Electronic **structure**

Electronic Structure for solids, and DFT method in molecules and solids

Xinzheng Li & Enge Wang, *Computer Simulations of Molecules and Condensed Matter*, 2018
单斌等，《材料学的纳米尺度计算模拟》，2015
Richard Martin, *Electronic Structure*
P. K. Misra, *Physics of Condensed Matter*, 2012

Yongle Li

Periodic condition

Bravais lattice $\mathbb{L} = \left\{ \boldsymbol{R} \,|\, \boldsymbol{R} = n_1\boldsymbol{a}_1 + n_2\boldsymbol{a}_2 + n_3\boldsymbol{a}_3,\ n_1, n_2, n_3 \in \mathbb{Z} \right\}$

Periodic potential $V(\boldsymbol{r} + \boldsymbol{R}) = V(\boldsymbol{r}) \qquad \forall \boldsymbol{r} \in \mathbb{R}^3, \quad \forall \boldsymbol{R} \in \mathbb{L}$

Unit cell $\Omega = \left\{ \boldsymbol{r} \,|\, \boldsymbol{R} = c_1\boldsymbol{a}_1 + c_2\boldsymbol{a}_2 + c_3\boldsymbol{a}_3,\ 0 \le c_1, c_2, c_3 \le 1 \right\}$

$$\boldsymbol{a}_\alpha \cdot \boldsymbol{b}_\beta = 2\pi\delta_{\alpha\beta}, \alpha, \beta = 1,2,3$$

Reciprocal lattice $\mathbb{L}^* = \left\{ \boldsymbol{G} \,|\, \boldsymbol{R} = n_1\boldsymbol{b}_1 + n_2\boldsymbol{b}_2 + n_3\boldsymbol{b}_3,\ n_1, n_2, n_3 \in \mathbb{Z} \right\}$

Reciprocal unit cell $\Omega^* = \left\{ \boldsymbol{r} \,|\, \boldsymbol{R} = c_1\boldsymbol{b}_1 + c_2\boldsymbol{b}_2 + c_3\boldsymbol{b}_3,\ -1/2 \le c_1, c_2, c_3 \le 1/2 \right\}$

Bloch theorem $\psi(\boldsymbol{r} + \boldsymbol{R}) = e^{i\boldsymbol{k}\cdot\boldsymbol{R}}u(\boldsymbol{r}) \quad u(\boldsymbol{r} + \boldsymbol{R}) = u(\boldsymbol{r} + \boldsymbol{R})$

$$\psi(\boldsymbol{r}) = e^{i\boldsymbol{k}\cdot\boldsymbol{r}}u(\boldsymbol{r})$$

Hamiltonian in periodic system

$$\psi(\boldsymbol{r}) = \psi_{n,\boldsymbol{k}}(\boldsymbol{r}) = e^{i\boldsymbol{k}\cdot\boldsymbol{r}} u_{n,\boldsymbol{k}}(\boldsymbol{r})$$

$$\hat{H}\psi(\boldsymbol{r}) = \left[\hat{T} + V(\boldsymbol{r})\right]\psi_{n,\boldsymbol{k}}(\boldsymbol{r})$$

$$\left[-\frac{1}{2}(\nabla + i\boldsymbol{k})^2 + V(\boldsymbol{r})\right] u_{n,\boldsymbol{k}}(\boldsymbol{r}) = E_{n,\boldsymbol{k}} u_{n,\boldsymbol{k}}(\boldsymbol{r})$$

$$\int_\Omega u^*_{n,\boldsymbol{k}}(\boldsymbol{r})\, u_{m,\boldsymbol{k}}(\boldsymbol{r})\, \mathrm{d}\boldsymbol{r} = \delta_{n,m}$$

$$\psi_{n,\boldsymbol{k}}(\boldsymbol{r}) = \psi_{n,\boldsymbol{k}+\boldsymbol{G}}(\boldsymbol{r}), \quad E_{n,\boldsymbol{k}+\boldsymbol{G}} = E_{n,\boldsymbol{k}}$$

Hartree-Fock for electron gas

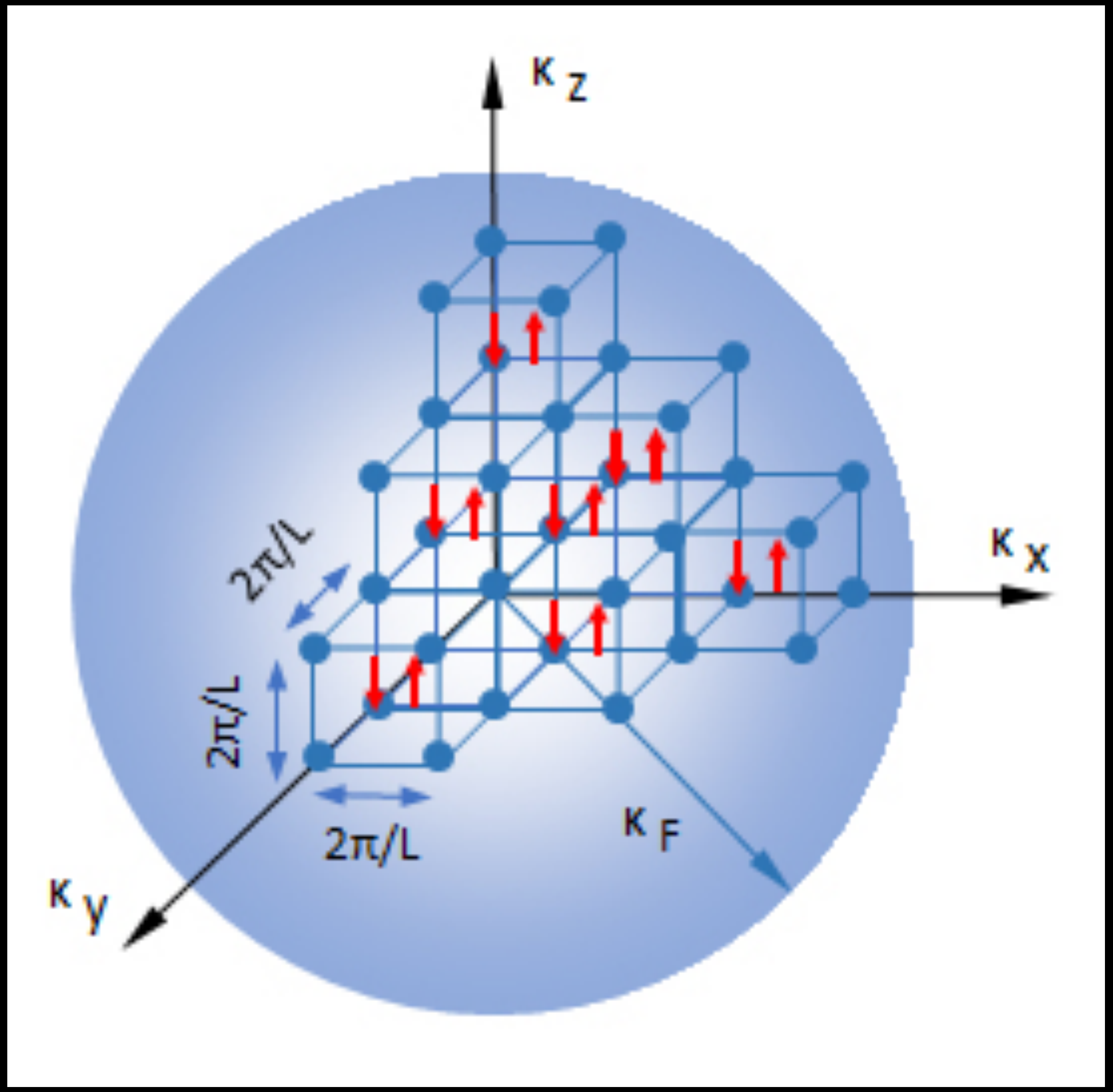
Jellium model $\rho^+ = \rho^-$

Mean free path of electron $\frac{4\pi}{3} r_s^3 = \frac{1}{\rho_0 a_0^3}$

$$N(\boldsymbol{k}_\mathrm{F}) = 2\frac{V(\boldsymbol{k}_\mathrm{F})}{(\Delta k^3)} = \frac{V}{(2\pi)^3}\frac{8\pi}{3}k_\mathrm{F}^3 \quad \Delta k_\alpha = \frac{2\pi}{L}, \alpha = x, y, z$$

$$\rho_0 = \frac{N}{V} = \frac{1}{(2\pi)^3}\frac{8\pi}{3}k_\mathrm{F}^3 = \frac{k_\mathrm{F}^3}{3\pi^2}$$

$$k_\mathrm{F}\, a_0 = (3\pi^2\rho_0)^{1/3} a_0 = \left(\frac{9\pi}{4}\right)^{1/3}\frac{1}{r_s} = \frac{1.9192}{r_s}$$

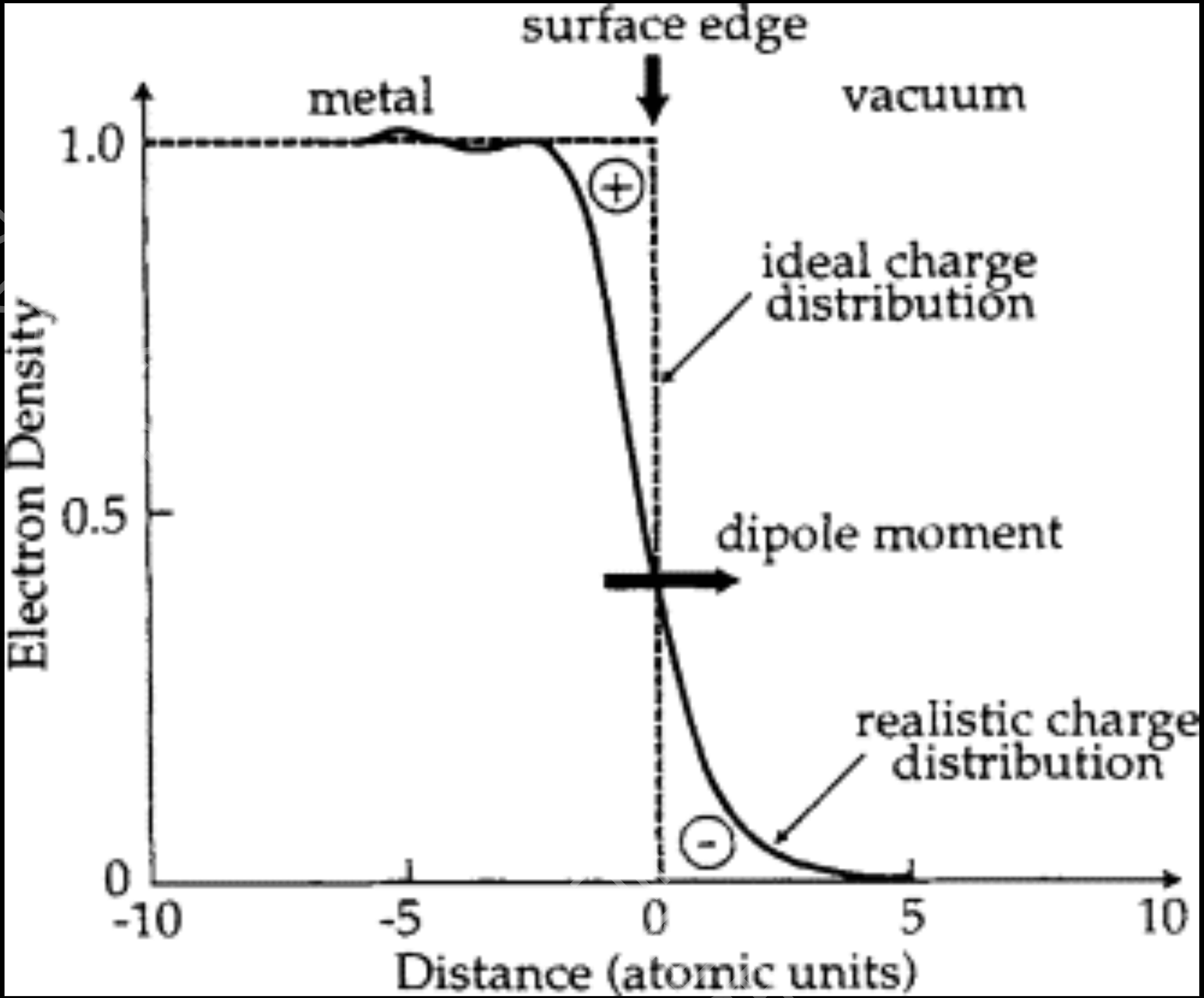


Jellium model

Lang & Kohn 1970

$$\lambda_{\mathrm{F}} = \frac{2\pi}{k_{\mathrm{F}}} = 3.46\ \text{Å}\ (r_s = 2)$$

$$\text{or}\ = 8.33\ \text{Å}\ (r_s = 5)$$



1. N. D. Lang, W. Kohn, Theory of Metal Surfaces: Charge Density and Surface Energy. *Phys. Rev. B*, 1:4555 (1970)
2. H. Over, S.Y. Tong, in *Handbook of Surface Science*, 1996

Coulomb energy

$$\rho^{-}(\boldsymbol{r}) = \rho^{+}(\boldsymbol{r}) = \rho_0 = \frac{V}{N}$$

$$U_{\mathrm{col}} = U_{\mathrm{ee}} + U_{\mathrm{II}} + U_{\mathrm{eI}} = e^2 \left(\frac{N}{V}\right)^2 \iint \left[\frac{1}{2}\frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|} + \frac{1}{2}\frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|} - \frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|}\right] \mathrm{d}\boldsymbol{r}\mathrm{d}\boldsymbol{r}'$$

So, in jellium model, there is no Coulomb energy.

