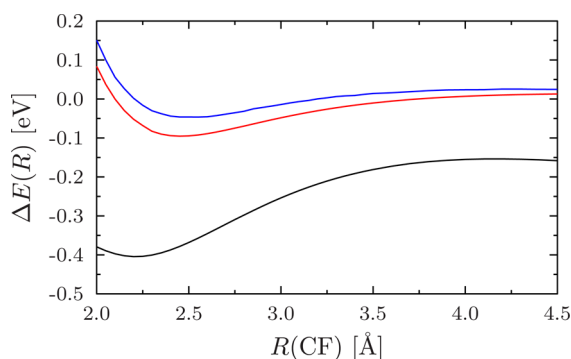# Correction to Variational, Self-Consistent Implementation of the Perdew−Zunger Self-Interaction Correction with Complex Optimal Orbitals

Susi Lehtola* and Hannes Jónsson

Upon further study, we have found that the optimization algorithm presented in our recent work[1] does not yield a

Figure 1. Binding energy of the $CH_3 + F^-$ complex. Shown are the result obtained using the PBEsol functional (black line), the earlier result of applying PZ-SIC to PBEsol from ref [1] (blue line), and the fully variational result using the gradient descent method presented here (red line).
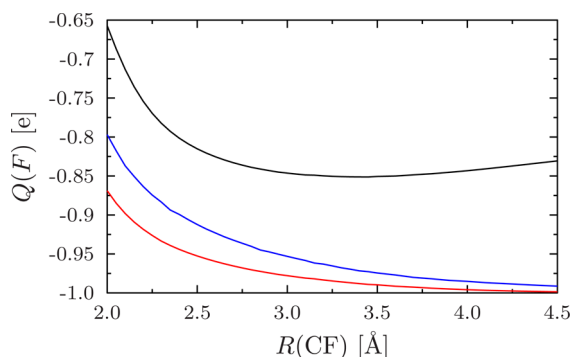
Figure 2. Mulliken charge on the fluorine atom in the $CH_3 + F^-$ complex. The legend is the same as in Figure 1.

proper minimum, as significant occupied−virtual (ov) orbital rotation gradients persist after convergence has apparently been reached. The effect can be seen for the H_2 molecule in a minimal basis set. The problem is that the approach in ref [1] uses a constant effective Fock matrix

$$\mathbf{F}^{\sigma}_{SIC} = -\left(\sum_{i=1}^{N_{\sigma}} \mathbf{F}^{i\sigma}\mathbf{P}^{i\sigma}\right)\mathbf{S} \tag{1}$$

(eq 36 in ref [1]) for updating the set of canonical orbitals in a self-consistent field (SCF) procedure. Here, $\mathbf{P}^{i\sigma}$ is the density matrix for orbital i of spin σ, $\mathbf{F}^{i\sigma}$ is the two-electron part of the

Fock matrix built from $\mathbf{P}^{i\sigma}$ (containing Coulomb, exchange, and correlation), $\mathbf{S}$ is the overlap matrix and N_{σ} is the number of occupied orbitals with spin σ. The use of a constant effective potential given by eq 1 amounts to linearizing the energy functional with respect to small orbital rotations in the vicinity of the current orbitals. However, nonlinear terms turn out to be important, and the canonical orbitals need to be updated in a different way.

Correspondingly, the solution of the SCF equations under the constant effective potential

$$(\mathbf{F}^{\sigma} + \mathbf{F}^{\sigma}_{SIC})\mathbf{C}^{\sigma} = \mathbf{S}\mathbf{C}^{\sigma}\mathbf{E}^{\sigma} \tag{2}$$

(eq 35 in ref [1]) should be replaced by a gradient descent optimization in the ov block. By parametrizing the orbital rotations as

$$\mathbf{c}^{\sigma} \rightarrow \mathbf{c}^{\sigma} \exp \boldsymbol{\theta}^{\sigma} \tag{3}$$

with $\mathbf{c}$ being the matrix of the optimal molecular orbital coefficients and $\boldsymbol{\theta}$ an antihermitian matrix, the orthonormality of the orbitals is automatically preserved. Defining the orbital density matrix as

$$P^{k\sigma}_{\mu\nu} = c^{\sigma*}_{\mu k} c^{\sigma}_{\nu k} \tag{4}$$

its change upon an infinitesimal rotation is obtained as

$$\left.\frac{\partial P^{k\sigma}_{\mu\nu}}{\partial \theta^{\sigma}_{pq}}\right|_{\theta=0} = c^{\sigma*}_{\mu q} c^{\sigma}_{\nu p}(\delta_{kq} - \delta_{kp}) = -\left.\frac{\partial P^{k\sigma}_{\mu\nu}}{\partial \theta^{\sigma*}_{qp}}\right|_{\theta=0} \tag{5}$$

