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Complex orbitals, multiple local minima and symmetry breaking in Perdew–Zunger self-interaction corrected density-functional theory calculations

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Abstract

The implementation of seminumerical stability analysis for calculations using the Perdew–Zunger self-interaction correction is described. It is shown that real-valued solutions of the Perdew–Zunger equations for gas phase atoms are unstable with respect to imaginary orbital rotations, confirming that a proper implementation of the correction requires complex-valued orbitals. The orbital density dependence of the self-interaction

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corrected functional is found to lead to multiple local minima in the case of the acrylic acid, H_6 and benzene molecules. In the case of benzene, symmetry breaking that results in incorrect ground state geometry is found to occur, which will erroneously lead to alternating bond lengths in the molecule.

Introduction

Kohn–Sham density-functional theory^{1,2} (KS-DFT) is a quintessential tool of modern quantum chemistry, with uses ranging from small molecules to large molecular clusters and all the way to the solid state. As a result of years of development of approximate density functionals, DFT is reaching chemical accuracy for a wide variety of applications. However, one of the still unresolved issues of modern density-functional theory is self-interaction error^{3–6} (SIE), which was discussed already in the 1930s by Fermi and Amaldi⁷. SIE remains a problem even for the most accurate (range-separated) hybrid functionals^{8–11}. It can be reduced with double hybrid functionals such as XYG3¹², ω B97X-2¹³ and PBE0-2¹⁴ thanks to being able to include a larger amount of exact exchange than in normal hybrids, as in ω B97X-2, for example. However, double hybrids incur the substantial additional cost of evaluating a Møller–Plesset¹⁵ type non-local correlation contribution.

SIE is an artefact of the approximate exchange-correlation functionals used in KS-DFT, in which an electron may spuriously repel or attract itself. This is especially a problem for charge transfer states in molecules^{3,5,6,11,16,17} and defect states of solids^{18–20}, for which KS-DFT often fails to reproduce even qualitatively correct behavior. Because of SIE, the electron participating in the charge transfer may fail to localize on one of the fragments. Instead, the fragments end up having fractional charges. Analogously, in solids the defect states become delocalized and fail to reproduce the charge distribution observed experimentally.

One of the procedures proposed²¹ for approximate removal of one-electron SIE was suggested by Perdew and Zunger^{22–24}. While the Perdew–Zunger self-interaction correction

(PZ-SIC) scheme has been used and studied in several contexts^{8,25–52}, it has only recently been proposed that a proper implementation of the variational procedure for the PZ-SIC functional requires complex-valued orbitals^{53–57}. To our knowledge, the only implementations to date that can achieve this are the ones by Klüpfel^{53,54}, Lehtola^{55–57}, and Borghi and coworkers⁵⁸. The use of complex-valued orbitals in PZ-SIC has been found to reproduce, *e.g.*, accurate charge transfer¹¹ and Rydberg states of molecules^{59–61}, as well as energies of defect states in solids²⁰.

In the present manuscript, a fully variational, all-electron treatment of PZ-SIC with complex-valued orbitals is used to study some aspects of PZ-SIC. With the use of finite-difference stability analysis, we show that real-valued extrema of the PZ-SIC functional are high-order saddle points in the complex-valued space of rotations between occupied orbitals, confirming earlier speculation that the use of complex-valued orbitals is necessary for correct minimization of the PZ-SIC energy functional^{53–55}. Based on the stability analysis, we propose a novel method for performing complex-orbital calculations, which is found to be more reliable than simple gradient descent in the complex space. We confirm the existence of multiple local minima for the PZ-SIC equations in the acrylic acid molecule that were found in earlier work^{55,57}. They arise due to the explicit dependence on the occupied orbital densities. The existence of multiple minima is further illustrated by calculations on symmetry breaking in the benzene and H₆ molecules, which have important ramifications for the application of PZ-SIC calculations on aromatic molecules, as well as larger polycyclic aromatics.

The organization of the manuscript is as follows. Next, in the Theory section, the formalism of PZ-SIC is briefly summarised. In the Implementation section, various aspects of the implementation are discussed. In the Results section, applications of PZ-SIC on the acrylic acid, H₆ and benzene molecules are discussed. The study concludes with a summary and discussion. Atomic units are used throughout the manuscript, unless stated otherwise.

Theory

The energy functional in KS-DFT is

$$E^{\text{KS}}[n] = V[n] + J[n] + T_s[n] + K[n], \quad (1)$$

with the first three terms representing the external potential

$$V[n] = \int n(\mathbf{r}) V(\mathbf{r}) \, d^3r, \quad (2)$$

the Coulomb repulsion energy

$$J[n] = \frac{1}{2} \iint \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, d^3r d^3r', \quad (3)$$

and the kinetic energy

$$T_s[n] = -\frac{1}{2} \sum_{\sigma} \sum_{I=1}^{N_{\sigma}} \langle \phi_I^{\sigma} | \nabla^2 | \phi_I^{\sigma} \rangle, \quad (4)$$

where ϕ_I^{σ} is the I^{th} orbital and N_{σ} the number of occupied states for spin σ . The last term in equation (1), $K[n]$, is the exchange-correlation energy functional, the form of which is not known in general. However, a large variety of approximations exist for K . The simplest approximation is the local density approximation^{2,62,63} (LDA) for which

$$K[n] = \int n(\mathbf{r}) \epsilon_{xc}(n_{\alpha}(\mathbf{r}), n_{\beta}(\mathbf{r})) \, d^3r, \quad (5)$$

where n_{α} and n_{β} denote the spin-up and spin-down densities, respectively, and ϵ_{xc} is the exchange-correlation energy density. More advanced approximations – the generalized gradient approximation⁶⁴ (GGA) and the meta-GGA⁶⁵ (mGGA) approximation – introduce further dependences on the density gradient and the kinetic energy density, respectively, in

the energy density.

The exact functional can be shown to satisfy²²

$$J[n_{i\sigma}] + K[n_{i\sigma}] = 0 \quad (6)$$

for any single-electron density $n_{i\sigma}$. However, approximate functionals do not satisfy equation (6), and thus some one-electron SIE persists. In the Perdew–Zunger procedure²² the one-electron SIE is approximately removed by explicitly subtracting it from the energy functional

$$E^{\text{PZ}}[n] = E^{\text{KS}}[n] - \sum_{i\sigma} (J[n_{i\sigma}] + K[n_{i\sigma}]). \quad (7)$$

Even if the one-electron SIE vanishes, there may still be many-electron SIE^{3–5,45,66}, which is easiest to understand as a “delocalization error”^{6,10}. Next, we will discuss how the electronic wave function is solved from equation (7).

