

# Simplified method for calculating the energy of weekly interacting fragments & applications

Discussion on papers by J. Harris & Antonio S. Torralba et al.

CSCI-699, April 16, 2018  
Ben Wang

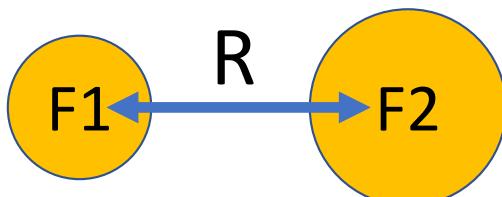
# Energy of weakly interacting fragments

J. Harris, Phys. Rev. B 31, 1770(1985)

- **Problem:** Kohn–Sham (K-S) scheme can be difficult: Poisson's equation, total energy.
- **Purpose:** design a new approximate scheme for calculating the interaction energy of two fragments
- **Idea:** expand the K-S energy expression about the density, and neglect quadratic terms.
- K-S energy expression:

$$E[n(x)] = T_0 + \int dx n(x) \left[ \frac{1}{2} \phi(x) + V_{ext}(x) \right] + E_{xc} + E_N$$

- Consider two fragments:



- K-S energy of F1 and total:

$$\bullet E_1 = \sum_n^1 a_n^1 \varepsilon_n^1 - \int dx n_1(x) \left[ \frac{1}{2} \varphi_1(x) + \mu_{xc}^{n_1}(x) \right] + E_{xc}[n_1] + E_N^1$$

$$\bullet E_R = \sum_n a_n \varepsilon_n - \int dx n(x) \left[ \frac{1}{2} \varphi(x) + \mu_{xc}^n(x) \right] + E_{xc}[n] + E_N^R$$

- Write:

$$n(\mathbf{x}) = n_f(\mathbf{x}) + \delta n(\mathbf{x}) \quad n_f(\mathbf{x}) = n_1(\mathbf{x}) + n_2(\mathbf{x})$$

- Construct a potential:

$$\tilde{V}(\mathbf{x}) = \phi_f(\mathbf{x}) + \mu_{xc}^{n_f}(\mathbf{x}) + V_{\text{ext}}(\mathbf{x})$$

- Calculate the difference between true SCF potential and :  $\tilde{V}(\mathbf{x})$

$$\Delta V(\mathbf{x}) = \phi(\mathbf{x}) - \phi_f(\mathbf{x}) + \mu_{xc}^n(\mathbf{x}) - \mu_{xc}^{n_f}(\mathbf{x})$$

- Assume  $\Delta V(x)$  is small:

$$\sum_n a_n \epsilon_n = \sum_n a_n \tilde{\epsilon}_n + \int d\mathbf{x} n(\mathbf{x}) \Delta V(\mathbf{x}) + O(\Delta V^2)$$

- Expand  $E_{xc}$  :

$$E_{xc}[n] = E_{xc}[n_f] + \int d\mathbf{x} \mu_{xc}^{n_f}(\mathbf{x}) \delta n(\mathbf{x}) + O(\delta n^2)$$

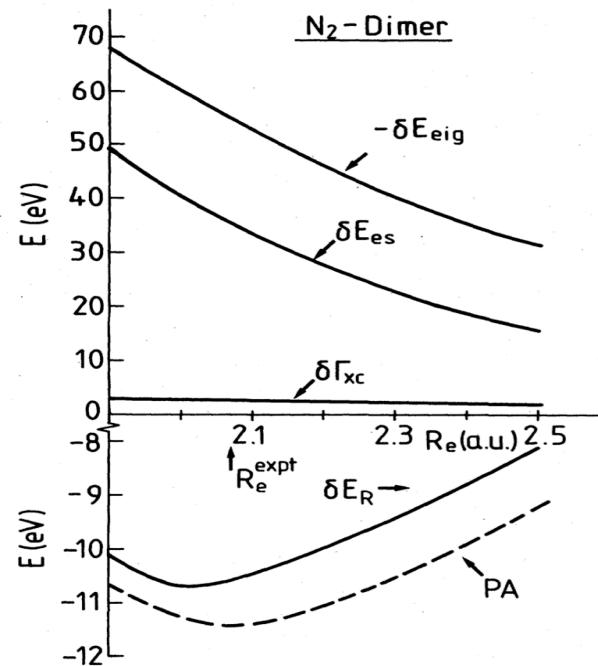
- Substituting in  $E_R$  to have the desired approximation:

$$\begin{aligned} E_R \simeq & \sum_n a_n \tilde{\epsilon}_n - \int d\mathbf{x} n_f(\mathbf{x}) [\frac{1}{2} \phi_f(\mathbf{x}) + \mu_{xc}^{n_f}(\mathbf{x})] \\ & + E_{xc}[n_f] + E_N^R \end{aligned}$$