Here, the indices i, j, and k denote occupied orbitals, a and b denote virtual orbitals, and p and q denote general indices. The gradient of the energy is

$$\left.\frac{\partial E}{\partial \theta^{\sigma}_{pq}}\right|_{\theta=0} = \sum_{k=1}^{N_{\sigma}} c^{\sigma*}_{\mu q}(F^{\sigma}_{\mu\nu} - F^{k\sigma}_{\mu\nu})\, c^{\sigma}_{\nu p}(\delta_{kq} - \delta_{kp}) \tag{6}$$

From this expression, the occupied−occupied (oo) gradient can be identified as the Pederson condition[2]

$$\frac{\partial E}{\partial \theta^{\sigma}_{ij}} = c^{\sigma*}_{\mu j}(F^{i\sigma}_{\mu\nu} - F^{j\sigma}_{\mu\nu})c^{\sigma}_{\nu i} = \kappa_{ij} \tag{7}$$

and the ov gradient as

$$\frac{\partial E}{\partial \theta^{\sigma}_{ib}} = -c^{\sigma*}_{\mu b}(F^{\sigma}_{\mu\nu} - F^{i\sigma}_{\mu\nu})c^{\sigma}_{\nu i} \tag{8}$$

In the present implementation, orbital optimization is performed using gradient descent with the gradients given by eqs 7 and 8, in contrast to using the unitary optimization algorithm discussed in ref 3 in the oo block and an SCF solver for the ov subspace as was done in ref 1. It is still beneficial to perform the oo and ov minimizations separately, as the energy scales involved in the two subspaces are disparate. An analogous approach for solid state calculations has recently been presented by Borghi et al.[4]

The ov block gradient can be efficiently preconditioned with an estimate for the diagonal Hessian,[5] and fast convergence with respect to ov rotations is typically observed. For the oo subspace, we have implemented the memory-limited Broyden−Fletcher−Goldfarb−Shanno algorithm[6,7] in ERKALE.[8,9]

The revised optimization algorithm gives lower energy for the test problems presented in ref 1, but the results turn out to be qualitatively similar. Figure 1 shows the binding energy curve for $CH_3 + F^-$ calculated using the PBEsol exchange-correlation functional,[10] and Figure 2 shows the resulting Mulliken charge on the fluorine ion.

A significant variation in the calculated values of the energy of the acrylic acid molecule found in ref 1 is also found with the present gradient descent minimization algorithm. The nature of these minima is being analyzed, and the results will be reported in a future publication.

■ REFERENCES

(1) Lehtola, S.; Jónsson, H. *J. Chem. Theory Comput.* **2014**, *10*, 5324−5337.

(2) Pederson, M. R.; Heaton, R. A.; Lin, C. C. *J. Chem. Phys.* **1984**, *80*, 1972.

(3) Lehtola, S.; Jónsson, H. *J. Chem. Theory Comput.* **2013**, *9*, 5365−5372.

(4) Borghi, G.; Park, C.-h.; Nguyen, N. L.; Ferretti, A.; Marzari, N. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2015**, *91*, 155112.

(5) Vydrov, O. A.; Scuseria, G. E. *J. Chem. Phys.* **2004**, *121*, 8187−93.

(6) Nocedal, J. *Math. Comput.* **1980**, *35*, 773.

(7) Nocedal, J.; Wright, S. *Numerical Optimization*; Springer Series in Operations Research and Financial Engineering; Springer : New York, 1999.

(8) Lehtola, S. ERKALE—HF/DFT from Hel: A Flexible Program Package for X-ray Properties of Atoms and Molecules, 2015; http://erkale.googlecode.com.

(9) Lehtola, J.; Hakala, M.; Sakko, A.; Hämäläinen, K. *J. Comput. Chem.* **2012**, *33*, 1572−85.

(10) Perdew, J. P.; Ruzsinszky, A.; Csonka, G. I.; Vydrov, O. A.; Scuseria, G. E.; Constantin, L. A.; Zhou, X.; Burke, K. *Phys. Rev. Lett.* **2008**, *100*, 136406.