The DFT

Starting from Chapter 3, DFT of atoms and molecules, Parr & Lee 1989

DFT- Thomas-Fermi model for atoms

- The theory showing how the N-electron wave function depending on 3N coordinates can be replaced by electron density depending only on 3 coordinates.
- The form of what we are looking for (optimal electron density) was simplified but the troubles (unknown mathematical form of the exact density functional) remained.
- Thomas 1927, electrons in atoms: el. are distributed uniformly in the 6D phase space, their effective potential is determined by nuclear charge and distribution of electrons

Space divided in cubes $\Delta V = l^3$ with fixed number of electrons ΔN behaving "like independent fermions".

$$\varepsilon(n_x, n_y, n_z) = \frac{h^2}{8ml^2}(n_x^2 + n_y^2 + n_z^2)$$

Energy levels, $n_{x,y,z} = 1,2,\ldots$, of particle in 3D infinite well box.

$$= \frac{h^2}{8ml^2} R^2$$

$$\Phi(\varepsilon) = \frac{1}{8}\left(\frac{4\pi R^3}{3}\right) = \frac{\pi}{6}\left(\frac{8ml^2\varepsilon}{h^2}\right)^{3/2}$$

Number of energy levels, states, with $E < \varepsilon$.

The number of energy levels between ε and $\varepsilon + \delta\varepsilon$ is accordingly

$$g(\varepsilon)\,\Delta\varepsilon = \Phi(\varepsilon + \delta\varepsilon) - \Phi(\varepsilon)$$

$$= \frac{\pi}{4}\left(\frac{8ml^2}{h^2}\right)^{3/2} \varepsilon^{1/2}\,\delta\varepsilon + \mathrm{O}((\delta\varepsilon)^2)$$

where the function $g(\varepsilon)$ is the *density of states at energy* ε.

Total energy for the cell with ΔN electrons

$$\Delta E = 2\int \varepsilon f(\varepsilon) g(\varepsilon)\, d\varepsilon$$

$$= 4\pi \left(\frac{2m}{h^2}\right)^{3/2} l^3 \int_0^{\varepsilon_F} \varepsilon^{3/2}\, d\varepsilon$$

$$= \frac{8\pi}{5}\left(\frac{2m}{h^2}\right)^{3/2} l^3 \varepsilon_F^{5/2}$$

2 – because α and β

ε – energy, "almost continuous" for high states

f - Fermi – Dirac distribution

g – number of energy levels in (ε, Δε) interval

ε_F – Fermi energy, zero temperature limit of chemical potential μ

$$f(\varepsilon) = \frac{1}{1 + e^{\beta(\varepsilon - \mu)}} \qquad f(\varepsilon) = \begin{cases} 1, & \varepsilon < \varepsilon_F \\ 0, & \varepsilon > \varepsilon_F \end{cases} \quad \text{as } \beta \to \infty$$

ΔN and ε_F are related by

$$\Delta N = 2\int f(\varepsilon) g(\varepsilon)\, d\varepsilon$$

$$= \frac{8\pi}{3}\left(\frac{2m}{h^2}\right)^{3/2} l^3 \varepsilon_F^{3/2}$$

Therefore we can substitute ΔN and obtain dependence of kinetic energy on el. density $\Delta N/l^3$.

$$\Delta E = \frac{3}{5}\Delta N\, \varepsilon_F$$

$$= \frac{3h^2}{10m}\left(\frac{3}{8\pi}\right)^{2/3} l^3 \left(\frac{\Delta N}{l^3}\right)^{5/3}$$

Note: $\rho = \Delta N/l^3$ is not constant but varying in space!

The Thomas-Fermi kinetic energy functional,
Called the LDA - Local Density Approximation

The total kinetic energy $T_{TF}[\rho] = C_F \int \rho^{5/3}(\mathbf{r})\, d\mathbf{r}, \qquad C_F = \frac{3}{10}(3\pi^2)^{2/3} = 2.871$

The limit $\Delta V \to 0$, with $\rho = \Delta N/\Delta V = \rho(\mathbf{r})$ finite
allows integration instead of summation

The electronic property, the kinetic energy, is thus determined with electron density obtained with local relations for homogenous electronic system.

Note: the kinetic energy T_{TF} is function of ρ(r), whereas the rigorous form for the kinetic energy is that in terms of first order density matrix:

$$
\begin{aligned}
E &= E[\rho_1(\mathbf{r}_1', \mathbf{r}_1), \rho_2(\mathbf{r}_1, \mathbf{r}_2)] = E[\rho_2(\mathbf{r}_1'\mathbf{r}_2, \mathbf{r}_1\mathbf{r}_2)] \\
&= \boxed{\int [-\tfrac{1}{2}\nabla_{\mathbf{r}}^2 \rho_1(\mathbf{r}', \mathbf{r})]_{\mathbf{r}'=\mathbf{r}}\, d\mathbf{r}} + \int v(\mathbf{r})\rho(\mathbf{r})\, d\mathbf{r} \\
&\quad + \iint \frac{1}{r_{12}} \rho_2(\mathbf{r}_1, \mathbf{r}_2)\, d\mathbf{r}_1\, d\mathbf{r}_2
\end{aligned}
$$

The total energy functional, **Thomas-Fermi model** for atoms (for molecules the el.-nucleus part is modified accordingly) covers only kinetic energy and classical electrostatic part for el.-nucleus end el.-el. interaction.

$$E_{\mathrm{TF}}[\rho(\mathbf{r})] = C_F \int \rho^{5/3}(\mathbf{r})\, d\mathbf{r} - Z \int \frac{\rho(\mathbf{r})}{\mathbf{r}}\, d\mathbf{r} + \frac{1}{2} \int\int \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}\, d\mathbf{r}_1\, d\mathbf{r}_2$$

Now, we wish to find the energy minimum, the extreme of the functional, (like in the case of HF theory). The same way - the boundary condition

$$N = N[\rho(\mathbf{r})] = \int \rho(\mathbf{r})\, d\mathbf{r}$$

and the ground state density variation is

$$\delta\left\{E_{\mathrm{TF}}[\rho] - \mu_{\mathrm{TF}}\left(\int \rho(\mathbf{r})\, d\mathbf{r} - N\right)\right\} = 0$$

The Euler-Lagrange equation that can be solved employing boundary condition is

$$\mu_{\mathrm{TF}} = \frac{\delta E_{\mathrm{TF}}[\rho]}{\delta \rho(\mathbf{r})} = \tfrac{5}{3} C_F \rho^{2/3}(\mathbf{r}) - \phi(\mathbf{r})$$

where Φ (r) is the electrostatic potential

$$\phi(\mathbf{r}) = \frac{Z}{r} - \int \frac{\rho(\mathbf{r}_2)}{|\mathbf{r} - \mathbf{r}_2|} d\mathbf{r}_2$$

The T-F theory is oversimplified, not working for molecules, unable to describe binding, and having also low accuracy even for atoms. The situation changed (the model was improved) in 1964 when Hohenberg-Kohn showed that T-F model may be regarded as approximation to the exact theory for ground states, the Density Functional Theory.

Thomas-Fermi and related models

We have proved that ρ determines N, v(r), and E[ρ] and that ρ(r) is solution of stationary principle

$$\delta\{E[\rho]-\mu N[\rho]\}=0$$

where μ is Lagrange multiplier and E[ρ] is defined

$$E[\rho]=T[\rho]+\int\rho(\mathbf{r})v(\mathbf{r})\,d\mathbf{r}+V_{ee}[\rho]$$

and classical part of V_{ee} is Coulomb energy

$$J[\rho]=\frac{1}{2}\iint\frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_2-\mathbf{r}_1|}\,d\mathbf{r}_1\,d\mathbf{r}_2$$

The problem (big problem) remains how to calculate T[ρ] and nonclassical part of V_{ee}

The traditional TF theory is the first approximation: “replace $V_{ee\ by}$ J[ρ] and take T[ρ] from the theory of noninteracting uniform gas”, T-F 1927.

The **Thomas-Fermi-Dirac model (TFD)** is the next step, accept T[ρ] and for V_{ee}add to J[ρ] the exchange formula for a uniform electron gas, Dirac 1930.

TF theory is thus obtained from TFD when ignoring the exchange contribution.

Consider the nondegenerate closed shell ground state described by single determinant wave function, density and first order density

$$\rho_1(\mathbf{r}_1, \mathbf{r}_1') = 2\sum_i^{N/2} \phi_i(\mathbf{r}_1)\phi_i^*(\mathbf{r}_1')$$

The energy is given by

$$E_{\mathrm{HF}}[\rho_1] = \int \left[-\frac{1}{2}\nabla_1^2\rho_1(\mathbf{r}_1, \mathbf{r}_2)\right]_{\mathbf{r}_2=\mathbf{r}_1} d\mathbf{r}_1 + \int \rho(\mathbf{r})v(\mathbf{r})\, d\mathbf{r}$$

$$+ J[\rho] - \frac{1}{4}\iint \frac{1}{r_{12}}\rho_1(\mathbf{r}_1, \mathbf{r}_2)\rho_1(\mathbf{r}_2, \mathbf{r}_1)\, d\mathbf{r}_1\, d\mathbf{r}_2$$

Comparison with $E[\rho] = T[\rho] + \int \rho(\mathbf{r})v(\mathbf{r})\, d\mathbf{r} + V_{ee}[\rho]$

gives $T[\rho] = \int [-\frac{1}{2}\nabla_1^2 \rho_1(\mathbf{r}_1, \mathbf{r}_2)]_{\mathbf{r}_2=\mathbf{r}_1}\, d\mathbf{r}_1$

$$V_{ee}[\rho] = J[\rho] - K[\rho]$$

Where K[ρ] is the HF exchange energy functional $K[\rho] = \frac{1}{4}\int \frac{1}{r_{12}} |\rho_1(\mathbf{r}_1, \mathbf{r}_2)|^2\, d\mathbf{r}_1\, d\mathbf{r}_2$

The expression for V_{ee} implies assumption that correlation effects can be ignored and we express T[ρ] and K[ρ] in form of the first-order density matrix. For an approximate solution we turn to description of uniform electron gas build from particle in box states with boundary condition $\psi(x + l) = \psi(x)$. leading to the orbitals

$$\psi(k_x, k_y, k_z) = \frac{1}{l^{3/2}} e^{i(k_x x + k_y y + k_z z)}$$

$$= \frac{1}{V^{1/2}} e^{i\mathbf{k}\cdot\mathbf{r}}$$

$$k_x = \frac{2\pi}{l} n_x, \qquad k_y = \frac{2\pi}{l} n_y, \qquad k_z = \frac{2\pi}{l} n_z \qquad\qquad n_x, n_y, n_z = 0, \pm 1, \pm 2 \cdots$$

$$E(n_x, n_y, n_z) = \frac{h^2}{8ml^2}\left[(2n_x)^2 + (2n_y)^2 + (2n_z)^2\right]$$

The density matrix becomes $\rho_1(\mathbf{r}_1, \mathbf{r}_2) = \frac{2}{V} \sum_{\text{all occupied } \mathbf{k}} e^{i\mathbf{k}\cdot(\mathbf{r}_1 - \mathbf{r}_2)}$

And for many occupied sates the summation becomes an integral

$$\begin{aligned}\rho_1(\mathbf{r}_1, \mathbf{r}_2) &= \frac{1}{4\pi^3} \int e^{i\mathbf{k}\cdot(\mathbf{r}_1 - \mathbf{r}_2)}\, d\mathbf{k} \\ &= \frac{1}{4\pi^3} \int_0^{k_F} k^2\, dk \iint e^{i\mathbf{k}\cdot\mathbf{r}_{12}} \sin\theta\, d\theta\, d\phi\end{aligned}$$

$$dn = (l/2\pi)^3\, d\mathbf{k} = (V/8\pi^3)\, d\mathbf{k}.$$

$$\rho(\mathbf{r}) = \frac{k_F^3}{3\pi^2}$$

The quantity k_F is determined by

$$\rho(\mathbf{r}) = \frac{k_F^3}{3\pi^2} \qquad \text{or} \qquad k_F(\mathbf{r}) = [3\pi^2\rho(\mathbf{r})]^{1/3}$$

For inhomogenous system the argument r of k_F(r) will be and average of r1 and r2 and we therefore introduce the following substitution

$$\mathbf{r} = \tfrac{1}{2}(\mathbf{r}_1 + \mathbf{r}_2), \qquad \mathbf{s} = \mathbf{r}_1 - \mathbf{r}_2$$

integrate ρ(r1,r1) and put the results into K[ρ], T[ρ].

$$\rho_1(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{4\pi^3}\int_0^{k_F} k^2\,dk \int_{\theta=0}^{\pi} \sin\theta\, e^{ikr_{12}\cos\theta}\,d\theta \int_0^{2\pi} d\phi$$

$$= 3\rho(\mathbf{r})\left[\frac{\sin t - t\cos t}{t^3}\right] = \rho_1(\mathbf{r}, s) \qquad\qquad t = k_F(\mathbf{r})s$$

This is first-order spin-less density matrix for a uniform gas in coordinates r, s.

