Problem Set 3 "Foundations of DFT"

Problem 5 Unif. scaling in 1D

$$\Psi_\gamma(x_1, \dots x_N) = \gamma^{N/2}\, \Psi(\gamma x_1, \dots \gamma x_N)$$

a) $\int dx_1 \dots \int dx_N\, |\Psi_\gamma(x_1, \dots x_N)|^2 =$

$= \int d(\gamma x_1) \dots \int d(\gamma x_N)\; |\Psi(\gamma x_1, \dots, \gamma x_N)|^2 = 1$

if $\int dx_1 \dots \int dx_N\, |\Psi(x_1, x_2, \dots x_N)|^2 = 1$

~~b) $T_s[n_\gamma]$~~

$$n_\gamma(x) = N \gamma^{N} \int dx_2 \dots \int dx_N\, |\Psi(\gamma x, \gamma x_2, \dots \gamma x_N)|^2$$

$$= \gamma\; N \int d\tilde{x}_2 \dots \int d\tilde{x}_N\, |\Psi(\gamma x, \tilde{x}_2, \dots \tilde{x}_N)|^2$$

where

$\tilde{x}_i = \gamma x_i$

$$= \gamma\, n(\gamma x)$$

with $n(x) = N \int dx_2 \dots \int dx_N\, |\Psi(x, x_2 \dots, x_N)|^2$

b) $T_s[n_\gamma] = \int dx_1 \dots \int dx_N\; \Psi^*_\gamma(x_1 \dots x_N) \left(-\frac{\partial^2_{x_1}}{2} - \dots - \frac{\partial^2_{x_N}}{2}\right) \Psi_\gamma(x_1 \dots x_N)$

$$= \gamma^N \int dx_1 \dots \int dx_N\, \Psi^*(\gamma x_1 \dots \gamma x_N)\, \gamma^2 \left(-\frac{1}{2}\frac{d^2}{d(\gamma x_1)^2} - \frac{1}{2}\frac{d^2}{d(\gamma x_2)^2} - \dots - \frac{1}{2}\frac{d^2}{d(\gamma x_N)^2}\right) \Psi(\gamma x_1, \dots \gamma x_N)$$

$\tilde{x}_i = \gamma x_i$

$$= \gamma^2 \int d\tilde{x}_1 \dots \int d\tilde{x}_N\; \Psi(\tilde{x}_1 \dots \tilde{x}_N) \left(-\frac{1}{2}\sum_{i=1}^{N} \frac{d^2}{d\tilde{x}_i^2}\right) \Psi(\tilde{x}_1, \dots \tilde{x}_N)$$

$$= \gamma^2\, T_s[n]$$

Nano-bio Spectroscopy Group and ETSF Centre for Scientific Development
Universidad del País Vasco UPV/EHU and Centro de Física de Materiales CFM CSIC - UPV/EHU - MPC
Edificio Joxe Mari Korta. Avenida de Tolosa 72, 20018 San Sebastián. Spain
Tel.: +34943018534 Fax: +34943018390 E-mail: manager-nano-bio@ehu.es Web: http://nano-bio.ehu.es
ETSF
eman ta zabal zazu
Universidad del País Vasco Euskal Herriko Unibertsitatea
CSIC

c) uniform, non-int. el. gas in 1D

↳ Orbitals $\varphi_k(x) = \frac{1}{\sqrt{L}} e^{ikx}$ L: length of system

$$n(x) = \sum_{k \le k_F} |\varphi_k(x)|^2 = \frac{1}{L} \sum_{k \le k_F} 1 = \int_0^{k_F} \frac{dk}{2\pi} = \frac{k_F}{2\pi}$$

non-int. kinetic energy per unit length

$$t_s(n) = \frac{T_s[n]}{L} = \frac{1}{L} \int dx \sum_{k \le k_F} \varphi_k^*(x) \left(-\frac{1}{2}\frac{d^2}{dx^2}\right) \varphi_k(x)$$

$$= \frac{1}{L} \sum_{k \le k_F} \underbrace{\int dx \frac{1}{L} e^{-ikx} \left(\frac{k^2}{2}\right) e^{ikx}}_{\frac{k^2}{2}}$$

$$= \int_0^{k_F} \frac{dk}{2\pi} \frac{k^2}{2} = \frac{1}{2\pi} \frac{k_F^3}{6}$$

with $k_F = 2\pi n$ $\leadsto t_s(n) = \frac{1}{2\pi} \frac{(2\pi)^3}{6} n^3$

$$= \frac{2\pi^2}{3} n^3$$

$$\leadsto T_s^{LDA}[n] = \int dx \, t_s(n)\Big|_{n = n(x)} = \frac{2\pi^2}{3} \int dx \, (n(x))^3$$

d) define a reduced density gradient

$$s(x) = \frac{\frac{\partial}{\partial x} n(x)}{n^2(x)} \quad \leadsto s_\gamma(x) = \frac{\frac{\partial}{\partial x} n_\gamma(x)}{n_\gamma^2(x)} = s(\gamma x)$$

$$T_s^{GEA}[n] = \frac{2\pi^2}{3} \int dx (n(x))^3 \left(1 + \alpha_s s^2(x)\right)$$

with constant coefficient α_s has correct scaling behavior

Nano-bio Spectroscopy Group and ETSF Centre for Scientific Development
Universidad del País Vasco UPV/EHU and Centro de Física de Materiales CFM CSIC - UPV/EHU - MPC
Edificio Joxe Mari Korta. Avenida de Tolosa 72, 20018 San Sebastián. Spain
Tel.: +34943018534 Fax: +34943018390 E-mail: manager-nano-bio@ehu.es Web: http://nano-bio.ehu.es

Problem 6 Hellmann-Feynman theorem

$$\hat{H}(\lambda)\,|\Psi^\lambda\rangle = E(\lambda)\,|\Psi^\lambda\rangle \qquad \langle\Psi^\lambda|\Psi^\lambda\rangle = 1$$

$$E(\lambda) = \langle\Psi^\lambda|\,\hat{H}(\lambda)\,|\Psi^\lambda\rangle$$

$$\frac{dE}{d\lambda} = \langle\frac{\partial\Psi^\lambda}{\partial\lambda}|\,\hat{H}(\lambda)\,|\Psi^\lambda\rangle + \langle\Psi^\lambda|\,\hat{H}(\lambda)\,|\frac{\partial\Psi^\lambda}{\partial\lambda}\rangle$$

$$+ \langle\Psi^\lambda|\frac{\partial\hat{H}(\lambda)}{\partial\lambda}|\Psi^\lambda\rangle$$

$$= E(\lambda)\underbrace{\left[\langle\frac{d\Psi^\lambda}{d\lambda}|\Psi^\lambda\rangle + \langle\Psi^\lambda|\frac{d\Psi^\lambda}{d\lambda}\rangle\right]}_{=\frac{d}{d\lambda}\left[\langle\Psi^\lambda|\Psi^\lambda\rangle\right] = 0}$$

$$+ \langle\Psi^\lambda|\,\frac{\partial\hat{H}(\lambda)}{\partial\lambda}\,|\Psi^\lambda\rangle$$

#

Nano-bio Spectroscopy Group and ETSF Centre for Scientific Development
Universidad del País Vasco UPV/EHU and Centro de Física de Materiales CFM CSIC - UPV/EHU - MPC
Edificio Joxe Mari Korta. Avenida de Tolosa 72, 20018 San Sebastián. Spain
Tel.: +34943018534 Fax: +34943018390 E-mail: manager-nano-bio@ehu.es Web: http://nano-bio.ehu.es