- Final expression:

$$E_R \simeq \sum_n a_n \tilde{\epsilon}_n - \int d\mathbf{x} n_f(\mathbf{x}) [\frac{1}{2} \phi_f(\mathbf{x}) + \mu_{xc}^{n_f}(\mathbf{x})] + E_{xc}[n_f] + E_N^R$$

- Involves **only the frozen fragment densities**
- Use constructed potential for K-S scheme
- Accuracy? N<sub>2</sub>-dimer



- Results for some homonuclear dimers:  $E_b$ ,  $R_e$ ,  $\omega_e$

Dimer	$E_b$ (eV)			$R_e$ (a.u.)			$\omega_e$ (meV)		
	(2.21)	PA	Expt.	(2.21)	PA	Expt.	(2.21)	PA	Expt.
$\text{Be}_2$	0.49	0.50	$\sim 0.1$	4.50	4.63	4.66	45	45	28
$\text{C}_2$ $(^1\Sigma_g^+)$	8.7	7.19	6.2	2.20	2.36	2.35	246	232	230
$\text{N}_2$	10.7	11.34	9.91	2.03	2.08	2.07	346	296	292
$\text{F}_2$	3.7	3.32	1.65	2.71	2.62	2.68	120	133	111
$\text{Cu}_2$	2.9	2.65	2.03	4.10	4.10	4.20	35	41	33

- Best case:  $\text{Be}_2$

# NSC DFT Exchange-correlation forces for GGA

J. Chem. Theory Comput. **2009**, 5, 1499-1505

- **Problem:** save computer efforts with lower precision calculations
- **Purpose:** develop generalized gradient approximation (GGA) NSC forces and implement with linear scaling DFT.
- **Idea:** Local orbital basis functions based on Harris-Foulkes expression

- **GGA:**  $E_{xc} = E_{xc}[n(r), \nabla n(r)] = \int dr f_{xc}(n(r), \nabla n(r))$

- **Linear-Scaling DFT:**

- electronic structure is local
- solve for density matrix:

$$\rho(\mathbf{r}, \mathbf{r}') = \sum_{i\alpha j\beta} \phi_{i\alpha}(\mathbf{r}) K_{i\alpha j\beta} \phi_{j\beta}(\mathbf{r}')$$

- **Support function:**

- $\phi_{i\alpha}(r)$  is local orbital basis

- The total energy:  $E_{\text{Tot}} = E_{\text{kin}} + E_{\text{ps}} + E_{\text{Har}} + E_{\text{XC}} + E_{\text{c}}$
- Charge density & K-S eigenstates:

$$n(r) = 2 \sum_n f_n |\psi_n(r)|^2, \psi_n(r) = \sum_{i\alpha} u_{i\alpha}^n \phi_{i\alpha}(r)$$

- Fixed charge density:  $n^{in}(r) = \sum_i \eta_i(|r - R_i|)$ ,
- $\delta n = n(r) - n^{in}(r)$
- NSC force:

$$\mathbf{F}_i^{\text{NSC}} = - \int d\mathbf{r} [\delta V_{\text{Har}}(\mathbf{r}) \nabla_i n^{in}(\mathbf{r}) + \delta n(\mathbf{r}) \nabla_i V_{\text{XC}}(\mathbf{r})]$$

- The exchange-correlation potential using GGA functional:

$$V_{\text{xc}}(\mathbf{r}) = \frac{\delta E_{\text{xc}}}{\delta n(\mathbf{r})} = \frac{\partial f_{\text{xc}}}{\partial n(\mathbf{r})} - \nabla \cdot \frac{\partial f_{\text{xc}}}{\partial \mathbf{g}(\mathbf{r})}$$