The kinetic energy becomes

$$\begin{aligned}[\nabla_1^2 \rho_1(\mathbf{r}_1, \mathbf{r}_2)]_{\mathbf{r}_2=\mathbf{r}_1} &= [(\tfrac{1}{4}\nabla_{\mathbf{r}}^2 + \nabla_s^2 + \nabla_{\mathbf{r}}\nabla_s)\rho_1(\mathbf{r}, s)]_{s=0} \\ &= \tfrac{1}{4}\nabla_{\mathbf{r}}^2 \rho(\mathbf{r}) - \tfrac{3}{5}(3\pi^2)^{2/3}\rho(\mathbf{r})^{5/3}\end{aligned}$$

Where $\nabla_{\mathbf{r}_1}^2 = \frac{1}{4}\nabla_{\mathbf{r}}^2 + \nabla_s^2 + \nabla_{\mathbf{r}}\nabla_s, \qquad \nabla_{\mathbf{r}_2}^2 = \frac{1}{4}\nabla_{\mathbf{r}}^2 + \nabla_s^2 - \nabla_{\mathbf{r}}\nabla_s$

and $\int \nabla^2 \rho(\mathbf{r})\, d\mathbf{r} = 0$

$$T_{\mathrm{TF}}[\rho] = C_F \int \rho(\mathbf{r})^{5/3}\, d\mathbf{r}, \qquad \text{with} \qquad C_F = \tfrac{3}{10}(3\pi^2)^{2/3} = 2.8712$$

This is Thomas – Fermi kinetic energy formula and the exchange energy by Dirac is

$$\begin{aligned}K_D[\rho] &= \frac{1}{4}\iint \frac{[\rho_1(\mathbf{r}, s)]^2}{s}\, d\mathbf{r}\, ds \\ &= 9\pi \int \rho^2(\mathbf{r}) \frac{1}{k_F^2}\, d\mathbf{r}\left[\int_0^\infty \frac{(\sin t - t\cos t)^2}{t^5}\, dt\right] \\ &= C_x \int \rho^{4/3}(\mathbf{r})\, d\mathbf{r}, \qquad \text{with} \qquad C_x = \frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3} = 0.7386\end{aligned}$$

The integral in previous slide can be evaluated when considering

$$q = (\sin t / t) \qquad \frac{dq}{dt} = -\left[\frac{\sin t - t\cos t}{t^2}\right] \qquad \text{and} \qquad \frac{d^2q}{dt^2} = -\frac{2}{t}\frac{dq}{dt} - q$$

$$\begin{aligned}\int_0^\infty \frac{(\sin t - t\cos t)^2}{t^5}\,dt &= \int_0^\infty \left(\frac{dq}{dt}\right)\left(\frac{1}{t}\frac{dq}{dt}\right)dt \\ &= \int_0^\infty \left(\frac{dq}{dt}\right)\left(-\frac{1}{2}q - \frac{1}{2}\frac{d^2q}{dt^2}\right)dt \\ &= -\frac{1}{4}\int_0^\infty \frac{d}{dt}\left[q^2 + \left(\frac{dq}{dt}\right)^2\right]dt = \frac{1}{4}\end{aligned}$$

The final energy functional becomes

$$E_{\text{TFD}}[\rho] = C_F \int \rho(\mathbf{r})^{5/3}\,d\mathbf{r} + \int \rho(\mathbf{r})v(\mathbf{r})\,d\mathbf{r} + J[\rho] - C_{\mathbf{x}} \int \rho(\mathbf{r})^{4/3}\,d\mathbf{r}$$

The Thomas-Fermi functional can be obtained by setting Cx = 0 and the corresponding Lagrange Euler equation is

$$\mu_{\mathrm{TFD}} = \tfrac{5}{3}C_F\rho^{2/3}(\mathbf{r}) - \tfrac{4}{3}C_x\rho^{1/3}(\mathbf{r}) - \phi(\mathbf{r})$$

where Φ is classical electrostatic potential.

Suppose the T[ρ] has a form of local density functional

$$T[\rho] = \int t(\rho)\, d\mathbf{r},$$

where t(ρ) is *function* of ρ and if we scale the wave-function according to

$$\Psi_\lambda \equiv \lambda^{3N/2}\Psi(\lambda\mathbf{r}_1, \lambda\mathbf{r}_2, \ldots; R_1, R_2, \ldots) \qquad T[\Psi_\lambda] = \lambda^2 T[\Psi_1]$$

The density becomes scaled density

$$\rho_\lambda(\mathbf{r}) = \lambda^3\rho(\lambda\mathbf{r})$$

and the kinetic energy assuming the scaling becomes

$$T[\rho_\lambda] = \int t(\lambda^3\rho(\lambda\mathbf{r}))\, d\mathbf{r} = \lambda^{-3}\int t(\lambda^3\rho(\mathbf{r}))\, d\mathbf{r}$$

$$= \lambda^2 \int t(\rho(\mathbf{r}))\, d\mathbf{r} = \lambda^2 T[\rho]$$

Accordingly

$$t(\lambda^3\rho(\mathbf{r})) = \lambda^5 t(\rho(\mathbf{r}))$$

$$t(\lambda\rho) = \lambda^{5/3} t(\rho)$$

And we say that t(ρ) is homogenous of degree 5/3 in ρ, the is T[ρ] = $A \int \rho^{5/3}\, d\mathbf{r}$ the Thomas-Fermi form.

Similarly, assuming the scaling we have

$$k(\rho_\lambda) = \lambda k[\rho]$$

$$k(\lambda\rho) = \lambda^{4/3} k(\rho)$$

And we say that k(ρ) is homogenous of degree 4/3 in ρ, K[ρ] = $B \int \rho^{4/3}\, d\mathbf{r}$ the Dirac form.

The total energy functional, following the assumption of locality, is of the form

$$E[\rho] = A \int \rho(\mathbf{r})^{5/3}\, d\mathbf{r} + \int \rho(\mathbf{r}) v(\mathbf{r})\, d\mathbf{r} + J[\rho] - B \int \rho(\mathbf{r})^{4/3}\, d\mathbf{r}$$

The solution to Euler equation for Thomas-Fermi

$$\mu_{\mathrm{TF}} = \frac{\delta E_{\mathrm{TF}}[\rho]}{\delta \rho(\mathbf{r})} = \tfrac{5}{3} C_F \rho^{2/3}(\mathbf{r}) - \phi(\mathbf{r})$$

and Thomas-Fermi-Dirac

$$\mu_{\mathrm{TFD}} = \tfrac{5}{3} C_F \rho^{2/3}(\mathbf{r}) - \tfrac{4}{3} C_{\mathbf{x}} \rho^{1/3}(\mathbf{r}) - \phi(\mathbf{r})$$

should be taken for granted.

The solution may or may not have al qualitative properties of exact Schrodinger density.

For example, the cusp (not to cause blow ups) $\frac{\partial}{\partial r_\alpha} \bar{\rho}(r_\alpha)\big|_{r_\alpha = 0} = -2Z_\alpha \bar{\rho}(0)$

but from $\phi(\mathbf{r}) = \frac{Z}{r} - \int \frac{\rho(\mathbf{r}_2)}{|\mathbf{r} - \mathbf{r}_2|} d\mathbf{r}_2$

it follows that Φ (0) = ∞ what is basic defect of TF and TFD theory.

For a neutral atom/molecule

$$\phi(\mathbf{r}) \rightarrow 0 \qquad \text{as } r \rightarrow \infty$$

and this must be also behavior of ρ

For $\mu_{\mathrm{TF}}(N = Z) = 0$

and $\mu_{\mathrm{TFD}}(N = Z) = 0$

Since $\rho^{2/3}$ decays faster than $\rho^{1/3}$ and at large distances $\phi \geq 0$ the formula

$$\mu_{\mathrm{TFD}} = \tfrac{5}{3} C_F \rho^{2/3}(\mathbf{r}) - \tfrac{4}{3} C_x \rho^{1/3}(\mathbf{r}) - \phi(\mathbf{r})$$

Becomes incorrect for neutral species at large r unless all electronic charge is contained within some critical radius, the TFD neutral atom has finite size $r = r_C$.

Explicit solution for ρ for TF neutral atom is following:

Using $\mu_{\mathrm{TF}} = \frac{\delta E_{\mathrm{TF}}[\rho]}{\delta \rho(\mathbf{r})} = \frac{5}{3} C_F \rho^{2/3}(\mathbf{r}) - \phi(\mathbf{r})$ $\phi(\mathbf{r}) = \frac{Z}{r} - \int \frac{\rho(\mathbf{r}_2)}{|\mathbf{r} - \mathbf{r}_2|} d\mathbf{r}_2$

and $\mu_{\mathrm{TF}}(N = Z) = 0$

we obtain

$$C\rho^{2/3}(\mathbf{r}) = \frac{Z}{r} - \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|} d\mathbf{r}' = \phi(\mathbf{r})$$

Alternatively ρ is function of electrostatic potential

$$\rho(\mathbf{r}) = \left(\frac{1}{C}\right)^{3/2} [\phi(\mathbf{r})]^{3/2}$$

Now we apply Poisson equation to the neutral atom

$$\nabla^2 \phi(\mathbf{r}) = 4\pi \rho(\mathbf{r}) - 4\pi Z\, \delta(\mathbf{r})$$

$$\nabla^2 \phi(\mathbf{r}) = 4\pi \left(\frac{1}{C}\right)^{3/2} [\phi(\mathbf{r})]^{3/2} - 4\pi Z\, \delta(\mathbf{r})$$

This is differential equation for ϕ(r) which depends like ρ only on r because the atom is spherically symmetric and thus we can define

$$\phi(\mathbf{r}) = \phi(r) = \frac{Z}{r}\chi(r)$$

and thus

$$\nabla^2\phi(\mathbf{r}) = \frac{Z}{r}\frac{d^2\chi(r)}{dr^2} - 4\pi Z\chi(0)\,\delta(\mathbf{r})$$

And the Poisson equation becomes

$$\frac{d^2\chi(r)}{dr^2} = 4\pi\left(\frac{1}{C}\right)^{3/2}\frac{Z^{1/2}}{r^{1/2}}[\chi(r)]^{3/2}$$

with the boundary condition χ(0) = 1, χ(∞) = 0.

The problem can be solved numerically and $x = \alpha r$

$$\rho(x) = \frac{32}{9\pi^3}\left[\frac{\chi(x)}{x}\right]^{3/2} Z^2 = \frac{32Z^2}{9\pi^3 x}\left[\frac{d^2\chi(x)}{dx^2}\right]$$

Near the nucleus

$$\rho(\text{small } r) \sim \frac{1}{r^{3/2}} \to \infty \qquad \text{as } r \to 0$$

and for large r

$$\chi(x) = \frac{144}{x^3} \qquad \text{for very large } x$$

$$\rho(\text{large } r) \sim \frac{1}{r^6} \to 0 \qquad \text{as } r \to \infty$$

The two limits can’t reproduce the correct behavior of exact atomic densities. The radial distribution function $r^2\rho$ is zero at origin, peaks at x = 0.42 and falls of to zero without showing any shell structure.

The total energy is $E_{\mathrm{TF}} = -0.7687Z^{7/3}$

because

$$\left(\frac{\partial E}{\partial Z}\right)_{N=Z} = \left(\frac{\partial E}{\partial Z}\right)_N = -\int \frac{\rho(\mathbf{r}, z)}{r}\, d\mathbf{r} \qquad E = -4\pi \int_0^Z dZ \int \frac{1}{\alpha^2} x\rho(x)\, dx$$

$$E = -\int_0^Z dZ\left[\int \frac{\rho(\mathbf{r})}{r}\, d\mathbf{r}\right] \qquad = -3/7(1.1295)[\chi'(\infty) - \chi'(0)]Z^{7/3} = -0.7687Z^{7/3}$$

The TF energies for neutral atoms are too low 54% for H, 35% for He, 20% for Kr and 15% for Rn.

The T_{FD} is even worse because K[ρ] is positive and E_{TFD} is more negative than E_{TF}.

$$K_D[\rho_{TF}] = 0.221 Z^{5/3}$$

This is negligible for large Z but it pulls energy down.

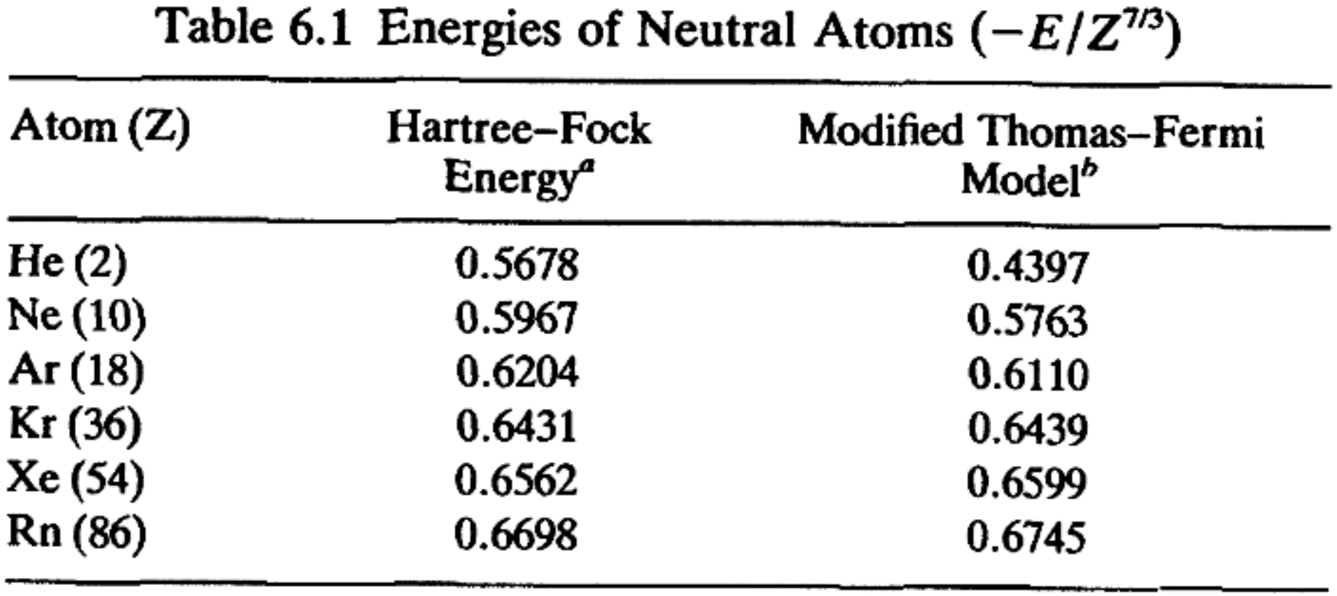


Table 6.1 Energies of Neutral Atoms ($-E/Z^{7/3}$)

Atom (Z)	Hartree–Fock Energy[a]	Modified Thomas–Fermi Model[b]
He (2)	0.5678	0.4397
Ne (10)	0.5967	0.5763
Ar (18)	0.6204	0.6110
Kr (36)	0.6431	0.6439
Xe (54)	0.6562	0.6599
Rn (86)	0.6698	0.6745

The Hohenberg – Kohn teorems

The ground state energy E and wave function ψ are described by minimization of the functional

$$E[\Psi] = \frac{\langle\Psi|\hat{H}|\Psi\rangle}{\langle\Psi|\Psi\rangle}$$

For N-electron system the external potential v(r) and number of electrons N (boundary condition) **determines** the ground state properties E,Ψ.

1st H-K theorem: **The external potential v(r) is determined within a constant by an electron density ρ(r)**.

The proof: Consider ρ(r) for non-degenerate ground state of N-electron system. It determines N (the norm) and also v(r), and all other ground state properties.

Suppose, v(r) and v’(r) differing by more than constant but providing the same ρ. Than we would have H and H’ Hamiltonians whose ground state densities would be the same although their Ψ and Ψ’ differ.