Implementation

Minimization

As discussed at length in the literature^{55,57,58,67}, the minimization of the PZ functional (equation (7)) is significantly more complicated than that of the KS functional (equation (1)). Here, we resort to a straightforward gradient descent approach. A description of the procedure used here has already been presented elsewhere⁵⁷, but for completeness it is reviewed and discussed here in more detail. The energy is minimized via orbital rotations

$$\mathbf{c} \rightarrow \mathbf{c}e^{\theta}, \quad (8)$$

where $c_{\mu i}$ is the μ^{th} coefficient of the i^{th} optimal molecular orbital, in the terminology of reference 55. The antihermitian rotation parameter matrix $\boldsymbol{\theta}$ is parametrized as

$$\boldsymbol{\theta} = \begin{pmatrix} \boldsymbol{\theta}_{oo} & \boldsymbol{\theta}_{ov} \\ -\boldsymbol{\theta}_{ov}^\dagger & \mathbf{0} \end{pmatrix}, \quad (9)$$

where $\boldsymbol{\theta}_{oo} = -\boldsymbol{\theta}_{oo}^\dagger$ contains rotations in the occupied–occupied (oo) block and $\boldsymbol{\theta}_{ov}$ those in the occupied–virtual (ov) as well as the virtual–occupied (vo) blocks. The KS functional is invariant to oo rotations, but this invariance is broken in the PZ functional. Both the KS and PZ functionals are invariant to virtual–virtual (vv) rotations. Therefore, the vv block has been set to zero in equation (9).

The number of free parameters in $\boldsymbol{\theta}$ is as follows. $\boldsymbol{\theta}_{ov}$ contains ov real and ov imaginary rotations, whereas $\boldsymbol{\theta}_{oo}$ contains $o(o-1)/2$ real rotations and $o(o-1)/2$ imaginary rotations. In principle, $\boldsymbol{\theta}_{oo}$ is also allowed to have a purely imaginary diagonal, the elements of which correspond to individual orbital phase transformations. But, as these would have no effect on the energy, they have been omitted from the parametrization.

The derivative of the energy with respect to the rotation parameters is easily obtained as

$$\frac{\partial E}{\partial \theta_{ij}^\sigma} = F_{\mu\nu}^\sigma \frac{\partial P_{\mu\nu}^\sigma}{\partial \theta_{ij}^\sigma} - \sum_{k=1}^{N_\sigma} F_{\mu\nu}^{k\sigma} \frac{\partial P_{\mu\nu}^{k\sigma}}{\partial \theta_{ij}^\sigma}, \quad (10)$$

where the Fock matrix $\mathbf{F}^\sigma$ has been identified as usual⁶⁸ as

$$F_{\mu\nu}^\sigma = \frac{\partial E}{\partial P_{\mu\nu}^\sigma},$$

and an analogous expression holds for the orbital-dependent counterpart, $\mathbf{F}^{k\sigma}$. The deriva-

tives of the orbital density matrices

$$P_{\mu\nu}^{k\sigma} = c_{\mu k}^{\sigma*} c_{\nu k}^{\sigma} \quad (11)$$

can be obtained to be

$$\frac{\partial P_{\mu\nu}^{k\sigma}}{\partial \theta_{ij}^{\sigma}} = c_{\mu j}^{\sigma*} c_{\nu i}^{\sigma} (\delta_{kj} - \delta_{ki}) = -\frac{\partial P_{\mu\nu}^{k\sigma}}{\partial \theta_{ji}^{\sigma*}}, \quad (12)$$

which gives the result

$$\text{oo: } \frac{\partial E}{\partial \theta_{ij}^{\sigma}} = c_{\mu j}^{\sigma*} (F_{\mu\nu}^{i\sigma} - F_{\mu\nu}^{j\sigma}) c_{\nu i}^{\sigma} \quad (13)$$

$$\text{ov: } \frac{\partial E}{\partial \theta_{ib}^{\sigma}} = -c_{\mu b}^{\sigma*} (F_{\mu\nu}^{\sigma} - F_{\mu\nu}^{i\sigma}) c_{\nu i}^{\sigma} \quad (14)$$

$$\text{vo: } \frac{\partial E}{\partial \theta_{aj}^{\sigma}} = c_{\mu j}^{\sigma*} (F_{\mu\nu}^{\sigma} - F_{\mu\nu}^{j\sigma}) c_{\nu a}^{\sigma} \quad (15)$$

for the oo, ov, and vo blocks, respectively. The oo derivative is the so-called Pederson condition³⁸.

Equations (13), (14) and (15) have been implemented in the ERKALE program^{69,70}, in which approximate exchange-correlation functionals are evaluated using the LIBXC library⁷¹. The minimization is performed separately in the oo and ov subblocks, as the blocks possess different structure. The optimization is deemed to have converged when the gradient norm vanishes simultaneously in the occupied-occupied block (used threshold $|\partial E / \partial \theta_{ij}^{\sigma}| \leq 10^{-4}$) and in the occupied-virtual (and virtual-occupied) block (used threshold $|\partial E / \partial \theta_{ij}^{\sigma}| \leq 10^{-5}$).

Alternatively, the optimization in a block is deemed to have converged if a line search results in a change of the energy $|\Delta E| \leq 10^{-10}$. A parabolic line search is used, which uses information on the energy and gradient vector at the current point, as well as the energy at

a trial step length $l_{\text{trial}}/5$ away, where

$$l_{\text{trial}} = \frac{\pi}{2\omega_{\text{max}}} \quad (16)$$

is the length scale of the highest frequency pseudo-oscillation along the search direction, ω_{max} denoting the largest absolute eigenvalue of the matrix of rotation parameters corresponding to the search direction⁷². An estimation of the energy as a fourth order Taylor series in the orbitals leads to equation (16).

We apply preconditioning of the ov block with the approximate Hessian

$$\frac{\partial^2 E}{\partial_{ia}^\sigma \partial_{jb}^\sigma} \approx (\epsilon_a - \epsilon_i) \delta_{ij} \delta_{ab}, \quad (17)$$

where ϵ_a and ϵ_i are canonical orbital energies in HF and KS-DFT, but lack a similar definition in PZ-SIC. Correspondingly, we have implemented two kinds of preconditioners. First, one that mimics the usual KS-DFT preconditioner by constructing a unified Hamiltonian operator^{25,33}, diagonalizing it, and then scaling the components of the ov gradient by the projection onto the canonical orbital constructed from the unified Hamiltonian. Second, following Vydrov and Scuseria⁸, one that simply defines the quantities ϵ_a and ϵ_i as expectation values of the orbital dependent Fock matrix $\mathbf{F}^\sigma - \mathbf{F}^{i\sigma}$ over the orbitals a and i , respectively. We have found these two preconditioners to generally yield similar results, and in the rest of the work the former preconditioner is used. The ov block descent direction to be preconditioned is determined using the Polak–Ribière conjugate gradient method⁷³.

In contrast, as we have not found a cost-efficient estimate for the diagonal Hessian in the oo space, we resort to a limited-memory Broyden–Fletcher–Goldfarb–Shanno (L-BFGS) Hessian⁷⁴. Parallel transport of the previous derivatives is not used in our L-BFGS algorithm.

PZ-SIC introduces significant overhead compared to KS-DFT not only due to the need to calculate N occupied orbital Fock matrices for a given trial wave function, but also by the introduction of the dependence on rotations in the oo space that define the optimal orbitals.

Due to the use of preconditioning, the ov minimization typically converges rapidly, within a few iterations. Correspondingly, the oo optimization is found to dominate the cost of the calculation, in line with earlier results⁵⁵.

