A new implementation of an accurate self-interaction-corrected correlation energy functional based on an electron gas with a gap

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Abstract - Density functional theory (DFT) is a very effective method for the computation of the electronic structure of atoms, molecules or solids. In practical applications of this theory, only the exchange-correlation contribution to the total energy needs to be approximated. Whereas a large number of approximations have been proposed for the exchange part, there are less correlation functionals, more difficult to model. However, Krieger, Chen, Saltate and Savin [1,2] have recently designed a meta-GGA correlation functional called KCIS that satisfied a large number of rigorous physical conditions. Furthermore, this functional, based on the idea of an uniform electron gas with a gap in the excitation spectrum [3], contains no empirical parameters. In order to test this functional and to build new accurate DFT models, we have in this work implemented KCIS in a self-consistent way in the quantum chemistry software GAUSSIAN. The search for the best exchange functionals which can be used with KCIS has led to two new hybrid models with the Becke 88 (B) and mPBE exchange functionals: B0KCIS and mPBE/KCIS. These models, both including 25% of exact exchange, contain only one empirical parameter in the exchange part. These two functionals have been tested over a variety of physico-chemical properties and have turned out to have performances better or at least equivalent to those provided by semi-empirical exchange-correlation functionals like B3LYP. A detailed analysis of the results suggests that the best improvements brought by our models concern the correlation contribution plays an important role like for atomization energies, energetic reaction barriers and magnetic properties.

1. Introduction

In order to obtain more accurate molecular properties, new approximations to the DFT exchange-correlation functional $E_x$ are expected, especially for the correlation contribution which is the most difficult part to model.

In this context, we have in this work:
- implemented a new, promising correlation functional named KCIS in a self-consistent way in the quantum chemistry software GAUSSIAN, as well as its second derivatives with respect to the occupied orbitals;
- identified the best exchange functionals that can be used with the KCIS functional in order to construct new accurate DFT models;
- evaluated the accuracy of these new DFT models over a wide set of physico-chemical properties.

2. The KCIS correlation functional (2)

$E_{xc}^{\text{KCIS}}(\rho_{\text{occ}}, \rho_{\text{unocc}}) = \int \rho_{\text{occ}}(\mathbf{r}) \mathbf{V}_{\text{xc}}(\mathbf{r}, \mathbf{r}_0) \rho_{\text{occ}}(\mathbf{r}_0) \, d\mathbf{r}_0$

where $\mathbf{V}_{\text{xc}}(\mathbf{r}, \mathbf{r}_0) = \sum_{n} \sum_{n'} \rho_{\text{occ}}(\mathbf{r}_0) \mathbf{V}_{n,n'}(\mathbf{r}, \mathbf{r}_0)$

KCIS satisfies several theoretical conditions, in particular:
- The slowly-varying limit $\lim_{E \to 0} \frac{E_{xc}^{\text{KCIS}}}{E} = \frac{3}{4}$
- The rapidly-varying limit $\lim_{E \to 0} \frac{E_{xc}^{\text{KCIS}}}{E} = 0$
- Saturation under uniform scaling to the high-density limit $\lim_{E \to \infty} \frac{E_{xc}^{\text{KCIS}}}{E} = 0$

The Self-Interaction Correction (SIC): $E_{xc}^{\text{SIC}}(\rho_{\text{occ}}, \rho_{\text{unocc}})$

KCIS is one of the most accurate correlation functionals.

3. Test of the KCIS functional

Mean absolute errors (MAE) on correlation energies of atoms from H to Ar (6-31G(d,p)/6-311G(d,p) basis set and Hartree-Fock densities):

<table>
<thead>
<tr>
<th>Method</th>
<th>MAE (Hartree)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBE</td>
<td>0.018</td>
</tr>
<tr>
<td>LYP</td>
<td>0.015</td>
</tr>
<tr>
<td>PKZB</td>
<td>0.009</td>
</tr>
<tr>
<td>KCIS</td>
<td>0.011</td>
</tr>
</tbody>
</table>

KCIS is one of the most accurate correlation functionals.

4. Test of BOKCIS: Molecular geometries

Mean absolute errors (MAE) on bond lengths of 32 molecules belonging to the G2 set (6-31G(d,p)/basis set):

<table>
<thead>
<tr>
<th>Method</th>
<th>MAE (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBE</td>
<td>0.011</td>
</tr>
<tr>
<td>B0LYP</td>
<td>0.007</td>
</tr>
<tr>
<td>B0KCIS</td>
<td>0.006</td>
</tr>
</tbody>
</table>

Compared to other hybrid functionals, BOKCIS gives similar results for molecular geometries.

5. Test of BOKCIS: Chemical reactivity

Symmetric S2: reaction: $\text{Cl} + \text{CH}_3\text{Cl} \rightarrow \text{CICH}_2\text{CH}_3 + (6-31G(d,p)/basis set)$

<table>
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<tr>
<th>Method</th>
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</tr>
</thead>
<tbody>
<tr>
<td>PBE</td>
<td>0.012</td>
</tr>
<tr>
<td>B0LYP</td>
<td>0.009</td>
</tr>
<tr>
<td>B0KCIS</td>
<td>0.008</td>
</tr>
</tbody>
</table>

6. Test of BOKCIS: Weak interactions

The isotropic hyperfine coupling constant of a nucleus $i$ is connected to the spin density at the nucleus $\rho_i$ by the following expression:

$$\gamma_i = -\frac{\hbar}{4mc} \beta_i \beta_j \rho_{ij}(\mathbf{r})$$

$\beta_i$ and $\beta_j$ are the spins of the nuclei $i$ and $j$.

BOKCIS gives very accurate hyperfine coupling constants for simple radicals without spin polarisation.

7. Test of BOKCIS: Magnetic properties

The intrinsic magnetic moment of a molecule is the vector sum of the magnetic moments of the constituent atoms.

[References]

Conclusion

- The KCIS correlation functional is generally more accurate than the other semi-empirical or theoretical functionals, like LYP or PBE.
- BOKCIS is globally more accurate than B0LYP for properties which strongly depend on the correlation contribution of the functional like atomization energies, energetic reaction barriers and magnetic properties.
- BOKCIS gives similar results for properties more depending on the exchange contribution of the functional like molecular geometries, weak interactions and excitation energies.
- Prospects: Construct more accurate DFT models by combining KCIS with some recently developed meta-GGA exchange functionals involving the Laplacian of the electron density.

References