Kinetic energy and exchange energy

$$|\boldsymbol{k}_i\rangle = \Omega^{-1/2} e^{i\boldsymbol{k}_i\cdot\boldsymbol{r}}$$

$$\Phi_0 = (N!)^{-1/2}\begin{vmatrix} \langle \boldsymbol{r}_1|\boldsymbol{k}_1\rangle\alpha & \langle \boldsymbol{r}_2|\boldsymbol{k}_1\rangle\alpha & \cdots & \langle \boldsymbol{r}_N|\boldsymbol{k}_1\rangle\alpha \\ \langle \boldsymbol{r}_1|\boldsymbol{k}_1\rangle\beta & \langle \boldsymbol{r}_2|\boldsymbol{k}_1\rangle\beta & \cdots & \langle \boldsymbol{r}_N|\boldsymbol{k}_1\rangle\beta \\ \langle \boldsymbol{r}_1|\boldsymbol{k}_2\rangle\alpha & \langle \boldsymbol{r}_2|\boldsymbol{k}_2\rangle\alpha & \cdots & \langle \boldsymbol{r}_N|\boldsymbol{k}_2\rangle\alpha \\ \vdots & \vdots & & \vdots \\ \langle \boldsymbol{r}_1|\boldsymbol{k}_{N/2}\rangle\beta & \langle \boldsymbol{r}_2|\boldsymbol{k}_{N/2}\rangle\beta & \cdots & \langle \boldsymbol{r}_N|\boldsymbol{k}_{N/2}\rangle\beta \end{vmatrix}$$

$$\hat{\mathscr{F}} e^{i\boldsymbol{k}\cdot\boldsymbol{r}} = \left[-\frac{\nabla^2}{2} - \sum_a K_a\right] e^{i\boldsymbol{k}\cdot\boldsymbol{r}} = \frac{k^2}{2} e^{i\boldsymbol{k}\cdot\boldsymbol{r}} - \frac{1}{\Omega}\sum_{\boldsymbol{k}'}^{(\mathrm{occ})} e^{i\boldsymbol{k}'\cdot\boldsymbol{r}} \int e^{-i\boldsymbol{k}'\cdot\boldsymbol{r}'} \frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|} e^{i\boldsymbol{k}\cdot\boldsymbol{r}'} \mathrm{d}\boldsymbol{r}'$$

$$= \frac{k^2}{2} e^{i\boldsymbol{k}\cdot\boldsymbol{r}} - \frac{1}{\Omega}\sum_{\boldsymbol{k}'}^{(\mathrm{occ})} e^{i\boldsymbol{k}'\cdot\boldsymbol{r}} \int \frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|} e^{-i(\boldsymbol{k}'-\boldsymbol{k})\cdot\boldsymbol{r}'} \mathrm{d}\boldsymbol{r}'$$

The kinetic energy is quite simple, that's $k^2/2$.

$$= \frac{k^2}{2} e^{i\boldsymbol{k}\cdot\boldsymbol{r}} - \frac{1}{\Omega}\sum_{\boldsymbol{k}'}^{(\mathrm{occ})} e^{i\boldsymbol{k}'\cdot\boldsymbol{r}} \int \frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|} e^{-i(\boldsymbol{k}'-\boldsymbol{k})\cdot(\boldsymbol{r}'\boxed{-\boldsymbol{r}+\boldsymbol{r}})} \mathrm{d}\boldsymbol{r}'$$

$$= \frac{k^2}{2} e^{i\boldsymbol{k}\cdot\boldsymbol{r}} - \frac{1}{\Omega}\sum_{\boldsymbol{k}'}^{(\mathrm{occ})} e^{i\boldsymbol{k}'\cdot\boldsymbol{r}} \int \frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|} e^{-i(\boldsymbol{k}'-\boldsymbol{k})\cdot(\boldsymbol{r}'-\boldsymbol{r})} \mathrm{d}\boldsymbol{r}' \boxed{e^{-i(\boldsymbol{k}'-\boldsymbol{k})\cdot\boldsymbol{r}}}$$

$$= \frac{k^2}{2} e^{i\boldsymbol{k}\cdot\boldsymbol{r}} - \frac{1}{\Omega}\sum_{\boldsymbol{k}'}^{(\mathrm{occ})} \boxed{e^{i\boldsymbol{k}\cdot\boldsymbol{r}}} \int \frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|} e^{-i(\boldsymbol{k}'-\boldsymbol{k})\cdot(\boldsymbol{r}'-\boldsymbol{r})} \mathrm{d}\boldsymbol{r}'$$

$$\hat{\mathscr{F}}\, e^{i\boldsymbol{k}\cdot\boldsymbol{r}} = \frac{k^2}{2} e^{i\boldsymbol{k}\cdot\boldsymbol{r}} - \frac{1}{\Omega} \sum_{\boldsymbol{k}'}^{(\mathrm{occ})} e^{i\boldsymbol{k}\cdot\boldsymbol{r}} \int \frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|} e^{-i(\boldsymbol{k}'-\boldsymbol{k})\cdot(\boldsymbol{r}'-\boldsymbol{r})} \mathrm{d}\boldsymbol{r}'$$

$$\hat{\mathscr{F}}\, e^{i\boldsymbol{k}\cdot\boldsymbol{r}} = \frac{k^2}{2} e^{i\boldsymbol{k}\cdot\boldsymbol{r}} - \frac{1}{\Omega} e^{i\boldsymbol{k}\cdot\boldsymbol{r}} \sum_{\boldsymbol{k}'}^{(\mathrm{occ})} \int \frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|} e^{-i(\boldsymbol{k}'-\boldsymbol{k})\cdot(\boldsymbol{r}'-\boldsymbol{r})} \mathrm{d}\boldsymbol{r}'$$

$$\boxed{\hat{\mathscr{F}}\, e^{i\boldsymbol{k}\cdot\boldsymbol{r}} = \left[\frac{k^2}{2} - \frac{1}{\Omega} \sum_{k'<k_{\mathrm{F}}} \frac{4\pi}{|\boldsymbol{k}'-\boldsymbol{k}|^2} \right] e^{i\boldsymbol{k}\cdot\boldsymbol{r}}}$$

Proof of the integration:

$$\int \frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|} e^{-i(\boldsymbol{k}'-\boldsymbol{k})\cdot(\boldsymbol{r}'-\boldsymbol{r})}\mathrm{d}\boldsymbol{r}'$$

$\Delta\boldsymbol{k} = \boldsymbol{k}' - \boldsymbol{k}$ $\boldsymbol{x} = \boldsymbol{r}' - \boldsymbol{r}$

$$= \frac{1}{-i\Delta\boldsymbol{k}}\int \frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|}\mathrm{d}e^{-i\Delta\boldsymbol{k}\cdot(\boldsymbol{r}'-\boldsymbol{r})} = \frac{1}{i\Delta\boldsymbol{k}}\cdot\int\left\{\nabla\frac{1}{|\boldsymbol{x}|}\right\}e^{-i\Delta\boldsymbol{k}\cdot\boldsymbol{x}}\mathrm{d}\boldsymbol{x}$$

Integrate by parts

$$= \frac{-1}{(\Delta k)^2}\int\left\{\nabla^2\frac{1}{|\boldsymbol{x}|}\right\}e^{-i\Delta\boldsymbol{k}\cdot\boldsymbol{x}}\mathrm{d}\boldsymbol{x}$$

Integrate by part again

$$\nabla^2\frac{1}{r} = -4\pi\delta(\boldsymbol{r})$$

$$= \frac{-1}{(\Delta k)^2}\int\left\{-4\pi\delta(\boldsymbol{x})\right\}e^{-i\Delta\boldsymbol{k}\cdot\boldsymbol{x}}\mathrm{d}\boldsymbol{x} = \frac{4\pi}{(\Delta k)^2} = \frac{4\pi}{|\boldsymbol{k}'-\boldsymbol{k}|^2}$$

Ashcroft & Mermin, *Solid State Physics*, pp. 351, problem 3.

$$\frac{1}{\Omega}\sum_{k'<k_\mathrm{F}}\frac{4\pi}{|\boldsymbol{k}'-\boldsymbol{k}|^2}=\frac{4\pi}{(2\pi)^3}\int_0^{k_\mathrm{F}}\int_0^{\pi}\int_0^{2\pi}\frac{k'^2\sin\theta\mathrm{d}k'\,\mathrm{d}\theta\,\mathrm{d}\phi}{k^2-2kk'\cos\theta+k'^2}$$

The integration over ϕ is simply 2π.

$$\frac{1}{\Omega}\sum_{\boldsymbol{k}}\cdot=\frac{1}{(2\pi)^3}\int\mathrm{d}^3k\,\cdot$$

$$=\frac{8\pi^2}{(2\pi)^3}\int_0^{k_\mathrm{F}}\int_0^{\pi}\frac{k'^2\sin\theta\mathrm{d}k'\,\mathrm{d}\theta}{k^2-2kk'\cos\theta+k'^2}$$

The integration over θ:

$$\int_0^{\pi}\frac{k'^2\sin\theta\mathrm{d}\theta}{(k^2+k'^2)-2kk'\cos\theta}=-\int_0^{\pi}\frac{k'^2\mathrm{d}\cos\theta}{(k^2+k'^2)-2kk'\cos\theta}$$

$$=\int_{-1}^{1}\frac{k'^2}{A-By}\mathrm{d}y \qquad y=\cos\theta \qquad A=k^2+k'^2 \qquad B=2kk'$$

$$=-\frac{k'^2}{B}\ln\left|\frac{A-B}{A+B}\right|=-\frac{k'^2}{2kk'}\ln\left|\frac{k^2+k'^2-2kk'}{k^2+k'^2+2kk'}\right|$$

$$=\frac{k'}{k}\ln\left|\frac{k+k'}{k-k'}\right|$$

Now let’s calculate the integration over r:

$$\frac{1}{\Omega}\sum_{k'<k_{\mathrm{F}}}\frac{4\pi}{|\boldsymbol{k}'-\boldsymbol{k}|^2} = \frac{1}{\pi k}\int_0^{k_{\mathrm{F}}} k'\ln\left|\frac{k+k'}{k-k'}\right| \mathrm{d}k'$$

Change the variable:

$$= \frac{1}{\pi k}\frac{1}{2}\int_0^{k_{\mathrm{F}}}\ln\left|\frac{k+k'}{k-k'}\right| \mathrm{d}k'^2$$

Integrate by parts:

$$= \frac{1}{2\pi k}\left\{ k'^2 \ln\left|\frac{k+k'}{k-k'}\right|\Bigg|_0^{k_{\mathrm{F}}} - \int_0^{k_{\mathrm{F}}}\frac{k'^2}{k'+k}\mathrm{d}k' + \int_0^{k_{\mathrm{F}}}\frac{k'^2}{k'-k}\mathrm{d}k'\right\}$$

$$= \frac{1}{2\pi k}\left\{k_{\mathrm{F}}^2\ln\left|\frac{k+k_{\mathrm{F}}}{k-k_{\mathrm{F}}}\right| + 2k\int_0^{k_{\mathrm{F}}}\frac{k'^2}{k'^2-k^2}\mathrm{d}k'\right\}$$