Initial guess

The dependence on oo rotations introduces significant complications to the minimization of the PZ-SIC functional, as convergence to different local minima in the oo space is possible. For this reason, in reference 55, the calculations were initialized with occupied canonical orbitals rotated with a random complex unitary matrix, resulting in a set of complex-valued orbitals. The use of pseudorandom initialization makes it possible to perform stochastic probing of the energy manifold. The initial orbitals can then be refined using an orbital localization method, such as Pipek–Mezey^{75,76}, Edmiston–Ruedenberg⁷⁷, von Niessen⁷⁸, Foster–Boys⁷⁹ or its variant, the fourth moment method⁸⁰. This set of localized guess orbitals is then hopefully close to the optimal set of orbitals for PZ-SIC, and is minimized using gradient descent. In the rest of the manuscript, we refer to this procedure as “Method 1”.

We have found that calculations restricted to real-valued orbitals converge much faster than those using complex-valued orbitals, as the optimization problem is then better conditioned. This can be explained by the fact that the KS-DFT part of the functional, which contributes most of the energy, only needs real-valued rotations. When imaginary rotations are also introduced, the KS-DFT part becomes ill-conditioned. A suitable workaround is to first converge the real-valued orbitals, and then run a stability analysis for real oo rotations. If instabilities are found, a line search is performed in the direction of the largest instability, and the minimization is restarted. If the wave function is stable to real rotations, another stability analysis is run with respect to purely imaginary oo rotations. If instabilities are found, a similar line search is performed, resulting in complex-valued orbitals, which are then optimized with gradient descent. Once convergence has been reached, the stability of the solution is checked for all possible rotations in the oo block: again, if instabilities are

found, the wave function is perturbed in the direction of the largest instability, and the optimization is restarted. In this scheme, referred to in the rest of the manuscript as “Method 2”, imaginary degrees of freedom are only introduced when the wavefunction is stable upon real rotations, but unstable to imaginary rotations.

Methods

In addition to the LDA^{62,63,81}, a variety of approximate exchange-correlation functionals are studied. As well as the Perdew–Burke–Ernzerhof^{82,83} (PBE) and the Tao–Perdew–Staroverov–Scuseria functionals^{84,85} (TPSS), we also examine a hybrid functional, B3LYP⁸⁶, which has been studied by Vydrov and Scuseria⁸ for calculations restricted to real-valued orbitals (denoted with the -RSIC suffix in the manuscript), and a range-separated functional (which to our knowledge have not been studied before with PZ-SIC) with 100% long-range exact exchange, ω B97X⁸⁷. These calculations are all done with the ERKALE program.

For reference, calculations using a range of all-electron post-Hartree–Fock (post-HF) methods are considered, from Møller–Plesset perturbation theory¹⁵ truncated at the second order (MP2) to coupled cluster theory⁸⁸ with single and double excitations⁸⁹ (CCSD) as well as full single and double and perturbative triple excitations⁹⁰ (CCSD(T)). The geometry optimizations and the post-HF calculations presented here have been carried out with a development version of Q-CHEM 4.2⁹¹. The correlation consistent cc-pVXZ basis sets⁹² are used throughout the work.

In large PZ-SIC calculations, the accumulation of the orbital Coulomb matrices can become a dominant contribution to the time requirements when the resolution of the identity (RI) technique⁹³ is not used. However, as orbital densities are not as smooth as the total density, normal Coulomb RI sets are not guaranteed to reproduce the correct orbital Coulomb energies. Instead, PZ-SIC RI calculations should be performed using auxiliary basis sets parametrized for fitting the exact exchange, which is an orbital dependent property. Here, we have avoided these problems by Cholesky decomposition of the electron repulsion integral

matrix⁹⁴ following the implementation in reference 95. The decomposition threshold was set to $\Delta_{\text{Cholesky}} = 10^{-5}$. The decomposition is only performed once at the beginning of the calculation, and constitutes an insignificant portion of the total runtime.

The integrals in the exchange-correlation contributions (e.g., equation (5)) are performed on Becke grids⁹⁶. As is well known^{8,46,55}, PZ-SIC calculations require finer grids than KS-DFT calculations. The KS-DFT and PZ-SIC calculations presented here have been performed on unpruned (100,590) grids, composed of 100 radial shells, each containing 590 angular points, which we have found to yield energies converged to microhartree level accuracy for first-row systems.

Analysis

The optimal orbitals produced by two calculations, $\{\psi_i\}_{i=1}^N$ and $\{\phi_i\}_{i=1}^N$, can be compared by computing the orbital projection matrix

$$O_{ij}^{\sigma} = |\langle \psi_{i\sigma} | \phi_{j\sigma} \rangle|^2. \quad (18)$$

The information contained in $\mathbf{O}$, when it has been properly sorted, can be represented by two numbers

$$\delta^{\sigma} = N_{\sigma} - \sum_i O_{ii}^{\sigma}, \quad (19)$$

$$\Delta^{\sigma} = N_{\sigma} - \sum_{ij} O_{ij}^{\sigma}. \quad (20)$$

The diagonal of $\mathbf{O}$, proxied by δ , reveals whether the two calculations have converged onto an identical set of occupied orbitals, while Δ measures how well the two total determinants match. Both δ and Δ vanish for matching sets of orbitals. Because the ordering of the optimal orbitals is not defined *a priori*, the rows i and columns j are matched for maximum overlap before δ is computed, the procedure for which is outlined in Appendix II. Δ is

invariant to reordering of the orbitals.

As we are dealing with complex wave functions, it is important to notice that a determinant composed of the orbitals $\{\psi_i\}_{i=1}^N$ will yield the same energy as its complex conjugate $\{\psi_i^*\}_{i=1}^N$, because the orbital densities they produce are identical. However, it is easy to see that while $\langle \psi_{i\sigma} | \psi_{i\sigma} \rangle = 1$, $\langle \psi_{i\sigma}^* | \psi_{i\sigma} \rangle \leq 1$, so one can determine if the two calculations have converged onto orbitals that are complex conjugates of each other by checking which of $\{\psi_i\}_{i=1}^N$ or $\{\psi_i^*\}_{i=1}^N$ result in the maximal Δ .

Results

Necessity of complex-valued orbitals

In earlier work^{53–55} it was shown that PZ-SIC implemented with complex-valued orbitals yields lower energies than an implementation restricted to real-valued orbitals. Through stability analysis, we have found that complex-valued orbitals are indeed strictly necessary for a proper implementation of PZ-SIC: calculations using “Method 2” discussed in the Implementation section show that the real-valued solutions have significant instabilities with respect to imaginary rotations already at the LDA-SIC level of theory, when applied to atoms in the gas phase. The obtained eigenvalues for the imaginary rotations are shown in table 1. The instabilities start occurring for atoms once there are three electrons per spin channel, and increase in number for heavier atoms, with 25%–50% of the eigenvalues of the imaginary rotations being negative for the atoms B – Ar. Similar results are also obtained at the GGA and mGGA levels of theory. These results carry on straightforwardly to the molecular case, for which instabilities with respect to imaginary rotations appear in all but systems composed exclusively of light atoms, and give strong testimony for the use of complex-valued orbitals in PZ-SIC calculations.