Taking Ψ’ for H

$$\begin{aligned} E_0 < \langle \Psi' | \hat{H} | \Psi' \rangle &= \langle \Psi' | \hat{H}' | \Psi' \rangle + \langle \Psi' | \hat{H} - \hat{H}' | \Psi' \rangle \\ &= E_0' + \int \rho(\mathbf{r})[v(\mathbf{r}) - v'(\mathbf{r})]\, d\mathbf{r} \end{aligned}$$

where E_0 and E_0’ are the ground state energies for H and H’, and the way around

$$\begin{aligned} E_0' < \langle \Psi | \hat{H}' | \Psi \rangle &= \langle \Psi | \hat{H} | \Psi \rangle + \langle \Psi | \hat{H}' - \hat{H} | \Psi \rangle \\ &= E_0 - \int \rho(\mathbf{r})[v(\mathbf{r}) - v'(\mathbf{r})]\, d\mathbf{r}. \end{aligned}$$

It follows that $E_0 + E'_0 < E'_0 + E_0$

what is contradiction!, and prove - two different v(r) can't have the same ρ.

Thus ρ determines N and v(r) and other ground state properties like T[ρ] and V[ρ] and also E[ρ].

Instead of

$$E_{\mathrm{TF}}[\rho(\mathbf{r})] = C_F \int \rho^{5/3}(\mathbf{r})\, d\mathbf{r} - Z \int \frac{\rho(\mathbf{r})}{\mathbf{r}}\, d\mathbf{r} + \frac{1}{2} \iint \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}\, d\mathbf{r}_1\, d\mathbf{r}_2$$

we have, E_v energy depending explicitly on v(r)

$$\begin{aligned} E_v[\rho] &= T[\rho] + V_{ne}[\rho] + V_{ee}[\rho] \\ &= \int \rho(\mathbf{r}) v(\mathbf{r})\, d\mathbf{r} + F_{\mathrm{HK}}[\rho] \end{aligned}$$

where $F_{\mathrm{HK}}[\rho] = T[\rho] + V_{ee}[\rho]$

and we may write $V_{ee}[\rho] = J[\rho] + \text{nonclassical term}$

The classical repulsion J is here complemented by elusive and very important "exchange-correlation energy".

The 2nd H-K theorem: For a trial density ρ, such as ρ(r) ≥ 0 and $\int \tilde{\rho}(\mathbf{r})\, d\mathbf{r} = N$

$$E_0 \leqslant E_v[\tilde{\rho}]$$

where $E_v[\rho]$ is the energy functional, E_0 exact energy of gr. state.

$$\begin{aligned} E_v[\rho] &= T[\rho] + V_{ne}[\rho] + V_{ee}[\rho] \\ &= \int \rho(\mathbf{r}) v(\mathbf{r})\, d\mathbf{r} + F_{\mathrm{HK}}[\rho] \end{aligned}$$

It is full analogy to variation principle for Ψ.
It provides justification for T-F variation principle, E_{TF} is approximate to E_0.

Prove:

The 1th HK theorem ensures that ρ' determines v'(r), H and Ψ' which can be taken as *trial function* for the problem of interest having defined potential v(r).

$$\langle\tilde{\Psi}|\,\hat{H}\,|\tilde{\Psi}\rangle = \int \tilde{\rho}(\mathbf{r})v(\mathbf{r})\,d\mathbf{r} + F_{\mathrm{HK}}[\tilde{\rho}] = E_v[\tilde{\rho}] \geqslant E_v[\rho]$$

The ground state density satisfies the stationary principle

$$\delta\left\{E_v[\rho] - \mu\left[\int \rho(\mathbf{r})\,d\mathbf{r} - N\right]\right\} = 0$$

Which gives the Euler-Lagrange equation, where μ is chemical potential

$$\mu = \frac{\delta E_v[\rho]}{\delta\rho(\mathbf{r})} = v(\mathbf{r}) + \frac{\delta F_{\mathrm{HK}}[\rho]}{\delta\rho(\mathbf{r})}$$

If we knew the exact F_{HK} the equation

$$\delta\left\{E_v[\rho] - \mu\left[\int \rho(\mathbf{r})\, d\mathbf{r} - N\right]\right\} = 0$$

is exact equation for the ground state.

Note: F_{HK} is defined independently of v(r)!

It is therefore **universal** and once its form is known (which is however not the case) it can be applied to any system.

This equation is the basic working equation of DFT.

The N- and v(r)- representability of ρ

Important, however, criteria for v(r)-representability are not yet known/defined. The N-condition is weaker (easy to test for any density) than v-representability condition and can be fulfilled more easily.

ρ is v-representable if it is associated with the anti-symmetric wave function of H with "some" potential v(r), (not necessarily the Coulomb potential).

ρ generally may or may not be v(r)-representable.
Not: the density for q-degenerated ground state $\rho(\mathbf{r}) = \sum_{i=1} C_i \rho_i(\mathbf{r}) \ \{\Psi_i,\ i = 1, \ldots, q\}$

1st H-K theorem says that there is one-to-one mapping of the ground state ψ and v-representable ρ.

When we say that all ground state properties are functionals of ρ, we mean that these functionals are defined only for the v(r)-representable densities, like F_{HK}

$$F_{\mathrm{HK}}[\rho] = \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle$$

and 2nd HK theorem states that for ALL v-representable densities we have

$$E_v[\rho] \equiv F_{\mathrm{HK}}[\rho] + \int v(\mathbf{r})\rho(\mathbf{r})\, d\mathbf{r} \geq E_v[\rho_0]$$

N-representability

ρ is N-representable when

$$\rho(\mathbf{r}) \geqslant 0, \qquad \int \rho(\mathbf{r})\, d\mathbf{r} = N, \qquad \text{and} \qquad \int |\nabla\rho(\mathbf{r})^{1/2}|^2\, d\mathbf{r} < \infty.$$

ρ can be constructed from N orthonormal orbitals based on *space partitioning* and hence generated from single-determinantal wave function (we know how).

Explicit construction uses N smooth, continuous, orthonormal orbitals for ANY density satisfying the above criteria. The required orbitals are:

$$\phi_k(x) = [\sigma(x)]^{1/2} \exp[i2\pi k q(x)]$$

$$\sigma(x) = \rho(x)/N$$

$$q(x) = \int_{x_1}^{x} \sigma(x)\, dx$$

$k = 0, \pm 1, \pm 2, \ldots$, or $k = \pm 1/2, \pm 3/2, \pm 5/2, \ldots$

All orbitals have same orbital density

$$|\phi_k(x)|^2 = \sigma(x)$$

0 ≤ q(x) ≤ 1, and

$$\frac{dq(x)}{dx} = \sigma(x)$$

The orbitals are orthonormal:

$$\begin{aligned}\int_{x_1}^{x_2} \phi_k^*(x)\phi_l(x)\,dx &= \int_{x_1}^{x_2} \sigma(x)\exp\left[2\pi q(x)(l-k)\right] dx \\ &= \int_{x_1}^{x_2} \exp\left[2\pi(l-k)q(x)\right]\frac{dq(x)}{dx}\,dx \\ &= \int_0^1 \exp\left[2\pi(l-k)q\right] dq = \delta_{kl}\end{aligned}$$

Any number of such orbitals thus can be constructed and any density can be represented by, $0 \le \lambda_k \le 1$, $\Sigma\ \lambda_k = N$

$$\rho(x) = \sum_k^M \lambda_k\,|\phi_k(x)|^2$$

If ρ is density from the ground state Ψ of Hamiltonian
With some external potential v(r) than ρ(r) is called
pure state v-representable.

$$\hat{H} = \sum_{i=1}^{N}\left(-\tfrac{1}{2}\nabla_i^2\right) + \sum_{i=1}^{N} v(\mathbf{r}_i) + \sum_{i<j}^{N}\frac{1}{r_{ij}}$$

If the Hamiltonian is not including the el.-el. interaction, than ρ(r) is called *noninteracting pure state v-representable.*

$$\hat{H} = \hat{T} + \sum_{i=1}^{N} v(i)$$

If ρ is constructed form degenerated ψ than ρ is said *ensemble v-representable* or *noninteracting ensemble v-representable.*

The Levy constrained search formulation

Search for Ψ_0 that is determined from ρ_0, search for the ground state wave-function.

The inverse problem is trivial.
But infinite number of wave-functions exist (not necessarily the ground state) giving the same density. How do we distinguish true ground-state Ψ_0 from from (many) $\Psi_{\rho 0}$ that integrates to the density ρ_0.

Levy (1979, 1982)

$$\langle \Psi_{\rho_0} | \hat{H} | \Psi_{\rho_0} \rangle \geqslant \langle \Psi_0 | \hat{H} | \Psi_0 \rangle = E_0$$

$$\hat{H} = \hat{T} + \hat{V}_{ee} + \textstyle\sum_i^N v(\mathbf{r}_i)$$

where

and since v(r) is functional of density, we have

$$\langle \Psi_{\rho_0} | \hat{T} + \hat{V}_{ee} | \Psi_{\rho_0} \rangle + \int v(\mathbf{r}) \rho_0(\mathbf{r}) \, d\mathbf{r} \geqslant \langle \Psi_0 | \hat{T} + \hat{V}_{ee} | \Psi_0 \rangle + \int v(\mathbf{r}) \rho_0(r) \, d\mathbf{r}$$

Among all wave-functions that integrate to ground state density ρ_0 only Ψ_0 minimizes the expectation value

$$\langle \Psi_{\rho_0} | \hat{T} + \hat{V}_{ee} | \Psi_{\rho_0} \rangle \geqslant \langle \Psi_0 | \hat{T} + \hat{V}_{ee} | \Psi_0 \rangle$$

The right hand side equals to $F_{HK}[\rho_0]$, the HK functional defined for any v-representable wave-function.

$$\begin{aligned} F_{\mathrm{HK}}[\rho_0] &= \langle \Psi_0 | \hat{T} + \hat{V}_{ee} | \Psi_0 \rangle \\ &= \underset{\Psi \rightarrow \rho_0}{\mathrm{Min}} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle \end{aligned}$$

This is definition of constrained search; searching over ALL anti-symmetric wave-functions yielding the ρ_0 density, $F_{HK}[\rho_0]$ delivers the minimum expectation value of $T+V_{ee}$ operators.

Defining $F_{HK}[\rho_0]$ in this way is new proof of HK 1st theorem and eliminates the original limitation concerning degeneracy, from all possible degenerated wave-functions is selected the one corresponding to ρ_0.

The variation search $\underset{\Psi\rightarrow\rho_0}{\mathrm{Min}}\ \langle\Psi|\ \hat{T}+\hat{V}_{ee}\ |\Psi\rangle$

is thus constrained because the space of trial functions comprises only to those giving ρ_0 in contract to the unconstrained minimum search for

$$\langle\Psi|\ \hat{T}+\hat{V}_{ee}+\textstyle\sum_i^N v(\mathbf{r}_i)\ |\Psi\rangle$$

whole Hilbert space.

In the constrained search for $F_{HK}[\rho_0]$ the ρ_0 is automatically v-representable if it is constructed from antisymmetric wave function. This fact permits us to extend the domain of v-representable to N-representable densities

$$F[\rho]=\underset{\Psi\rightarrow\rho}{\mathrm{Min}}\ \langle\Psi|\ \hat{T}+\hat{V}_{ee}\ |\Psi\rangle$$

where ρ is only N-representable.

$$F_{\mathrm{HK}}[\rho_0]=F[\rho_0]$$

The ground-state minimization is divided into two steps

$$\begin{aligned} E_0 &= \operatorname*{Min}_{\Psi} \langle \Psi | \hat{T} + \hat{V}_{ee} + \sum_{i}^{N} v(\mathbf{r}_i) | \Psi \rangle \\ &= \operatorname*{Min}_{\rho} \left\{ \operatorname*{Min}_{\Psi \to \rho} \langle \Psi | \hat{T} + \hat{V}_{ee} + \sum_{i}^{N} v(\mathbf{r}_i) | \Psi \rangle \right\} \\ &= \operatorname*{Min}_{\rho} \left\{ \operatorname*{Min}_{\Psi \to \rho} \left[\langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle + \int v(\mathbf{r}) \rho(\mathbf{r})\, d\mathbf{r} \right] \right\} \end{aligned}$$

the inner minimization (second row) is constrained to Ψs giving ρ, the outer minimization searches for all such ρs.

$$\begin{aligned} E_0 &= \operatorname*{Min}_{\rho} \left\{ F[\rho] + \int v(\mathbf{r}) \rho(\mathbf{r})\, d\mathbf{r} \right\} \\ &= \operatorname*{Min}_{\rho} E[\rho] \end{aligned}$$

The variation is over all N-representative ρs (the three basic conditions on ρ). Importantly, the v-representability was thus removed.

The constrained search by Levy – search for minimum of the universal functional F[ρ] for noninteracting fermions is based on Perkus's partitioning of the N-electron Hilbert space.

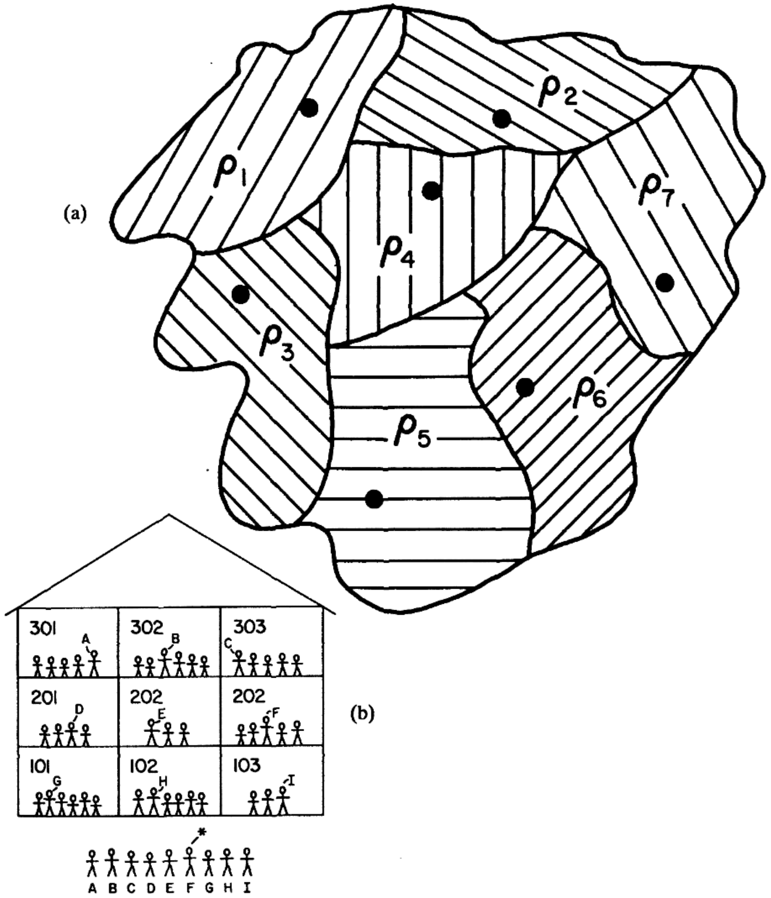


Figure 3.1(a) Percus partition of the N-electron Hilbert space. Each shaded area shown is the set of all Ψ that integrate to a particular ρ. The minimization in (3.4.5) for a particular ρ is constrained to the shaded area associated with this ρ, and is realized by only one point (denoted by ●) in this shaded area. The minimization in (3.4.8) is over all such points.