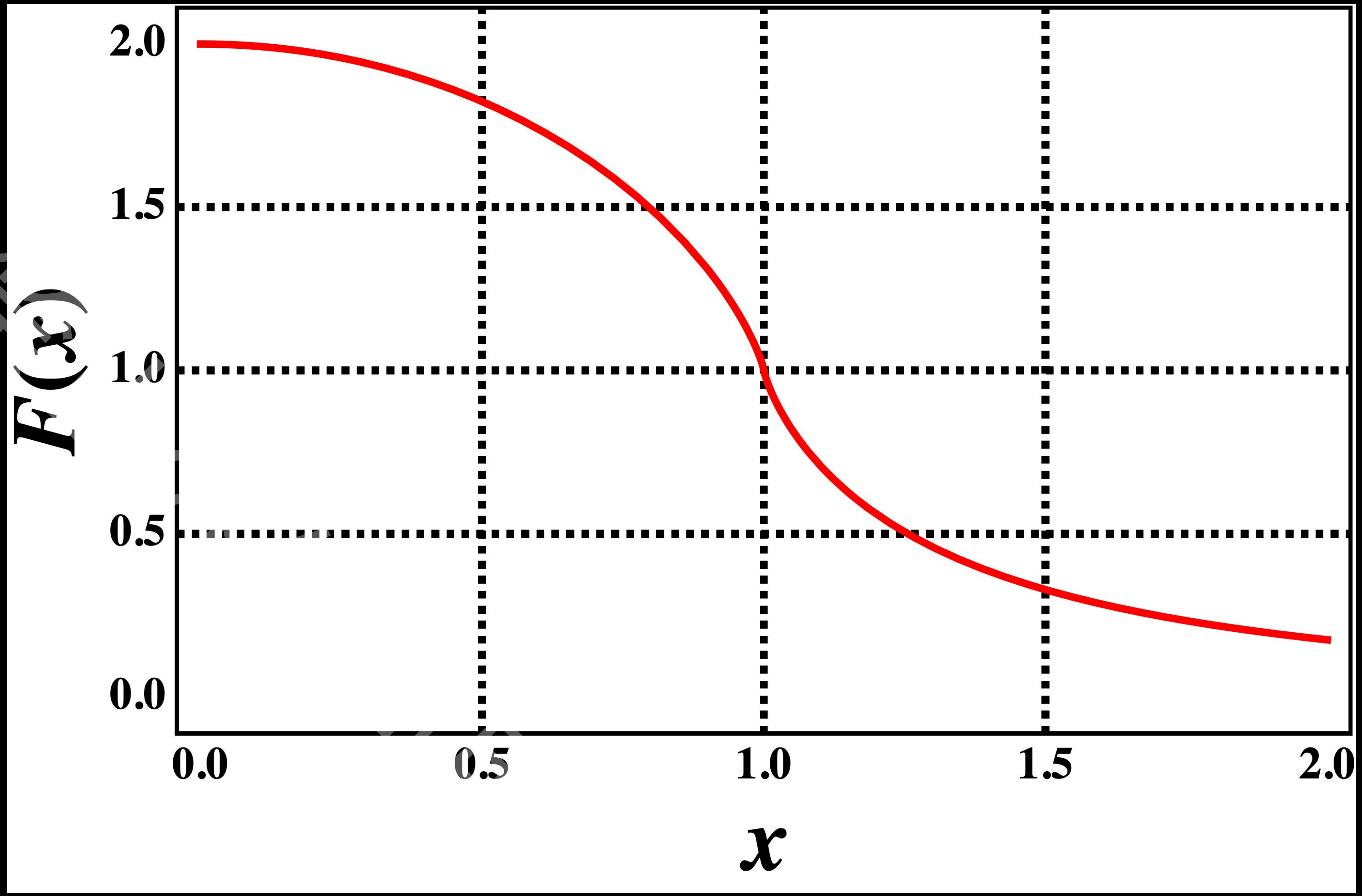
$$= \frac{1}{2\pi k}\left\{k_{\mathrm{F}}^2\ln\left|\frac{k+k_{\mathrm{F}}}{k-k_{\mathrm{F}}}\right| + 2k\int_0^{k_{\mathrm{F}}}\mathrm{d}k' + (2k)k^2\int_0^{k_F}\frac{1}{k'^2-k^2}\mathrm{d}k'\right\}$$

The third term of the integration:

$$
\begin{aligned}
&(2k)k^2\int_0^{k_\mathrm{F}}\frac{1}{k'^2-k^2}\mathrm{d}k'\\
&=(2k)k^2\frac{1}{2k}\int_0^{k_\mathrm{F}}\left[\frac{1}{k'-k}-\frac{1}{k'+k}\right]\mathrm{d}k'\\
&=-(2k)(\frac{k}{2})\ln|\frac{k+k_\mathrm{F}}{k-k_\mathrm{F}}|
\end{aligned}
$$

Finally we obtain the expression of the part of exchange energy.

$$
\begin{aligned}
&\frac{1}{\pi k}\int_0^{k_\mathrm{F}} k' \ln\left|\frac{k+k'}{k-k'}\right| \mathrm{d}k' \\
&= \frac{1}{2\pi k}\left\{k_\mathrm{F}^2 \ln\left|\frac{k+k_\mathrm{F}}{k-k_\mathrm{F}}\right| + 2k\int_0^{k_\mathrm{F}} \mathrm{d}k' + (2k)k^2\int_0^{k_F} \frac{1}{k'^2-k^2}\mathrm{d}k'\right\} \\
&= \frac{1}{2\pi k}\left\{k_\mathrm{F}^2 \ln\left|\frac{k+k_\mathrm{F}}{k-k_\mathrm{F}}\right| + 2k\left(k_\mathrm{F} - \frac{k}{2}\ln\left|\frac{k+k_\mathrm{F}}{k-k_\mathrm{F}}\right|\right)\right\} \\
&= \frac{1}{\pi}\left\{k_\mathrm{F} + \left(\frac{k_\mathrm{F}^2}{2k} - \frac{k}{2}\right)\ln\left|\frac{1+(k/k_\mathrm{F})}{1-(k/k_\mathrm{F})}\right|\right\} \\
&= \frac{k_\mathrm{F}}{\pi}F\left(\frac{k}{k_\mathrm{F}}\right) \qquad F(x) = 1 + \frac{1-x^2}{2x}\ln\left|\frac{1+x}{1-x}\right|
\end{aligned}
$$



$$\boxed{\hat{\mathscr{F}} e^{i\boldsymbol{k}\cdot\boldsymbol{r}} = \left[\frac{k^2}{2} - \frac{k_\mathrm{F}}{\pi} F\left(\frac{k}{k_\mathrm{F}}\right)\right] e^{i\boldsymbol{k}\cdot\boldsymbol{r}} = \varepsilon_k e^{i\boldsymbol{k}\cdot\boldsymbol{r}}}$$

$$k_\mathrm{F}\, a_0 = \frac{1.9192}{r_s} \qquad \varepsilon_k = \frac{k^2}{2} - \frac{1.9192}{r_s a_0 \pi} F(kr_s)$$

Here we can see, although the electrons are plane waves, their energy $\varepsilon(\boldsymbol{k})$ is the free plane wave plus a term.

Here the number 2 comes from the spin. But in exchange part, it countered by correction of double-counting.

$$E_0^{\mathrm{HF}} = 2\sum_{k<k_{\mathrm{F}}} \frac{k^2}{2} - \sum_{k<k_{\mathrm{F}}} \frac{k_{\mathrm{F}}}{\pi} F(\frac{k}{k_{\mathrm{F}}}) = \frac{8\pi\Omega}{(2\pi)^3} \int_0^{k_{\mathrm{F}}} k^2 \left[\frac{k^2}{2} - \frac{k_{\mathrm{F}}}{2\pi} F(\frac{k}{k_{\mathrm{F}}}) \right] \mathrm{d}k = \left[\frac{3}{5}\frac{k_{\mathrm{F}}^2}{2} - \frac{3}{4}\frac{k_{\mathrm{F}}}{\pi} \right] N$$

$$\boxed{E_0^{\mathrm{HF}} = \left[\frac{3}{5}\frac{k_{\mathrm{F}}^2}{2} - \frac{3}{4}\frac{k_{\mathrm{F}}}{\pi} \right] N}$$

$$N = \frac{8\pi\Omega k_{\mathrm{F}}^3}{3(2\pi)^3} \qquad E_0^{\mathrm{HF}} = N\bar{E}_0 \qquad V_{\mathrm{x}}(\boldsymbol{r}) \propto \rho(\boldsymbol{r})^{1/3} \qquad \rho_0 = \frac{k_{\mathrm{F}}^3}{3\pi^2}$$

$$\bar{E}_0 = \frac{3}{5}\frac{k_{\mathrm{F}}^2}{2} - \frac{3}{4}\frac{k_{\mathrm{F}}}{\pi}$$

$$\rho_0 = \frac{k_\mathrm{F}^3}{3\pi^2}$$

Kinetic energy density:

$$\varepsilon_\mathrm{k}(\boldsymbol{r}) = \frac{3}{10}k_\mathrm{F}^2 = \frac{3}{10}(6\pi^2\rho^\sigma)^{2/3}$$

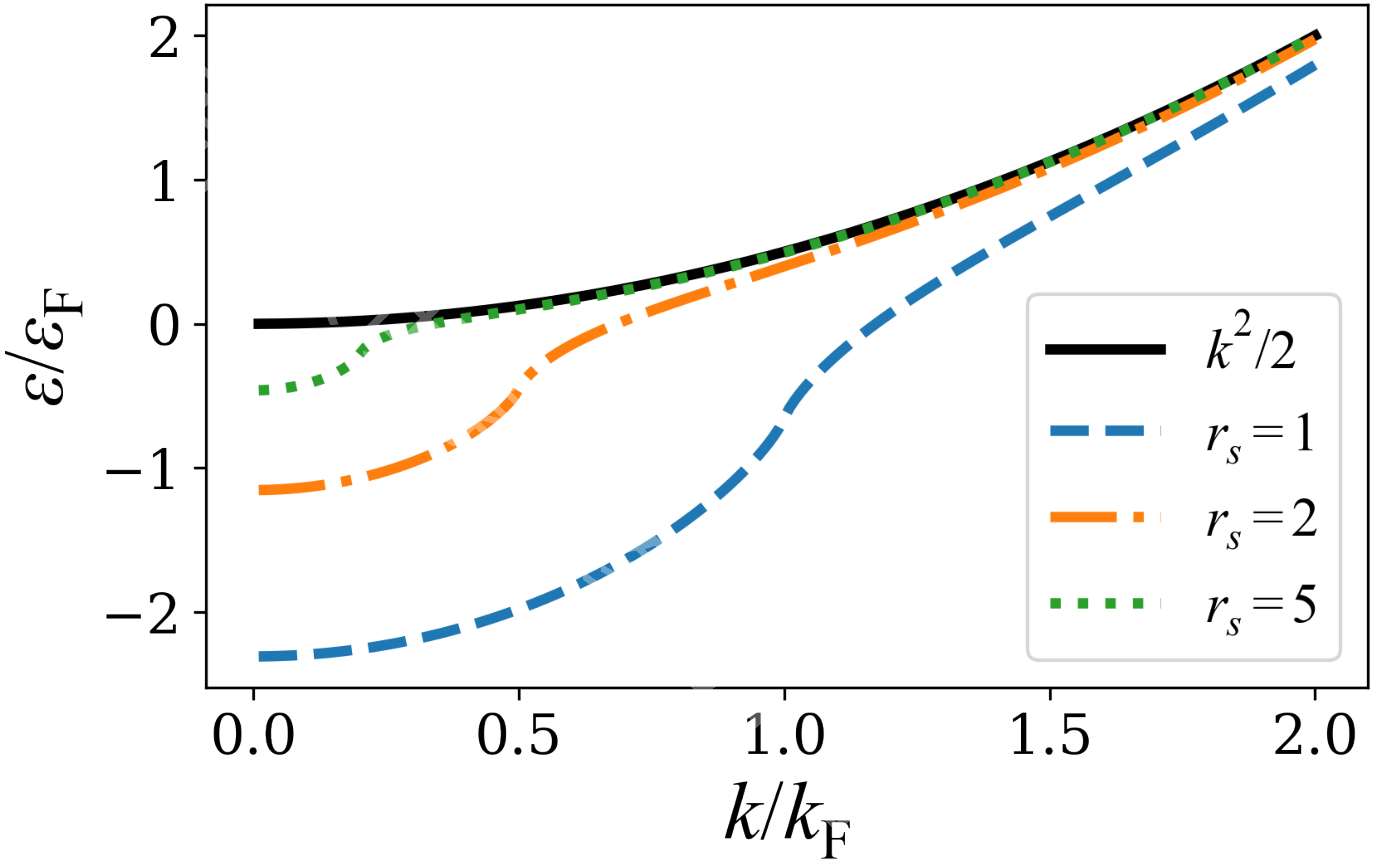
$$\varepsilon_\mathrm{K}^\uparrow(\boldsymbol{r}) = \varepsilon_\mathrm{K}^\downarrow(\boldsymbol{r}) = \frac{3}{10}(3\pi^2\rho^\mathrm{tot})^{2/3}$$

