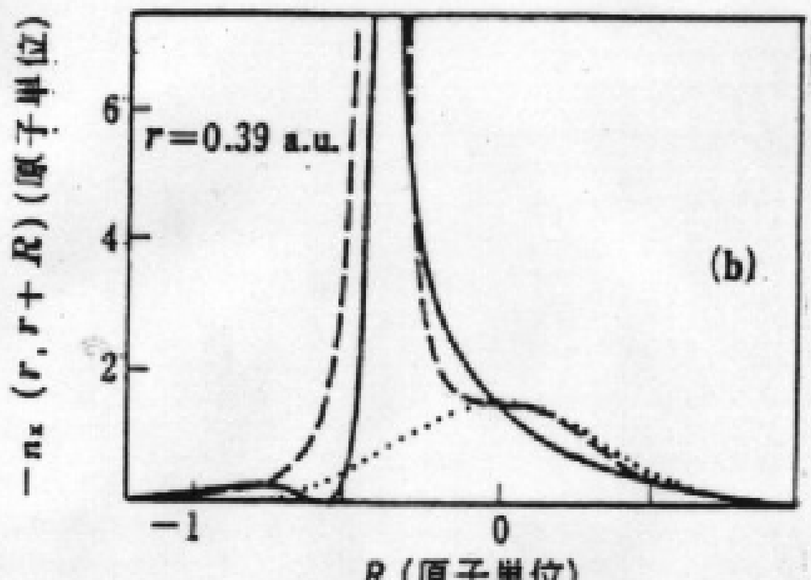
$$E_{xc} = \pi^{1/2} \int d\boldsymbol{r} n(\boldsymbol{r}) \int_0^{\infty} dr' r'^2 n_{00}(\boldsymbol{r}, r') \frac{1}{r'}$$

