DONOSTIA INTERNATIONAL PHYSICS CENTER

# Recent Advances and future developments in NOFT

## SEMINARIO

Donostia / San Sebastian

16 de enero de 2008

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- Introducción a la teoría del funcional de orbitales naturales.


- M. Piris, "Natural Orbital Functional Theory" in *Reduced-Density-Matrix Mechanics: With Applications to Many-electron Atoms and Molecules*, edited by D. A. Mazziotti, Advances in Chemical Physics, Volume 134, Chapter 14, Wiley, New York, April 2007.

- M. Piris, X. Lopez, J. M. Ugalde, "Dispersion interactions within the PNOF theory: the helium dimer", Journal of Chemical Physics 126, 214103, 2007.

- M. Piris, X. Lopez, J. M. Ugalde, "Natural orbital functional description of van der Waals interactions: A case study of the effect of the basis set for the helium dimer", Int. J. Quantum Chem. 108, 2008 (early view).

# Índice

- Introducción a la teoría del funcional de orbitales naturales.
- Obtención de los orbitales naturales.
- Curvas de energía potencial para el dímero de Helio.
- Huecos de correlación en el dímero de Helio.

# El funcional de la Energía

- La energía electrónica $E_0$ de un sistema de $N$ electrones es un funcional exacto y explícito de las MDRs de 1er y 2do órdenes ($\Gamma$ y $D$):

$$E_0[N,\Gamma,D] = \sum_{ij} h_{ij}\ \Gamma_{ji} + \sum_{ijkl} \langle ij|kl\rangle D_{kl,ij}$$

Remplazamos el último término por un funcional de $\Gamma$:

$$E_0[N,\Gamma,D] \quad \Longrightarrow \quad E_0[N,\Gamma] = h[N,\Gamma] + \mathrm{V}_{ee}[N,\Gamma]$$

$$\mathrm{V}_{ee}[N,\Gamma] = \min_{D\in D(\Gamma)} U[N,D] \qquad \left( U[N,D] = \sum_{ijkl} \langle ij|kl\rangle D_{kl,ij} \right)$$

# El funcional de orbitales naturales

- La MDR-1 (Γ) se puede diagonalizar con una transformación unitaria:

$$\Gamma_{ji} = n_i \delta_{ji} \qquad \left( \Gamma\left(\mathbf{x}_1^{'}, \mathbf{x}_1\right) = \sum_{ij} \Gamma_{ji} \phi_i\left(\mathbf{x}_1^{'}\right) \phi_j^{*}\left(\mathbf{x}_1\right) \right)$$

Funciones propias $\left\{ \phi_i\left(\mathrm{x}\right) \right\}$: Los spin orbitales naturales

Valores propios $\left\{ n_i \right\}$: Los números de ocupación

- En adelante nos referimos a la base de orbitales naturales:

$$E_0\left[N,\Gamma\right] \Longrightarrow E_0\left[N,\left\{n_i\right\},\left\{\phi_i\left(\mathbf{x}\right)\right\}\right]$$

# MDR-2

$$D_{kl,ij} = \tfrac{1}{2}\left(\Gamma_{ki}\cdot\Gamma_{lj} - \Gamma_{kj}\cdot\Gamma_{li}\right) + \lambda_{kl,ij}$$

$$D^{\alpha\alpha}_{rt,pq} = \frac{n_q n_p}{2}\left(\delta_{rp}\delta_{tq} - \delta_{rq}\delta_{tp}\right) + \lambda^{\alpha\alpha}_{rt,pq}\ ,\qquad \lambda^{\alpha\alpha}_{rt,pq} = -\frac{\Delta_{qp}}{2}\delta_{rp}\delta_{tq} + \frac{\Delta_{qp}}{2}\delta_{rq}\delta_{tp}$$

$$D^{\alpha\beta}_{rt,pq} = \frac{1}{2}n_q n_p \delta_{rp}\delta_{tq} + \lambda^{\alpha\beta}_{rt,pq}\qquad \lambda^{\alpha\beta}_{rt,pq} = -\frac{\Delta_{qp}}{2}\delta_{rp}\delta_{tq} + \frac{\Pi_{tp}}{2}\delta_{rt}\delta_{pq}$$

$$\Pi_{tp} = n_t n_p - \Delta_{tp} - \Lambda_{tp}$$

PNOF:

$$\boldsymbol{E}_0 = 2\sum_{p}\boldsymbol{n}_p\boldsymbol{h}_{pp} + 2\sum_{pq}\left(\boldsymbol{n}_q\boldsymbol{n}_p - \Delta_{qp}\right)\boldsymbol{J}_{pq} - \sum_{pq}\Lambda_{qp}\boldsymbol{K}_{pq}$$