Exchange energy density:

$$\varepsilon_\mathrm{x}(\boldsymbol{r}) = -\frac{3}{4}\frac{k_\mathrm{F}}{\pi} = -\frac{3}{4}\left(\frac{6\rho^\sigma}{\pi}\right)^{1/3}$$

$$\varepsilon_\mathrm{x}^\uparrow(\boldsymbol{r}) = \varepsilon_\mathrm{x}^\downarrow(\boldsymbol{r}) = -\frac{3}{4}\frac{k_\mathrm{F}}{\pi} = -\frac{3}{4}\left(\frac{3\rho^\mathrm{tot}}{\pi}\right)^{1/3}$$

$$k_\mathrm{F}\,a_0 = \frac{1.9192}{r_s} \quad \Rightarrow \quad \bar{E}_0 = \frac{3}{10}(k_\mathrm{F}a_0)^2\frac{1}{a_0} - \frac{3}{4\pi}\frac{k_\mathrm{F}a_0}{a_0} = \frac{1.1050}{r_s^2} - \frac{0.4581}{r_s}$$



$$\varepsilon^{\mathrm{HF}} = \bar{E}_0 = \frac{1.1050}{r_s^2} - \frac{0.4581}{r_s}$$

$$\varepsilon_k = \frac{k^2}{2} - \frac{1.9192}{r_s a_0 \pi} F(k r_s)$$

Correlation in periodic system

Gell-Mann & Brueckner 1957, large density:

M. Gell-Mann & K. Brueckener, *Phys. Rev.* 106, 364 (1957)

$$E_\mathrm{c} = 0.0311 \times \ln r_s - 0.048$$

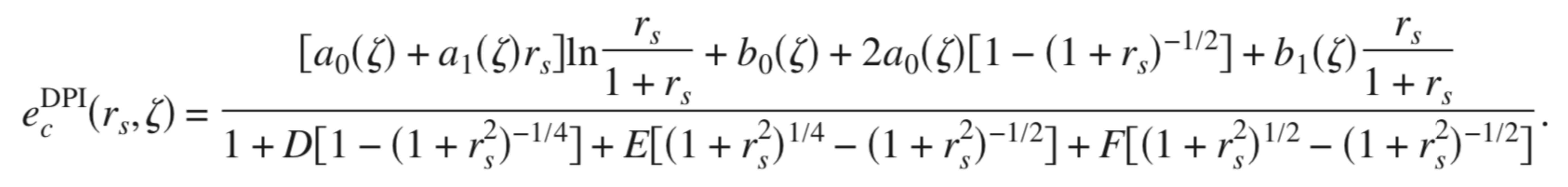
Eugene Wigner, small density:

E. Wigner, *Phys. Rev.* 46, 1002 (1934)

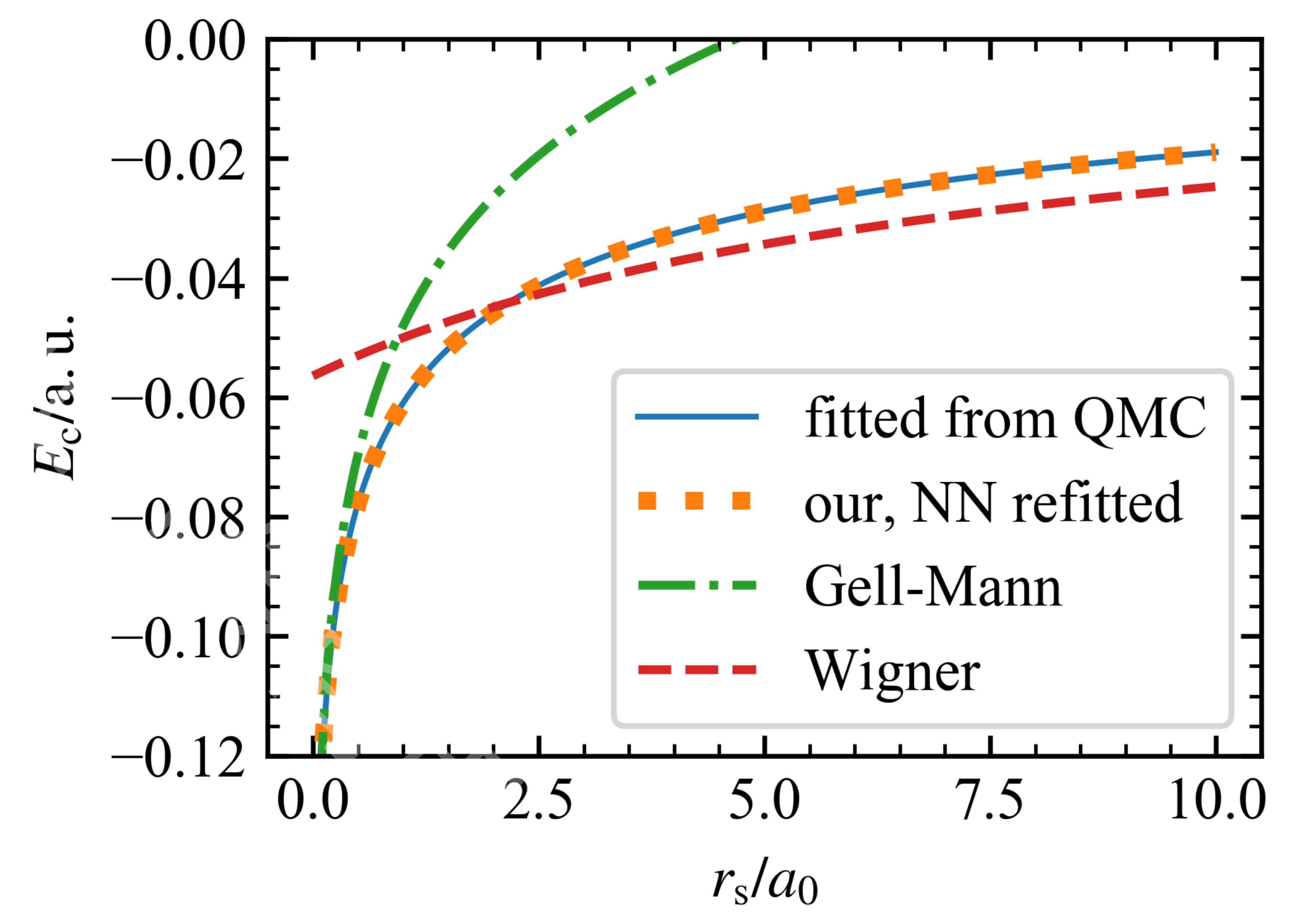
$$E_\mathrm{c} = -\frac{0.44}{r_s + 7.8}$$

Fitted from Quantum Monte Carlo

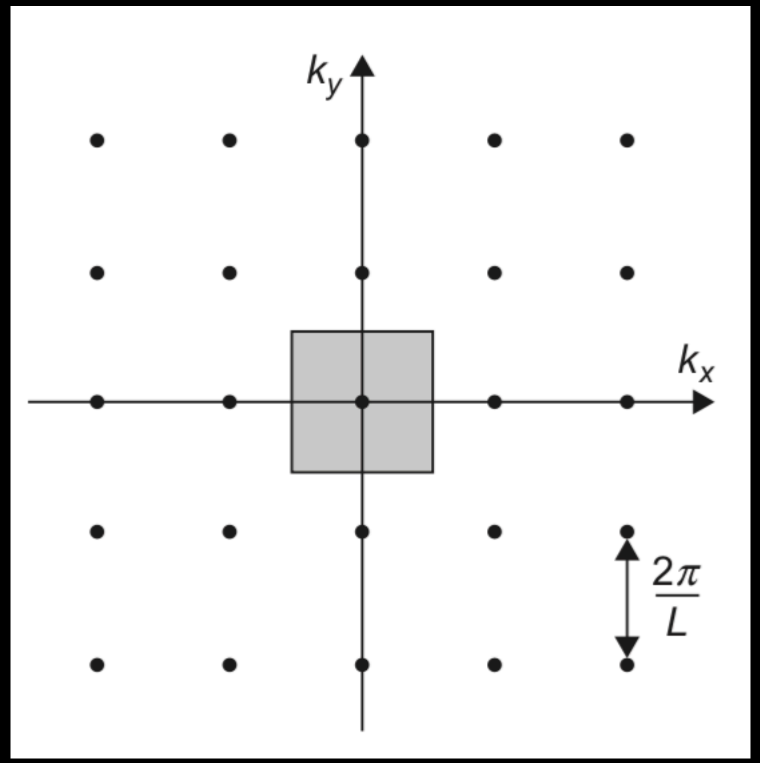
Jianwei Sun, John Perdew, M. Seidl,
Phys. Rev. B 81, 085123 (2010)



$$e_c^{\mathrm{DPI}}(r_s,\zeta) = \frac{[a_0(\zeta)+a_1(\zeta)r_s]\ln\frac{r_s}{1+r_s} + b_0(\zeta) + 2a_0(\zeta)[1-(1+r_s)^{-1/2}] + b_1(\zeta)\frac{r_s}{1+r_s}}{1 + D[1-(1+r_s^2)^{-1/4}] + E[(1+r_s^2)^{1/4} - (1+r_s^2)^{-1/2}] + F[(1+r_s^2)^{1/2} - (1+r_s^2)^{-1/2}]}.$$



Thomas-Fermi-Dirac model (1927)



Free electron gas

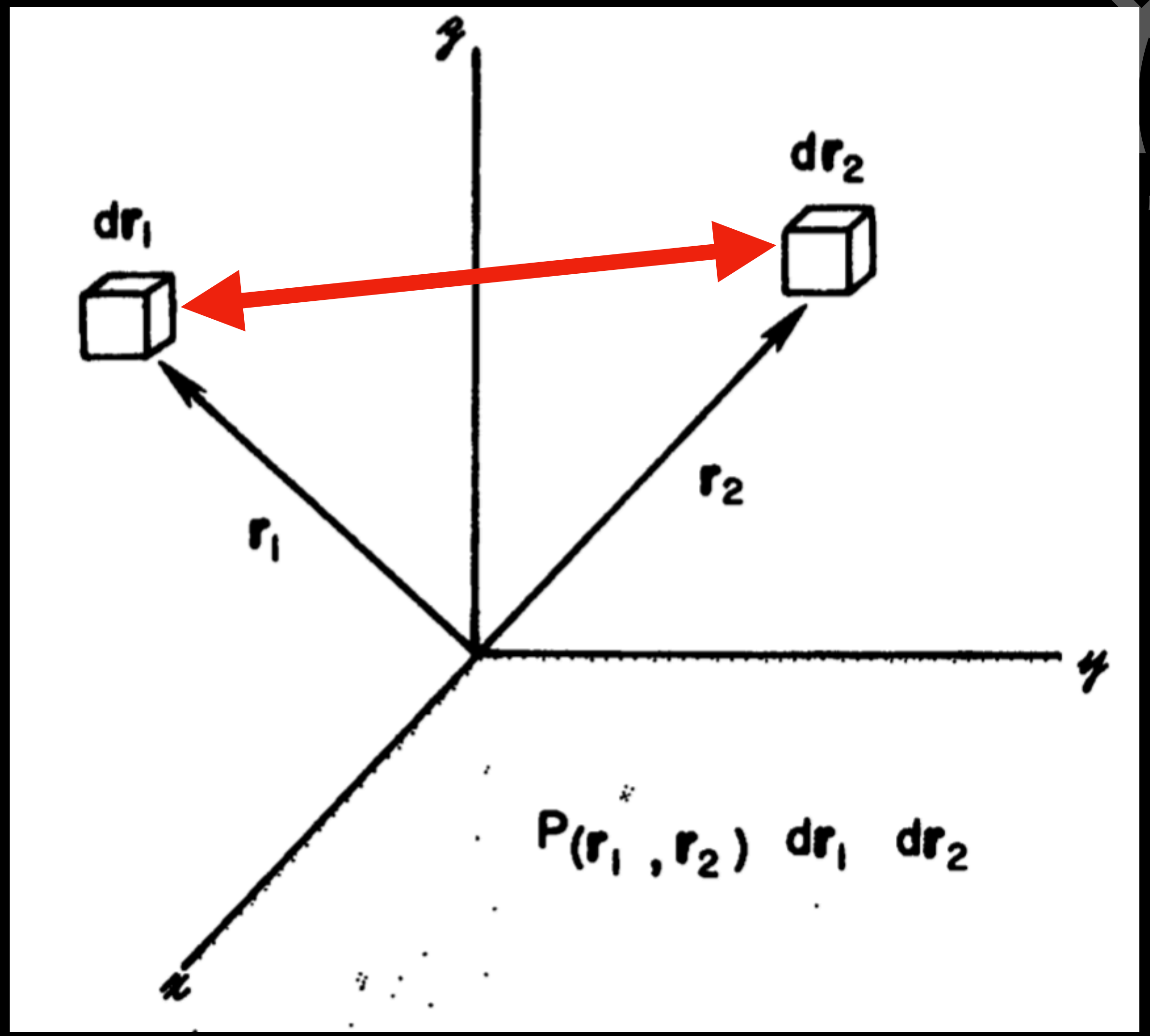
$$E = T = \frac{\hbar^2 k^2}{2m} = \frac{h^2 n^2}{2mL^2} \qquad k = \frac{2\pi n}{L}$$

