Electrical response of molecular systems: the power of self-interaction corrected Kohn-Sham theory

T. Körzdörfer, M. Mundt, and S. Kümmel Physics Institute, University of Bayreuth, D-95440 Bayreuth, Germany (Dated: July 17, 2007)

The accurate prediction of electronic response properties of extended molecular systems has been a challenge for conventional, explicit density functionals. We demonstrate that a self-interaction correction implemented rigorously within Kohn-Sham theory via the Optimized Effective Potential (OEP) yields polarizabilities close to the ones from highly accurate wavefunction-based calculations and exceeding the quality of exact-exchange-OEP. The orbital structure obtained with the OEP-SIC functional and approximations to it are discussed.

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Gaining microscopic insight into the quantummechanical electronic effects that govern energy- and charge transfer in processes like light-harvesting, chargeseparation in organic solar cells, or the response of molecular opto-electronic devices would be extremely beneficial to the understanding of these phenomena. But the computational complexity of solving the manyelectron Schrödinger equation leaves little hope that wave-function based approaches can address these problems any time soon. The formulation of quantum mechanics without wavefunction, i.e., density functional theory (DFT) in the Kohn-Sham framework, is computationally much more efficient and allows to handle systems with up to several hundreds of electrons. Therefore, it appears as the ideal tool for investigating the above mentioned problems. However, the predictive power of DFT calculations depends crucially on the approximations made in the description of the exchange-correlation effects. Structural, ground-state molecular properties are obtained with reasonable to excellent accuracy using standard, explicit density functionals like the Local Spin Density Approximation (LSDA) or Generalized Gradient Approximations (GGAs). But these functionals notoriously fail in the description of charge transfer processes [1, 2] and associated problems like predicting the response [3] or transport [4] properties of extended molecular systems. There is, thus, a serious need for exchange-correlation approximations that allow to calculate response properties like polarizabilities of extended systems reliably on a quantitative scale and with bearable computational costs.

It has been demonstrated that improvements in the density-functional description of the response of conjugated polymers can be achieved based on current density functional theory [5] and related ideas [6], or by incorporating full [3, 7, 8] or partial [9] exact exchange. It has also been argued that correlation effects play a non-negligible role in the proper description of response properties [10]. However, evaluating the Fock integrals in exact exchange approaches increases numerical costs substantially, and the computational complexity of ap-

proaches using exact exchange with "compatible" correlation is significant [11].

In this manuscript we demonstrate that these problems can be overcome with a self-interaction correction (SIC) employed rigorously within Kohn-Sham theory. In the SIC-scheme, only direct, i.e., self-exchange integrals need to be evaluated, thus computational costs are lowered. OEP-SIC yields highly accurate results for the response of extended molecular systems without involving empirical parameters.

The first "modern" SIC was proposed by Perdew and Zunger as a correction to LSDA [13]. They devised the LSDA-SIC functional

$$E_{\text{xc}}^{\text{SIC}}[n_{\uparrow}, n_{\downarrow}] = E_{\text{xc}}^{\text{LSDA}}[n_{\uparrow}, n_{\downarrow}] - \left[\sum_{\sigma = \uparrow, \downarrow} \sum_{i=1}^{N_{\sigma}} E_{\text{H}}[n_{i,\sigma}] + E_{\text{xc}}^{\text{LSDA}}[n_{i,\sigma}, 0]\right],$$
(1)

where $E_{\rm xc}^{\rm LSDA}$ is the LSDA exchange-correlation energy functional, $E_{\rm H}$ the Hartree (classical Coulomb) energy, n_{\uparrow} and n_{\downarrow} the up- and down-spin densities, respectively, N_{\uparrow} and N_{\downarrow} the numbers of occupied spin-orbitals, and $n_{i,\sigma}$ the orbital spin densities. Eq. (1) is not the only way in which a SIC can be defined [14], but it is plausible and straightforward: The spurious self-interaction effects that are contained in the Hartree energy and the LSDA functional are subtracted on an orbital-by-orbital basis. However, a subtlety is buried in this seemingly simple equation: The functional depends on the orbitals explicitly, i.e., it is not an explicit density functional. The traditional way of approaching this problem has been to minimize the total energy with respect to the orbitals [13, 15, 16]. This approach is within the realm of the Hohenberg-Kohn theorem, but it is outside the foundations of Kohn-Sham theory: minimizing with respect to the orbitals leads to single-particle equations with orbital specific potentials instead of a global, local Kohn-Sham potential for all orbitals. But the existence of a common, local potential is one of the features that makes Kohn-Sham DFT attractive: Only with a local