Figure 3.1(b) An analogous constrained-search problem. To identify the tallest child in a school, one does not have to line up all of the children in the schoolyard. Instead, one can simply ask the tallest child from each room to come to the schoolyard.

The constrained search by Levy – search for minimum of the universal functional for noninteracting fermions.

Existence of the minimum for $F[\rho] = \underset{\Psi \to \rho}{\mathrm{Min}} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle$ employing trial $\psi_{\rho}^{\min}$ was proved by Lieb in 1982

$$\begin{aligned} F[\rho] &= \langle \psi_{\rho}^{\min} | \hat{T} + \hat{V}_{ee} | \psi_{\rho}^{\min} \rangle \\ &= T[\rho] + V_{ee}[\rho] \end{aligned}$$

The F[ρ] is universal because it is independent of v(r). The same F[ρ] is applied to hydrogen atom and protein. So we look for method to deal with F[ρ] that is rigorously defined for any N-representative ρ. However, F[ρ] is highly difficult to approximate because we changed from many-variable variation function ψ to single three variable ρ.

The electronic energy is functional of second-order reduced density matrix Γ_2 and its variation is set of N-representable Γ_2 matrices which is unknown.
The constrained search for F[ρ] is approximated by bounds

$$F[\rho] \leqslant \underset{\substack{\Psi \to \rho \\ \Psi \in S}}{\mathrm{Min}} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle$$

$$F[\rho] \leqslant \langle \Psi_{\rho} | \hat{T} + \hat{V}_{ee} | \Psi_{\rho} \rangle$$

where S is any subspace of Hilbert space giving ρ.
The existence was proved and energy functional minimum was thus established.

The Chemical Potential

Chemical potential in the grand canonical ensemble at zero temperature

The principle equation for obtaining ρ(r) of ground state includes μ.

$$\delta\left\{E_v[\rho]-\mu\left[\int\rho(\mathbf{r})\,d\mathbf{r}-N\right]\right\}=0$$

E ➔ canonical ➔ grand-canonical ensemble gives us route to μ.

a) For the the ground state E[ρ] riches minimum among all densities integrating to N.

b) For en equilibrium state at temperature Θ in a canonical ensemble the Helmhotz free energy A[ρ] riches its minimum among all densities integrating to N.

$$A[\rho]=F[\rho]+\int v(\mathbf{r})\rho(\mathbf{r})\,d\mathbf{r}$$

were F[ρ] is universal functional of ρ containing the kinetic energy, particle-particle and entropy term

$$F[\rho]=T[\rho]+U[\rho]-\theta S[\rho]$$

c) For an equilibrium state at temperature Θ and chemical potential μ in a grand-canonical ensemble the grand potential functional Ω[ρ] riches its minimum

$$\Omega[\rho(\mathbf{r})] = F[\rho(\mathbf{r})] + \int \rho(\mathbf{r})(v(\mathbf{r}) - \mu)\, d\mathbf{r}$$

Note, μ appears only as combination of v(r) – μ.

$$\begin{aligned} F[\rho(\mathbf{r})] &= T[\rho(\mathbf{r})] + U[\rho(\mathbf{r})] - \theta S[\rho(\mathbf{r})] \\ &= \mathrm{Tr}\left[\hat{\Gamma}_{\rho}^{\min}\left(\hat{T} + \hat{U} + \frac{1}{\beta}\ln \hat{\Gamma}_{\rho}^{\min}\right)\right] \end{aligned}$$

$\Gamma^{\min}$ is the operator that minimized operators in the () and gives ρ.

The equilibrium state density ρ_0 determines the density operator Γ_0 and hence the properties of ground state.

There holds the grand potential variation principle in terms of particle density with the universal functional F[ρ].

At the zero temperature limit, $\theta = 0$, $\beta \rightarrow \infty$, $\Theta S[\rho] \rightarrow 0$, the equilibrium state and ground state become the same. We consider the grand canonical (GC) ensemble

$$F_{\mathrm{GC}}[\rho(\mathbf{r})] = \underset{\Gamma \rightarrow \rho}{\mathrm{Min}}\ \mathrm{Tr}\,[\hat{\Gamma}(\hat{T} + \hat{V}_{ee})]$$

where F_{GC} is the universal ground state functional (proposed in 1982) extending the Levy's constrained search to general density operator Γ in Fock space.

$$\hat{\Gamma} = \sum_{N} \sum_{i} p_{Ni} |\Psi_{Ni}\rangle \langle \Psi_{Ni}|$$

The grand potential at the zero temperature limits to

$$\Omega[\rho] = F_{\mathrm{GC}}[\rho] + \int \rho(\mathbf{r})(v(\mathbf{r}) - \mu)\, d\mathbf{r}$$

$$= E_{\mathrm{GC}}[\rho] - \mu N$$

where $E_{GC}[\rho]$ is the grand-canonical-ensemble energy functional

$$E_{\mathrm{GC}}[\rho] = F_{\mathrm{GC}}[\rho] + \int \rho(\mathbf{r}) v(\mathbf{r})\, d\mathbf{r}$$

Considering the β → ∞ limit for variational principle Ω[Γ]

$$\Omega^0 = \Omega[\hat{\Gamma}^0] = \underset{\Gamma}{\mathrm{Min}}\ \mathrm{Tr}\left[\hat{\Gamma}\left(\hat{H} - \mu\hat{N} + \frac{1}{\beta}\ln\hat{\Gamma}\right)\right]$$

$$= \underset{\rho}{\mathrm{Min}}\left\{\underset{\Gamma\to\rho}{\mathrm{Min}}\ \mathrm{Tr}\left[\hat{\Gamma}\left(\hat{T} + \hat{U} + \frac{1}{\beta}\ln\hat{\Gamma}\right)\right] + \int (v(\mathbf{r}) - \mu)\rho(\mathbf{r})\, d\mathbf{r}\right\}$$

the limit becomes

$$\Omega^0 = E^0(N) - \mu N \leqslant \mathrm{Tr}\,\hat{\Gamma}(\hat{H} - \mu\hat{N})$$

where $E^0(N)$ and μ is the energy and chemical potential of the ground state with N electrons. Following the variational principle for Ω[Γ] the density functional principle is

$$E^0(N) - \mu N \leqslant E_{GC}[\rho(\mathbf{r})] - \mu\int\rho(\mathbf{r})\, d\mathbf{r}$$

From which follows the variational equation for the ground state density and energy

$$\delta\left\{E_{GC}[\rho] - \mu\int\rho(\mathbf{r})\, d\mathbf{r}\right\} = 0$$

and the Euler-Lagrange

$$\frac{\delta E_{GC}[\rho]}{\delta\rho(\mathbf{r})} - \mu = 0$$

Consider Γ describes ground state with average number of electrons N+ΔN = Tr ΓN. Following the

$$\Omega^0 = E^0(N) - \mu N \leqslant \mathrm{Tr}\,\hat{\Gamma}(\hat{H} - \mu\hat{N})$$

we have for two systems with N+/-ΔN

$$E^0(N) - \mu N \leqslant E^0(N + \Delta N) - \mu \cdot (N + \Delta N)$$
$$E^0(N) - \mu N \leqslant E^0(N - \Delta N) - \mu \cdot (N - \Delta N)$$

If E(N) is differentiable, than

$$\mu = \frac{\partial E^0(N)}{\partial N}$$

And function $E^0(N)$ is therefore convex

$$E^0(N + \Delta N) + E^0(N - \Delta N) - 2E^0(N) \geqslant 0$$

If E(N) is twice differentiable, than

$$\frac{\partial^2 E^0(N)}{\partial N^2} \geqslant 0$$

Setting ΔN = 1 we obtain

$$E^0(N+1) - E^0(N) \geqslant E^0(N) - E^0(N-1)$$

$$I(N+1) \geqslant I(N)$$

where I(N) is ionization potential.

The successive ionization potentials are NOT decreasing for the same external potential. This holds for atoms, molecules although the first principle prove has never been given.

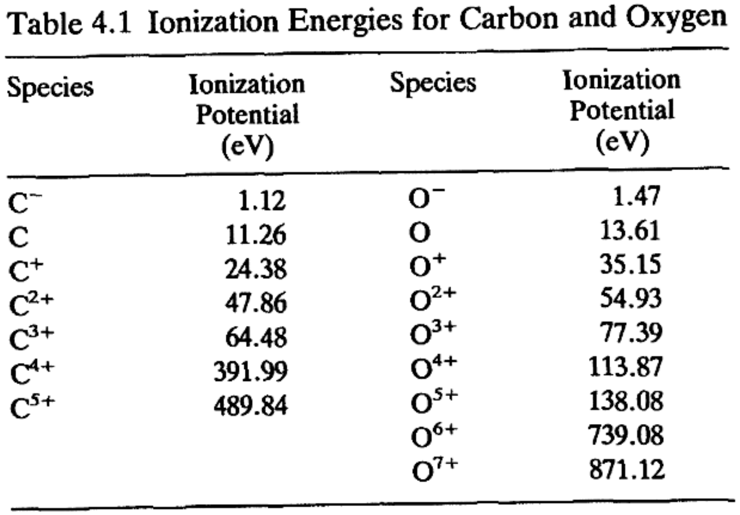


Table 4.1 Ionization Energies for Carbon and Oxygen

Species	Ionization Potential (eV)	Species	Ionization Potential (eV)
C^-	1.12	O^-	1.47
C	11.26	O	13.61
C^+	24.38	O^+	35.15
C^{2+}	47.86	O^{2+}	54.93
C^{3+}	64.48	O^{3+}	77.39
C^{4+}	391.99	O^{4+}	113.87
C^{5+}	489.84	O^{5+}	138.08
		O^{6+}	739.08
		O^{7+}	871.12

Physical meaning of the chemical potential

In DFT it measures the “escaping tendency” of an electron cloud.

It is constant throughout the space for ground state of molecule, atom, solid state.

Equals to the ΔE/ΔN slope for constant v(r).

It is the negative of electronegativity by Pauling and Mulliken $\mu \approx -\frac{I+A}{2}$

Chemical potential derivatives

Change from one ground-state to another is described by

$$dE = \mu\, dN + \int \rho(\mathbf{r})\, dv(\mathbf{r})\, d\mathbf{r}$$

The proof for equilibrium state of grand canonical ensemble at zero temperature:

The total differential of energy

$$dE = \left(\frac{\partial E}{\partial N}\right)_v dN + \int \left[\frac{\delta E}{\delta v(\mathbf{r})}\right]_N dv(\mathbf{r})\, d\mathbf{r}$$

must be the same as differential of E[ρ]

$$dE = \int \left[\frac{\delta E}{\delta \rho(\mathbf{r})}\right]_v d\rho(\mathbf{r})\, d\mathbf{r} + \int \left[\frac{\delta E}{\delta v(\mathbf{r})}\right]_\rho dv(\mathbf{r})\, d\mathbf{r}$$

From $\mu = \left[\frac{\delta E}{\delta \rho}\right]_v = v(\mathbf{r}) + \frac{\delta F[\rho]}{\delta \rho(\mathbf{r})}$

we know that

$$\left[\frac{\delta E}{\delta \rho(\mathbf{r})}\right]_v = \mu = \text{constant}$$

While from the first order energy $E_k^{(1)} = \int \Psi_k^{0*} \, \Delta V \Psi_k^0 \, dx^N = \int \rho_k(\mathbf{r}_1) \, \Delta v(\mathbf{r}_1) \, d\mathbf{r}_1$

it follows that
$$\left[\frac{\delta E}{\delta v(\mathbf{r})}\right]_\rho = \left[\frac{\delta E}{\delta v(\mathbf{r})}\right]_N = \rho(\mathbf{r})$$

and therefore we proved
$$dE = \mu \, dN + \int \rho(\mathbf{r}) \, dv(\mathbf{r}) \, d\mathbf{r}$$

and also we can write
$$\mu = \left(\frac{\partial E}{\partial N}\right)_v$$

The change of μ due to change in N or v(r) is given by

$$d\mu = \left(\frac{\partial \mu}{\partial N}\right)_v dN + \int \left[\frac{\delta \mu}{\delta v(\mathbf{r})}\right]_N dv(\mathbf{r})\, d\mathbf{r}$$

or by "Maxwell relation"

$$d\mu = 2\eta\, dN + \int f(\mathbf{r})\, dv(\mathbf{r})\, d\mathbf{r}$$

where we defined

$$2\eta = \left(\frac{\partial \mu}{\partial N}\right)_v \qquad f(\mathbf{r}) = \left[\frac{\delta \mu}{\delta v(\mathbf{r})}\right]_N = \left[\frac{\partial \rho(\mathbf{r})}{\partial N}\right]_v$$

The Maxwell relation is pertinent to chemical concept as μ is negative of electronegativity, η is called hardness and both η and μ are global properties while *f*(r) is local property depending on r called Fukui function.

For obtaining ρ(r) we need the linear response function

$$\left[\frac{\delta\rho(\mathbf{r})}{\delta v(\mathbf{r}')}\right]_N = \frac{\delta^2 E}{\delta v(\mathbf{r})\,\delta v(\mathbf{r}')} = \left[\frac{\delta\rho(\mathbf{r}')}{\delta v(\mathbf{r})}\right]_N$$

The ground state energy is assumed to be continuous and differentiable function of E[N,v(r)].

For the zero temperature grand canonical ground state of N noninteracting electrons we have μ equal to -I ($\Delta N < 0$) or –EA ($\Delta N > 0$).