	ω_1	ω_2	ω_3	ω_4	ω_5	ω_6	ω_7	ω_8	ω_9	ω_{10}	n_ω
B α	-0.08										3
C α	-0.12	-0.12									6
N α	-0.25	-0.25	-0.14	-0.14	-0.14						10
O α	-0.30	-0.30	-0.17	-0.17	-0.16						10
O β	-0.14										3
F α	-0.34	-0.34	-0.19	-0.19	-0.19						10
F β	-0.19	-0.19									6
Ne $\alpha\beta$	-0.76	-0.76	-0.43	-0.43	-0.43						10
Na α	-0.44	-0.44	-0.24	-0.24	-0.24						15
Na β	-0.45	-0.45	-0.24	-0.24	-0.24						10
Mg $\alpha\beta$	-1.02	-1.02	-0.54	-0.53	-0.53						15
Al α	-0.58	-0.58	-0.30	-0.30	-0.30	-0.05					21
Al β	-0.57	-0.57	-0.30	-0.30	-0.30						15
Si α	-0.64	-0.64	-0.33	-0.33	-0.32	-0.06	-0.06				28
Si β	-0.64	-0.63	-0.32	-0.32	-0.32						15
P α	-0.71	-0.71	-0.35	-0.35	-0.35	-0.12	-0.12	-0.06	-0.06	-0.06	36
P β	-0.70	-0.70	-0.35	-0.35	-0.35						15
S α	-0.78	-0.78	-0.39	-0.39	-0.39	-0.14	-0.14	-0.07	-0.06	-0.06	36
S β	-0.77	-0.76	-0.39	-0.38	-0.38	-0.07					21
Cl α	-0.85	-0.85	-0.42	-0.42	-0.42	-0.15	-0.15	-0.07	-0.07	-0.07	36
Cl β	-0.84	-0.84	-0.42	-0.42	-0.40	-0.07	-0.07				28
Ar $\alpha\beta$	-1.83	-1.83	-0.90	-0.89	-0.89	-0.34	-0.34	-0.15	-0.15	-0.15	36

Table 1: Negative eigenvalues for imaginary rotations in each spin block for PZ-SIC calculations on gas phase atoms with the LDA functional. The last column shows the total number of imaginary rotations in the spin block.

Existence of multiple solutions

Figure 1: The acrylic acid molecule.

In references 55 and 57, several values of the converged energy were found for the acrylic acid molecule, depending on initial conditions and minimization method. These were tentatively attributed to the presence of multiple local minima. We have reproduced the calculations at the PBE, B3LYP and ω B97X levels of theory with the two strategies discussed above in the Implementation section. The geometry from reference 55 and the cc-pVTZ basis set were used. A set of 20 different calculations initialized with random rotations in the oo space were performed for all methods. Initial localization of the guess orbitals was not performed, as our purpose here is to thoroughly probe the orbital manifolds.

The KS-DFT energies are -266.962470 Ha, -267.273392 Ha and -267.196295 Ha for PBE, B3LYP and ω B97X, respectively. For RSIC calculations Methods 1 and 2 coincide, and the energy of the real solution was found to be -266.880626 Ha for PBE-RSIC, -266.979669 Ha for B3LYP-RSIC, and -266.072458 Ha for ω B97X-RSIC, with all 20 random initial rotations converging onto the same energy. For PBE-RSIC and B3LYP-RSIC, the oxygen and carbon 1s orbitals were found to have positive self-interaction energy, thus making the correction negative, while all the valence orbitals were found to have negative self-interaction energies, slightly raising the total energy. Similar results have been presented by Vydrov and Scuseria⁸. For ω B97X-RSIC, all the orbitals were found to have negative self-interaction energies, which is why the PZ-SIC energy is higher than the KS-DFT one. Thus, counterintuitively, the functional with SIE only in the short range is more affected by PZ-SIC than functionals that bear the full range of SIE.

For PBE-RSIC and B3LYP-RSIC, the orbital diagnostics of equations (20) and (19) were found to be small ($\delta \lesssim 3 \times 10^{-5}$, $\Delta \leq 3 \times 10^{-7}$), indicating that all the calculations had

converged to the same set of orbitals. For the ω B97X-RSIC the differences are much larger: $\delta \approx 4 \times 10^{-3}$ and $\Delta \approx 10^{-5}$, indicating that the resulting total density is still somewhat similar between the solutions obtained from different initial points, but the sets of orbitals have significant differences. This result is expected due to the nature of the range-separated functional: self-interaction only occurs at short range, so a large set of different local solutions can be expected. The range-separation parameter in ω B97X is 0.3 bohr^{-1} , which is small compared to the length scale of the molecule. A more pronounced SIE and an ill-defined minimum even just with real-valued orbitals indicate that ω B97X does not benefit from application of the PZ-SIC.

The results for the calculations with complex-valued orbitals (denoted with the suffix -SIC), shown in order of decreasing energy in table 2, possess more structure. Note that calculations with both methods are carried out with stability analysis, and the results are stable to rotations within the oo block. But, all the calculations with Method 1 were found to converge to local minima *without any help from the stability analysis*, demonstrating the versatility of the used line search approach.

These results indicate that PBE-SIC has two solutions, with Method 2 consistently finding the lower solution, and Method 1 converging onto the higher lying solution in 6 cases out of 20. Surprisingly, a consecutively run full stability analysis with respect to real and imaginary oo and ov rotations shows that the higher lying solution is a true local minimum.

A visual inspection of the occupied orbitals of the two solutions with different energies show no discernible differences in the shapes of the isomagnitude surfaces. But, the δ and Δ diagnostics are large ($\delta \approx 4.6$, $\Delta \approx 0.01$), indicating that the densities and the sets of orbitals are different in the two local minima. But, the δ and Δ diagnostics are also of the same magnitude even within the sets of solutions with the same energy with Method 1, which makes reproduction of results difficult. In contrast, for Method 2 the values shown in table 3 are obtained. From these values, one can distinguish two groups of solutions shown in table 4, which all share the same energy. Visualizing the density difference between the

two groups (figure 2) shows that the symmetry of the wave function is broken in PZ-SIC. Interestingly, this did not occur with PZ-RSIC. Going back to the calculations with Method 1, it is seen that the differences between the calculations here as well mostly arise from symmetry breaking around the plane. Unlike Method 2, the solutions for Method 1 appear all to be different, barring a classification of the solutions. We tentatively attribute this dispersion to the complex conjugation symmetry. While in Method 2, a consistent complex phase was found for all orbitals, such that two calculations either yielded the same orbitals or were complex conjugates of each other, we believe Method 1 often yields mixed determinants, where orbital i is conjugated from some reference but orbital j is not.

Next, for B3LYP-SIC, three classes of solutions are found with Method 1. As for the PBE-SIC results above, the B3LYP-SIC solutions turn out to be proper local minima. Method 2 again shows considerably better convergence properties, converging onto the lowest energy solution in all but one calculation. Last, for ω B97X, two classes of solutions are also found, which also turn out to be stable minima.