# PNOF - 2

$$\Delta_{qp} = h_q h_p \theta(n_q - 0.5)\theta(n_p - 0.5) + n_q n_p \theta(0.5 - n_q)\theta(0.5 - n_p)$$
$$+ f_q f_p [\theta(n_q - 0.5)\theta(0.5 - n_p) + \theta(0.5 - n_q)\theta(n_p - 0.5)]$$

$$f_p = \frac{(1-S)}{\sum_{q=F+1}^{\infty} f_q} h_p \quad \text{if } p \leqslant F \qquad \sum_{p=1}^{F} f_p \sum_{q=F+1}^{\infty} f_q = S(1-S)$$

$$f_p = \frac{(1-S)}{\sum_{q=F+1}^{\infty} f_q} h_p \quad \text{if } p \leqslant F$$

$$S = \sum_{q=1}^{F} h_q = \sum_{q=F+1}^{\infty} n_q$$

$$\Lambda_{qp} = \theta(n_q - 0.5)\theta(n_p - 0.5)(\sqrt{n_q n_p} + \sqrt{h_q h_p})$$
$$+ \theta(n_q - 0.5)\theta(0.5 - n_p)(\sqrt{n_q n_p} - \sqrt{h_q n_p})$$
$$+ \theta(0.5 - n_q)\theta(n_p - 0.5)(\sqrt{n_q n_p} - \sqrt{n_q h_p})$$

# PNOF - 2

$$E_0 = 2\sum_{p=1}^{\infty} n_p h_{pp} - \sum_{p,q=1}^{\infty} \Lambda_{qp} K_{pq} + 2\sum_{p,q=1}^{\infty}{}' n_q n_p J_{pq}$$

$$-2\sum_{p,q=1}^{F}{}' h_q h_p J_{pq} - 2\sum_{p,q=F+1}^{\infty}{}' n_q n_p J_{pq}$$

$$-2\frac{1-S}{S}\left( \sum_{q=1}^{F} \sum_{p=F+1}^{\infty} h_q n_p J_{pq} + \sum_{q=F+1}^{\infty} \sum_{p=1}^{F} n_q h_p J_{pq} \right)$$

$$\mathrm{Tr}(\Gamma) = 2\sum_{q=1}^{\infty} n_q = N \quad \Longrightarrow \quad S = \sum_{q=1}^{F} h_p = \sum_{q=F+1}^{\infty} n_q$$

# Obtención de los orbitales naturales

$$\Omega\left[N,\{\gamma_i\},\{\phi_i(\mathbf{x})\}\right] = E - \mu\left(\sum_i \cos^2\gamma_i - N\right) - \sum_{ik}\lambda_k^i\left(\langle\phi_k|\phi_i\rangle - \delta_i^k\right)$$

$$\delta\Omega = \sum_i \sin(2\gamma_i)\left[\mu - \frac{\partial E}{\partial n_i}\right]d\gamma_i + \sum_i \int d\mathbf{x}\,\delta\phi_i^*(\mathbf{x})\left[\frac{\delta E}{\delta\phi_i^*(\mathbf{x})} - \sum_k \lambda_i^k\phi_k(\mathbf{x})\right]$$
$$+\sum_i \int d\mathbf{x}\left[\frac{\delta E}{\delta\phi_i(\mathbf{x})} - \sum_k \lambda_k^i\phi_k^*(\mathbf{x})\right]\delta\phi_i(\mathbf{x}) = 0$$

Ecuaciones de Euler: $\dfrac{\partial E}{\partial n_i} = h_i^i + \dfrac{\partial V_{ee}}{\partial n_i} = \mu \quad , \quad n_i = \cos^2\gamma_i$

$$n_i\widehat{V}(\mathbf{x})\,\phi_i(\mathbf{x}) = \sum_k \lambda_i^k\phi_k(\mathbf{x}) \quad , \quad \widehat{V}(\mathbf{x}) = \widehat{h}(\mathbf{x}) + \frac{1}{n_i\phi_i(\mathbf{x})}\frac{\delta V_{ee}}{\delta\phi_i^*(\mathbf{x})}$$