Natural variables in equations for *d*E and *d*μ are N and v(r). Like in macroscopic termodynamics it is conveniet to define new, appropriate state functions

$$F = E - \int \rho(\mathbf{r}) v(\mathbf{r})\, d\mathbf{r}$$

$$\Omega = E - N\mu$$

and for the change of one ground state to any other we have

$$dF = \mu\, dN - \int v(\mathbf{r})\, d\rho(\mathbf{r})\, d\mathbf{r} = \int [\mu - v(\mathbf{r})]\, d\rho(\mathbf{r})\, d\mathbf{r}$$

$$d\Omega = -N\, d\mu + \int \rho(\mathbf{r})\, dv(\mathbf{r})\, d\mathbf{r}$$

The function F is Hohenberg – Kohn F since

$$E = T + V_{ee} + V_{ne} = F + V_{ne}$$

and Ω is zero temperature grand potential and therefore we have

$$\Omega = F - \int \frac{\delta F}{\delta \rho(\mathbf{r})} \rho(\mathbf{r})\, d\mathbf{r}$$

and the following quantities corresponding to Maxwell relations of classical thermodynamics

$$\left[\frac{\delta \rho(\mathbf{r})}{\delta v(\mathbf{r}')}\right]_N = \left[\frac{\delta \rho(\mathbf{r}')}{\delta v(\mathbf{r})}\right]_N$$

$$\left[\frac{\delta N}{\delta v(\mathbf{r})}\right]_\mu = -\left[\frac{\partial \rho(\mathbf{r})}{\partial \mu}\right]_v$$

$$\left[\frac{\delta \rho(\mathbf{r})}{\delta v(\mathbf{r}')}\right]_\mu = \left[\frac{\delta \rho(\mathbf{r}')}{\delta v(\mathbf{r})}\right]_\mu$$

Electronegativity and electronegativity equation

The chemical potential μ is global property of ground state, constant throughout the space in atom/molecule, in principle calculable. For change from one to another ground state we have

$$d\mu = 2\eta\, dN + \int f(\mathbf{r})\, dv(\mathbf{r})\, d\mathbf{r}$$

When atoms of different chemical potential form molecule with its own characteristic μ their formerly different chemical potentials must equalize. (Sanderson 1951, 1976 – Principle of electronegativity equalization).

This has parallel in classical macroscopic thermodynamics – two phases put together come to equilibrium with equalized chemical potential. The flow of a substance is from the phase with high μ to that with low μ. For A, B electronic systems $\mu_B^0 > \mu_A^0$ electrons should flow from B to A while forming AB. To show this we consider

$$E_\mathrm{A} = E_\mathrm{A}^0 + \mu_\mathrm{A}^0(N_\mathrm{A} - N_\mathrm{A}^0) + \eta_\mathrm{A}(N_\mathrm{A} - N_\mathrm{A}^0)^2 + \cdots$$
$$E_\mathrm{B} = E_\mathrm{B}^0 + \mu_\mathrm{B}^0(N_\mathrm{B} - N_\mathrm{B}^0) + \eta_\mathrm{B}(N_\mathrm{B} - N_\mathrm{B}^0)^2 + \cdots$$

The total energy depending on $\Delta N = N_B^0 - N_B = N_A - N_A^0$ will be

$$E_A + E_B = E_A^0 + E_B^0 + (\mu_A^0 - \mu_B^0)\,\Delta N + (\eta_A + \eta_B)(\Delta N)^2 + \cdots$$

for $\mu_B^0 > \mu_A^0$

we have positive ΔN and flow from B to A stabilizes system. The energy stabilization due to such charge transfer is second order in $\mu_B^0 - \mu_A^0$.

The explicit formula can be obtained by minimizing $E_A + E_B$ with respect to ΔN, i.e. the result is $\mu_A = \mu_B$ where

$$\mu_A = \left(\frac{\partial E_A}{\partial N_A}\right)_v = \mu_A^0 + 2\eta_A\,\Delta N + \cdots$$

$$\mu_B = \left(\frac{\partial E_B}{\partial N_B}\right)_v = \mu_B^0 - 2\eta_B\,\Delta N + \cdots$$

and consequently to the first order $\Delta N = \dfrac{\mu_B^0 - \mu_A^0}{2(\eta_A + \eta_B)}$

The charge transfer to the first order is proportional to the different of original chemical potentials.

Such DFT implementation where the binding energy is obtained from atomic charges and DFT functional is approximated by simple adding of atomic contributions is primitive.

The join with structural chemistry was achieved by identification of μ with negative of electronegativity χ

$$\mu = \left(\frac{\partial E}{\partial N}\right)_v = -\chi$$

that is

1) state property calculable from DFT or determinable from experiment,
2) different chemical potentials drive electron transfer, electron flow from high to low chemical potential proportional to the original chemical potential difference and the energy stabilization is proportional to its square,
3) on formation of a molecule former electronegativities equalize/neutralize.

$$\Delta E = -\frac{(\mu_B^0 - \mu_A^0)^2}{4(\eta_A + \eta_B)}$$

These principles are well known, however, now they were shown to follow tom DFT.

Development of electronegativity concept

Pauling (1960) used the concept as descriptive indicator for electron-attracting power. He made relative scale based on bond energies and dipole moments and termed the stabilization due to charge transfer as extra-ionic resonance energy that equals to square of electronegativity differences.

Mulliken did not think that electronegativity is slope E versus N curve but he proposed that electronegativity depends on valence state of atoms that is followed by DFT.

Sanderson (1976) proposed geometric mean equalization principle

$$\chi_{AB} = (\chi_A^0 \chi_B^0)^{1/2}$$

$$\mu_{AB} = -(\mu_A^0 \mu_B^0)^{1/2}$$

Roughly correct but incorrectly describing the homonuclear bonding.

As the atomic number of neutral atom increases the chemical potential is proportional to $Z^{-1/3}$ when going down the column of periodic table.

The electronegativity is property of system that behaves much like the chemical potential of macroscopic thermodynamics. It measures escaping tendency of electron and is constant for system at equilibrium.

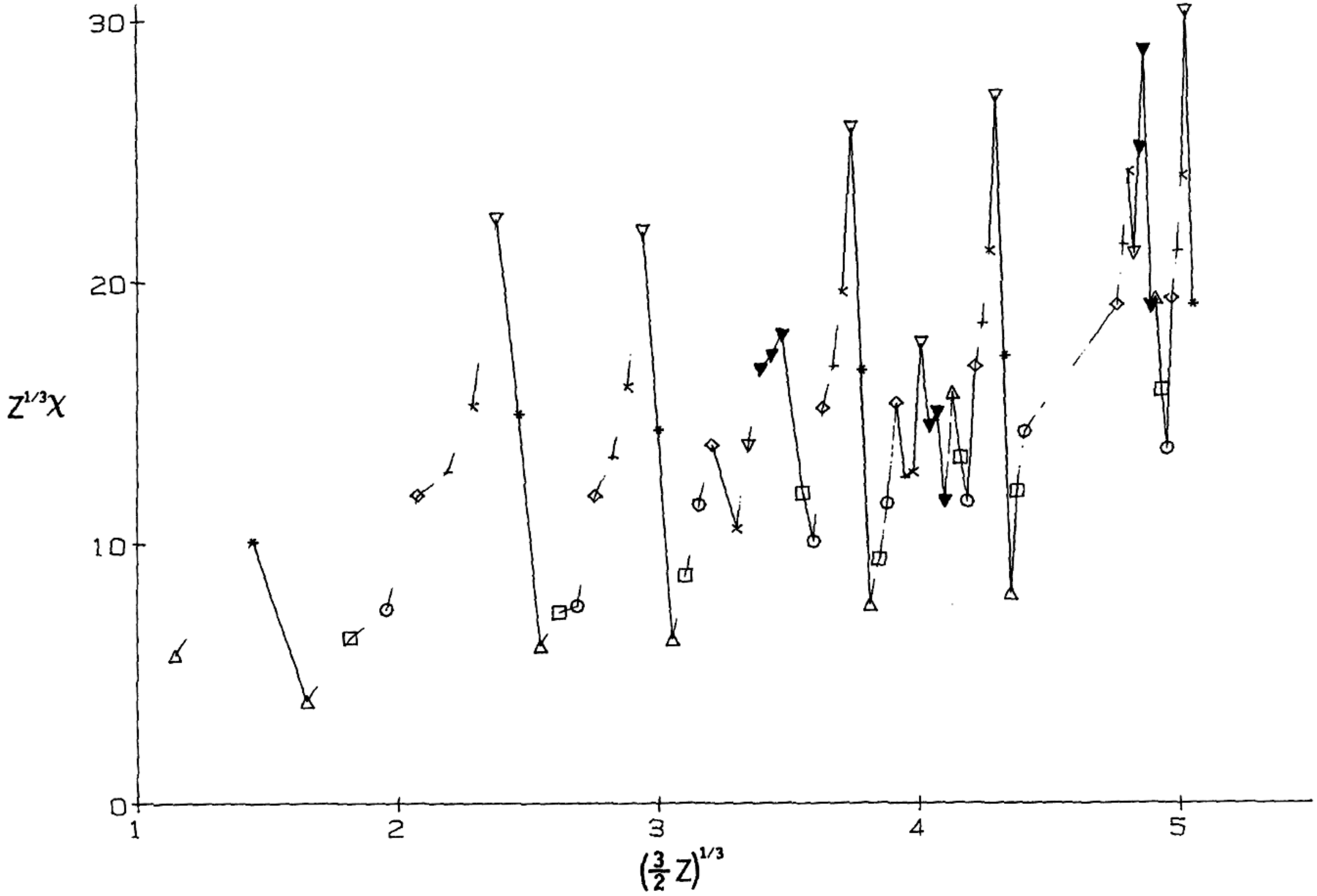


Figure 5.1 Periodic behavior of the chemical potential (after Gázquez, Vela, and Galvan, 1986).

Hardness and softness

The absolute harness (Parr, Pearson 1983) $\eta = \frac{1}{2}\left(\frac{\partial \mu}{\partial N}\right)_v = \frac{1}{2}\left(\frac{\partial^2 E}{\partial N^2}\right)_v$

Its inverse is softness (Young, Parr 1985) $S = \frac{1}{2\eta} = \left(\frac{\partial N}{\partial \mu}\right)_v$

The property is $\eta \geq 0$ due to convexity assumption and $\eta \approx \frac{I - A}{2}$

For an insulator or semiconductor the hardness is half of the band gap.

The first (chemical potential) and second (harness) derivative of E with N is important

The physical meaning of hardness

Consider deprotonation reaction where electron is taken from S and given to S

$$\dot{S} + \dot{S} \rightarrow S^+ + \ddot{S}^-$$

The energy change $\Delta E_s = I_s - A_s$ is hardness. Small hardness thus means that it is easy to move electron from one S to the other S; that is S is soft species.

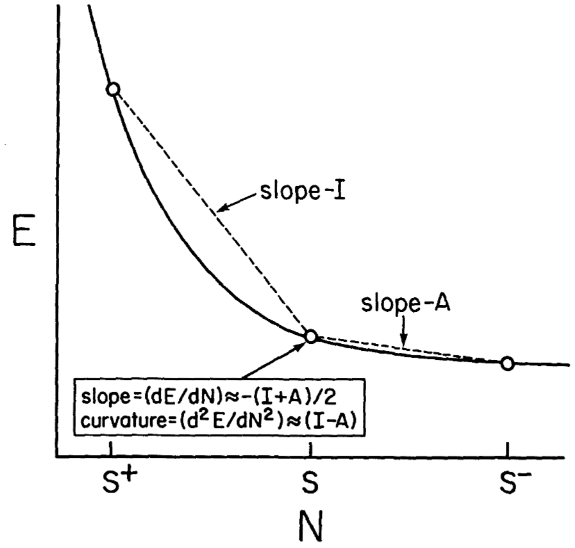


Figure 5.2 Energy versus number of electrons for a typical species S.

The disprotonation reaction was important in devolopment of orbital theories. Suppose, the two electrons in $\ddot{S}^-$ each had the same energy, the same energy as the energy of one electron in $\dot{S}$ the energy $\Delta E_s = I_s - A_s$ than would be zero, the typical, wrong result of Huckel method.

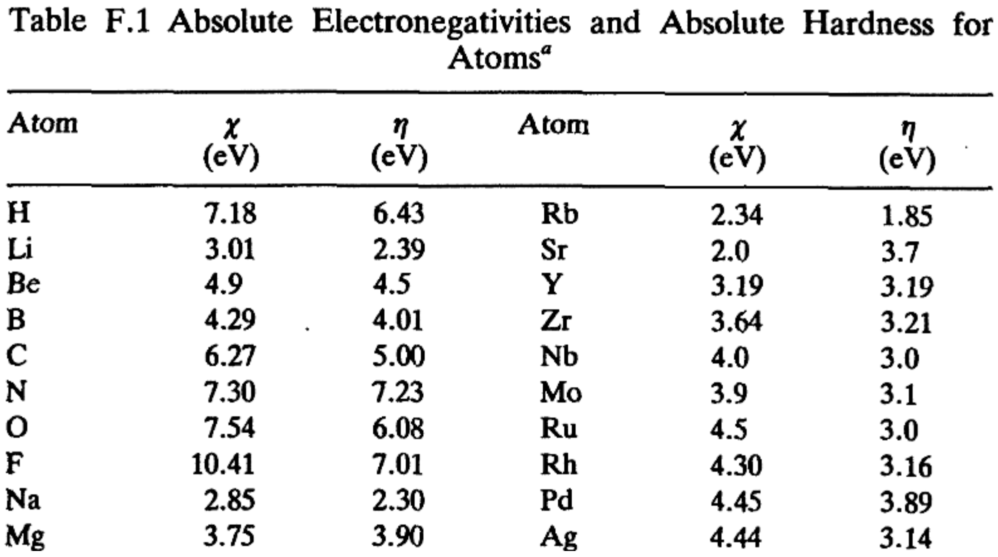


Table F.1 Absolute Electronegativities and Absolute Hardness for Atoms[a]

Atom	χ (eV)	η (eV)	Atom	χ (eV)	η (eV)
H	7.18	6.43	Rb	2.34	1.85
Li	3.01	2.39	Sr	2.0	3.7
Be	4.9	4.5	Y	3.19	3.19
B	4.29	4.01	Zr	3.64	3.21
C	6.27	5.00	Nb	4.0	3.0
N	7.30	7.23	Mo	3.9	3.1
O	7.54	6.08	Ru	4.5	3.0
F	10.41	7.01	Rh	4.30	3.16
Na	2.85	2.30	Pd	4.45	3.89
Mg	3.75	3.90	Ag	4.44	3.14

Better approximation to ΔE_s is repulsion between the two electrons in $\ddot{S}^-$ calculated as

$$\Delta E_s = (ss \mid ss)$$

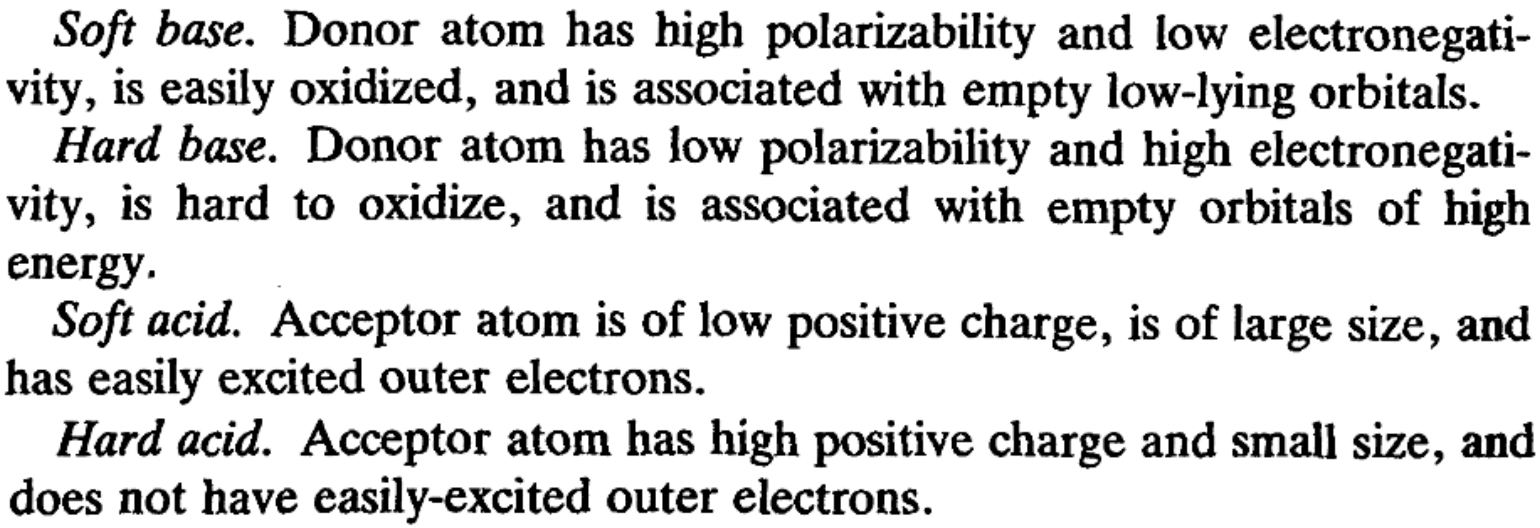
This description, working idea in 1945-51, is not correct due to the frozen-core assumption.