The number of line searches necessary for the calculations in table 2 is shown in table 5. The convergence of the procedure is excruciatingly slow, as is known from earlier work^{58,67}, and converging the complex-valued orbitals is at least two times more work than converging the real-valued orbitals. On average, Method 2 requires 0.93–2.31 times the number of line searches necessary for Method 1, indicating that Method 1 may actually be optimal in some cases.

However, if an initial localization is performed, the two methods will likely converge in fewer iterations because while the canonical orbitals are delocal, the optimal PZ-SIC orbitals usually turn out to be localized. Initial localization should then give reasonable guess orbitals. But, the initial localization may also change the minima on which the calculations converge: it might be energetically preferable for an orbital to delocalize, instead of localize. To investigate whether this happens in this case, we repeated the energy sampling with guess orbitals localized using the Edmiston–Ruedenberg procedure before the PZ-SIC calculation.

This yielded the energies shown in table 6 for the calculations with complex-valued orbitals, while the calculations with real-valued orbitals all gave the same energies as above. For PBE-SIC, the initial localization makes all calculations with Method 1 find the same minimum, while without localization six calculations converged onto a higher lying local minimum. For ω B97X-SIC, initial localization also appears to be helpful, with all initial guesses now converging onto similar energies. However, for B3LYP-SIC the localization appears to be even counterproductive as for Method 1 instead of one calculation converging on a higher lying local minimum without localization, now 9 calculations converge on a local minimum over 2 mHa higher than the lowest found minimum.

The number of line searches necessary with the use of localized guess orbitals is shown in table 7. Initial localization reduces the number of iterations necessary to converge calculations with real-valued orbitals by 3.6–11 times. However, initial localization does not (and should not) affect the demands of the complex-valued optimization in Method 2, because the procedure always begins from a real-valued minimum. For Method 1, the results in tables 5 and 7 are contradicting: localization decreases the number of iterations necessary for B3LYP-SIC and ω B97X-SIC by roughly three to four hundred iterations, but increases the effort for PBE-SIC by roughly 500 iterations.

Due to the large variation in the number of line searches between calculations within the same method, we cannot determine if initial localization is helpful or not in small systems. However, as the size of the system grows, the choice of the initial set of orbitals will become more important, as PZ-SIC will then allow multiple solutions⁹⁷. When localized initial orbitals are chosen, the minimization will likely yield local orbitals. But, if delocalized initial orbitals are used, the minimization might yield delocal optimal orbitals, because the self-interaction correction vanishes for extended orbitals²².

While Method 2 may not be faster to converge, it does possess clearly superior convergence properties over Method 1 by converging more often onto lower minima. If RSIC solutions are also wanted, the use of Method 2 is optimal, and in the rest of the manuscript,

Method 2 with initial localization will be used.

Before finishing the analysis of acrylic acid, we will cycle back to the beginning and have another look at why the range-separated ω B97X functional counterintuitively appears to suffer from larger self-interaction error than pure functionals. In addition to the three functionals studied above, we will also study the pure HCTH/93 functional⁹⁸, the hybrid B97 functional⁹⁹, as well as the range-separated PBE functional variants LC- ω PBE¹⁰⁰, LRC- ω PBE¹⁰¹ and LRC- ω PBEh¹⁰¹. The total energies at the KS-DFT and PZ-SIC levels of theory with all the functionals are shown in table 8. The differences $E^{\text{PZ-SIC}} - E^{\text{KS-DFT}}$ and $E^{\text{PZ-SIC}} - E^{\text{KS-DFT}}$ can be used as estimates of the total self-interaction error in the parent functional. From these results, it is apparent that PZ-SIC with real-valued orbitals overestimates self-interaction compared to the correction with complex-valued orbitals. Furthermore, the largest self-interaction is seen with empirical functionals: (B3LYP,) B97, HCTH and ω B97X; while the correction is small with the *ab initio* functionals: PBE, LC- ω PBE, LRC- ω PBE, and LC- ω PBEh. This result is easy to interpret: the optimal exchange-correlation functional with PZ-SIC is likely different to one that is optimal for KS-DFT¹⁰², and thus empirical functionals fitted at the KS-DFT level of theory do not fare well at the PZ-SIC level of theory.

Symmetry breaking

The dependence on the occupied orbital densities introduced in PZ-SIC suggests it may be prone to symmetry breaking defects, in analogy to coupled cluster valence bond and local valence correlation models^{104–109}. To test this, we study symmetry breaking in the allyl radical, as well as the breaking of the D_{6h} symmetry in H_6 and benzene. In all three systems, there are two equivalent Kekulé structures at the equilibrium geometry, shown in figure 3. As the symmetry of the molecule is broken, one localized solution will likely fall and the other will rise in energy.

The geometry of H_6 was optimized at the CCSD(T)/cc-pVQZ level of theory. For ben-

Table 2: Energy of acrylic acid at PBE-SIC, B3LYP-SIC and ω B97X-SIC levels of theory with randomly rotated guess orbitals, sorted in order of decreasing energy.

Guess	PBE-SIC		B3LYP-SIC		ω B97X-SIC	
	Method 1	Method 2	Method 1	Method 2	Method 1	Method 2
1	-267.044203	-267.044474	-267.162810	-267.162882	-266.368440	-266.369606
2	-267.044203	-267.044474	-267.165391	-267.165585	-266.368441	-266.369606
3	-267.044203	-267.044474	-267.165393	-267.165585	-266.368441	-266.369607
4	-267.044203	-267.044474	-267.165393	-267.165585	-266.369607	-266.369607
5	-267.044203	-267.044474	-267.165393	-267.165585	-266.369607	-266.369607
6	-267.044203	-267.044474	-267.165393	-267.165585	-266.369607	-266.369607
7	-267.044474	-267.044474	-267.165393	-267.165585	-266.369607	-266.369607
8	-267.044474	-267.044474	-267.165393	-267.165585	-266.369607	-266.369607
9	-267.044474	-267.044474	-267.165584	-267.165585	-266.369607	-266.369607
10	-267.044474	-267.044474	-267.165584	-267.165585	-266.369607	-266.369607
11	-267.044474	-267.044474	-267.165584	-267.165585	-266.369607	-266.369607
12	-267.044474	-267.044474	-267.165585	-267.165585	-266.369614	-266.369607
13	-267.044474	-267.044474	-267.165585	-267.165585	-266.369614	-266.369607
14	-267.044474	-267.044474	-267.165585	-267.165585	-266.369614	-266.369607
15	-267.044474	-267.044474	-267.165585	-267.165585	-266.369614	-266.369607
16	-267.044474	-267.044474	-267.165585	-267.165585	-266.369614	-266.369607
17	-267.044474	-267.044474	-267.165585	-267.165585	-266.369614	-266.369607
18	-267.044474	-267.044474	-267.165585	-267.165585	-266.369614	-266.369607
19	-267.044474	-267.044474	-267.165585	-267.165585	-266.369614	-266.369607
20	-267.044474	-267.044474	-267.165585	-267.165585	-266.369614	-266.369607