$$E = 2\sum_{k\le k_\mathrm{F}} \frac{\hbar^2 k^2}{2m} = 2\sum_{k\le k_\mathrm{F}} \left[\frac{V}{(2\pi)^3} E(\boldsymbol{k})\Delta \boldsymbol{k}\right] = 2\frac{V}{(2\pi)^3}\int_{k\le k_\mathrm{F}} \frac{\hbar^2 k^2}{2m}\mathrm{d}^3 k$$

$$E = \frac{V\hbar^2 k_\mathrm{F}^5}{10\pi^2 m} \qquad V = L^3 \quad N(\boldsymbol{k}_\mathrm{F}) = \frac{V(\boldsymbol{k}_\mathrm{F})}{(\Delta k^3)} = \frac{V k_\mathrm{F}^3}{3\pi^2}$$

$$\varepsilon_K = \frac{E}{N} = \frac{3\hbar^2 k_\mathrm{F}^2}{10m} = \frac{3}{5}\left(\frac{\hbar^2 k_\mathrm{F}^2}{2m}\right) = \frac{3}{5}\varepsilon_\mathrm{F} \qquad \rho_0 = \frac{N}{V} = \frac{k_\mathrm{F}^3}{3\pi^2}$$

$$E_K = \varepsilon_K \rho_0 \qquad E_K = \int t[\rho_0]\rho_0 \mathrm{d}r = \int \varepsilon_K \rho_0 \mathrm{d}r = C_1 \int \rho_0^{5/3}\mathrm{d}r \quad C_1 = \frac{3(3\pi^2)^{2/3}}{10} \approx 2.871$$



$$E_K = 2.871 \int \rho_0^{5/3}(\boldsymbol{r}) \mathrm{d}^3 r$$

$$V^{\mathrm{Hartree}} = \frac{1}{2} \int\int \mathrm{d}^3 r\, \mathrm{d}^3 r' \, \frac{\rho(\boldsymbol{r})\rho(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|}$$

$$= \frac{1}{2} \int v^{\mathrm{H}} \rho(\boldsymbol{r}) \mathrm{d}^3 r$$

This is not pure Coulomb interaction, since it contains self-interaction.

$$v^{\mathrm{H}} = \int \mathrm{d}^3 r' \, \frac{\rho(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|}$$

$$V_{\mathrm{ext}} = -\int \mathrm{d}^3 r \, \frac{Z\rho(\boldsymbol{r})}{|\boldsymbol{R} - \boldsymbol{r}|} = \int \mathrm{d}^3 r \, v_{\mathrm{ext}} \rho(\boldsymbol{r}) \mathrm{d}^3 r$$

$$v_{\mathrm{ext}} = -\frac{Z}{|\boldsymbol{R} - \boldsymbol{r}|}$$

Dirac’s correction: exchange

$$V_{\mathrm{x}} = \int \varepsilon_{\mathrm{x}}(\boldsymbol{r}) \rho(\boldsymbol{r}) \mathrm{d}^3 r = -\frac{3}{4} \int \left(\frac{3\rho(\boldsymbol{r})}{\pi} \right)^{1/3} \rho(\boldsymbol{r}) \mathrm{d}^3 r$$

$$= C_2 \int \rho(\boldsymbol{r})^{4/3} \mathrm{d}^3 r \qquad C_2 = -\frac{3}{4} \left(\frac{3}{\pi} \right)^{1/3} = -0.739$$

$$E_{\mathrm{TFD}}[\rho(\boldsymbol{r})] = 2.871\int \rho^{5/3}(\boldsymbol{r})\mathrm{d}^3r + \frac{1}{2}\int\int \mathrm{d}^3r\,\mathrm{d}^3r'\,\frac{\rho(\boldsymbol{r})\rho(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} - \int \frac{Z\rho(\boldsymbol{r})}{|\boldsymbol{R}-\boldsymbol{r}|}\mathrm{d}^3r - 0.739\int \rho(\boldsymbol{r})^{4/3}\mathrm{d}^3r$$

There is a constraint:

$$N = \int \rho(\boldsymbol{r})\mathrm{d}^3r$$

$$\frac{\delta\left[E_{\mathrm{TFD}}[\rho] - \mu\left(\int \rho(\boldsymbol{r})\mathrm{d}r - N\right)\right]}{\delta\rho(\boldsymbol{r})} = 0$$

Problem: how to calculate this ‘differentiation’?

Answer: we need to extend the definition by introducing *functional derivatives*.

Functional derivatives

Functional derivative

$$\delta F = \int \frac{\delta F}{\delta f(x)} \delta f(x) \mathrm{d}x$$

$$\lim_{\varepsilon \to 0} \left[\frac{F[f + \varepsilon \phi] - F[f]}{\varepsilon} \right] = \left\{ \frac{\mathrm{d}}{\mathrm{d}\varepsilon} F[f + \varepsilon \phi] \right\}_{\varepsilon = 0} = \int \frac{\delta F}{\delta f(x)} \phi(x) \mathrm{d}x$$

$$\boxed{\begin{gathered} \frac{\delta(C_1 F_1 + C_2 F_2)}{\delta f(x)} = C_1 \frac{\delta F_1}{\delta f(x)} + C_2 \frac{\delta F_2}{\delta f(x)} \\[2ex] \frac{\delta(F_1 F_2)}{\delta f(x)} = \frac{\delta F_1}{\delta f(x)} F_2 + F_1 \frac{\delta F_2}{\delta f(x)} \end{gathered}}$$

Example 1

$$E_K[\rho] = 2.871\int \rho^{5/3}(\boldsymbol{r})\mathrm{d}^3r \quad\Longrightarrow\quad E_K[\rho+\delta\rho] = 2.871\int [\rho+\delta\rho]^{5/3}(\boldsymbol{r})\mathrm{d}^3r$$

$$= 2.871\int \left[\rho^{5/3}(\boldsymbol{r}) + \frac{5}{3}\rho^{2/3}(\boldsymbol{r})\delta\rho + \cdots\right]\mathrm{d}^3r$$

$$= E_K[\rho] + \frac{5}{3}2.871\int \rho^{2/3}(\boldsymbol{r})\delta\rho(\boldsymbol{r})\mathrm{d}^3r + \cdots$$

$$\Big\Downarrow$$

$$\boxed{\frac{\delta E_K[\rho]}{\delta\rho(\boldsymbol{r})} = \frac{5}{3}2.871\rho^{2/3}(\boldsymbol{r})}$$

Example 2

$$V^{\text{Hartree}} = \frac{1}{2}\int\!\!\int \mathrm{d}^3r\,\mathrm{d}^3r'\,\frac{\rho(\boldsymbol{r})\rho(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}$$

$$\begin{aligned} V^{\text{Hartree}}[\rho(\boldsymbol{r})+\delta\rho(\boldsymbol{r})] &= \frac{1}{2}\int\!\!\int \mathrm{d}^3r\,\mathrm{d}^3r'\,\frac{[\rho(\boldsymbol{r})+\delta\rho(\boldsymbol{r})]\rho(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} \\ &+ \frac{1}{2}\int\!\!\int \mathrm{d}^3r'\,\mathrm{d}^3r\,\frac{\rho(\boldsymbol{r}')[\rho(\boldsymbol{r})+\delta\rho(\boldsymbol{r})]}{|\boldsymbol{r}'-\boldsymbol{r}|} \end{aligned}$$

$$\Downarrow$$

$$\boxed{\frac{\delta V^{\text{Hartree}}[\rho(\boldsymbol{r})]}{\delta\rho(\boldsymbol{r})} = \int \frac{\rho(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}\mathrm{d}^3r'}$$

Example 3

$$V_{\mathrm{W}}[\rho(\boldsymbol{r})] = \frac{1}{8}\int \frac{\nabla\rho(\boldsymbol{r})\cdot\nabla\rho(\boldsymbol{r})}{\rho(\boldsymbol{r})}\mathrm{d}\boldsymbol{r}$$

$$V_{\mathrm{W}}[\rho(\boldsymbol{r})+\delta\rho(\boldsymbol{r})] = \frac{1}{8}\int \frac{\nabla(\rho(\boldsymbol{r})+\delta\rho(\boldsymbol{r}))\cdot\nabla(\rho(\boldsymbol{r})+\delta\rho(\boldsymbol{r}))}{(\rho(\boldsymbol{r})+\delta\rho(\boldsymbol{r}))}\mathrm{d}\boldsymbol{r}$$

$$\frac{1}{1+x} \overset{x\to 0}{\approx} 1-x$$

$$\begin{aligned}
V_{\mathrm{W}}[\rho(\boldsymbol{r})+\delta\rho(\boldsymbol{r})] &= \frac{1}{8}\int \nabla(\rho(\boldsymbol{r})+\delta\rho(\boldsymbol{r}))\cdot\nabla(\rho(\boldsymbol{r})+\delta\rho(\boldsymbol{r}))\left[1-\frac{\delta\rho(\boldsymbol{r})}{\rho(\boldsymbol{r})}\right]\frac{1}{\rho(\boldsymbol{r})}\mathrm{d}\boldsymbol{r} \\
&= \frac{1}{8}\int \left[\nabla\rho(\boldsymbol{r})\cdot\nabla\rho(\boldsymbol{r})+2\nabla\rho\cdot\nabla\delta\rho\right]\left[1-\frac{\delta\rho(\boldsymbol{r})}{\rho(\boldsymbol{r})}\right]\frac{1}{\rho(\boldsymbol{r})}\mathrm{d}\boldsymbol{r} \\
&= V_{\mathrm{W}}[\rho(\boldsymbol{r})] - \frac{1}{8}\int \frac{\nabla\rho(\boldsymbol{r})\cdot\nabla\rho(\boldsymbol{r})\delta\rho(\boldsymbol{r})}{\rho^2(\boldsymbol{r})}\mathrm{d}\boldsymbol{r} + \boxed{\frac{1}{8}\int \frac{2\nabla\rho(\boldsymbol{r})\cdot\nabla\delta\rho(\boldsymbol{r})}{\rho}\mathrm{d}\boldsymbol{r}}
\end{aligned}$$

$$-\frac{1}{8}\int \frac{\nabla\rho(\boldsymbol{r})\cdot\nabla\rho(\boldsymbol{r})\delta\rho(\boldsymbol{r})}{\rho^2(\boldsymbol{r})}\mathrm{d}\boldsymbol{r} \Rightarrow -\frac{1}{8}\int\left[\frac{\nabla\rho(\boldsymbol{r})\cdot\nabla\rho(\boldsymbol{r})}{\rho^2(\boldsymbol{r})}\right]\delta\rho(\boldsymbol{r})\mathrm{d}\boldsymbol{r}$$

$$\begin{aligned}\boxed{\frac{1}{8}\int\frac{2\nabla\rho(\boldsymbol{r})\cdot\nabla\delta\rho(\boldsymbol{r})}{\rho}\mathrm{d}\boldsymbol{r}} &= \frac{1}{4}\int\frac{\nabla\rho(\boldsymbol{r})}{\rho(\boldsymbol{r})}\cdot\mathrm{d}\left[\delta\rho(\boldsymbol{r})\boldsymbol{n}\right]\\ &= -\frac{1}{4}\int\left[\delta\rho(\boldsymbol{r})\boldsymbol{n}\right]\cdot\mathrm{d}\left[\frac{\nabla\rho(\boldsymbol{r})}{\rho(\boldsymbol{r})}\right]\\ &= -\frac{1}{8}\int\left[\frac{2\nabla^2\rho(\boldsymbol{r})}{\rho(\boldsymbol{r})}-\frac{2\nabla\rho(\boldsymbol{r})\cdot\nabla\rho(\boldsymbol{r})}{\rho^2(\boldsymbol{r})}\right]\delta\rho(\boldsymbol{r})\mathrm{d}\boldsymbol{r}\end{aligned}$$

$$V_{\mathrm{W}}[\rho(\boldsymbol{r})+\delta\rho(\boldsymbol{r})]=V_{\mathrm{W}}[\rho(\boldsymbol{r})]-\frac{1}{8}\int\frac{\nabla\rho(\boldsymbol{r})\cdot\nabla\rho(\boldsymbol{r})\delta\rho(\boldsymbol{r})}{\rho^{2}(\boldsymbol{r})}\mathrm{d}\boldsymbol{r}+\frac{1}{8}\int\frac{2\nabla\rho(\boldsymbol{r})\cdot\nabla\delta\rho(\boldsymbol{r})}{\rho}\mathrm{d}\boldsymbol{r}$$