potential is the non-interacting kinetic energy density a well-defined density functional, a local potential considerably simplifies numerical efforts, it facilitates the interpretation of results, and it yields not only corrected occupied eigenvalues, but also corrected unoccupied ones. But on the other hand, Perdew-Zunger SIC [13] has become popular in some areas of solid state physics exactly for the reason that it does not work with one common local potential but with several orbital specific ones, because orbital specific potentials straightforwardly allow to take into account orbital localization effects: SIC with orbital-specific potentials can treat, e.g., p- and dorbitals of a crystalline solid on a different footing. In this way, Perdew-Zunger SIC can naturally distinguish between localized and delocalized states. In order to benefit from the advantages of working with a local potential without loosing the ability to describe localization effects, schemes have been devised which make use of the fact that Eq. (1) is not invariant under transformations of the orbitals that change the individual orbital densities but leave the total density unchanged. Calculating orbitals from a common Hamiltonian and then subject these orbitals to localizing transformations has proved to be a successful scheme for solids [21, 22] and molecules [23, 24, 25].

However, localizing orbital transformations can become computationally involved in large finite systems and in time-dependent calculations. Therefore, yet another variant of the SIC has become popular. It uses the Krieger-Li-Iafrate (KLI) construction [12] to obtain the KLI-potential corresponding to Eq. (1) and evaluates Eq. (1) directly with the KLI orbitals [17, 18, 19, 20]. This approach has been justified as an approximation to the OEP-version of SIC (OEP-SIC), which is defined by evaluating Eq. (1) with the orbitals obtained from the SIC Kohn-Sham potential that follows from the Optimized Effective Potential (OEP) formalism [11]. But to the best of our knowledge, the performance of the OEP-SIC approach itself has remained largely unexplored, and tests of the KLI-SIC approach were restricted to spherical atoms [17]. In this manuscript we demonstrate that OEP-SIC, but not KLI-SIC, allows to predict electric response coefficients of molecular systems very reliably and may thus become an important tool to investigate chargetransfer questions.

One of the most demanding tests of a functional's ability to adequately describe charge transfer is calculating the polarizability of hydrogen chains. It has been shown that obtaining the response of hydrogen chains correctly is even more difficult than obtaining the response of real polymers like polyacetylene [5]. Therefore, calculating the polarizability of hydrogen chains has become a benchmark test for many-particle approaches from both the density functional [3, 5, 6, 7, 8] and the wave-function worlds [28, 29]. Since a response quantity like the polarizability determines how a system reacts to a field

that induces a density shift, calculating the polarizability also probes the ability to correctly describe charge transfer. As a second, positive side effect, investigating hydrogen chains also allows us to address the question of size-consistency of the OEP-SIC functional [13, 26, 27].

Our calculations are based on a real space approach [30] which we employed to calculate the ground-state of hydrogen chains with alternating interatomic distances of 2 and 3 a₀ using KLI-SIC. From the converged KLI-SIC solution we calculated the true OEP following the iterative procedure described in [31], which is more cumbersone for the SIC-LDA functional than for pure exchange, but does converge. The ground-state calculations (no electrical field applied yet) lead to a remarkable result. For the sake of clarity we discuss it using the specific example of the shortest chain, H₄. The KLIsolution is spatially symmetric as expected and as depicted in the left part of Fig. 1. It is also manifestly spin-unpolarized, i.e., the self-consistent KLI iteration returns to a spin-unpolarized solution from a spin-polarized starting guess. But starting from the spin-unpolarized KLI solution and iterating the OEP to self-consistency without restriction on the spin polarization, we observe a spontaneous change in symmetry. After a few iterations of the OEP self-consistency cycle, the up- and down-spin orbitals separate and each orbital starts to center around one nucleus. For the interatomic distances of 2 and 3 a_0 frequently used in the literature [3, 8, 28, 32], the effect is moderate but clearly visible, as shown in the middle of Fig. (1). If the interatomic distances are increased further, e.g., to 2.5 and 3 a_0 as shown in the right part of Fig. (1), the orbital localization becomes pronounced and one can undoubtedly associate one orbital with one nucleus. This effect is not only observed for H₄, but also for the other hydrogen chains we studied.