# El operador *V* para el PNOF

$$n_p \widehat{V}^p(\mathbf{r}_1)\varphi_p(\mathbf{r}_1) = \sum_r \lambda_p^r \varphi_r(\mathbf{r}_1)$$

$$\widehat{V}^p(\mathbf{r}_1) = \widehat{h}(\mathbf{r}_1) + \widehat{v}^p(\mathbf{r}_1)$$

$$\widehat{v}^p(\mathbf{r}_1) = \sum_q{}' \left(n_q - \frac{\Delta_q^p}{n_p}\right)\left[2\widehat{J}_q(\mathbf{r}_1) - \widehat{K}_q(\mathbf{r}_1) + \widehat{L}_q(\mathbf{r}_1)\right] - \sum_q \frac{\Lambda_q^p}{n_p}\widehat{L}_q(\mathbf{r}_1)$$

$$\widehat{J}_q(\mathbf{r}_1) = \int d\mathbf{r}_2 \varphi_q^*(\mathbf{r}_2) r_{12}^{-1} \varphi_q(\mathbf{r}_2)$$

$$\widehat{K}_q(\mathbf{r}_1) = \int d\mathbf{r}_2 \varphi_q^*(\mathbf{r}_2) r_{12}^{-1} \widehat{P}_{12} \varphi_q(\mathbf{r}_2)$$

$$\widehat{L}_q(\mathbf{r}_1) = \int d\mathbf{r}_2 \varphi_q(\mathbf{r}_2) r_{12}^{-1} \widehat{I}(2) \widehat{P}_{12} \varphi_q(\mathbf{r}_2)$$

# El potencial no-local

Gilbert: $\frac{\delta V_{ee}}{\delta \phi_i^* (\mathbf{x})} = n_i \phi_i (\mathbf{x}) \widehat{\upsilon}_{ee} (\mathbf{x}) \longrightarrow [\lambda, {}^1\mathbf{D}] = 0$

$$\left[\widehat{h} (\mathbf{x}) + \widehat{\upsilon}_{ee} (\mathbf{x})\right] \phi_i (\mathbf{x}) = \lambda_i n_i^{-1} \phi_i (\mathbf{x}) = \varepsilon_i \phi_i (\mathbf{x}) \ , \quad \varepsilon_i = \frac{\lambda_i}{n_i} = \mu$$

Pernal: $\lambda_i^k - \left(\lambda_k^i\right)^* = 0$

$$\lambda_i^k = V_i^k n_i = h_i^k n_i + \left(g_k^i\right)^*$$

$$(n_i - n_k) h_i^k + \left(g_k^i\right)^* - g_i^k = 0$$

$$(n_i - n_k) (\upsilon_{ee})_i^k = \left(g_k^i\right)^* - g_i^k$$

$$g_i^k = \int d\mathbf{x} \frac{\delta V_{ee}}{\delta \phi_k (\mathbf{x})} \phi_i (\mathbf{x})$$

$\longrightarrow$

$$\left[\mathbf{F}, {}^1\mathbf{D}\right] = \left[\mathbf{h} + \upsilon_{ee}, {}^1\mathbf{D}\right] = 0$$

$$\left[\widehat{h} (\mathbf{x}) + \widehat{\upsilon}_{ee} (\mathbf{x})\right] \phi_i (\mathbf{x}) = \varepsilon_i \phi_i (\mathbf{x})$$

¿ $(\upsilon_{ee})_i^i = \frac{\partial V_{ee}}{\partial n_i} \ , \quad \varepsilon_i = \mu$ ?