$$\sqrt{4\pi} \int dr' r'^2 n_{00}(\boldsymbol{r}, r') = -1$$

Ne原子の交換ホール

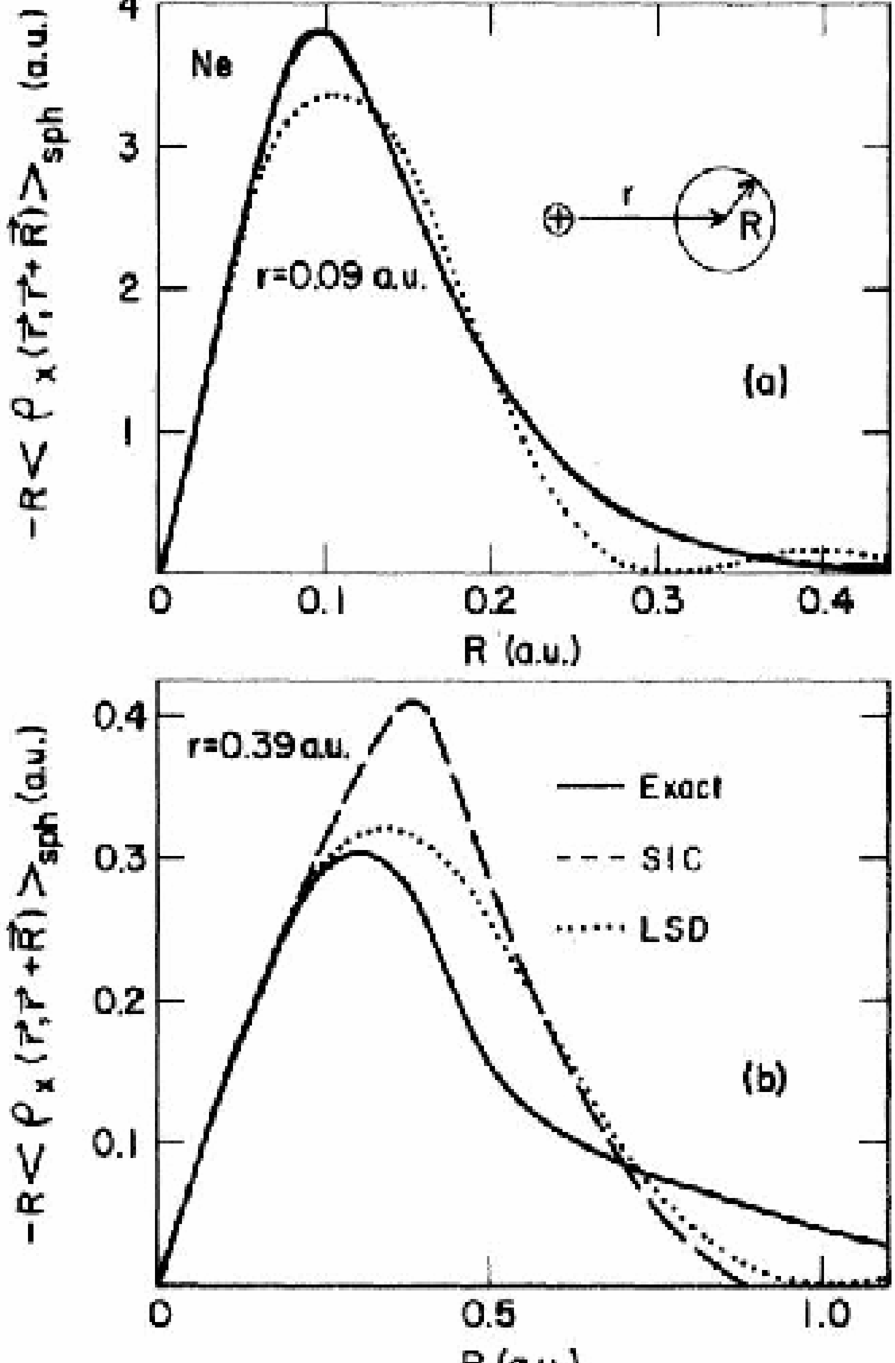


Ne
r=0.09 a.u.
R R
r
(a)
150
100
50
−0.2
−0.1
0
0.1
R (原子単位)
−n_x (r, r+R) (原子単位)



r=0.39 a.u.
(b)
6
4
2
−1
0
−n_x (r, r+R) (原子単位)

Ne原子の交換ホール



Ne
r=0.09 a.u.
r
R
(a)
-R< ρx(r,r+R)>sph (a.u.)
R (a.u.)
r=0.39 a.u.
Exact
SIC
LSD
(b)
-R< ρx(r,r+R)>sph (a.u.)