Pariser (1953) suggested semiempirical way where the integral is not computed but rather approximated

$$(ss \mid ss) = I_s - A_s$$

in number of semiempirical methods like CNDO, INDO,…, starting since 1951. They provided correct electronegativities and hardness for atoms.

Unification of terminology



Soft base. Donor atom has high polarizability and low electronegativity, is easily oxidized, and is associated with empty low-lying orbitals.

Hard base. Donor atom has low polarizability and high electronegativity, is hard to oxidize, and is associated with empty orbitals of high energy.

Soft acid. Acceptor atom is of low positive charge, is of large size, and has easily excited outer electrons.

Hard acid. Acceptor atom has high positive charge and small size, and does not have easily-excited outer electrons.

Politzer (1987) showed that softness is linearly correlated with polarizability and showed how it can be linked with capacity to accept charge.

Reactivity index – Fukui function, f(r) is natural index of chemical reactivity, independent of molecular model

$$f(\mathbf{r}) = \left[\frac{\delta\mu}{\delta v(\mathbf{r})}\right]_N = \left[\frac{\partial\rho(\mathbf{r})}{\partial N}\right]_v$$

is normalized $\int f(\mathbf{r})\, d\mathbf{r} = 1$

measures how sensitive is chemical potential of a system with respect to external perturbation (first definition) and is quantity involving valence region of a molecule.

$$f^{+}(\mathbf{r}) = \left[\frac{\partial\rho(\mathbf{r})}{\partial N}\right]_v^{+} \qquad \text{(derivative as } N \text{ increases from } N_0 \text{ to } N+\delta\text{)}$$

$$f^{-}(\mathbf{r}) = \left[\frac{\partial\rho(\mathbf{r})}{\partial N}\right]_v^{-} \qquad \text{(derivative as } N \text{ increases from } N_0-\delta \text{ to } N_0\text{)}$$

$$f^{0}(\mathbf{r}) = \tfrac{1}{2}[f^{+}(\mathbf{r}) + f^{-}(\mathbf{r})] \qquad \text{(mean of left and right derivatives)}$$

The derivatives can be approximated

$$f^{+}(\mathbf{r}) \approx \rho_{\mathrm{LUMO}}(\mathbf{r})$$

$$f^{-}(\mathbf{r}) \approx \rho_{\mathrm{HOMO}}(\mathbf{r})$$

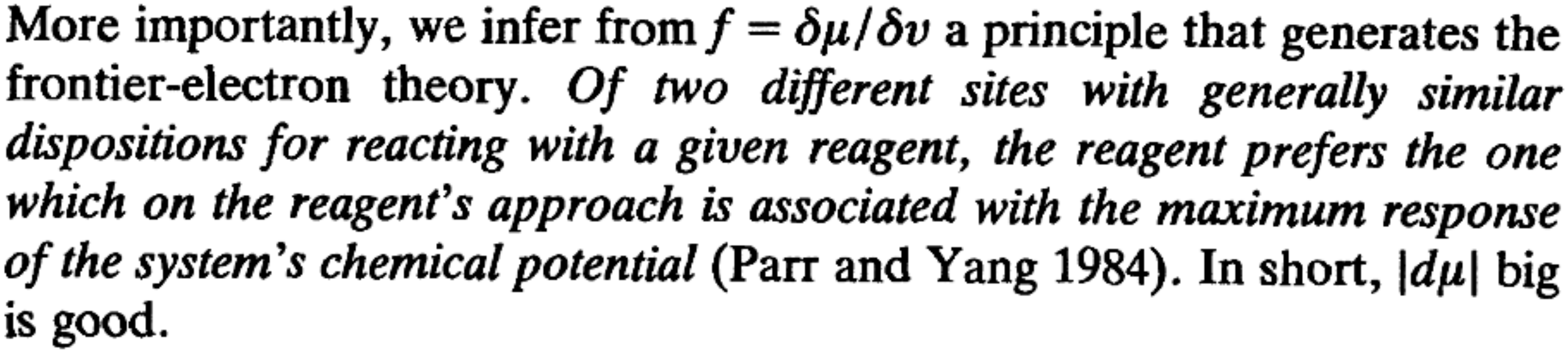
$$f^{0}(\mathbf{r}) \approx \tfrac{1}{2}[\rho^{\mathrm{HOMO}}(\mathbf{r}) + \rho_{\mathrm{HOMO}}(\mathbf{r})]$$

Fukui (1952):

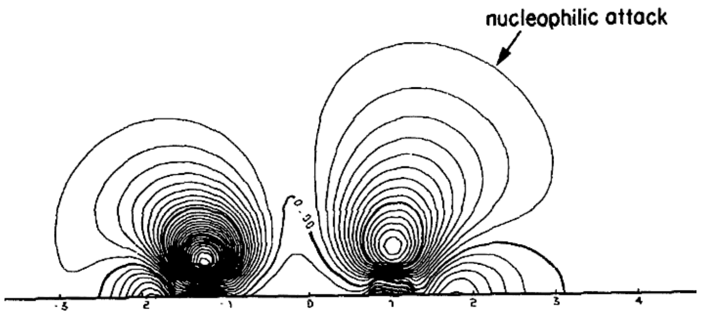
$f^{+}(\mathbf{r}) \approx \rho_{\mathrm{LUMO}}(\mathbf{r})$ measures reactivity toward a nucleophilic reagent

$f^{-}(\mathbf{r}) \approx \rho_{\mathrm{HOMO}}(\mathbf{r})$ measures reactivity toward an electrophilic reagent

$f^{0}(\mathbf{r}) \approx \tfrac{1}{2}[\rho_{\mathrm{HOMO}}(\mathbf{r}) + \rho_{\mathrm{LUMO}}(\mathbf{r})]$ measures reactivity toward an innocuous (radical) reagent

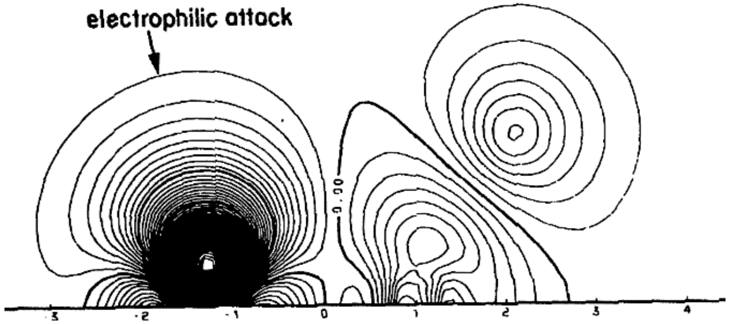


More importantly, we infer from $f = \delta\mu/\delta v$ a principle that generates the frontier-electron theory. *Of two different sites with generally similar dispositions for reacting with a given reagent, the reagent prefers the one which on the reagent's approach is associated with the maximum response of the system's chemical potential* (Parr and Yang 1984). In short, $|d\mu|$ big is good.



O C

$f^{+}(r)$ (left) contours on the plane perpendicular to the H2CO molecular plane.



O C

$f^{-}(r)$ (right) contours on the H2CO molecular plane.

Local softness and hardness

The absolute hardness and softness are independent of space coordinate

$$\eta = \frac{1}{2}\left(\frac{\partial \mu}{\partial N}\right)_v = \frac{1}{2}\left(\frac{\partial^2 E}{\partial N^2}\right)_v \qquad S = \frac{1}{2\eta} = \left(\frac{\partial N}{\partial \mu}\right)_v$$

The soft molecules have larger propensity to form covalent bonds and reactivity index f(r) can identify the relevant site for reaction. One can expect that η and S should be somehow related to f(r). Exploring this relationship leads to local harness/ softness definition.

Parr, Yang (1982) defined local softness

$$s(\mathbf{r}) = \left[\frac{\partial \rho(\mathbf{r})}{\partial \mu}\right]_{v(\mathbf{r})} \qquad S = \int s(\mathbf{r})\, d\mathbf{r}$$

Considering the identity $\left[\frac{\partial \rho(\mathbf{r})}{\partial \mu}\right]_v = \left[\frac{\partial \rho(\mathbf{r})}{\partial N}\right]_v \left[\frac{\partial N}{\partial \mu}\right]_v$

and definition of Fukui function f(r) we can write

$$s(\mathbf{r}) = f(\mathbf{r})S; \qquad f(\mathbf{r}) = \frac{s(\mathbf{r})}{S}$$

S, s(r) and f(r) are known in theory of metals where $g(\varepsilon_F, r)$ and $g(\varepsilon_F)$ are local density of states at Fermi level and total density of states at Fermi level at 0 K.

$$s(\mathbf{r}) = g(\varepsilon_F, \mathbf{r}) \qquad f(\mathbf{r}) = \frac{g(\varepsilon_F, \mathbf{r})}{g(\varepsilon_F)}$$
$$S = g(\varepsilon_F)$$

Young, Parr (1985) s(r) is given by fluctuations in a grand canonical ensebmle

$$s(\mathbf{r}) = \frac{1}{kT}\{\langle N\rho(\mathbf{r})\rangle - \langle N\rangle\langle\rho(\mathbf{r})\rangle\}$$

Berkowitz and Parr (1988) did derivation of local softness that reveals relation to local hardness. They defined two-variable kernels for hardness and softness and than they defined local properties.

Because ρ(r) determines all properties, it determines μ, v(r) and also modified potential

$$u(\mathbf{r}) = v(\mathbf{r}) - \mu = -\frac{\delta F[\rho]}{\delta\rho(\mathbf{r})}$$

As u(r) is functional of ρ the derivative δu(r)/δρ(r’) exits and we define the hardness kernel

$$-2\eta(\mathbf{r},\mathbf{r}') \equiv \frac{\delta u(\mathbf{r})}{\delta\rho(\mathbf{r}')} = \frac{\delta u(\mathbf{r}')}{\delta\rho(\mathbf{r})}$$

and similarly δρ(r)/δu(r’) exists and we define the softness kernel

$$-s(\mathbf{r},\mathbf{r}') \equiv \frac{\delta\rho(\mathbf{r})}{\delta u(\mathbf{r}')} = \frac{\delta\rho(\mathbf{r}')}{\delta u(\mathbf{r})}$$

We have proper reciprocity because

$$2\int s(\mathbf{r},\mathbf{r}')\eta(\mathbf{r}',\mathbf{r}'')\,d\mathbf{r}' = \delta(\mathbf{r}-\mathbf{r}'')$$

The hardness and softness kernel are reciprocals of each other and we can define the local softness

$$s(\mathbf{r}) = \int s(\mathbf{r},\mathbf{r}')\,d\mathbf{r}'$$

and local hardness

$$\eta(\mathbf{r}) = \frac{1}{N}\int \eta(\mathbf{r},\mathbf{r}')\rho(\mathbf{r}')\,d\mathbf{r}'$$

reciprocal

$$2\int s(\mathbf{r})\eta(\mathbf{r})\,d\mathbf{r} = 1$$

To prove this we multiply $2\int s(\mathbf{r},\mathbf{r}')\eta(\mathbf{r}',\mathbf{r}'')\,d\mathbf{r}' = \delta(\mathbf{r}-\mathbf{r}'')$ by $\rho(r')$ and integrate over r''

$$2\int s(\mathbf{r}',\mathbf{r})\eta(\mathbf{r}')\,d\mathbf{r}' = \frac{\rho(r)}{N}$$

and than integrate over r.