# Matriz de Fock generalizada para el PNOF

$$F_p^r = h_p^r + (\upsilon_{ee})_p^r$$

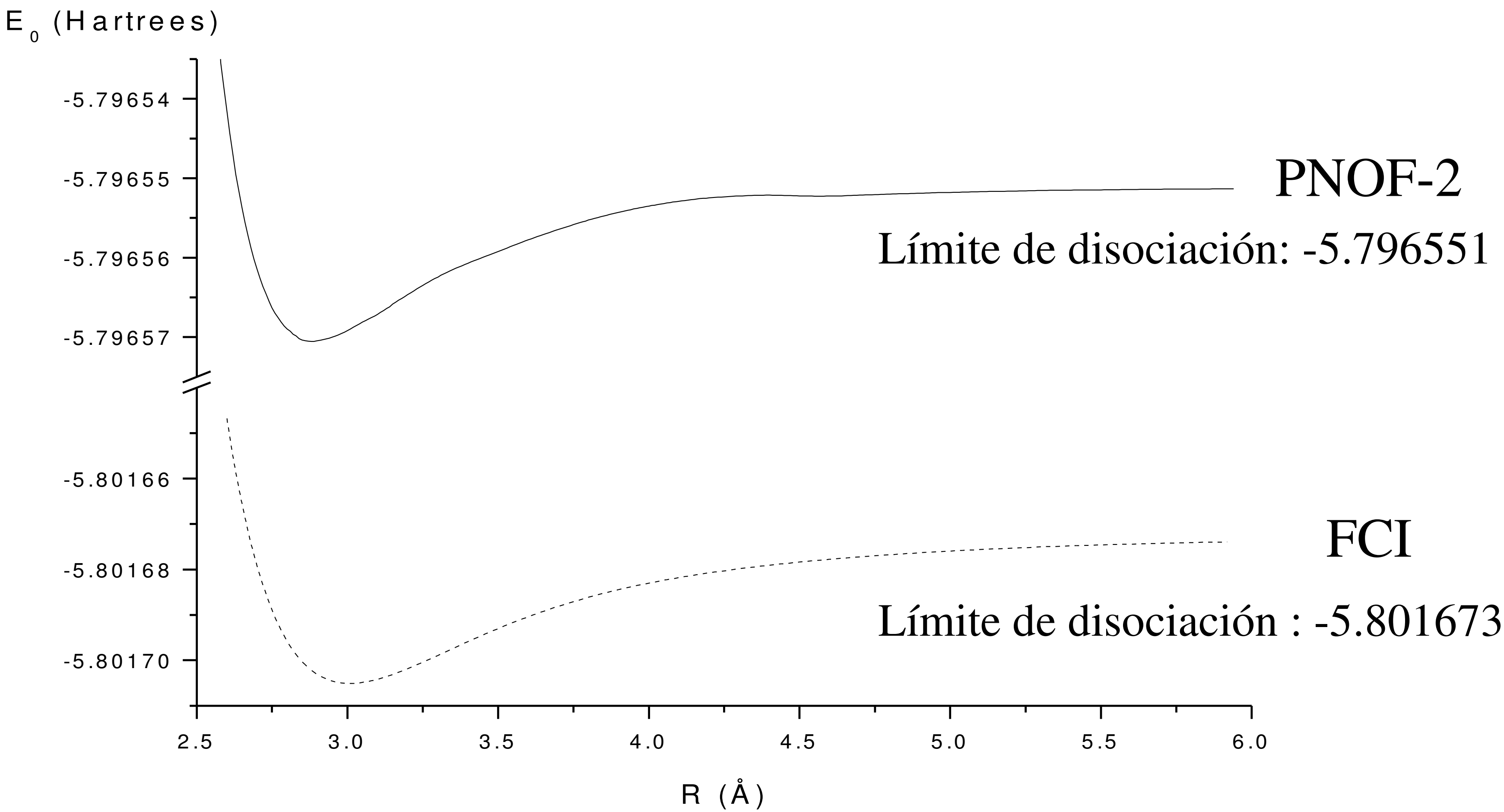
$$(\upsilon_{ee})_p^r = \frac{\partial V_{ee}}{\partial n_p}\delta_p^r + \frac{1-\delta_p^r}{n_p - n_r}\int d\mathbf{r}\varphi_r^*(\mathbf{r})\left[n_p\widehat{\upsilon}^p(\mathbf{r}) - n_r\widehat{\upsilon}^r(\mathbf{r})\right]\varphi_p(\mathbf{r})$$

$$L_q^p = K_{pq} \longrightarrow \frac{\partial V_{ee}}{\partial n_p} = J_{pp} + 2\sum_q{}'\left(n_q - \frac{\partial \Delta_q^p}{\partial n_p}\right)J_{pq} - \sum_q{}'\frac{\partial \Lambda_q^p}{\partial n_p}K_{pq}$$

$$\widehat{\upsilon}^p(\mathbf{r}) = \widehat{J}_p(\mathbf{r}) + 2\sum_q{}'\left(n_q - \frac{\Delta_q^p}{n_p}\right)\widehat{J}_q(\mathbf{r}) - \sum_q{}'\Lambda_q^p\widehat{K}_q(\mathbf{r})$$

# Curvas de Energía Potencial

Base: aug-cc-pVTZ



# aug-cc-pVxZ (x = D - 5)

- Distancias de Equilibrio en Å ( $R_e$ = 2.98 Å )

| Base | PNOF-2 | CCSD(T) |
|---|---|---|
| aug-cc-pVDZ | 2.86 (0.12) | 3.00 (0.02) |
| aug-cc-pVTZ | 2.96 (0.02) | 3.02 (0.04) |
| aug-cc-pVQZ | 2.99 (0.01) | 2.99 (0.01) |
| aug-cc-pV5Z | 2.99 (0.01) | 2.99 (0.01) |