交換エネルギーと相関エネルギー

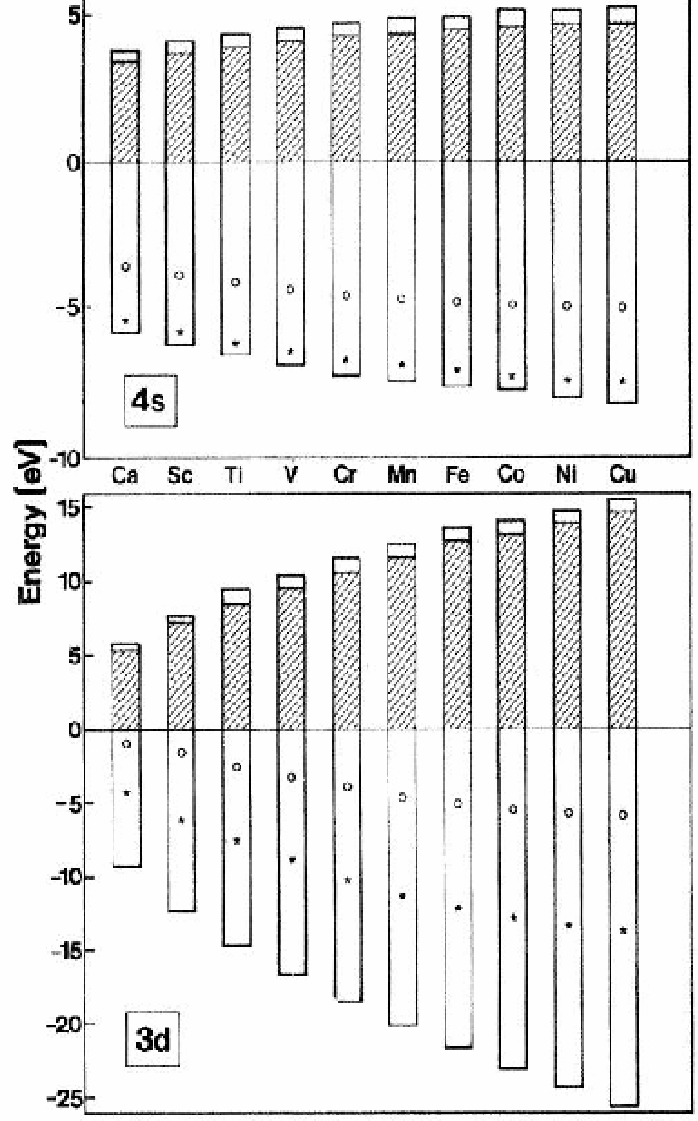


FIG. 5. Breakdown of the orbital energies in the SIC-LSD formalism for spin-up 4s and 3d orbitals of transition atoms in the $d^{n-1}s\uparrow$ configuration. White area: self-Coulomb; dashed: self-exchange; dotted: self-correlation. Open circles: LSD eigenvalues; asterisks: SIC eigenvalues.

バンドギャップのLDAと実験結果

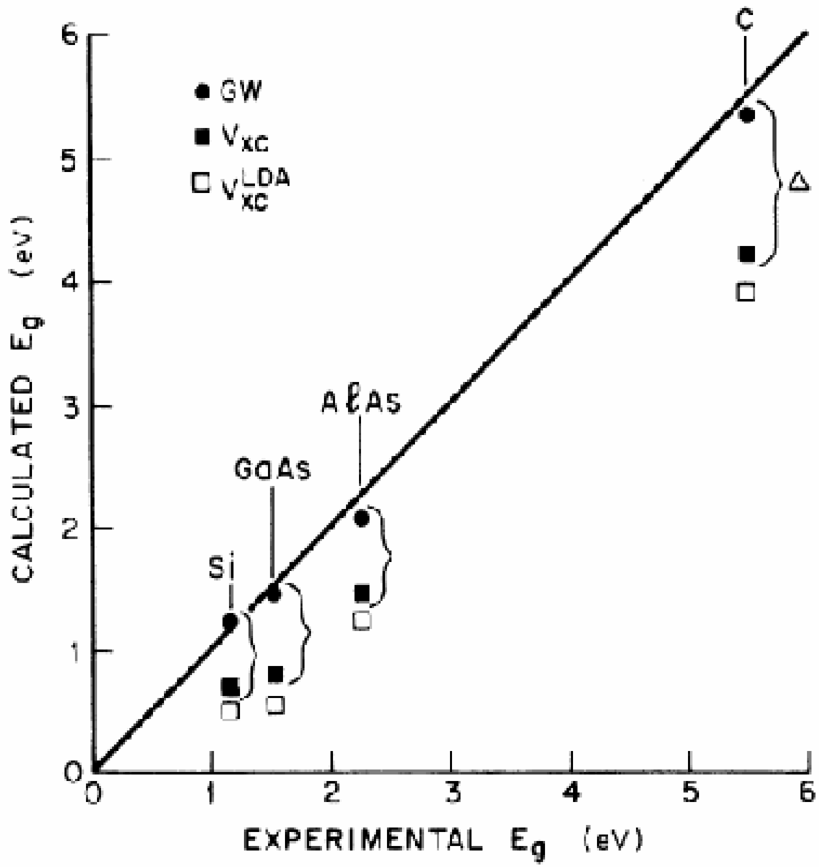


FIG. 10. The calculated minimum band gap in (i) the *GW* approximation, (ii) DFT, and (iii) the LDA plotted against the experimental band gap. The 45° line is a guide to the eye. Δ, the discontinuity in the exchange-correlation potential, is indicated.

図 33: GW, LDA によるバンドギャップの比較. (R.W. Godby et at, Phys. Rev. B 37, 10159 (1988))