Single-Electron Potential

$$V(r) = V_{ext}(r) + V_H(r) + V_{xc}(r) \tag{1}$$

— External (nucleus) potential

$$V_{ext}(r) = -\frac{Ze^2}{r} \tag{2}$$

In the Rydberg unit

$$V_{ext}(r) \cdot \frac{2a}{e^2} = -\frac{Ze^2}{a(r/a)} \cdot \frac{2a}{e^2} = -\frac{2Z}{r/a}$$

$\longrightarrow$ Rydberg factor

$$\therefore V_{ext}(r) = -\frac{2Z}{r} \tag{3}$$

— Electron density

$\longrightarrow$ spin degeneracy

$$\rho(\vec{r}) = \boxed{2} \sum_{(n,\ell) \in \{occupied\}} \sum_{m=-\ell}^{\ell} \frac{\chi_{n\ell}^2(r)}{r^2} |Y_\ell^m(\theta,\varphi)|^2 \tag{4}$$

Here, we have assumed that all (degenerated) m states are equally occupied.

Note the addition theorem,

$$P_\ell(\cos\gamma) = \frac{4\pi}{2\ell+1} \sum_{m=-\ell}^{\ell} Y_\ell^m(\theta_1,\varphi_1) Y_\ell^{m*}(\theta_2,\varphi_2) \tag{5}$$
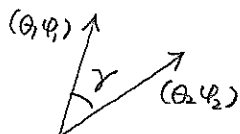
Setting $(\theta_1,\varphi_1) = (\theta_2,\varphi_2)$,

$$P_\ell(1) = \frac{4\pi}{2\ell+1} \sum_{m=-\ell}^{\ell} |Y_\ell^m(\theta,\varphi)|^2 \tag{6}$$

From the definition of Legendre polynomials,

$$\frac{1}{\sqrt{1-2tx+t^2}} = \sum_{l=0}^{\infty} P_l(x)\, t^l \qquad (|t| \leq 1) \qquad (7)$$

For $t = 1$,

$$\frac{1}{\sqrt{1-2t+t^2}} = \sum_{l=0}^{\infty} P_l(1)\, t^l$$

$$\Longrightarrow \quad \frac{1}{1-t} = \sum_{l=0}^{\infty} t^l$$

$$\therefore \quad P_l(1) = 1 \qquad (8)$$

Substituting Eq. (8) in (6),

$$\sum_{m=-l}^{l} |Y_l^m(\theta, \varphi)|^2 = \frac{2l+1}{4\pi} \qquad (9)$$

Therefore, if all m states are occupied for each l, Eqs. (4) and (9) produce

$$P(r) = 2 \sum_{(n,l)\in\{occ\}} \frac{\chi_{nl}^2(r)}{r^2} \cdot \frac{2l+1}{4\pi} \qquad (10)$$

— Hartree potential

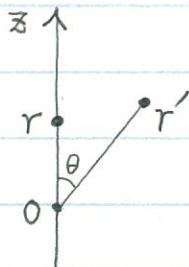$$V_H(r) = \int d\vec{r}' \frac{e^2}{|\vec{r} - \vec{r}'|} \rho(r') \tag{11}$$

In the Bohr-Rydberg unit,

$$V_H(r) \cdot \frac{2a}{e^2} = \frac{2a}{e^2} \cdot \int a^3 d\left(\frac{\vec{r}'}{a}\right) \frac{e^2}{a} \frac{1}{|\vec{r}/a - \vec{r}'/a|} \frac{1}{a^3} \rho(\vec{r}')$$

→ Rydberg factor

$$\therefore V_H(r) = \int d\vec{r}' \frac{②}{|\vec{r} - \vec{r}'|} \rho(r') \tag{12}$$

$$V_H(r) = 2\pi \int_0^\infty r'^2 dr' \, 2\rho(r') \int_{-1}^1 d\cos\theta \frac{1}{\sqrt{r^2 - 2rr'\cos\theta + r'^2}}$$

$$= 4\pi \int_0^r dr' r'^2 \rho(r') \int_{-1}^1 d\cos\theta \frac{1}{r\sqrt{1 - 2\frac{r'}{r}\cos\theta + \left(\frac{r'}{r}\right)^2}} \quad \frac{r'}{r} < 1$$

$$+ 4\pi \int_r^\infty dr' r'^2 \rho(r') \int_{-1}^1 d\cos\theta \frac{1}{r'\sqrt{1 - 2\frac{r}{r'}\cos\theta + \left(\frac{r}{r'}\right)^2}} \quad \frac{r}{r'} < 1 \tag{13}$$