# aug-cc-pVxZ (x = D - 5)

- Energías de disociación en kcal/mol ( $D_e$ = 0.021 kcal/mol )

| Base | PNOF | CCSD(T) |
|---|---|---|
| aug-cc-pVDZ | 0.0277 (0.0067) | 0.0265 (0.0055) |
| aug-cc-pVTZ | 0.0133 (0.0077) | 0.0196 (0.0014) |
| aug-cc-pVQZ | 0.0120 (0.0090) | 0.0202 (0.0008) |
| aug-cc-pV5Z | 0.0119 (0.0091) | 0.0204 (0.0006) |

# La densidad Intracular

$$I(\mathbf{u}) = \sum_{i<j} \langle \Psi | \delta(\mathbf{u} - \mathbf{r}_i + \mathbf{r}_j) | \Psi \rangle = \int d(\mathbf{r}_1, \mathbf{r}_2) \delta(\mathbf{u} - \mathbf{r}_1 + \mathbf{r}_2) \, d\mathbf{r}_1 d\mathbf{r}_2$$

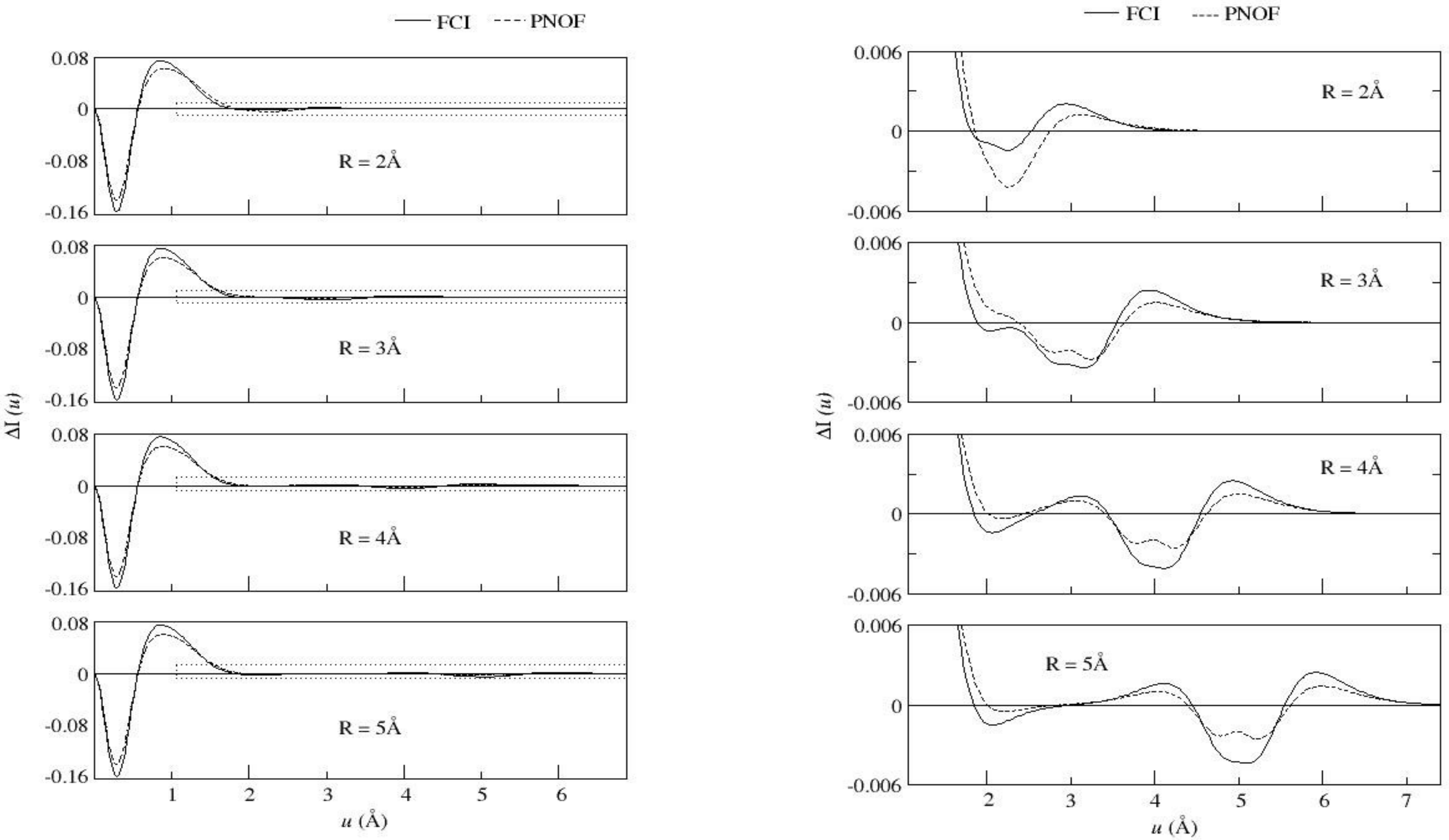
$d(\mathbf{r}_1, \mathbf{r}_2)$: Densidad de pares electrónicos, $\delta$ : La función delta de Dirac