$$=V_{\mathrm{W}}[\rho(\boldsymbol{r})]-\frac{1}{8}\int\left[\frac{\nabla\rho(\boldsymbol{r})\cdot\nabla\rho(\boldsymbol{r})}{\rho^{2}(\boldsymbol{r})}\right]\delta\rho(\boldsymbol{r})\mathrm{d}\boldsymbol{r}-$$

$$\frac{1}{8}\int\left[\frac{2\nabla^{2}\rho(\boldsymbol{r})}{\rho(\boldsymbol{r})}-\frac{2\nabla\rho(\boldsymbol{r})\cdot\nabla\rho(\boldsymbol{r})}{\rho^{2}(\boldsymbol{r})}\right]\delta\rho(\boldsymbol{r})\mathrm{d}\boldsymbol{r}$$

$$=V_{\mathrm{W}}[\rho(\boldsymbol{r})]+\frac{1}{8}\int\left[\frac{\nabla\rho(\boldsymbol{r})\cdot\nabla\rho(\boldsymbol{r})}{\rho^{2}(\boldsymbol{r})}\right]\delta\rho(\boldsymbol{r})\mathrm{d}\boldsymbol{r}-\frac{1}{4}\int\frac{\nabla^{2}\rho(\boldsymbol{r})}{\rho(\boldsymbol{r})}\delta\rho(\boldsymbol{r})\mathrm{d}\boldsymbol{r}$$

$$\boxed{\frac{\delta V_{\mathrm{W}}[\rho(\boldsymbol{r})]}{\delta\rho(\boldsymbol{r})}=\frac{1}{8}\left[\frac{\nabla\rho(\boldsymbol{r})\cdot\nabla\rho(\boldsymbol{r})}{\rho^{2}(\boldsymbol{r})}\right]-\frac{1}{4}\frac{\nabla^{2}\rho(\boldsymbol{r})}{\rho(\boldsymbol{r})}}$$

$$E_{\mathrm{TFD}}[\rho(\boldsymbol{r})] = 2.871\int \rho^{5/3}(\boldsymbol{r})\mathrm{d}^3r + \frac{1}{2}\int\int \mathrm{d}^3r\,\mathrm{d}^3r'\,\frac{\rho(\boldsymbol{r})\rho(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} - \int \frac{Z\rho(\boldsymbol{r})}{|\boldsymbol{R}-\boldsymbol{r}|}\mathrm{d}^3r - 0.739\int \rho(\boldsymbol{r})^{4/3}\mathrm{d}^3r$$

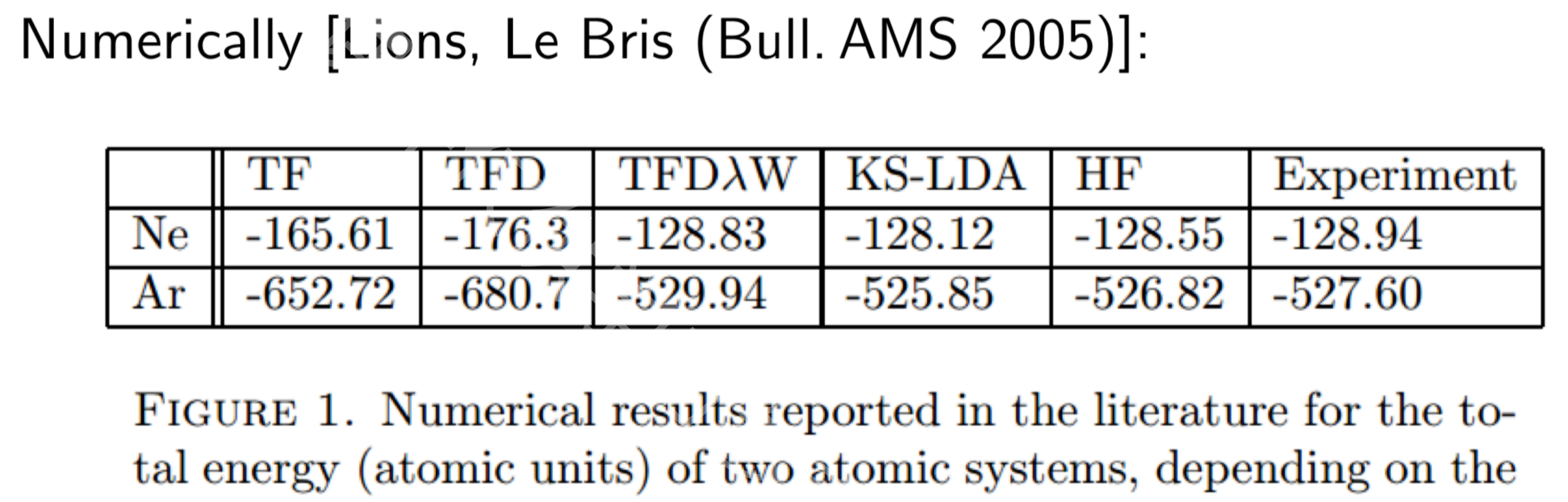
There is a constraint: $N = \int \rho(\boldsymbol{r})\mathrm{d}^3r$

$$\frac{\delta\left[E_{\mathrm{TFD}}[\rho] - \mu(\int \rho(\boldsymbol{r})\mathrm{d}r - N)\right]}{\delta\rho(\boldsymbol{r})}$$

$$\mu - \frac{5}{3}(2.871)\rho^{2/3} - \int \frac{\rho(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}\mathrm{d}\boldsymbol{r}' + \boxed{\frac{Z}{|\boldsymbol{R}-\boldsymbol{r}|}} + \frac{4}{3}(0.739)\rho^{1/3}(\boldsymbol{r}) = 0$$

Known chemical potential and external potential, one can solve the electron density.

This part is named ***external potential***, and is the potential generated by nuclei. Here only the simplest one is shown, but it can also be complicated, such as a periodic potential.



Numerically [Lions, Le Bris (Bull. AMS 2005)]:

	TF	TFD	TFDλW	KS-LDA	HF	Experiment
Ne	-165.61	-176.3	-128.83	-128.12	-128.55	-128.94
Ar	-652.72	-680.7	-529.94	-525.85	-526.82	-527.60

FIGURE 1. Numerical results reported in the literature for the total energy (atomic units) of two atomic systems, depending on the

The accuracy of TFD model is very poor. Later further corrections are proposed, such as *von Weizsacker* (von Weizsacker 1935) and others (such as Kirzhnits 1957), but it's later proved all the corrections are in a perturbation series and can only provide limited refinement to the original TFD model.

$$\frac{\delta V_{\mathrm{W}}[\rho(\boldsymbol{r})]}{\delta\rho(\boldsymbol{r})} = \frac{1}{8}\left[\frac{\nabla\rho(\boldsymbol{r})\cdot\nabla\rho(\boldsymbol{r})}{\rho^2(\boldsymbol{r})}\right] - \frac{1}{4}\frac{\nabla^2\rho(\boldsymbol{r})}{\rho(\boldsymbol{r})}$$

Density Functional Theory

Figure 1. Walter Kohn was presented receiving an honorary Doctor of Science degree by the Harvard University (AP Photo/Steven Senne).

K. Schwarz, Lu J. Sham, A. E. Mattsson, M. Scheffler

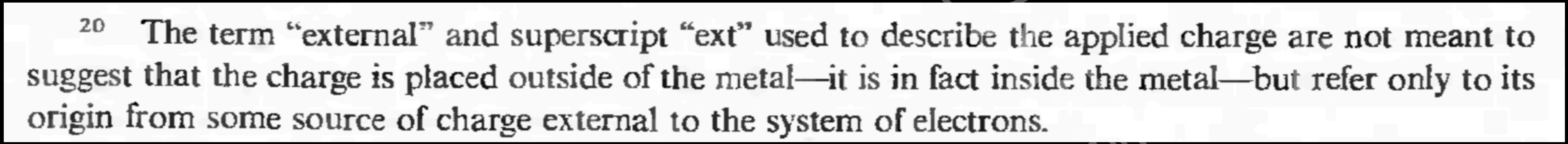
Obituary for Walter Kohn (1923–2016)

Computation **2016**, *4*, 40;
doi:10.3390/computation4040040

Hohenberg-Kohn theorem

First theorem: For any system of interacting particles in an external potential $V_{\text{ext}}(\boldsymbol{r})$, the potential $V_{\text{ext}}(\boldsymbol{r})$ is determined uniquely, except a constant, by the ground state particle density $\rho_0(\boldsymbol{r})$.

Corollary 1: Since the hamiltonian is thus fully determined, except for a constant shift of the energy, it follows that the many-body wave functions for all states (ground & excited) are determined. Therefore all properties of the system are completely determined given only the ground state density $\rho_0(\boldsymbol{r})$.



[20] The term "external" and superscript "ext" used to describe the applied charge are not meant to suggest that the charge is placed outside of the metal—it is in fact inside the metal—but refer only to its origin from some source of charge external to the system of electrons.

Ashcroft & Mermin, *Solid State Physics*, pp. 338

$$\begin{aligned} E_a^0 &< \langle \psi_b^0 | \hat{H}_a | \psi_b^0 \rangle \\ &= \langle \psi_b^0 | \hat{H}_a - \hat{H}_b + \hat{H}_b | \psi_b^0 \rangle \\ &= \langle \psi_b^0 | \hat{v}_a - \hat{v}_b | \psi_b^0 \rangle + E_b^0 \end{aligned}$$

$$E_a^o < \int d\mathbf{r}[v_a - v_b] n^0(\mathbf{r}) + E_b^0$$

$$E_b^o < \int d\mathbf{r}[v_b - v_a] n^0(\mathbf{r}) + E_a^0$$

$$E_a^0 + E_b^0 < E_a^0 + E_b^0$$

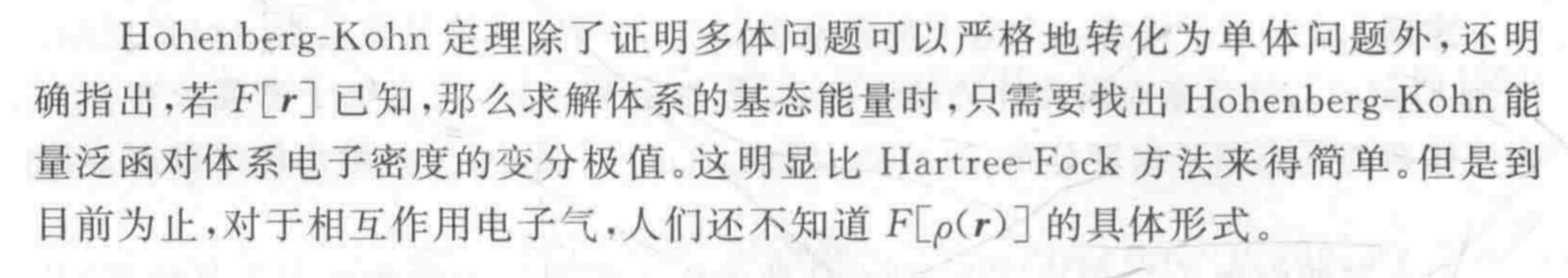
Hohenberg-Kohn Theorem (2)

Second theorem: A universal functional for the energy $E[n]$ in terms of the density $n(\boldsymbol{r})$ can be defined, valid for any external potential $V_{\text{ext}}(\boldsymbol{r})$, the exact ground state energy of the system is the global minimum value of this functional, and the density $n(\boldsymbol{r})$ that minimizes the functional is the exact ground state density $n_0(\boldsymbol{r})$.

$$E_v[n] = \int d\mathbf{r} v(\mathbf{r}) n(\mathbf{r}) + F[n]$$

Corollary 2: The functional $E[n]$ alone is sufficient to determine the exact ground state energy and density. (In general, excited states of the electrons must be determined by other means.)

$$\begin{aligned} E &= \min_{\psi} \langle \psi \mid \hat{H} \mid \psi \rangle = \min_{n} \min_{\psi \to n} \langle \psi \mid \hat{H} \mid \psi \rangle \\ &= \min_{n} [\min_{\psi \to n} \langle \psi \mid \hat{T} + \hat{U} \mid \psi \rangle + \int d\mathbf{r} v(\mathbf{r}) n(\mathbf{r})] \\ &= \min_{n} \{F[n] + \int d\mathbf{r} v(\mathbf{r}) n(\mathbf{r})\} \end{aligned}$$



Hohenberg-Kohn 定理除了证明多体问题可以严格地转化为单体问题外，还明确指出，若 $F[\boldsymbol{r}]$ 已知，那么求解体系的基态能量时，只需要找出 Hohenberg-Kohn 能量泛函对体系电子密度的变分极值。这明显比 Hartree-Fock 方法来得简单。但是到目前为止，对于相互作用电子气，人们还不知道 $F[\rho(\boldsymbol{r})]$ 的具体形式。