Index	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
1		-2.7	-7.7	-7.9	-8.2	-8.2	-9.2	-8.3	-9.7	-2.7	-2.7	-2.7	-2.7	-2.7	-2.7	-2.7	-2.7	-2.7	-7.2	-2.7
2	0.0		-2.7	-2.7	-2.7	-2.7	-2.7	-2.7	-2.7	-7.8	-8.7	-8.8	-2.7	-7.3	-7.0	-7.2	-7.3	-7.7	-2.7	-7.9
3	-5.6	0.0		-7.2	-7.3	-8.3	-7.5	-8.2	-7.6	-2.7	-2.7	-2.7	-2.7	-2.7	-2.7	-2.7	-2.7	-2.7	-6.8	-2.7
4	-5.9	0.0	-5.1		-9.1	-7.5	-8.1	-7.5	-8.0	-2.7	-2.7	-2.7	-2.7	-2.7	-2.7	-2.7	-2.7	-2.7	-7.6	-2.7
5	-6.1	0.0	-5.2	-7.0		-7.6	-8.5	-7.7	-8.2	-2.7	-2.7	-2.7	-2.7	-2.7	-2.7	-2.7	-2.7	-2.7	-7.5	-2.7
6	-6.1	0.0	-6.3	-5.4	-5.5		-8.0	-9.5	-8.1	-2.7	-2.7	-2.7	-2.7	-2.7	-2.7	-2.7	-2.7	-2.7	-6.9	-2.7
7	-7.0	0.0	-5.5	-6.1	-6.4	-5.9		-8.1	-9.3	-2.7	-2.7	-2.7	-2.7	-2.7	-2.7	-2.7	-2.7	-2.7	-7.2	-2.7
8	-6.2	0.0	-6.2	-5.4	-5.6	-7.2	-5.9		-8.3	-2.7	-2.7	-2.7	-2.7	-2.7	-2.7	-2.7	-2.7	-2.7	-7.0	-2.7
9	-7.2	0.0	-5.6	-5.9	-6.1	-6.1	-7.0	-6.1		-2.7	-2.7	-2.7	-2.7	-2.7	-2.7	-2.7	-2.7	-2.7	-7.2	-2.7
10	0.0	-5.8	0.0	0.0	0.0	0.0	0.0	0.0	0.0		-7.6	-7.6	-2.7	-8.0	-7.4	-7.7	-8.0	-9.0	-2.7	-2.7
11	0.0	-6.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	-5.5		-9.8	-2.7	-7.2	-6.9	-7.0	-7.2	-7.5	-2.7	-2.7
12	0.0	-6.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	-5.6	-7.3		-2.7	-7.2	-6.9	-7.0	-7.2	-7.5	-2.7	-2.7
13	-5.8	0.0	-5.1	-7.2	-6.6	-5.3	-6.0	-5.4	-5.8	0.0	0.0	0.0	-2.7	-2.7	-2.7	-2.7	-2.7	-2.7	-2.7	-2.7
14	0.0	-5.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	-5.9	-5.1	-5.1	0.0		-7.9	-8.7	-10.3	-8.3	-2.7	-2.7
15	0.0	-4.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	-5.3	-4.8	-4.8	0.0	-5.9		-8.4	-8.0	-7.5	-2.7	-2.7
16	0.0	-5.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	-5.6	-5.0	-5.0	0.0	-6.6	-6.3		-8.8	-7.9	-2.7	-2.7
17	0.0	-5.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	-5.9	-5.1	-5.1	0.0	-7.8	-5.9	-6.7		-8.2	-2.7	-2.7
18	0.0	-5.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	-6.8	-5.4	-5.4	0.0	-6.2	-5.4	-5.8	-6.1		-2.7	-2.7
19	-5.1	0.0	-4.7	-5.5	-5.4	-4.9	-5.2	-4.9	-5.1	0.0	0.0	0.0	-5.6	0.0	0.0	0.0	0.0	0.0	0.0	-2.7
20	0.0	-5.8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	-7.1	-5.6	-5.6	0.0	-5.9	-5.3	-5.6	-5.8	-6.7	0.0	0.0

Table 3: Orbital diagnostics $\lg \delta$ (lower triangle) and $\lg \Delta$ (upper triangle) for the PBE-SIC with Method 2 shown in table 2. Small values are shown in bold.

Table 4: Grouping of PBE-SIC solutions to classes with table 3.

	Calculations in group
Group 1	1, 3–9, 13, 19
Group 2	2, 10–12, 14–18, 20

Table 5: Line searches necessary to attain convergence when initial localization of the orbitals is not used. The notation is minimum – maximum (average). ^aThe line searches after stability analysis of the RSIC solution.

	RSIC	SIC, Method 2 ^a	SIC, Method 1
PBE	235 – 403 (278)	927 – 1800 (1522)	310 – 1941 (780)
B3LYP	199 – 314 (260)	502 – 1285 (1064)	288 – 1963 (1116)
ω B97X	420 – 914 (634)	552 – 826 (632)	479 – 3607 (1363)

Figure 2: Density difference between the two classes of solutions of PBE-SIC with Method 2. The isosurface value is 0.001 electrons/bohr³, with the positive surface shown in blue and the negative shown in red. The difference is antisymmetric around the molecular plane, and is centered on the oxygen of the carbonyl group. The rendering was done with Jmol¹⁰³.

Table 6: Energy of acrylic acid at PBE-SIC, B3LYP-SIC and ω B97X-SIC levels of theory with initial Edmiston–Ruedenberg localization of the occupied orbitals, sorted in order of decreasing energy.

Guess	PBE-SIC		B3LYP-SIC		ω B97X-SIC	
	Method 1	Method 2	Method 1	Method 2	Method 1	Method 2
1	-267.044474	-267.044474	-267.162845	-267.162884	-266.369606	-266.369606
2	-267.044474	-267.044474	-267.162875	-267.165585	-266.369606	-266.369606
3	-267.044474	-267.044474	-267.162875	-267.165585	-266.369607	-266.369606
4	-267.044474	-267.044474	-267.162876	-267.165585	-266.369607	-266.369606
5	-267.044474	-267.044474	-267.162882	-267.165585	-266.369607	-266.369607
6	-267.044474	-267.044474	-267.162882	-267.165585	-266.369607	-266.369607
7	-267.044474	-267.044474	-267.162882	-267.165585	-266.369607	-266.369607
8	-267.044474	-267.044474	-267.162882	-267.165585	-266.369607	-266.369607
9	-267.044474	-267.044474	-267.162882	-267.165585	-266.369607	-266.369607
10	-267.044474	-267.044474	-267.165393	-267.165585	-266.369607	-266.369607
11	-267.044474	-267.044474	-267.165585	-267.165585	-266.369607	-266.369607
12	-267.044474	-267.044474	-267.165585	-267.165585	-266.369607	-266.369607
13	-267.044474	-267.044474	-267.165585	-267.165585	-266.369607	-266.369607
14	-267.044474	-267.044474	-267.165585	-267.165585	-266.369607	-266.369607
15	-267.044474	-267.044474	-267.165585	-267.165585	-266.369607	-266.369607
16	-267.044474	-267.044474	-267.165585	-267.165585	-266.369607	-266.369607
17	-267.044474	-267.044474	-267.165585	-267.165585	-266.369614	-266.369607
18	-267.044474	-267.044474	-267.165585	-267.165585	-266.369614	-266.369607
19	-267.044474	-267.044474	-267.165585	-267.165585	-266.369614	-266.369614
20	-267.044474	-267.044474	-267.165585	-267.165585	-266.369614	-266.369614

Table 7: Line searches necessary to attain convergence with initial Edmiston–Ruedenberg localization of the guess orbitals. The notation is minimum – maximum (average). ^aThe line searches after stability analysis of the RSIC solution.