Densidad esférica promedio: $h(u) = \frac{1}{4\pi} \int d\Omega_u I(\mathbf{u})$

Distribución de probabilidad radial de pares: $4\pi u^2 h(u)$

Hueco Coulomb: $\Delta I_{Coul}(u) = 4\pi u^2 [h_{exact}(u) - h_{HF}(u)]$ (Löwdin)

# Hueco de Coulomb (Löwdin)



# La distribución de probabilidad radial de pares

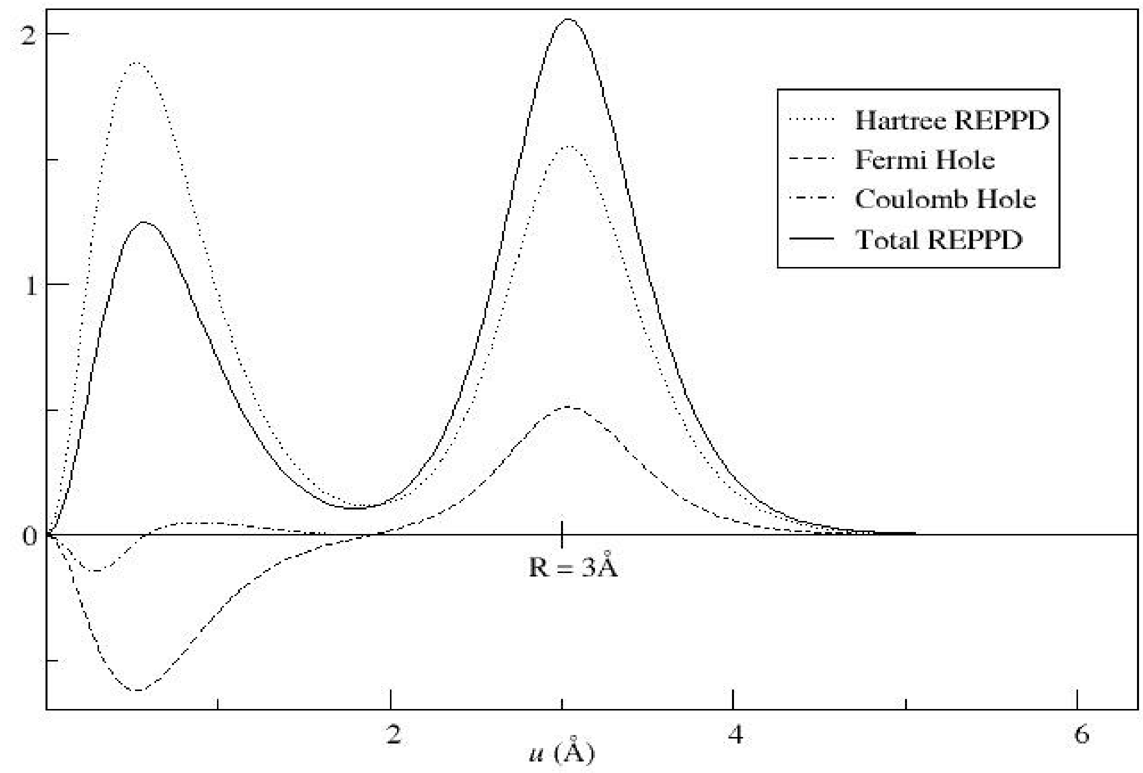
Desarrollo orbital $\Longrightarrow$ $I(\mathbf{u}) = \sum_{pqrt} \sum_{\sigma\sigma'} D^{\sigma\sigma'}_{rt,pq} \left\langle pq \middle| \delta(\mathbf{u}) \middle| rt \right\rangle$

$$4\pi u^2 h(u) = u^2 \int d\Omega_u I(\mathbf{u}) = u^2 \int d\Omega_u \sum_{pqrt} \sum_{\sigma\sigma'} D^{\sigma\sigma'}_{rt,pq} \left\langle pq \middle| \delta(\mathbf{u}) \middle| rt \right\rangle$$

