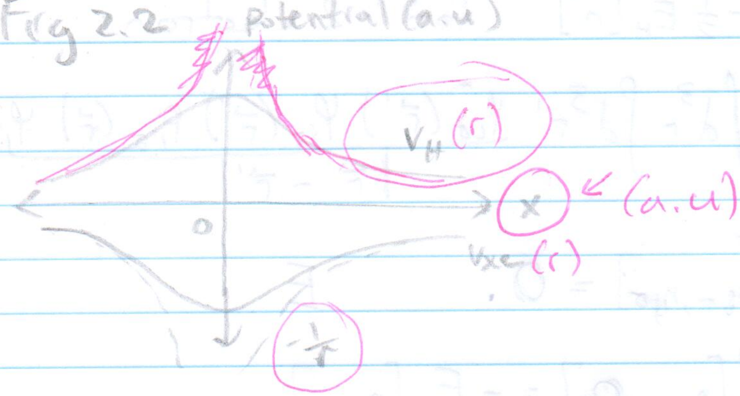
Ullrich Ch 1 & 2
- Prob 2.4, 2.7, 2.11 & Fig 2.2

Fig 2.2



2.4) Check Kato's theorem for the case of the hydrogen atom. Show that slope of hydrogenic density at cusp determines the nuclear charge.

$$\Rightarrow Z_i = \frac{-1}{2n(\vec{r})} \left.\frac{\partial \bar{n}(\vec{r})}{\partial r}\right|_{\vec{r}=\vec{R}_i}$$

$$\phi_{1s}(r) = \frac{1}{\sqrt{\pi}} e^{-r} \qquad n(r) = \frac{1}{\pi} e^{-2r}$$

$$\frac{\partial n(r)}{\partial r} = -\frac{2}{\pi} e^{-2r}$$

$$Z_i = \frac{-1}{\cancel{\frac{2}{\pi}} \cancel{e^{-2r}}} \cdot \left(\frac{-\cancel{2}}{\cancel{\pi}} \cancel{e^{-2r}} \right) = 1 \quad \text{for hydrogen atom} \quad \square$$

2.7) Consider a two-e^- system with a doubly occupied KS orbital (e.g. He). Show that the exact exchange energy (2.51) is minus 1/2 of E_H.

$$E_x^{exact} = -\frac{1}{2} \sum_\sigma \sum_{i,j=1}^{N_\sigma} \int d^3r \int d^3r' \frac{\varphi_{i\sigma}^*(\vec{r}')\varphi_{j\sigma}(\vec{r}')\varphi_{i\sigma}(\vec{r})\varphi_{j\sigma}^*(\vec{r})}{|\vec{r}-\vec{r}'|}$$

$$E_H[n] = \frac{1}{2} \int d^3r \int d^3r' \frac{n(\vec{r})n(\vec{r}')}{|\vec{r}-\vec{r}'|}$$

KS eqn: $\varepsilon_j \varphi_j(\vec{r}) = \left(\frac{-\nabla^2}{2} + v_s[n](\vec{r})\right)\varphi_j(\vec{r})$ $\quad v_s[n](\vec{r}) = v_{ext}(\vec{r}) + v_H(\vec{r}) + v_{xc}[n](\vec{r})$

$n_0(\vec{r}) = \sum_{j=1}^{N} |\varphi_j(\vec{r})|^2$ $\quad v_{xc}[n](\vec{r}) = \frac{\delta E_{xc}[n]}{\delta n(\vec{r})}$

2.7) ⇒ show $E_x^{exact}[n] = -\frac{1}{2} E_H[n]$ for 2 electrons

$$E_x^{exact} = -2\left(\frac{1}{2}\sum_{i,j=1}^{N_\sigma}\right)\int d^3r \int d^3r' \frac{\varphi_{i\sigma}^*(\vec{r}')\,\varphi_{j\sigma}(\vec{r}')\,\varphi_{i\sigma}(\vec{r})\,\varphi_{j\sigma}^*(\vec{r})}{|\vec{r}-\vec{r}'|}$$

$$\Rightarrow E_H[n_{j\sigma}] + E_x^{exact}[n_{i\sigma}, n_{j\sigma}] = 0 \qquad E$$

$$2E_x^{exact}[n_{i\sigma}, 0] = -E_H[n_{j\sigma}]$$

$$E_x^{exact}[n_{i\sigma}, 0] = -\frac{1}{2}E_H[n_{j\sigma}] \quad \square$$

2.11) Check the Oliver-Perdew spin-scaling relation (2.93) for the LSDA.

⇒ Show $E_x[n_\uparrow, n_\downarrow] = \frac{1}{2}E_x[2n_\uparrow] + \frac{1}{2}E_x[2n_\downarrow]$

$$E_x[n_\uparrow, n_\downarrow] = E_x[n_\uparrow, 0] + E_x[0, n_\downarrow]$$

$$E_x^{unpol}[n] = E_x[\tfrac{1}{2}n, 0] + E_x[0, \tfrac{1}{2}n] = 2E_x[\tfrac{1}{2}n, 0]$$

This follows:

$$E_x[n_\uparrow, n_\downarrow] = \frac{1}{2}E_x[2n_\uparrow, 0] + \frac{1}{2}E_x[0, 2n_\downarrow] \quad \square$$