	RSIC	SIC, Method 2 ^a	SIC, Method 1
PBE	64 – 70 (65)	896 – 1755 (1415)	821 – 2036 (1311)
B3LYP	67 – 80 (72)	601 – 1308 (1069)	362 – 1472 (814)
ω B97X	54 – 60 (57)	582 – 3692 (933)	539 – 3228 (912)

Table 8: Another look at self-interaction in acrylic acid with results for additional functionals.

Functional	$E^{\text{KS-DFT}}$	$E^{\text{PZ-RSIC}} - E^{\text{KS-DFT}}$	$E^{\text{PZ-SIC}} - E^{\text{KS-DFT}}$
PBE	-266.962470	0.081844	-0.082004
B3LYP	-267.273392	0.293723	0.107807
ω B97X	-267.196295	1.123837	0.826681
B97	-267.176832	0.455077	0.274962
HCTH/93	-267.180914	0.790832	0.500648
LC- ω PBE	-267.092693	0.221559	0.084387
LRC- ω PBE	-267.041053	0.168703	0.022744
LRC- ω PBEh	-267.001583	0.153014	0.026778

zene, a recently reported CCSD(T)/aug-cc-pVTZ geometry was used¹¹⁰. The corresponding radii for the geometries are 0.987 Å for H₆ and 1.398 Å for benzene. For the allyl radical, a geometry optimized at RI-MP2/cc-pVTZ level of theory was used. The KS-DFT and PZ-SIC calculations for all molecules, as well as the CCSD results for H₆ shown below, made use of the cc-pVTZ basis set.

Figure 3: Two possible localized bond configurations in the allyl radical and benzene.

In contrast to the unrestricted perfect pairing model¹⁰⁵ which predicts two different CC bond lengths in the allyl radical, PZ-SIC was found to maintain the symmetric structure when the length difference of the two bonds was altered. For H₆, PZ-SIC was found to have two local solutions corresponding to the two ways for dissociating into three separated hydrogen molecules. The total energy as a function of the symmetry breaking angle is shown in figure 4 at the LDA and LDA-SIC levels of theory^{62,63,111}, with the PBE and TPSS functionals yielding similar results. Two LDA-SIC curves are shown in figure 4: one scanning the energy from the left to the right, and another going from the right to the left. Except

for the initial points in the calculations, stability analysis was not used to adjust the wave function. Here, LDA-SIC and LDA-RSIC coincide, as no imaginary instabilities were found. For comparison, data calculated at the CCSD level of theory, which should account for all the static correlation in the system, are also shown.

The barrier at $\theta = 0$ is too low in KS-DFT compared to CCSD, when pure functionals are used. The LDA barrier is 6.7 mHa, while CCSD gives 30.4 mHa. The barrier to hydrogen abstraction in $\text{H}_2 + \text{H} \rightarrow \text{H} + \text{H}_2$ is also too low in KS-DFT, but is near perfect in PZ-SIC as was found by Johnson and coworkers in work using a perturbative approach with approximate (Foster–Boys localized), real-valued orbitals¹¹², and later confirmed variationally by Klüpfel and coworkers using complex-valued orbitals⁵⁴. However, for H_6 the barrier is overcorrected by PZ-SIC to over two times the CCSD value, 74.7 mHa. In turn, this finding is in agreement with earlier results by Klüpfel et al⁵⁴ that the application of PZ-SIC to PBE and similar functionals tends to overcorrect, but scaling of SIC by one half tends to give good atomization energies and band gaps¹⁸. Going back to figure 4, a pronounced cusp is seen at the D_{6h} symmetry where the two localized solutions are degenerate. PZ-SIC does still reproduce the locations of the minima better than KS-DFT. All of the data points represent proper local minima in the oo space, implying there is an energy barrier that prevents passing from one local solution to the other. The solutions can be followed beyond the cusp, up to $\theta \approx \pm 5^\circ$, where they collapse to the other localized solution, possibly due to numerical noise in the projection of the orbitals from the earlier step.

For benzene, a similar kind of behavior is observed. The results at the LDA, LDA-RSIC and LDA-SIC levels of theory are shown in figure 5, with PBE and TPSS again yielding similar results. While LDA yields a parabola centered on the origin, LDA-RSIC and LDA-SIC result in two parabolas representing the two different Kekulé structures, again exhibiting a pronounced cusp at the symmetric geometry, and strongly demonstrating a symmetry breaking artifact produced by PZ-SIC. Because the angles that minimize the RSIC and SIC energies are non-zero, PZ-RSIC and PZ-SIC will break the symmetry of the

Figure 4: Two localized solutions in H_6 . The legend is the following: LDA (black boxes), LDA-SIC scanning left→right (blue diamonds) and right→left (red diamonds), and CCSD (black crosses). PBE and TPSS give similar results.

molecule. For LDA-RSIC, the cusp at the origin is twice higher (9.7 mHa vs 4.4 mHa), and the symmetry breaking angle is 50% larger than in LDA-SIC (2.4° vs 1.6°). These results translate to alternating CC bond lengths of 1.35 Å and 1.45 Å, and 1.36 Å and 1.43 Å for the LDA-RSIC and LDA-SIC models, respectively. A full relaxation of the geometry with finite difference gradients predicts alternating CC bond lengths of 1.32 Å and 1.40 Å, and 1.33 and 1.39 Å for the LDA-RSIC and LDA-SIC models, respectively, while the relaxed CH bond lengths are 1.06 Å and 1.05 Å, respectively, and the molecule still maintains a planar geometry.

Interestingly, when restricted to real-valued orbitals the algorithm is not always able to follow the same solution as happens for the complex-valued orbitals. Instead, the calculations with real-valued orbitals collapse to the minimal solutions at $\theta \approx \pm 2.2^\circ$, which we again tentatively attribute to numerical noise. Even more intriguing is that while the left→right scan collapses directly to the minimum solution at $\theta \approx 2.2^\circ$, the right→left scan collapses to an *intermediate* solution at $\theta \approx -1.7^\circ$ that it follows till $\theta \approx -2.2^\circ$ where it collapses to the minimum solution. Stability analysis shows the intermediate solution is stable upon

rotations in the oo block. To further investigate the intermediate solution encountered in the right→left scan, we take the solution at $\theta = -1.6^\circ$ and reperform the calculations in both directions, and obtain the results presented in red in figure 6. The left branch is the same as in figure 5. However, the right branch reveals yet another local minimum solution in the oo block that can be followed to $\theta \approx 1.9^\circ$, where it collapses to a lower lying solution. Starting another set of calculations with this solution, one ends up with the set of results shown in figure 6.