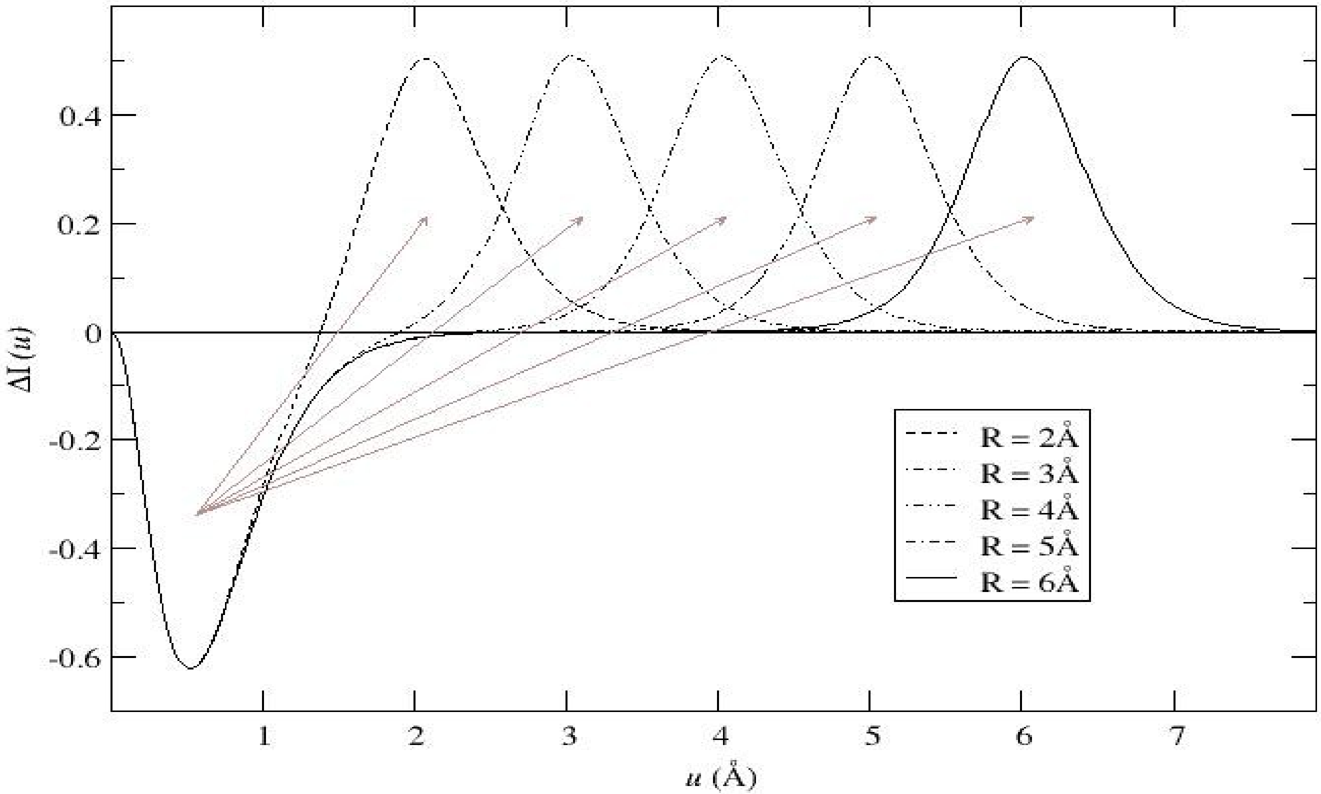
$$D^{\sigma\sigma}_{rt,pq} = \frac{n_q n_p}{2} \delta_{rp} \delta_{tq} - \frac{n_q n_p}{2} \delta_{rq} \delta_{tp} + \lambda^{\sigma\sigma}_{rt,pq} \qquad (\sigma\sigma = \alpha\alpha, \beta\beta)$$

$$D^{\sigma\sigma'}_{rt,pq} = \frac{n_q n_p}{2} \delta_{rp} \delta_{tq} + \lambda^{\sigma\sigma'}_{rt,pq} \qquad (\sigma\sigma' = \alpha\beta, \beta\alpha)$$