A conclusion from this finding is that the KLI-SIC potential is not necessarily a good approximation to the OEP-SIC potential. In order to understand this one should recall that the KLI-potential is justified as a meanfield approximation [11, 12, 19]: The difference between the true OEP and the KLI-potential is a term of the kind $(1/n(\mathbf{r}))\nabla \cdot \mathbf{f}(\mathbf{r})$, where $\mathbf{f}(\mathbf{r})$ is a well defined function depending on the full spectrum of Kohn-Sham orbitals. Averaged over the density, the term vanishes [12, 19]. But implicitly this mean-field argument assumes that the "averaged" term has little influence in the self-consistent iteration so that the density obtained with and without the neglected term are very similar. However, our calculations show that this is not the case for the SIC functional: taking into account the term that is neglected in the KLI potential drives the self-consistent iteration to a very different solution. This is possible because the neglected term contains all orbitals and is thus relevant for unitary (in)variance and greater variational freedom. The breakdown of the KLI-SIC approximation may be a surprise in view of its good performace for atoms [17],



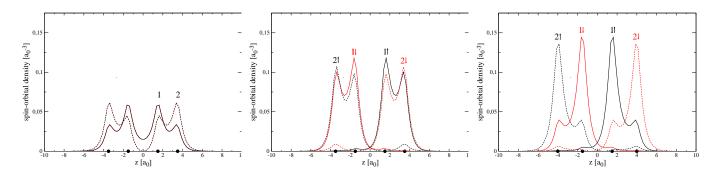


FIG. 1: Left: Orbital densities of H_4 with interatomic distances of 2 and 3 bohr (a_0) , respectively, obtained from self-consistent KLI-SIC calculation. Up- and down-spin orbitals are identical. Middle: Spin-orbital densities for the same system obtained from self-consistent OEP-SIC calculation. Right: Spin-orbital densities of H_4 with interatomic distances of 2.5 and 3 a_0 , respectively, obtained from self-consistent OEP-SIC calculation. The orbital localization increases with increasing interatomic distance.

but appears less surprising in view of other drawbacks [34].

The hydrogen chain ground-state results also naturally trigger thoughts about the bulk limit that one would reach by adding ever more atoms. We briefly want to ponder this case. Recall that for an infinite lattice of hydrogen atoms with a lattice constant that tends to infinity, the exact Kohn-Sham orbitals are delocalized Bloch orbitals for which the self-interaction correction vanishes on a per-atom basis [13]. Using such orbitals in Eq. (1) yields the (wrong) uncorrected LSDA energy. Inherent to the logic of this argument is a certain order of taking the two "infinity limits": first the number of atoms tends to infinity, i.e., an infinite lattice is built, and then the lattice constant is made ever larger.

Our calculations suggest that a different result is obtained if the order of taking these two limits is interchanged. For finite systems of largely separated hydrogen atoms, our OEP-SIC calculations lead to localized orbitals and thus, a self-interaction corrected energy. Now imagine building up an ever larger lattice of hydrogen atoms with ever larger interatomic separation by adding atoms to a finite starting system. At each step of this buildup process, one will be dealing with a large but finite system. Our calculations suggest that at each stage of the build-up process, OEP-SIC will yield localized orbitals and thus a self-interaction corrected energy. This idea is in line with earlier findings that revealed that it makes a great difference whether the surface of an extended system is explicitly taken into account or not [33]. In any case our results show that OEP-SIC can yield localized orbitals that differ greatly from the KLI orbitals. How strong the OEP-SIC localization is will depend on the specific system. Generally speaking, we expect localization effects to be even more pronounced in SIC schemes using orbital dependent potentials [13] or orbital localizing transformations [21, 22, 23, 24, 25].

