

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

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

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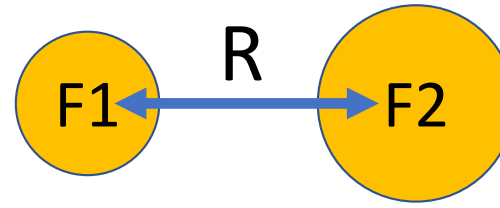
Energy of weakly interacting fragments

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:



- $E_1 = \sum_n^1 a_n^1 \varepsilon_n^1 - \int d\mathbf{x} n_1(\mathbf{x}) \left[\frac{1}{2} \varphi_1(\mathbf{x}) + \mu_{xc}^{n_1}(\mathbf{x}) \right] + E_{xc}[n_1] + E_N^1$
- $E_R = \sum_n a_n \varepsilon_n - \int d\mathbf{x} n(\mathbf{x}) \left[\frac{1}{2} \varphi(\mathbf{x}) + \mu_{xc}^n(\mathbf{x}) \right] + E_{xc}[n] + E_N^R$
- 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} :

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

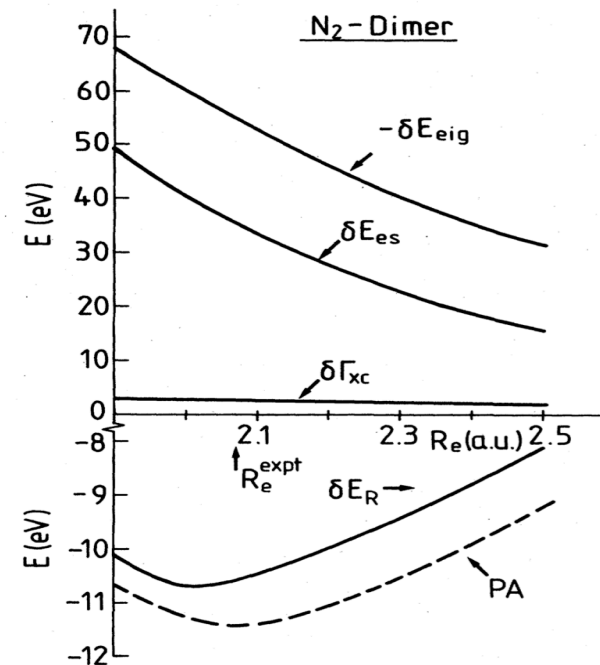
- Substituting in E_R to have the desired approximation:

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

- Final expression:

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

- Involves **only the frozen fragment densities**
- Use constructed potential for K-S scheme
- Accuracy? N₂-dimer



- Results for some homonuclear dimers: E_b, R_e, ω_e

| Dimer | E_b (eV) | | | R_e (a.u.) | | | ω_e (meV) | | |
|--|------------|-------|-------|--------------|------|-------|------------------|-----|-------|
| | (2.21) | PA | Expt. | (2.21) | PA | Expt. | (2.21) | PA | Expt. |
| Be ₂ | 0.49 | 0.50 | ~0.1 | 4.50 | 4.63 | 4.66 | 45 | 45 | 28 |
| C ₂ (¹ Σ _g ⁺) | 8.7 | 7.19 | 6.2 | 2.20 | 2.36 | 2.35 | 246 | 232 | 230 |
| N ₂ | 10.7 | 11.34 | 9.91 | 2.03 | 2.08 | 2.07 | 346 | 296 | 292 |
| F ₂ | 3.7 | 3.32 | 1.65 | 2.71 | 2.62 | 2.68 | 120 | 133 | 111 |
| Cu ₂ | 2.9 | 2.65 | 2.03 | 4.10 | 4.10 | 4.20 | 35 | 41 | 33 |

- Best case: Be₂

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

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

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

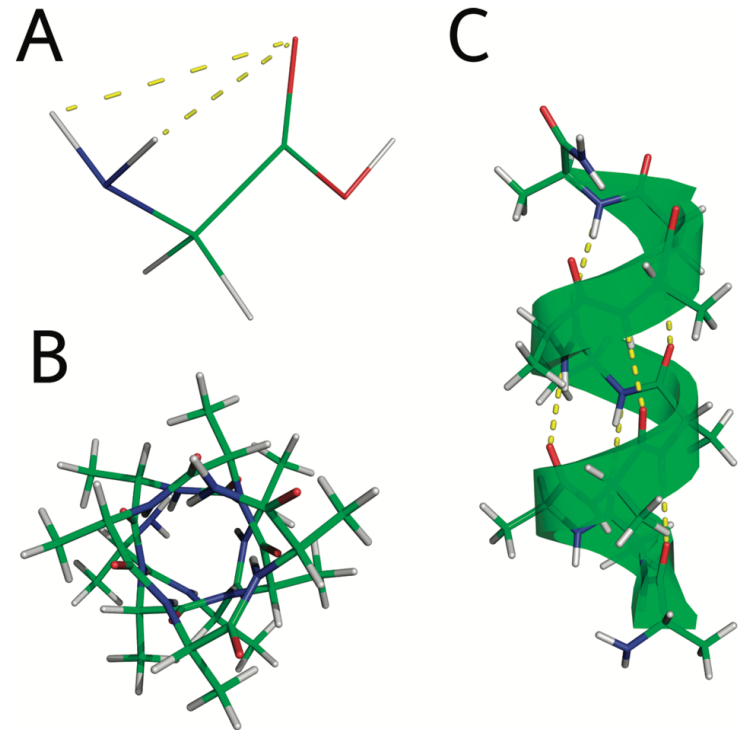
$$\mathbf{g}_l = \frac{1}{N} \sum_{m,l'} i\mathbf{G}_m n_{l'} e^{i\mathbf{G}_m \cdot (\mathbf{r}_l - \mathbf{r}_{l'})}$$

- **NSC force**: $\mathbf{F}_i^{\text{NSC},xc} = -\omega \sum_l \delta n_l \nabla_i V_{xc,l}$

- **Implementation**: the kernel only depends on the magnitude of gradient

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

- 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 ^b | CG steps | 32 | 16 | 48 | 21 |
| | functional evaluations | 116 | 733 | 849 | 805 |
| | total energy (Ha) | -56.625449 | -56.475861 | | -56.475870 |
| penta-alanine ^c | CG steps | 105 | 23 | 128 | 53 |
| | functional evaluations | 373 | 1180 | 1553 | 2961 |
| | total energy (Ha) | -242.121314 | -241.541173 | | -241.541182 |
| deca-alanine ^d | 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 $L_l^{\text{tot}} = L_l^{(1)} + L_l^{(2)} + L_l^{(3)} + L_l^{(4)}$

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

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

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