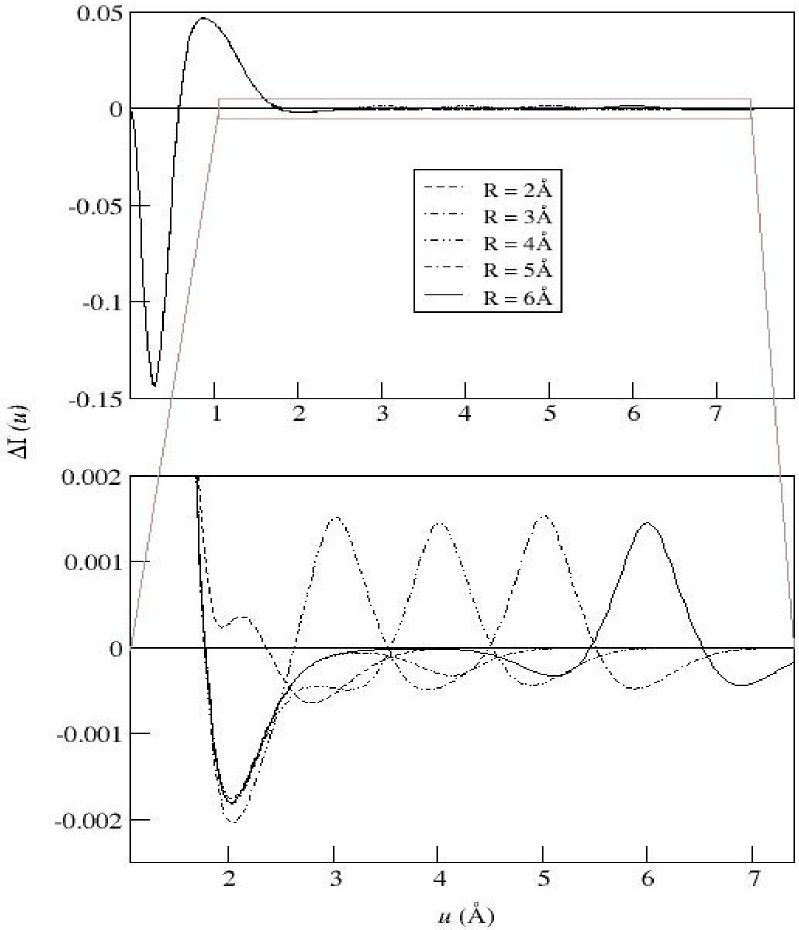
# Descomposición de la distribución de probabilidad radial de pares $4\pi u^2 h(u)$

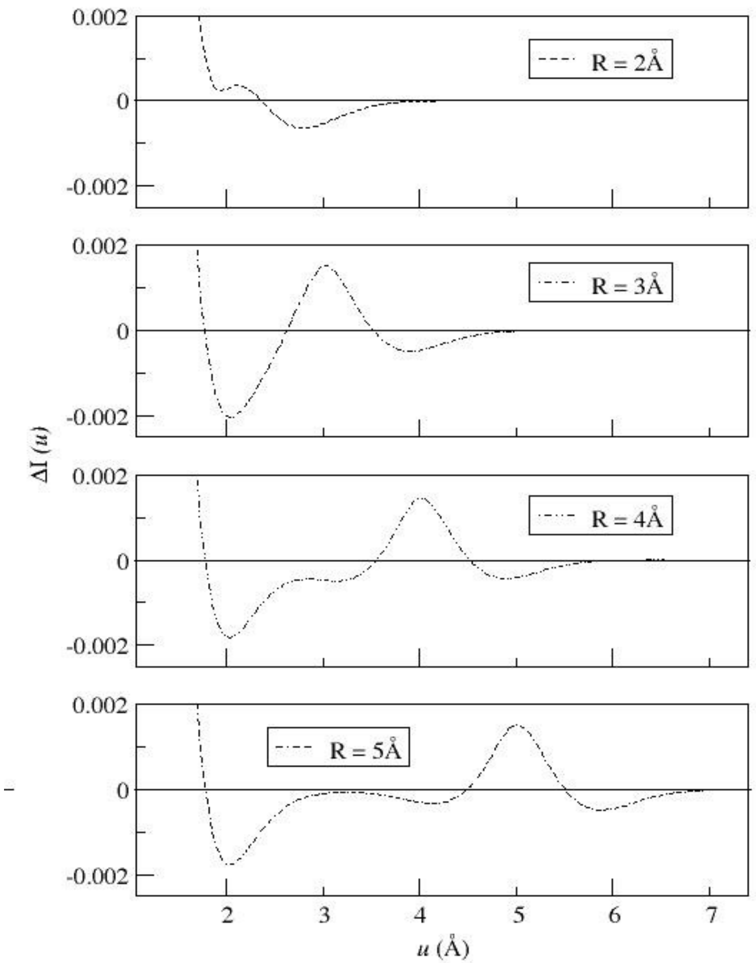


# Hueco de Fermi



# Hueco de Coulomb



# Hueco de Correlación