With the ground-state structure of OEP-SIC discussed we come to the most important aspect of this manuscript,

the calculation of the electrical response. As a first test we calculated the response of the two dimers Na₂ and N₂, which can be seen as representing the "extreme ends" of dimer bonding with a soft single and a strong triple bond, respectively. The OEP-SIC polarizability (tensor average in a_0^3) is obtained as 274 for Na₂ (KLI-SIC performs similar) and 10.3 for N_2 (no convergence for KLI-SIC). The value for the sodium dimer compares favorably with the most recent experimental result of 270 [35], the value for the nitrogen dimer is too low but not unreasonable [36]. It is a noteworthy observation that OEP-SIC increases the polarizability (by 12%) for Na₂ (where LDA underestimates) while it decreases it (by 18%) for N₂ (where LDA overestimates), i.e., it works "in the right direction" in both systems. OEP-SIC also yields greatly improved eigenvalues. For CH₄, e.g., OEP-SIC yields $\varepsilon_{\rm HOMO}^{\rm OEP-SIC}=14.56~{\rm eV},$ which compares much better with the experimental ionization energy of 14.42 eV than the LDA value $\varepsilon_{\text{HOMO}}^{\text{LDA}} = 9.52 \text{ eV}.$

The true and most important test is how OEP-SIC performs for the response of extended systems where semilocal functionals fail badly. This is tested by calculating the response of the hydrogen chains. The Kohn-Sham SIC longitudinal static electric polarizabilities obtained from an accurate finite field approach [37] are shown in

	H_4	H_6	H_8	H_{10}	H_{12}
LSDA	37.6	73	115	162	211
KLI-SIC	19.4	60.3	98.2	131.7	193.6
OEP-EXX	32.2	56.6	84.2	n/a	138.1
OEP-SIC	30.6	48.7	80.1	98.8	129.8
MP4	29.5	51.6	75.9	n/a	126.9

TABLE I: Longitudinal polarizability of hydrogen chains in a_0^3 obtained with different exchange-correlation approximations. Møller-Plesset- (MP4) results taken from [38], exact-exchange OEP (OEP-EXX) from [8]. KLI polarizabilities were calculated from the dipole moment, see discussion in [37].

Table I together with LSDA, exact-exchange OEP (OEP-EXX), and fourth-order Møller-Plesset perturbation theory (MP4) results. The MP4 results are close to the exact values and serve as the quasi-exact benchmark. The first observation is that the KLI-SIC results vary unsystematically – the polarizability of H₄ is substantially underestimated, whereas the polarizability of all other chains is overestimated. Comparison with OEP-EXX and LSDA shows that KLI-SIC improves over LSDA, but is less accurate than exchange-only theory. The picture changes when SIC is employed with the true, self-consistent OEP instead of with the KLI-approximation: KLI-SIC and OEP-SIC polarizabilities are rather different. Comparing OEP-SIC to the wavefunction based results shows that OEP-SIC polarizabilities are within a few percent of the MP4 results in all cases and are noticeably closer to the MP4 values than the exchange-only OEP results, which up to now represented the best density functional results for such systems.

One may wonder why the SIC functional, in which localization of the orbitals plays an important role, and exact exchange, which is unitarily invariant and thus independent of orbital localization, can both lead to a reasonable description of the chain response. The solution lies in the interpretation of the exchange part of the SIC functional: The Hartree self-interaction correction corresponds to the self-exchange part of the EXX functional, and it is well known that the diagonal (self-)exchange integrals are the dominant part of exchange, i.e., they are noticeably larger than the off-diagonal exchange integrals. The larger the diagonal "classical" parts of the exchange energy are in comparison with its off-diagonal parts, the more accurate becomes the SIC description which neglects the off-diagonal parts. Since the diagonal parts are typically maximal for localized orbitals, it becomes clear why localized orbitals are crucial in the SIC-approach. So from this perspective, SIC takes into account the most important part of EXX at the cost of needing to employ localized orbitals, but with the huge benefit of greatly reducing the number of exchange integrals that have to be evaluated. In addition, SIC offers an improvement over bare EXX that can be attributed to the non-EXX parts of the functional. Following [3] one can also show that the improved OEP-SIC polarizabilities stem from a field-counteracting-term in the response-part of the exchange-correlation-potential [39]. Thus, OEP-SIC is an approach which allows to reliably investigate the electrical response of a broad range of molecular systems.

Note added after submission: We learned of studies by Pemmaraju, Sanvito, and Burke, and Ruzsinszky, Perdew, Csonka, Scuseria, and Vydrov, which also find that SIC improves the response.

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