单斌等，《材料学的纳米尺度计算模拟》，2015 pp. 146

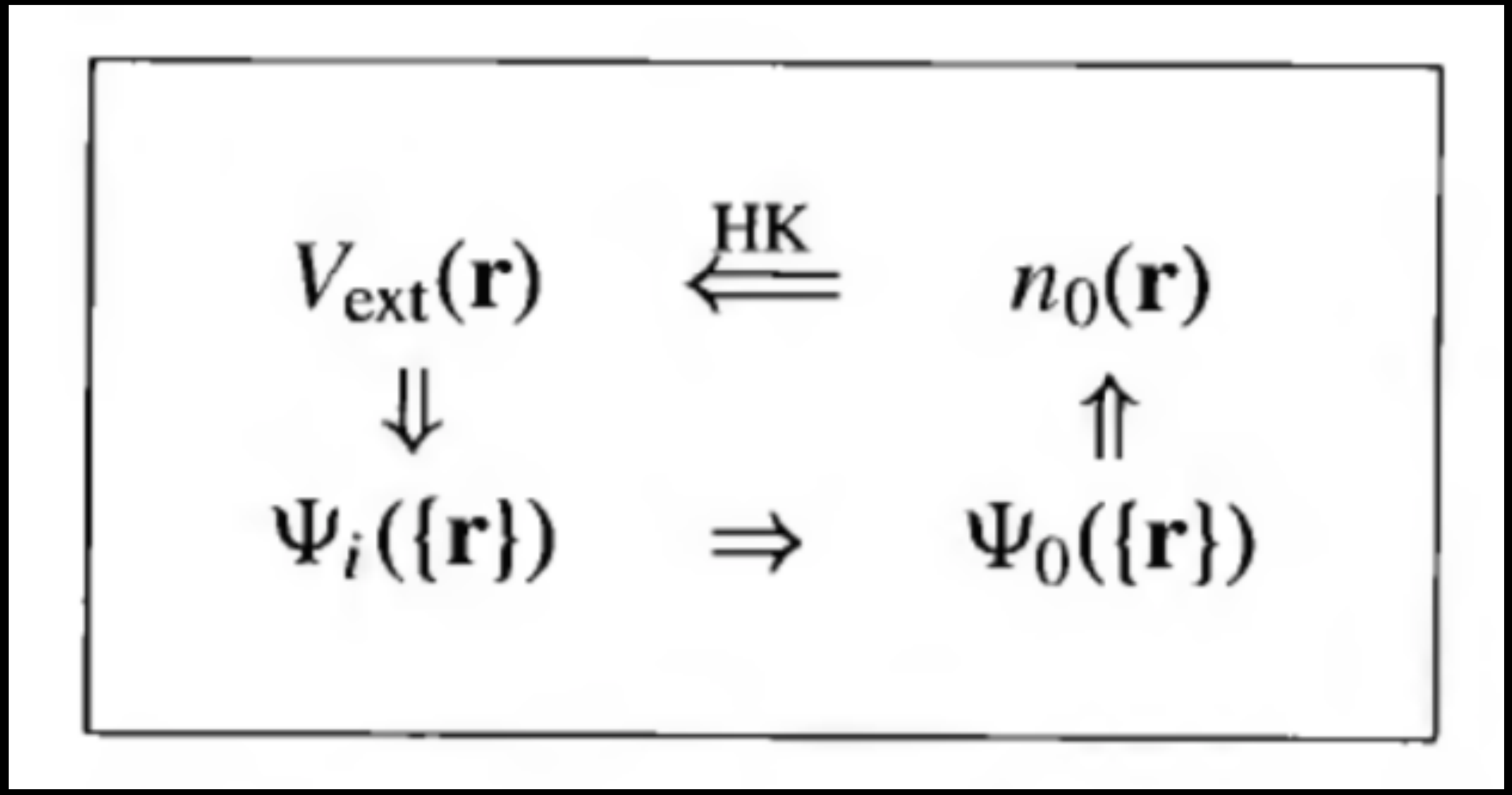
Kohn-Sham equation

$$E[\rho] = F[\rho] + V_{\text{ext}} = T_{\text{S}} + V_{\text{ext}} + V_{\text{H}} + v_{\text{XC}}$$

$$\rho(\boldsymbol{r}) = \sum_{i=1}^{\text{occ}} \int |\phi_i(\boldsymbol{r})|^2 \mathrm{d}^3 r$$

$$T_{\text{S}}[\rho] = -\frac{1}{2}\sum_{i=1}^{N} \int \psi_i^*(\boldsymbol{r})\, \nabla^2 \psi_i(\boldsymbol{r}) \mathrm{d}\boldsymbol{r}$$

$$V_{\text{H}} = \frac{1}{2} \int\int \mathrm{d}^3 r\, \mathrm{d}^3 r' \,\frac{\rho(\boldsymbol{r})\rho(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}$$



$$\begin{tikzcd} V_{\text{ext}}(\mathbf{r}) \arrow[d, Rightarrow] & n_0(\mathbf{r}) \arrow[l, Rightarrow, "\text{HK}"'] \\ \Psi_i(\{\mathbf{r}\}) \arrow[r, Rightarrow] & \Psi_0(\{\mathbf{r}\}) \arrow[u, Rightarrow] \end{tikzcd}$$

$$v_{\text{XC}} = E_{\text{tot}} - T_{\text{S}} - V - V_{\text{H}} = (T - T_{\text{S}}) + (V - V_{\text{H}})$$

$$\left[-\frac{1}{2}\nabla^2 + v_{\text{ext}}(\boldsymbol{r}) + v_{\text{H}}(\boldsymbol{r}) + v_{\text{XC}}(\boldsymbol{r})\right] \phi_i(\boldsymbol{r}) = \varepsilon_i \phi_i(\boldsymbol{r})$$

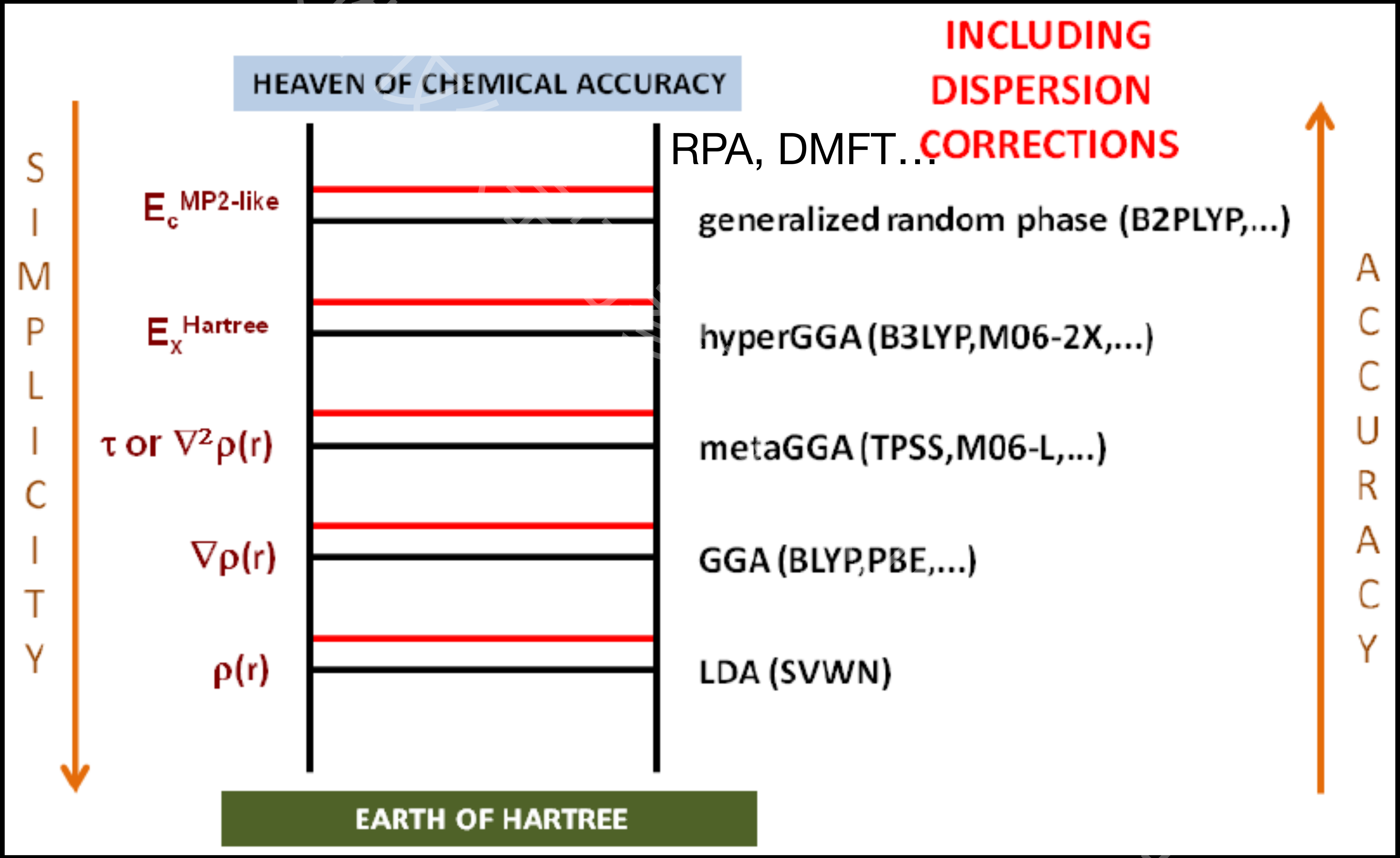
Total energy

$$E = \sum_{k=1}^{N} \varepsilon_k - \frac{1}{2} \int \mathrm{d}^3 r \, \mathrm{d}^3 r' \, \frac{n(\boldsymbol{r}) n(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} + E_{\mathrm{XC}}[n] - \int \mathrm{d}^3 r \, V_{\mathrm{XC}}[n(\boldsymbol{r})] n(\boldsymbol{r})$$

1. Kohn-Sham orbital is not the single electron orbital. It has no corresponding multi-electron wave function. Only the density generated by it is meaningful.
2. Overall the KS orbitals are a good basis for qualitative interpretation of molecular orbitals.
3. Koopmans' theorem in DFT: the eigenvalue of the uppermost occupied KS orbital equals the exact ionization potential.

JACS **1999**, 121, 3414; *PRL* **1982**, 49, 1691; *PRB* **1985**, 31, 3231
And papers from F. M. Bickelhaupt

LDA and GGA and then



Local density approximation, LDA for E_{X}

$$E_{\mathrm{XC}}^{\mathrm{LDA}}[\rho] = \int \mathrm{d}^3 r \varepsilon_{\mathrm{XC}}(n) n(\boldsymbol{r})$$

$$E_{\mathrm{XC}}^{\mathrm{LDA,\ Tot}}[\rho] = \int \mathrm{d}^3 r (\varepsilon_{\mathrm{XC}}[n] - v_{\mathrm{XC}}) n(\boldsymbol{r})$$

Recall Dirac’s exchange:

$$E_{\mathrm{x}}[\rho(\boldsymbol{r})] = V_{\mathrm{x}} = \int \varepsilon_{\mathrm{x}}(\boldsymbol{r})\rho(\boldsymbol{r})\mathrm{d}^3 r = -\frac{3}{4}\int \left(\frac{3\rho(\boldsymbol{r})}{\pi}\right)^{1/3} \rho(\boldsymbol{r})\mathrm{d}^3 r$$

$$\varepsilon_{\mathrm{X}}[\rho(\boldsymbol{r})] = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3} \rho^{1/3}(\boldsymbol{r}) \qquad = C_2 \int \rho(\boldsymbol{r})^{4/3}\mathrm{d}^3 r \qquad C_2 = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3} = -0.739$$