The $\eta(r)$ is given explicitly by

$$2\eta(\mathbf{r}) = \frac{1}{N}\int \frac{\delta^2 F[\rho]}{\delta\rho(\mathbf{r})\,\delta\rho(\mathbf{r}')}\rho(\mathbf{r}')\,d\mathbf{r}'$$

and total harness can be obtained from the local

$$\eta = \int f(\mathbf{r})\eta(\mathbf{r})\,d\mathbf{r}$$

We show that the following definitions are synonymous

$$s(\mathbf{r}) = \int s(\mathbf{r}, \mathbf{r}')\, d\mathbf{r}' \qquad\qquad s(\mathbf{r}) = \left[\frac{\partial \rho(\mathbf{r})}{\partial \mu}\right]_{v(\mathbf{r})}$$

We have

$$\begin{aligned} d\rho(\mathbf{r}) &= \int \frac{\delta \rho(\mathbf{r})}{\delta u(\mathbf{r}')}\, du(\mathbf{r}')\, d\mathbf{r}' \\ &= \int s(\mathbf{r}, \mathbf{r}')[dv(\mathbf{r}') - d\mu]\, d\mathbf{r}' \\ &= 2s(\mathbf{r})\eta\, dN + \int [-s(\mathbf{r}, \mathbf{r}') + s(\mathbf{r})f(\mathbf{r}')]\, dv(\mathbf{r}')\, d\mathbf{r}' \end{aligned}$$

and also

$$d\rho(\mathbf{r}) = f(\mathbf{r})\, dN + \int \left[\frac{\delta \rho(\mathbf{r})}{\delta v(\mathbf{r}')}\right]_N dv(\mathbf{r}')\, d\mathbf{r}$$

Hence

$$s(\mathbf{r}) = \frac{f(\mathbf{r})}{2\eta} = f(\mathbf{r})S$$

And relation of conventional response function to softness, local softness and softness kernel is

$$\left[\frac{\delta \rho(\mathbf{r})}{\delta v(\mathbf{r}')}\right]_N = -s(\mathbf{r}, \mathbf{r}') + \frac{s(\mathbf{r})s(\mathbf{r}')}{S}$$

The Kohn-Sham theory, the basic principles

The ground state energy of a many-electron system can be obtained as minimum of energy functional

$$E[\rho] = \int \rho(\mathbf{r}) v(\mathbf{r})\, d\mathbf{r} + F[\rho]$$

$$F[\rho] = T[\rho] + V_{ee}[\rho]$$

The ground state density minimizes E[ρ] and thus satisfies the Euler equation

$$\mu = v(\mathbf{r}) + \frac{\delta F[\rho]}{\delta \rho(\mathbf{r})}$$

with the boundary condition

$$\int \rho(\mathbf{r})\, d\mathbf{r} = N$$

Among all possible solutions for μ one takes which minimizes E[ρ] as opposed to those associated with other extremes.

How one can do better than TF or TFD. TF constitutes direct approach with explicit forms of T[ρ] and V_{ee}[ρ] and the equation involve the el. density alone. There are insurmountable difficulties when going beyond the simplified level of assumptions.

KS (1965) invented indirect approach for T[ρ] and made DFT a practical and accurate for rigorous calculations.

KS introduced orbitals in such a way that the kinetic energy can be computed simply to good accuracy leaving small residual correction treated separately. For better understanding we start with exact formula of ground state kinetic energy

$$T = \sum_{i}^{N} n_i \langle \psi_i | -\tfrac{1}{2}\nabla^2 | \psi_i \rangle$$

where Ψi and ni are natural spin orbitals and occupation numbers, 0≤ni≤1.

T is functional of total density ρ

$$\rho(\mathbf{r}) = \sum_{i}^{N} n_i \sum_{s} |\psi_i(\mathbf{r}, s)|^2$$

For any interacting system there is a infinite number of terms in the formula. HK showed that one can build simpler formulas

$$T_s[\rho] = \sum_{i}^{N} \langle \psi_i | -\tfrac{1}{2}\nabla^2 | \psi_i \rangle \qquad \rho(\mathbf{r}) = \sum_{i}^{N} \sum_{s} |\psi_i(\mathbf{r}, s)|^2$$

describing special case where ni = 1 for N orbitals and ni = 0 for the rest. This assumption holds exact for the determinantal wave function describing non-interacting electrons.

We know that any nonnegative, continuous and normalized density can be decomposed in this way, but given a ρ how can we have a *unique decomposition* in terms of orbitals so as to give a unique value to T[ρ] through this formula?

In analogy with the HK definition of universal functional $F_{HK}[\rho]$ Kohn and Sham invoked corresponding *noninteracting system* with the Hamiltonian without electron-electron repulsion term for which the ground state density is exactly ρ.

$$\hat{H}_s = \sum_i^N \left(-\tfrac{1}{2}\nabla_i^2\right) + \sum_i^N v_s(\mathbf{r})$$

For this system there will be an exact determinantal ground-state wave function

$$\Psi_s = \frac{1}{\sqrt{N!}} \det \left[\psi_1 \psi_2 \cdots \psi_N\right]$$

where Ψi are the N lowest eigenstates of the one-electron Hamiltoninan

$$\hat{h}_s \psi_i = \left[-\tfrac{1}{2}\nabla^2 + v_s(\mathbf{r})\right]\psi_i = \varepsilon_i \psi_i$$

The kinetic energy is given by

$$\begin{aligned} T_s[\rho] &= \langle \Psi_s | \sum_i^N \left(-\tfrac{1}{2}\nabla_i^2\right) | \Psi_s \rangle \\ &= \sum_{i=1}^N \langle \psi_i | -\tfrac{1}{2}\nabla^2 | \psi_i \rangle \end{aligned}$$

This definition leaves the undesirable restriction on density that needs to be noninteracting and v-representable, i.e. there must exist noninteracting ground state with density ρ.

The Ts[ρ] domain is any density derived from antisymmetric wave-function. However, the Ts[ρ] is not the exact density functonal T[ρ]! The KS idea was to set up the exact solution for Ts[ρ] and than to improve the independent-particle model.

The separation of Ts[ρ] proceeds according to

$$F[\rho] = T_s[\rho] + J[\rho] + E_{xc}[\rho]$$

where

$$E_{xc}[\rho] \equiv T[\rho] - T_s[\rho] + V_{ee}[\rho] - J[\rho]$$

is the exchange-correlation energy functional containing the difference between T and Ts, presumably small and the nonclassical part Vee.

The Euler equation becomes

$$\mu = v_{\text{eff}}(\mathbf{r}) + \frac{\delta T_s[\rho]}{\delta \rho(\mathbf{r})}$$

where KS effective potential is defined by

$$\begin{aligned} v_{\text{eff}}(\mathbf{r}) &= v(\mathbf{r}) + \frac{\delta J[\rho]}{\delta \rho(\mathbf{r})} + \frac{\delta E_{xc}[\rho]}{\delta \rho(\mathbf{r})} \\ &= v(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' + v_{xc}(\mathbf{r}) \end{aligned}$$

with the exchange-correlation functional defined

$$v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[\rho]}{\delta \rho(\mathbf{r})}$$

The explicit form of Ts[ρ] I terms of density is yet unknown.

The solution by KS implies that $\mu = v_{\mathrm{eff}}(\mathbf{r}) + \frac{\delta T_s[\rho]}{\delta \rho(\mathbf{r})}$ with the boundar $\int \rho(\mathbf{r})\, d\mathbf{r} = N$

is the same same equation as for conventioal DFT applied for *noninteracting* electrons moving in external potential $v_s(r) = v_{\mathrm{eff}}(r)$.

Therefore, for one $v_{\mathrm{eff}}(r)$ we can obtain ρ satisfying $\mu = v_{\mathrm{eff}}(\mathbf{r}) + \frac{\delta T_s[\rho]}{\delta \rho(\mathbf{r})}$

by solving the equations

$$[-\tfrac{1}{2}\nabla^2 + v_{\mathrm{eff}}(\mathbf{r})]\psi_i = \varepsilon_i \psi_i$$

$$\rho(\mathbf{r}) = \sum_i^N \sum_s |\psi_i(\mathbf{r}, s)|^2$$

The $v_{\mathrm{eff}}(r)$ depends on ρ(r) through $v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[\rho]}{\delta \rho(\mathbf{r})}$

and the equations must be solved therefore self-consistently.

One can begin with guessed ρ(r) constructed $v_{\mathrm{eff}}(r)$ and find new ρ from the equations called Kohn-Sham equations.

Derivation of KS equations

The energy is given by

$$E[\rho] = T_s[\rho] + J[\rho] + E_{xc}[\rho] + \int v(\mathbf{r})\rho(\mathbf{r})\, d\mathbf{r}$$

$$= \sum_i^N \sum_s \int \psi_i^*(\mathbf{r})(-\tfrac{1}{2}\nabla^2)\psi_i(\mathbf{r})\, d\mathbf{r} + J[\rho] + E_{xc}[\rho] + \int v(\mathbf{r})\rho(\mathbf{r})\, d\mathbf{r}$$

where the electron density is defined by $\rho(\mathbf{r}) = \sum_i^N \sum_s |\psi_i(\mathbf{r}, s)|^2$

The energy is expressed in terms of N orbitals allowed to vary over the defined space. The variational search can be done in space Ψi. To do it one most constrain orthonormality

$$\int \psi_i^*(\mathbf{x})\psi_j(\mathbf{x})\, d\mathbf{x} = \delta_{ij}$$

because otherwise T[ρ] would not be valid.

Define functional of N orbitals

$$\Omega[\{\psi_i\}] = E[\rho] - \sum_i^N \sum_j^N \varepsilon_{ij} \int \psi_i^*(\mathbf{x})\psi_j(\mathbf{x})\, d\mathbf{x}$$

Where E[ρ] is the known energy functional and εij are the Lagrange multipliers. For E[ρ] to be minimum the functional variation must fulfill

$$\delta\Omega[\{\psi_i\}] = 0$$

leading to the equations

$$\hat{h}_{\text{eff}}\psi_i = [-\tfrac{1}{2}\nabla^2 + v_{\text{eff}}]\psi_i = \sum_j^N \varepsilon_{ij}\psi_j$$

with the defined operator v_{eff} and one-electron Hermitian operator h_{eff} that can be diagonalized by unitary transformation of the orbitals.

$$\begin{aligned} v_{\text{eff}}(\mathbf{r}) &= v(\mathbf{r}) + \frac{\delta J[\rho]}{\delta\rho(\mathbf{r})} + \frac{\delta E_{xc}[\rho]}{\delta\rho(\mathbf{r})} \\ &= v(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\, d\mathbf{r}' + v_{xc}(\mathbf{r}) \end{aligned}$$

The canonical Kohn-Sham equations are thus defined

$$[-\tfrac{1}{2}\nabla^2 + v_{\mathrm{eff}}]\psi_i = \varepsilon_i \psi_i$$

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

where

$$\rho(\mathbf{r}) = \sum_i^N \sum_s |\psi_i(\mathbf{r}, s)|^2$$

The total energy is given by

$$E = \sum_i^N \varepsilon_i - \frac{1}{2} \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}\, d\mathbf{r}' + E_{xc}[\rho] - \int v_{xc}(\mathbf{r})\rho(\mathbf{r})\, d\mathbf{r}$$

the sum of orbital energies is similar to that in HF (but see the difference)

$$E_{\mathrm{HF}} = \sum_{i=1}^N \varepsilon_i - V_{ee} \qquad V_{ee} = \int \Psi_{\mathrm{HF}}^*(\mathbf{x}^N)\Big(\sum_{i<j} \frac{1}{r_{ij}}\Big)\Psi_{\mathrm{HF}}(\mathbf{x}^N)\, d\mathbf{x}^N$$

$$= \tfrac{1}{2} \sum_{i,j=1}^N (J_{ij} - K_{ij})$$

The KS equations:

Major advantage is that introducing the N orbitals we cover dominant part of true T[ρ] by the $T_s[\rho]$ which is calculated exactly! The price is that we have to solve N equations instead of one in original TF model. Keep in mind that $E_{xc}[\rho]$ is unknown.

The KS equations containing more general $v_{eff}(r)$ have the same form as HF equations and the numerical computational requirements are thus similar. F, HF and KS theories provide one-electron equations for many-electron system.

The KS theory is in principle exact because it incorporates rigorously the exchange-correlation effects, though the exact functional is unknown yet.

The correlation effects are not covered by HF equations and their improvement represents different way from improvement of KS equations represented by improvement of $E_{xc}[\rho]$ in order to provide the exact ρ and E.

Since $v_{eff}(r)$ doesn't contain spin the solution is double degenerated and spatial orbitals can be complemented by spin arbitrarily

$$\rho(\mathbf{r}) = 2\rho^{\alpha}(\mathbf{r}) = 2\rho^{\beta}(\mathbf{r}) = 2\sum_{i}^{N/2} |\phi_i(\mathbf{r})|^2 \qquad \rho(\mathbf{r}) = \rho^{\alpha}(\mathbf{r}) + \rho^{\beta}(\mathbf{r})$$

This prescription agrees with RHF method but HF and KS are different in nature: the restriction on spatial orbitals in KS theory is natural whereas the restriction on RHF is further qualification on the determinantal-wave-function approximation. Therefore exists the spin-density functional theory in analogy to HF which allows spin dependence of $v_{eff}(r)$.

The Hamiltonian

$$\hat{H}_s = \sum_{i}^{N} \left(-\frac{1}{2}\nabla_i^2\right) + \sum_{i}^{N} v_s(\mathbf{r})$$

defines the reference *non-interacting* system. The question is which orbitals should be chosen to form the KS density? Rigorous answer is: the set of N orbitals determined self-consistently according to KS equations to miminize total energy. In practice only the set of orbitals giving the lowest εi is chosen.

Becke3 + LeeYangParr xc funkcionál

$$E_{xc} = (1-a_0)E_x^{LDA} + a_0 E_x^{HF} + a_x \Delta E_x^{B88} + (1-a_c)E_c^{VWN} + a_c \Delta E_c^{LYP},$$

$$a_0 = 0{,}20 \qquad a_x = 0{,}72 \qquad a_c = 0{,}81.$$

$$E_x^{LDA}[\rho(r)] = \int \varepsilon_x[\rho(r)]\rho(r)\,dr = \int c_x \rho^{4/3}(r)\,dr$$

$$E_x^{B88}[\rho] = E_x^{D30}[\rho] - b\int \rho^{4/3} \frac{x_s^2}{1+6b\,x_s \sinh^{-1}(x_s)}\,dr; \quad b = 0{,}0042.$$

$$E_c^{LYP}[\rho] = -a\int \frac{\rho}{1+d\rho^{-1/3}} - \frac{11b}{24}\rho^2|\nabla\rho|^2 + b\left[\frac{3}{10}(3\pi^2)^{2/3}\rho^{8/3} + |\nabla\rho|^2\left(\frac{5}{12} - \frac{7\delta}{72}\right)\right]\omega\rho^2\,d\mathbf{r}$$

$$\omega = \frac{\exp(-c\rho^{-1/3})}{1+d\rho^{-1/3}}\rho^{-11/3}$$

$$\delta = c\rho^{-1/3} + \frac{d\rho^{-1/3}}{1+d\rho^{-1/3}}$$

In the case of a spin-polarized system where there is nonvanishing spin polarization,

$$\zeta = \frac{\rho^\alpha - \rho^\beta}{\rho^\alpha + \rho^\beta} \neq 0$$

the kinetic and exchange energy are also known: (8.2.9) and (8.2.18). From (8.2.19), the exchange energy is

$$E_x[\rho^\alpha, \rho^\beta] = \int \rho \varepsilon_x(\rho, \xi)\, d\mathbf{r} \qquad \text{(E.15)}$$

$$\varepsilon_x(\rho, \xi) = \varepsilon_x^0(\rho) + [\varepsilon_x^1(\rho) - \varepsilon_x^0(\rho)] f(\zeta) \qquad \text{(E.16)}$$

magnetic” case, $\varepsilon_x^1(\rho) = \varepsilon_x(\rho, 1)$. The corresponding correlation energy formula is

$$\varepsilon_c[\rho^\alpha, \rho^\beta] = \int \rho \varepsilon_c(\rho, \zeta)\, d\mathbf{r} \qquad \text{(E.18)}$$

but there is no simple exact formula like (E.16) relating ε_c to the limiting spin-compensated and spin-polarized correlation energies per particle, ε_c^0 and ε_c^1.