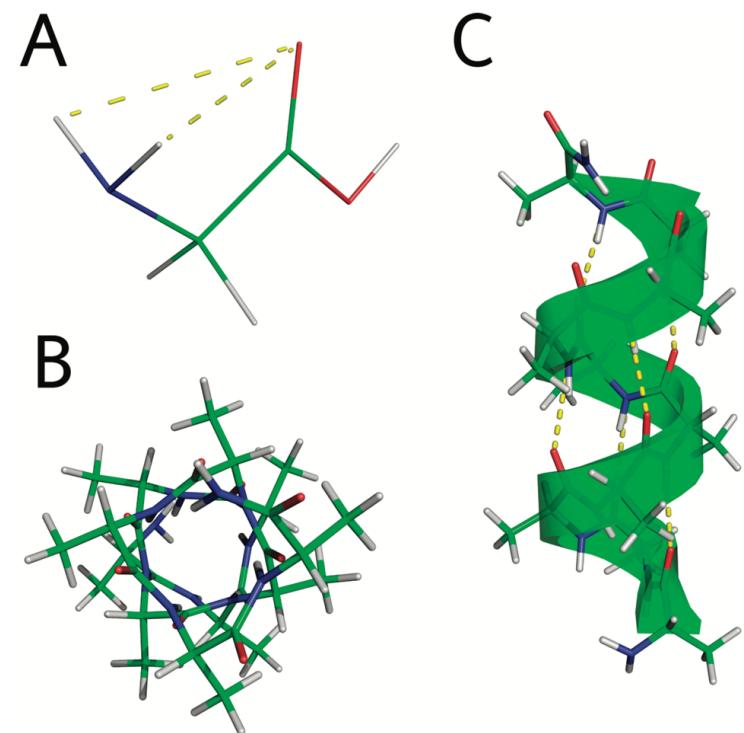
- Approximate GGA XC energy by:  $E_{\text{xc}}[\{n_l\}] = \omega \sum_l f_{\text{xc}}(n_l, \mathbf{g}_l)$
- **White-Bird (1994) approach:** the derivatives on the minimal grid are linear transformations on the same grid.

$$\mathbf{g}_l = \frac{1}{N} \sum_{m,l'} i\mathbf{G}_m n_{l'} e^{i\mathbf{G}_m \cdot (\mathbf{r}_l - \mathbf{r}_{l'})}$$

- **NSC force:**  $\mathbf{F}_i^{\text{NSC,xc}} = -\omega \sum_l \delta n_l \nabla_i V_{\text{xc},l}$
- **Implementation:** the kernel only depends on the magnitude of gradient

$$\frac{\partial^2 f_{\text{xc}}}{\partial n_l \partial \mathbf{g}_l} = \frac{\partial^2 f_{\text{xc}}}{\partial n_l \partial |\mathbf{g}_l|} \frac{\mathbf{g}_l}{|\mathbf{g}_l|}$$

- Test of NSC DFT on:
  - A: self-consistently relaxed structure of Glycine
  - B, C: Amide-terminated deca-alanine
- **Two methods:**
  - A: NSC first, then SCF
  - B: complete SCF
- Conjugate gradient algorithm for structural relaxations



- Comparasion of Relaxations with and without NSC pre-relaxation:

		method A		method B	
		step 1 (NSC)	step 2 (SCF)	total 1 + 2	only SCF
glycine <sup>b</sup>	CG steps	32	16	48	21
	functional evaluations	116	733	849	805
	total energy (Ha)	−56.625449	−56.475861		−56.475870
penta-alanine <sup>c</sup>	CG steps	105	23	128	53
	functional evaluations	373	1180	1553	2961
	total energy (Ha)	−242.121314	−241.541173		−241.541182
deca-alanine <sup>d</sup>	CG steps	73	28	101	75
	functional evaluations	299	1081	1380	3036
	total energy (Ha)	−474.779129	−473.372474		−473.372670

- **Conclusion:** the NSC pre-relaxation can save energy computations significantly.

# Appendix

- The final expression for the NSC exchange correlation force is:

$$\mathbf{F}_i^{\text{NSC,xc}} = - \sum_l L_l^{\text{tot}} \nabla_i n_l = - \sum_l L_l^{\text{tot}} \nabla_i \eta_i(|\mathbf{r}_l - \mathbf{R}_i|)$$

- With  $L_l^{\text{tot}} = L_l^{(1)} + L_l^{(2)} + L_l^{(3)} + L_l^{(4)}$

$$L_l^{(1)} = \omega \delta n_l \frac{\partial^2 f_{\text{xc},l}}{\partial n_l^2} \quad L_l^{(2)} = \omega \sum_{l'q} \delta n_{l'} \frac{\partial^2 f_{\text{xc},l}}{\partial g_{lq} \partial n_l} e_{l,l'}^q$$

$$L_l^{(3)} = -\omega \sum_{l'q} \delta n_{l'} \frac{\partial^2 f_{\text{xc},l'}}{\partial n_{l'} \partial g_{l'q}} e_{l,l'}^q$$

$$L_l^{(4)} = -\omega \sum_{l'r} M_{l'r} e_{l,l'}^r \quad M_{lr} = \sum_{l'q} \delta n_{l'} \frac{\partial^2 f_{\text{xc},l}}{\partial g_{lq} \partial g_{lr}} e_{l,l'}^q$$