The pair of solutions shown in figure 6 are intriguing. The results demonstrate that in addition to the real-valued minimum energy solutions that break the symmetry more than the complex-valued minimum solutions, there are also higher-lying solutions that would result in less symmetry breaking. A full stability analysis reveals that the solutions corresponding to the minima at $\theta = \pm 1.3^\circ$ have three negative eigenvalues around $\omega \approx -10^{-2}$ that correspond to combined oo and ov rotations, which suggests that these are not local minima but rather saddle point solutions.

Summary and discussion

The results presented here highlight the importance of complex-valued orbitals in the implementation of the Perdew–Zunger self-interaction correction (PZ-SIC). For atoms and molecules, we have shown that calculations restricted to real-valued orbitals converge onto solutions that are high-order saddle points in the space of all possible complex unitary rotations. For benzene we have shown that calculations restricted to real-valued orbitals break the symmetry more than those based on complex-valued orbitals. Unfortunately, the appearance of the imaginary degrees of freedom significantly complicate the minimization of the functional.

In addition to the large additional prefactor introduced by the orbital dependent correction, the dependence on the set of occupied orbitals also introduces the possibility of local

Figure 5: Symmetry breaking in benzene. LDA (black boxes), LDA-SIC with real-valued orbitals scanning left→right (blue diamonds) and right→left (red diamonds), and LDA-SIC with complex-valued orbitals scanning left→right (filled blue circles) and right→left (filled red circles). PBE and TPSS give similar results.

Figure 6: Further scans for the intermediate solution found for benzene using LDA-RSIC in figure 5. Data in red are obtained from starting calculations in both directions from solution at $\theta = -1.6$. Data in blue are in a similar fashion, starting from red datapoint at $\theta = 1.9$.

minima of the energy functional. We have confirmed the existence of multiple local minima in the acrylic acid molecule, and we further illustrated the existence of multiple solutions for H_6 and benzene. Depending on the system, convergence onto the lowest-lying solution may be a non-trivial matter, as the problem requires global optimization techniques. Interestingly, when stability analysis is not applied, calculations restricted to real-valued orbitals have more tendency of collapsing onto a different solution, as was demonstrated with the energy scans on benzene.

The results suggest that care should be taken in applying PZ-SIC calculations to polyaromatic hydrocarbons, as the number of possible Kekulé structures grows with the increasing number of aromatic rings. Furthermore, the nature of the localized solutions makes geometry optimization difficult, as the resulting geometry will be sensitive to the initial set of occupied orbitals.

The calculations on acrylic acid indicated the electron density reproduced by the PZ-SIC with complex-valued orbitals break inversion symmetry with respect to the plane of the molecule. This kind of spontaneous symmetry breaking suggests that PZ-SIC may also incorrectly predict non-planar ground state geometries for planar molecules. In the case of the CH_3 radical, it has been shown that PZ-SIC with real-valued orbitals predicts a non-planar geometry⁵¹, while the correct planar geometry is obtained with complex-valued orbitals⁵⁴.

The results of this work illustrate the numerical problems associated with the PZ-SIC method. While PZ-SIC is $O(n^3)$ scaling like conventional KS-DFT, the large prefactor poses limits on the applicability of the method, and the existence of multiple local minima makes the correct use of the procedure require a large amount of expertise. Still, SIC calculations can be carried out for large systems where they show promising results^{20,59–61}. Leaning on the experience with the large systems, we believe that the use of effective core potentials (ECPs) to eliminate the core electrons would be highly beneficial to PZ-SIC calculations, as the ECPs take out the core orbital densities that may be numerically challenging to optimize

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3 due to the nonlinearity of the exchange-correlation functional and the large density gradients
4 involved with core orbitals. ECPs also decrease the number of electrons that need explicit
5 description, all the while they still can guarantee proper description of the chemically inactive
6 core.
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11 As we have seen in the present work, the complex-valued orbitals result in reduced
12 symmetry breaking than calculations using real-valued orbitals. An alternative approach
13 to PZ-SIC based on Fermi orbitals¹¹³ (FO) has been recently proposed by Pederson and
14 coworkers^{114–117}. Depending on the point of view, the FO approach can either be viewed as
15 an approximation to PZ-SIC with real-valued orbitals, or as a completely new way of formu-
16 lating a self-interaction corrected approach. The FO approach leads to a significantly smaller
17 number of degrees of freedom compared to the use of full unitary transformations. Initial
18 results of the approach have been promising; although as far as we know, a fully variational
19 implementation of the Fermi orbital approach does not yet exist. It would be interesting
20 to see benchmarks of the use of Fermi orbitals, of real orthogonal orbitals, and of complex
21 unitary orbitals to see the relative accuracies of these methods in different applications, and
22 to determine whether the FO-SIC approach also has local solutions like PZ-SIC.
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36 Dabo and coworkers have recently suggested another kind of one-electron self-interaction
37 correction motivated by Koopmans' theorem^{118–124}. Because of the similar introduction of the
38 dependence on the set of occupied orbitals, we expect our results on the orbital dependence
39 of PZ-SIC to carry unchanged to the Koopmans-corrected functionals.
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46 Appendix I

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49 The stability of the wave function is determined by computing the eigenvalues of the Hessian
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$$52 H_{ij} = \frac{\partial^2 E(\mathbf{C}')}{\partial \theta_i \partial \theta_j} \bigg|_{\boldsymbol{\theta}=0} . \quad (21)$$

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The Hessian matrix is computed seminumerically by central finite differences of the analytic gradient with a step size of $h = \epsilon^{1/3} \approx 6 \times 10^{-6}$, where ϵ denotes the machine epsilon.

The stability of the unitary optimization is determined by the θ_{oo} rotations, which have $o(o-1)$ independent parameters. Filling the Hessian requires $O(o^2)$ evaluations of the orbital Fock matrices, which typically dominates the cost due to its large prefactor. If exact diagonalization of the Hessian is used, an asymptotical $O(o^6)$ cost for stability analysis in the oo block is obtained. As storing the oo Hessian requires $O(o^4)$ memory, for large systems a method with smaller memory requirements based on the Davidson algorithm¹²⁵ may be desirable¹²⁶.

Appendix II

The mappings for the rows and columns, π_i and π_j , in the orbital projection matrix O (or the density difference matrix τ) are determined as follows:

1. Initialize $\pi_i = (1 \ 2 \ \dots \ N)^T = \pi_j$. Set $k = 1$.
2. Obtain $\mathbf{O}$ (or $\boldsymbol{\tau}$) in the new order as $\tilde{O}_{ij} = O_{\pi_i(i), \pi_j(j)}$ (or $\tilde{\tau}_{ij} = \tau_{\pi_i(i), \pi_j(j)}$).
3. Determine the maximum value of $\tilde{\mathbf{O}}$ (or minimal value of $\tilde{\tau}$) in the lower righthand submatrix $k \leq i \leq N$, $k \leq j \leq N$, resulting in indices $i_{\max}$ and $j_{\max}$.
4. Swap $\pi_i(k) \leftrightarrow \pi_i(i_{\max})$ and $\pi_j(k) \leftrightarrow \pi_j(j_{\max})$.
5. If $k < N$ return to step 2.

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