Note that

$$\int_{-1}^1 dx \frac{1}{\sqrt{1 - 2tx + t^2}} = \sum_{\ell=0}^\infty \int_{-1}^1 dx \, P_\ell(x) \, t^\ell$$

$$= \sum_{\ell=0}^\infty t^\ell \int_{-1}^1 dx \, P_\ell(x) \, P_0(x) = 2 \tag{14}$$

$$\underbrace{\frac{2}{2\ell+1} \delta_{\ell,0} = 2\delta_{\ell,0}}$$

$$\therefore \, V_H(r) = \; 4\pi \int_0^r dr' r'^2 \rho(r') \, \frac{2}{r} \; + \; 4\pi \int_r^\infty dr' r' \rho(r') \cdot 2$$

$$V_H(r) = \frac{8\pi}{r} \int_0^r dr' r'^2 \rho(r') \; + \; 8\pi \int_r^\infty dr' r' \rho(r') \tag{15}$$

— Exchange-correlation potential

In the local-density approximation,

$$E_{xc}[n(\vec{r})] = \int d\vec{r}\; \epsilon_{xc}(\rho(\vec{r}))\,\rho(\vec{r}) \tag{16}$$

where $\epsilon_{xc}(\rho)$ is the exchange-correlation energy per electron at density ρ.

The exchange correlation potential, $V_{xc}(\vec{r})$, is defined as

$$\upsilon_{xc}(\vec{r}) \equiv \frac{\delta E_{xc}}{\delta\rho(\vec{r})}$$

$$= \frac{\partial}{\partial\rho(r)}\left[\epsilon_{xc}(\rho(\vec{r}))\,\rho(\vec{r})\right]$$

$$= \epsilon_{xc}(\rho) + \rho\frac{\partial\epsilon_{xc}}{\partial\rho} \quad\sim\quad \begin{array}{l}\text{exchange-correlation}\\ \text{chemical potential, } \mu_{xc}\end{array} \tag{17}$$

The coupling constant, r_s, is defined as

$$\frac{4\pi}{3}a_{mean}^3 = \frac{1}{\rho}$$

$$r_s \equiv \left(\frac{3}{4\pi\rho}\right)^{1/3}\frac{me^2}{\hbar^2} = a_{mean}/a_{Bohr} \tag{18}$$

$$\mu_{xc} = \epsilon_{xc} + \rho\underbrace{\left(\frac{dr_s}{d\rho}\right)}_{-\frac{1}{3}\frac{r_s}{\rho}}\frac{\partial\epsilon_{xc}}{\partial r_s} = \epsilon_{xc} - \frac{r_s}{3}\frac{\partial\epsilon_{xc}}{\partial r_s} \tag{19}$$

$$\therefore\; \upsilon_{xc}(r) = \epsilon_{xc} - \frac{r_s}{3}\frac{\partial\epsilon_{xc}}{\partial r_s}\bigg|_{r_s = [3/4\pi\rho(r)]^{1/3} \text{ in a.u.}} \qquad (Ry) \tag{20}$$

— Exchange chemical potential. (Ry)

$$\begin{cases} \epsilon_x = -\dfrac{3}{2\pi\lambda r_s} & (21) \\[2mm] \lambda = (4/9\pi)^{1/3} & (22) \end{cases}$$

$$\mu_x = \epsilon_{xc} - \underbrace{\frac{r_s}{3}\frac{\partial \epsilon_{xc}}{\partial r_s}}_{-\frac{\epsilon_x}{r_s}} = \frac{4}{3}\epsilon_x = -\frac{2}{\pi\lambda r_s} \qquad (23)$$

— Correlation chemical potential (a.u.)

We use Perdew-Zunger parametrization of the GFMC correlation energy by Ceperley and Alder.

[J. P. Perdew & A. Zunger, Phys. Rev. B23, 5048 ('81)]

$$\begin{cases} \epsilon_c = c_1 + c_2 \ln r_s + c_3 r_s + c_4 r_s \log r_s \quad (r_s \le 1) & (24) \\[2mm] c_1 = -0.0269, \; c_2 = 0.01555, \; c_3 = -0.0116, \; c_4 = 0.0020 \\[2mm] \mu_c = c_1 - \frac{1}{3}c_2 + c_2 \ln r_s + \frac{2c_3 - c_4}{3} r_s + \frac{2}{3}c_4 r_s \log r_s \quad (r_s \le 1) & (25) \end{cases}$$

$$\begin{cases} \epsilon_c = b_1 / (1 + b_2 \sqrt{r_s} + b_3 r_s) & (r_s > 1) \quad (26) \\[2mm] b_1 = -0.1423, \; b_2 = 1.0529, \; b_3 = 0.3334 \\[2mm] \mu_c = \epsilon_c \cdot \dfrac{1 + \frac{7}{6}b_2\sqrt{r_s} + \frac{4}{3}b_3 r_s}{1 + b_2\sqrt{r_s} + b_3 r_s} & (r_s \ge 1) \quad (27) \end{cases}$$