Vosko, Wilk, and Nusair (1980) made a careful analysis of the random phase approximation and proposed the more accurate description

$$\varepsilon_c^{\mathrm{VWN}}(r_s, \zeta) = \varepsilon_c^0(r_s) + \alpha(r_s)\left[\frac{f(\zeta)}{f''(0)}\right][1 + \beta(r_s)\zeta^4] \qquad \text{(E.25)}$$

where $\alpha(r_s)$ is the spin stiffness, which is related to spin susceptibilities, and $\beta(r_s)$ is chosen to satisfy $\varepsilon_c(r_s, 1) = \varepsilon_c^1(r_s)$, namely,

$$1 + \beta(r_s) = f''(0)\frac{\varepsilon_c^1(r_s) - \varepsilon_c^0(r_s)}{\alpha(r_s)}. \qquad \text{(E.26)}$$

Tables of $\alpha(r_s)$ and $\beta(r_s)$ may be found in the original paper. Another advance in the work of Vosko, Wilk, and Nusair is that Padé-approximant interpolations were made of accurate numerical calculations of uniform electron gas ε_c^0 and ε_c^1 that had been made by Ceperley and Alder. Ceperley and Alder (1980) had calculated the total energy for the uniform electron gas in spin-compensated and ferromagnetic states for several different values of r_s, using the quantum Monte Carlo method. The correlation energy was obtained by subtracting the corresponding kinetic and exchange energies from the total energy (E.5). The VWN interpolations for ε_c^0 and ε_c^1 also incorporate the high- and low-density limits. The final form for both ε_c^0 and ε_c^1 is

$$\begin{aligned}\varepsilon_c(r_s) = \frac{A}{2}\Bigg\{ &\ln\frac{x}{X(x)} + \frac{2b}{Q}\tan^{-1}\frac{Q}{2x+b} \\ &- \frac{bx_0}{X(x_0)}\left[\ln\frac{(x-x_0)^2}{X(x)} + \frac{2(b+2x_0)}{Q}\tan^{-1}\frac{Q}{2x+b}\right]\Bigg\} \qquad \text{(E.27)}\end{aligned}$$

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.

of the approximation assumed in this method. We start with the following time-dependent Kohn–Sham (KS) equation

$$\sum_q \{F_{pq\sigma} P_{qr\sigma} - P_{pq\sigma} F_{qr\sigma}\} = i \frac{\partial P_{pr\sigma}}{\partial t}, \tag{1}$$

with the idem-potency condition

$$\sum_q P_{pq\sigma} P_{qr\sigma} = P_{pr\sigma}, \tag{2}$$

where F and P are the KS Hamiltonian and density matrices, respectively, represented by orthonormal basis functions $\{\phi_p(\boldsymbol{r})\}$, and p,q,r are basis set indexes, and σ denotes spin. The KS Hamiltonian matrix elements are written explicitly as

$$F_{pq\sigma} = \int \phi^*_{p\sigma}(\boldsymbol{r}) \left(-\tfrac{1}{2}\nabla^2 + \sum_A \frac{-Z_A}{|\boldsymbol{r} - \boldsymbol{R}_A|} + \int \frac{\rho(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|}\, \mathrm{d}\boldsymbol{r}' + \frac{\delta E_{\mathrm{XC}}}{\delta \rho_\sigma(\boldsymbol{r})} \right) \phi_{q\sigma}(\boldsymbol{r})\, \mathrm{d}\boldsymbol{r}, \tag{3}$$

where the adiabatic approximation is used from the outset for the sake of simplicity. Spin density $\rho_\sigma(\boldsymbol{r})$ is related to the density matrix by

$$\rho_\sigma(\boldsymbol{r}) = \sum_{pq} P_{pq\sigma}\, \phi_{p\sigma}(\boldsymbol{r})\, \phi^*_{q\sigma}(\boldsymbol{r}). \tag{4}$$

We assume that the molecule is initially in a stationary state, the electronic structure of which is suitably described by time-independent KS density functional theory and that the orthonormal basis functions $\{\phi_p(\boldsymbol{r})\}$ are the KS orbitals for this unperturbed ground state. The KS Hamiltonian and density matrices for the ground state, which are superscripted with '(0)', are simply

$$F^{(0)}_{pq\sigma} = \delta_{pq}\, \varepsilon_{p\sigma}, \tag{5}$$

and

$$P^{(0)}_{ij\sigma} = \delta_{ij}, \tag{6}$$

$$P^{(0)}_{ia\sigma} = P^{(0)}_{ai\sigma} = P^{(0)}_{ab\sigma} = 0, \tag{7}$$

where ε are one-electron energies, and we use i,j for occupied orbitals, a,b for virtual orbitals, and p,q,r,s,t for general orbitals. These KS Hamiltonian and density matrices satisfy the time-independent KS equation

$$\sum_q \left(F^{(0)}_{pq\sigma} P^{(0)}_{qr\sigma} - P^{(0)}_{pq\sigma} F^{(0)}_{qr\sigma} \right) = 0, \tag{8}$$

with the idem-potency condition

$$\sum_q P^{(0)}_{pq\sigma} P^{(0)}_{qr\sigma} = P^{(0)}_{pr\sigma}. \tag{9}$$

We now apply an oscillatory perturbation, which can be described as a single Fourier component,

$$g_{pq\sigma} = \tfrac{1}{2}\left[f_{pq\sigma} \exp(-\mathrm{i}\omega t) + f^*_{qp\sigma} \exp(\mathrm{i}\omega t) \right], \tag{10}$$

where the matrix f represents a one-electron operator describing the details of the perturbation. The first-order (linear) response of the density matrix P' to this applied perturbation is

$$P_{pq\sigma} = P^{(0)}_{pq\sigma} + P'_{pq\sigma}, \tag{11}$$

with

$$P'_{pq\sigma} = \tfrac{1}{2}\left[d_{pq\sigma} \exp(-\mathrm{i}\omega t) + d^*_{qp\sigma} \exp(\mathrm{i}\omega t) \right]. \tag{12}$$

The first-order change in the KS Hamiltonian matrix is composed of two terms: the change in the one-electron part described by Eq. (10) and the change in the two-electron part induced by the first-order response of the density matrix, namely,

$$F_{pq\sigma} = F^{(0)}_{pq\sigma} + g_{pq\sigma} + \sum_{rs\tau} \frac{\partial F_{pq\sigma}}{\partial P_{rs\tau}} P'_{rs\tau} , \qquad (13)$$

with

$$\frac{\partial F_{pq\sigma}}{\partial P_{rs\tau}} = (p_\sigma q_\sigma | s_\tau r_\tau) + (p_\sigma q_\sigma | w_{\sigma\tau} | s_\tau r_\tau), \qquad (14)$$

where the regular two-electron integrals are expressed in the Mulliken notation, and

$$\begin{aligned} &(p_\sigma q_\sigma | w_{\sigma\tau} | s_\tau r_\tau) \\ &\quad = \int \phi^*_{p\sigma}(\boldsymbol{r}) \phi_{q\sigma}(\boldsymbol{r}) \frac{\delta^2 E_{\mathrm{XC}}}{\delta\rho_\sigma(\boldsymbol{r}) \delta\rho_\tau(\boldsymbol{r}')} \\ &\qquad \times \phi^*_{s\tau}(\boldsymbol{r}') \phi_{r\tau}(\boldsymbol{r}') \, \mathrm{d}\boldsymbol{r} \, \mathrm{d}\boldsymbol{r}' . \qquad (15) \end{aligned}$$

Substituting Eqs. (10) to (13) to the time-dependent KS Eq. (1) and collecting the terms which are multiplied by the $\exp(-\mathrm{i}\omega t)$ factor, we obtain

$$\begin{aligned} &\sum_q \Bigg[F^{(0)}_{pq\sigma} d_{qr\sigma} - d_{pq\sigma} F^{(0)}_{qr\sigma} \\ &\quad + \left(f_{pq\sigma} + \sum_{st\tau} \frac{\partial F_{pq\sigma}}{\partial P_{st\tau}} d_{st\tau} \right) P^{(0)}_{qr\sigma} \\ &\quad - P^{(0)}_{pq\sigma} \left(f_{qr\sigma} + \sum_{st\tau} \frac{\partial F_{qr\sigma}}{\partial P_{st\tau}} d_{st\tau} \right) \Bigg] \\ &\quad = \omega d_{pr\sigma} . \qquad (16) \end{aligned}$$

The terms multiplied by the $\exp(\mathrm{i}\omega t)$ factor lead to the conjugate complex of the above equation.

The idem-potency condition (Eq. (2)) strongly restricts the possible form of the d matrix in Eq. (12); occupied–occupied and virtual–virtual elements of the d matrix are zero. In TDDFT, all the possible non-zero elements of the d matrix, namely, virtual–occupied and occupied–virtual elements, are taken into account. Thus, writing

$$d_{ai\sigma} = x_{ai\sigma} , \qquad (17)$$

$$d_{ia\sigma} = y_{ai\sigma} , \qquad (18)$$

and using the diagonal nature of the unperturbed KS Hamiltonian and density matrices (Eqs. (5) and (6)), we obtain a pair of equations

$$\begin{aligned} &F^{(0)}_{aa\sigma} x_{ai\sigma} - x_{ai\sigma} F^{(0)}_{ii\sigma} \\ &\quad + \left[f_{ai\sigma} + \sum_{bj\tau} \left(\frac{\partial F_{ai\sigma}}{\partial P_{bj\tau}} x_{bj\tau} + \frac{\partial F_{ai\sigma}}{\partial P_{jb\tau}} y_{bj\tau} \right) \right] P^{(0)}_{ii\sigma} \\ &\quad = \omega x_{ai\sigma} , \qquad (19) \end{aligned}$$

and

$$F^{(0)}_{ii\sigma} y_{ai\sigma} - y_{ai\sigma} F^{(0)}_{aa\sigma} - P^{(0)}_{ii\sigma}\left[f_{ia\sigma} + \sum_{bj\tau} \left(\frac{\partial F_{ia\sigma}}{\partial P_{bj\tau}} x_{bj\tau} + \frac{\partial F_{ia\sigma}}{\partial P_{jb\tau}} y_{bj\tau} \right) \right] = \omega y_{ai\sigma} . \tag{20}$$

Remembering that $F^{(0)}_{pp\sigma} = \varepsilon_{p\sigma}$ (Eq. (5)) and $P^{(0)}_{ii\sigma} = 1$ (Eq. (6)) and assuming that the electronic transitions occur with an infinitesimal perturbation ($f_{ia\sigma} = f_{ai\sigma} = 0$), we obtain a non-Hermitian eigenvalue equation

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} = \omega \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} , \tag{21}$$

with

$$A_{ai\sigma,bj\tau} = \delta_{ij}\delta_{ab}\delta_{\sigma\tau}(\varepsilon_{a\sigma} - \varepsilon_{i\tau}) + (a_\sigma i_\sigma | j_\tau b_\tau) + (a_\sigma i_\sigma | w_{\sigma\tau} | j_\tau b_\tau) , \tag{22}$$

$$B_{ai\sigma,bj\tau} = (a_\sigma i_\sigma | b_\tau j_\tau) + (a_\sigma i_\sigma | w_{\sigma\tau} | b_\tau j_\tau) . \tag{23}$$

Eqs. (21) and (23) are solved to obtain the TDDFT excitation energies ω.

In TDDFT/TDA, only the virtual–occupied elements of the d matrix are considered; in other words, the Tamm–Dancoff approximation amounts to neglecting the occupied–virtual elements of the d matrix. Writing

$$d_{ai\sigma} = x_{ai\sigma} , \tag{24}$$

we obtain

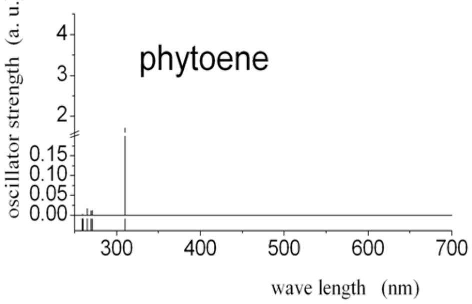
$$\sum_a F^{(0)}_{aa\sigma} x_{ai\sigma} - \sum_i x_{ai\sigma} F^{(0)}_{ii\sigma} + \sum_i \left(f_{ai\sigma} + \sum_{bj\tau} \frac{\partial F_{ai\sigma}}{\partial P_{bj\tau}} x_{bj\tau} \right) P^{(0)}_{ii\sigma} = \omega x_{ai\sigma} . \tag{25}$$

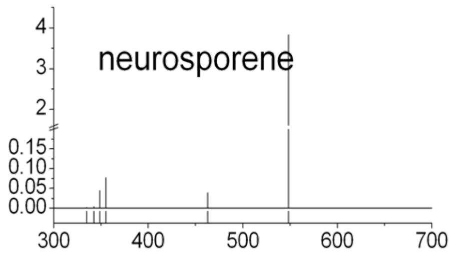
Substituting Eqs. (5) and (6) and assuming $f_{ai\sigma} = 0$ leads to a Hermitian eigenvalue equation the dimension of which is one-half that of the TDDFT working equation

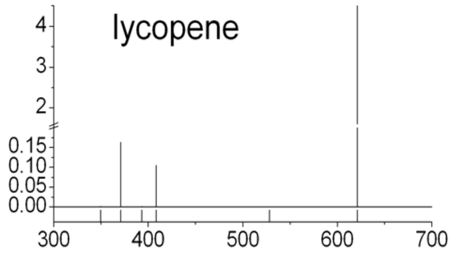
$$\mathbf{AX} = \omega \mathbf{X} , \tag{26}$$

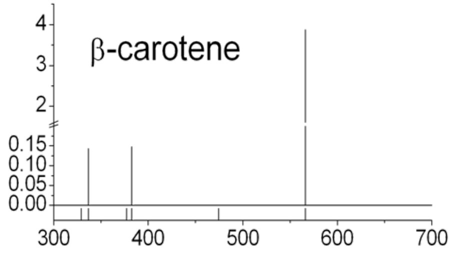
where the definition of the **A** matrix elements are the same as before (Eq. (22)).

TDDFT









TDA/TDDFT

*Vliv délky chromoforu, **b**-cyklů a přítomnosti hydroxylové skupiny.*