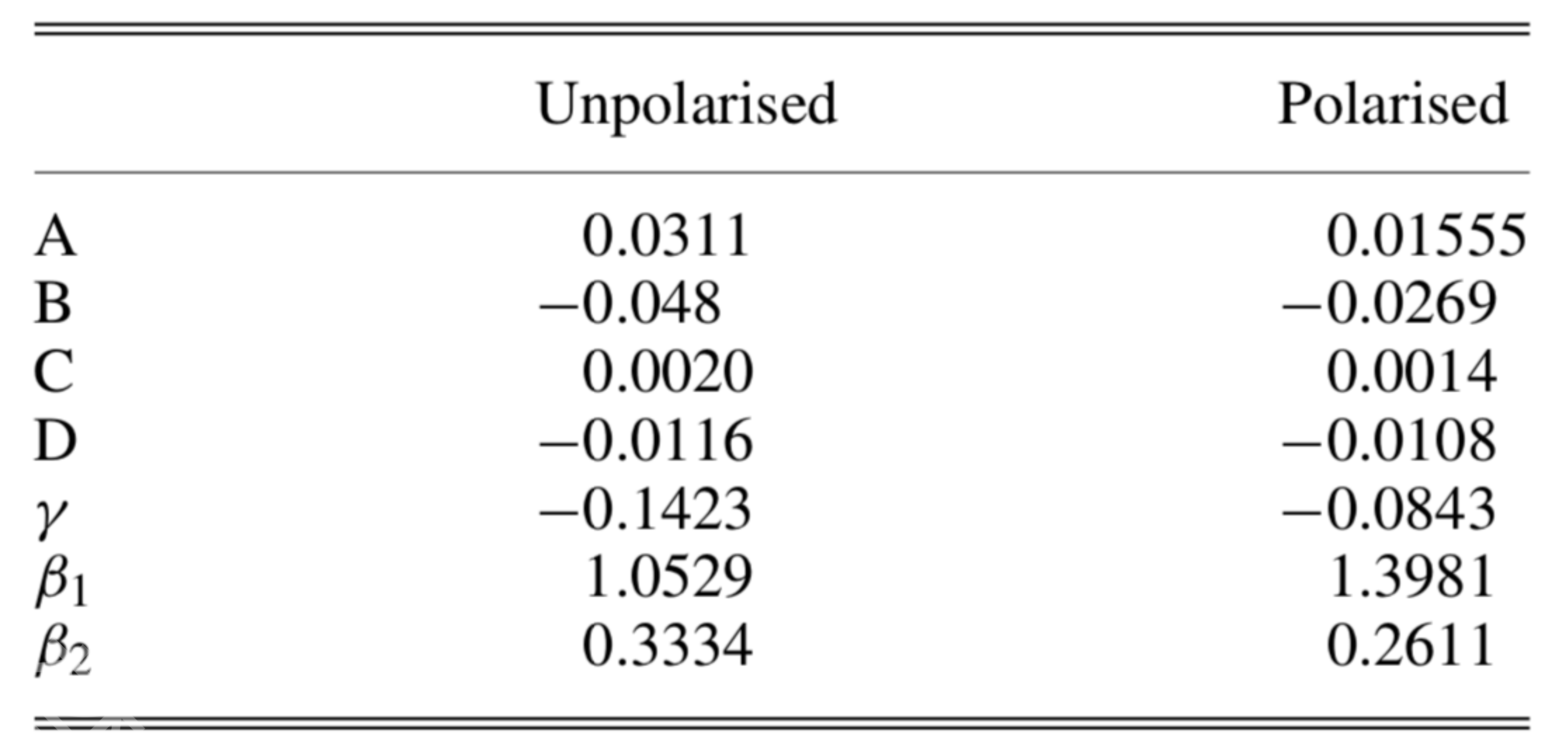
$$v_{\mathrm{X}}[\rho(\boldsymbol{r})] = \frac{\delta E_{\mathrm{X}}[\rho(\boldsymbol{r})]}{\delta \rho(\boldsymbol{r})} = -\left(\frac{3}{\pi}\right)^{1/3} \rho^{1/3}(\boldsymbol{r})$$

Local density approximation, LDA for E_{C}

Usually fitted from QMC results. Popular data used is from Ceperly and Alder.

$$\varepsilon_{\mathrm{C}} = \frac{\gamma}{1 + \beta_1\sqrt{r_s} + \beta_2 r_s}, \quad r_s \geq 1$$

$$\varepsilon_{\mathrm{C}} = A \ln r_s + B + C r_s \ln r_s + D r_s, \quad r_s < 1$$



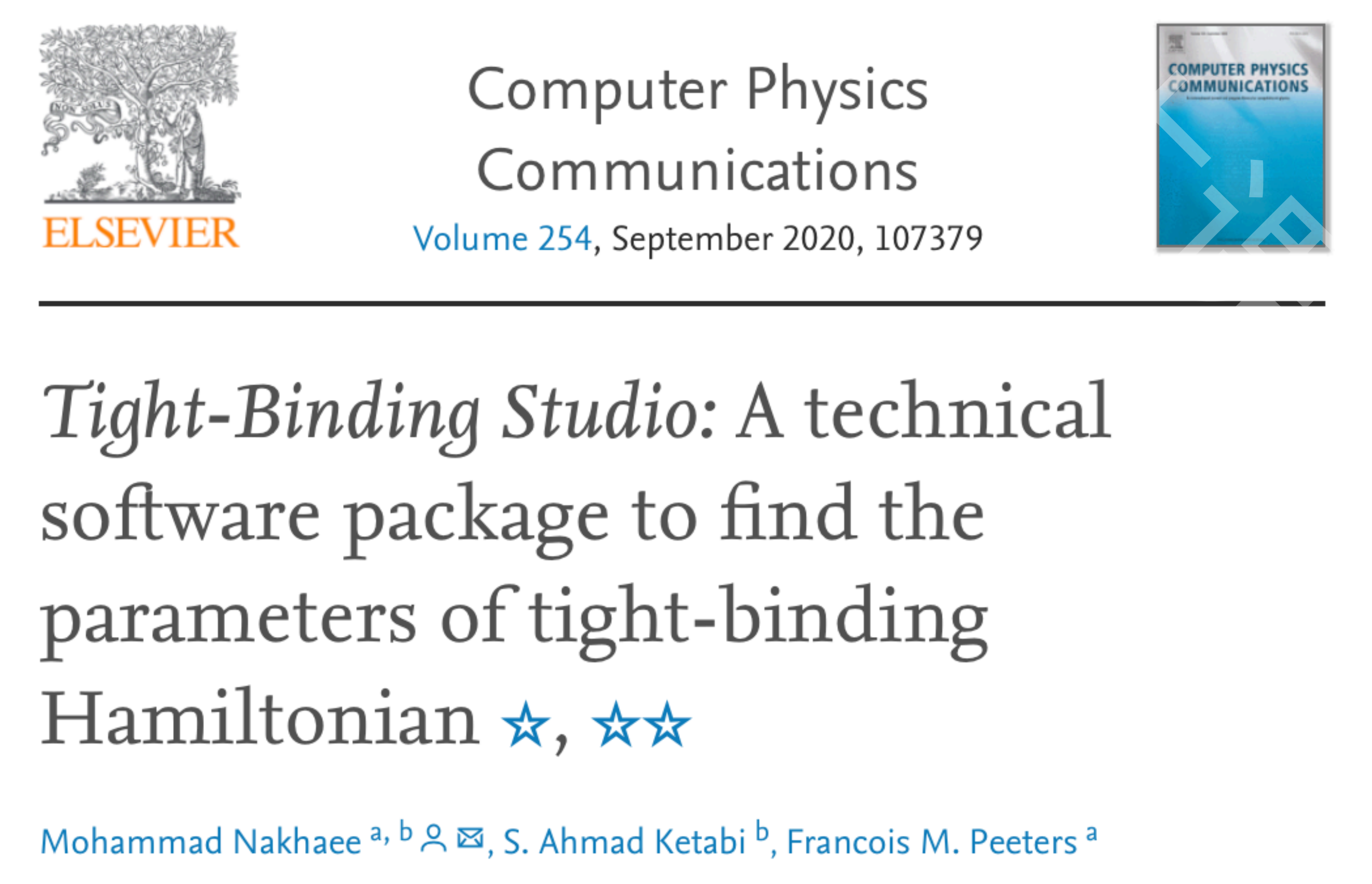
	Unpolarised	Polarised
A	0.0311	0.01555
B	−0.048	−0.0269
C	0.0020	0.0014
D	−0.0116	−0.0108
γ	−0.1423	−0.0843
β_1	1.0529	1.3981
β_2	0.3334	0.2611

$$v_{\mathrm{C}} = \varepsilon_{\mathrm{C}} \frac{1 + (7/6)\beta_1\sqrt{r_s} + (4/3)\beta_2 r_s}{1 + \beta_1\sqrt{r_s} + \beta_2 r_s}, \quad r_s \geq 1$$

$$v_{\mathrm{C}} = A \ln r_s + B - A/3 + \frac{2}{3} C r_s \ln r_s + \frac{(2D - C)}{3} r_s, \quad r_s < 1$$

[1] J. P. Perdew and A. Zunger, *Phys. Rev. B*, 23 (1981), 5048–79.
[2] D. M. Ceperley, B. Alder, *Phys. Rev. B*, 18 (1978), 3126–38.

Approximation method: tight binding



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Computer Physics Communications

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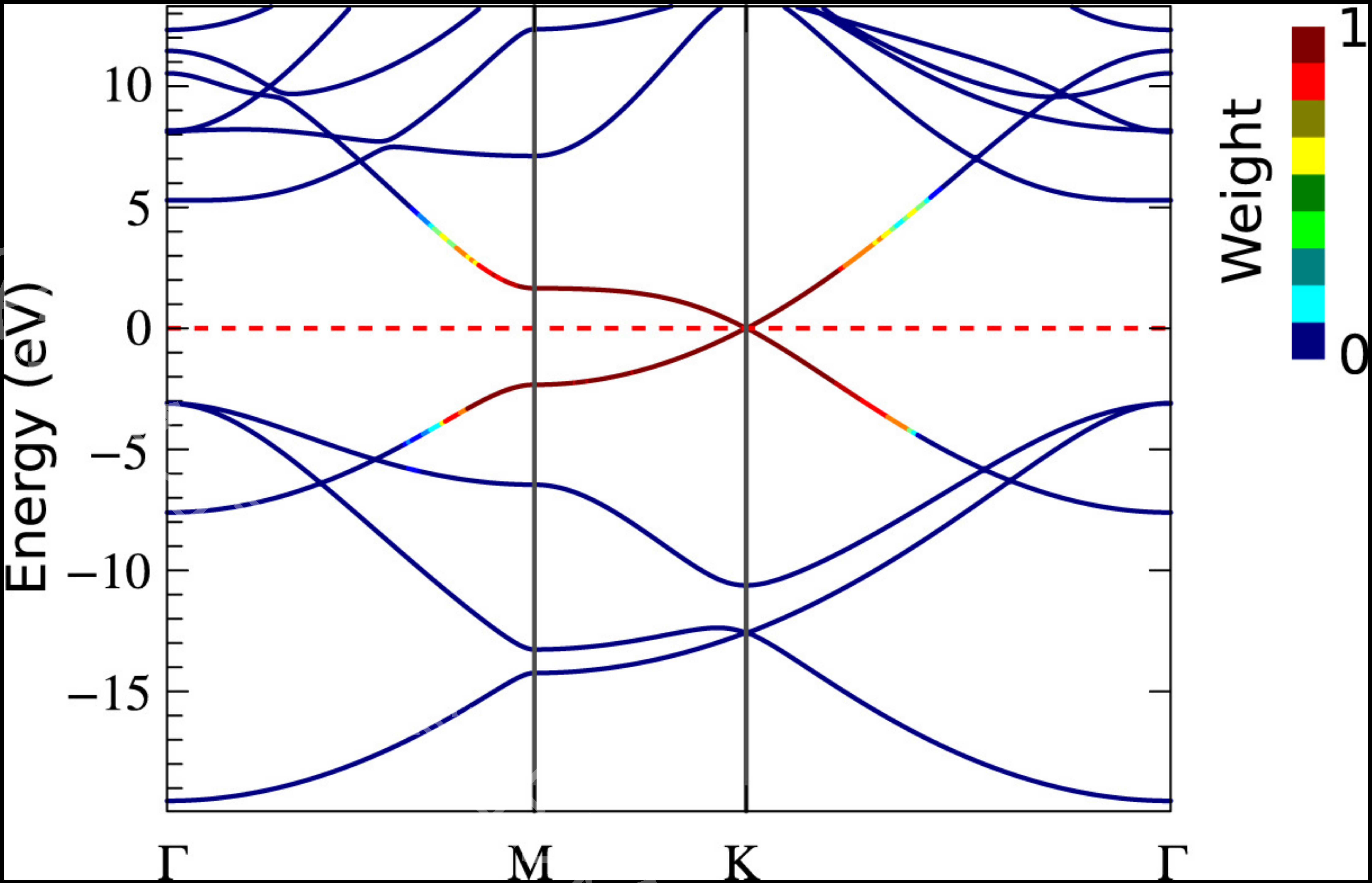
Tight-Binding Studio: A technical software package to find the parameters of tight-binding Hamiltonian ☆, ☆☆

Mohammad Nakhaee [a, b], S. Ahmad Ketabi [b], Francois M. Peeters [a]

A quantum technical software package to find Tight-Binding Hamiltonian for nano-structures
Email: developer.support@tight-binding.com



https://github.com/awvwgk/skprogs
https://dftb.org/parameters/download/

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